Supplementary Information (DT-ART-11-2017-004327)

Preparation and Reactivity of Iron Complexes Bearing Anionic Carbazole-Based PNP-Type Pincer Ligands toward Catalytic Nitrogen Fixation

Junichi Higuchi, Shogo Kuriyama, Aya Eizawa, Kazuya Arashiba, Kazunari Nakajima, and Yoshiaki Nishibayashi*[†]

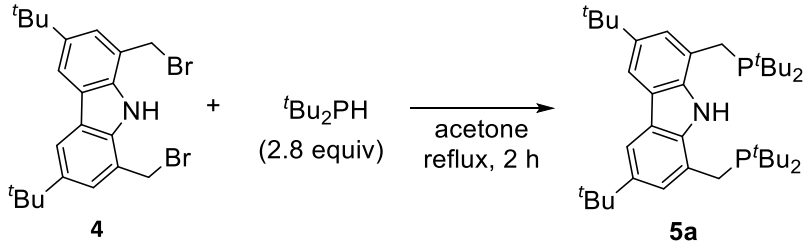
Department of Systems Innovation, School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

General Methods.

^{1}H NMR (270 MHz), and ^{31}P{^{1}H} NMR (109 MHz) spectra were recorded on a JEOL Excalibur 270 spectrometer in suitable solvent, and spectra were referenced to residual solvent (^{1}H) or external standard (^{31}P{^{1}H}: H_3PO_4). IR spectra were recorded on a JASCO FT/IR 4100 Fourier Transform infrared spectrometer. Magnetic susceptibility was measured in solution by using Evans' method.[S1] Absorption spectra were recorded on a Shimadzu MultiSpec-1500. Evolved dihydrogen and methane were quantified by a gas chromatography using a Shimadzu GC-8A with a TCD detector and a SHINCARBON ST (6 m × 3 mm). Elemental analyses were performed at Microanalytical Center of The University of Tokyo.

All manipulations were carried out under an atmosphere of nitrogen by using standard Schlenk techniques or glovebox techniques unless otherwise stated. Solvents were dried by general methods, and degassed before use. 1,8-bis(bromomethyl)-3,6-di-*tert*-butyl-9H-carbazole (**4**),[S2] $[FeCl_2(thf)_{1.5}]$ (thf = tetrahydrofuran),[S3] KC_8,[S4] and $[H(OEt_2)_2]BAr^F_4$ (Ar^F = 3,5-$(CF_3)_2C_6H_3$)[S5] were prepared according to the literature method. All the other reagents were commercially available.

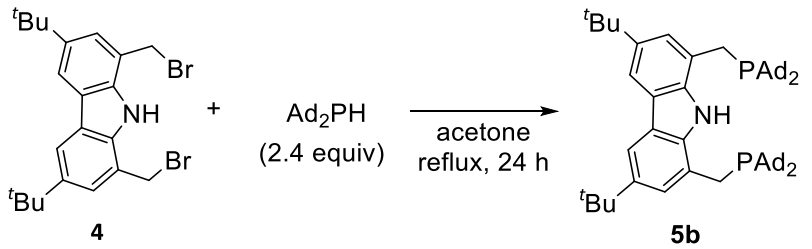
Preparation of 5a.



Pincer ligands **5a** and **5b** were prepared by a similar method to Gade's procedure.[S2]

To a solution of **4** (885 mg, 1.90 mmol) in acetone (15 mL) was added di-*tert*-butylphosphine (1.00 mL, 5.40 mmol) at room temperature, and the resultant mixture was heated at reflux temperature for 2 h. After the reaction mixture was cooled to room temperature, the solvent was removed *in vacuo*. The obtained solid was washed with Et_2O (5 mL, 3 times) and dried *in vacuo*. After sodium acetate (4.3 g), degassed water (15 mL) and Et_2O (15 mL) were added to the residue, the mixture was stirred at room temperature for 20 min. The mixture was extracted with Et_2O (10 mL, 3 times) and the combined extracts were dried over anhydrous $MgSO_4$. After filtration, the solvent was removed, and the residue was dried *in vacuo* to give **5a** as a pale-yellow solid (1.09 g, 1.83 mmol, 96%). ^{1}H NMR (C_6D_6) δ 10.20 (br s, N*H*, 1H), 8.18 (pseudo d, *J* = 1.6 Hz, Ar-*H*, 2H), 7.55 (s, Ar-*H*, 2H), 3.22 (s, ArC*H*$_2$P, 4H), 1.50 (s, Ar^t*Bu*, 18H), 1.14 (d, *J* = 10.5 Hz, ^{t}*Bu*$_2$P, 36H). ^{31}P{^{1}H} NMR (C_6D_6) δ 17.7 (s). Anal. Calcd. for $C_{38}H_{63}NP_2$: C, 76.60; H, 10.66; N, 2.35. Found: C, 76.52; H, 10.21; N, 2.74.

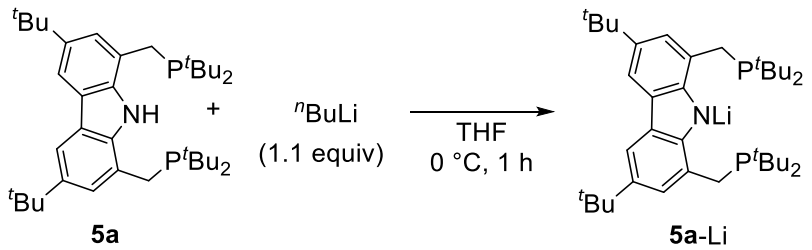
Preparation of 5b.



To a solution of **4** (83.2 mg, 0.179 mmol) in acetone (3 mL) was added di-1-adamantylphosphine (131 mg, 0.433 mmol) at room temperature and the resultant mixture was heated at reflux temperature for 24 h. After the reaction mixture was cooled to room temperature, the solvent was removed *in vacuo*. The obtained solid was washed with Et_2O (2 mL, 3 times) and dried *in vacuo*. After sodium acetate (0.90 g, 11 mmol), degassed water (4 mL) and Et_2O (5 mL) were added to the

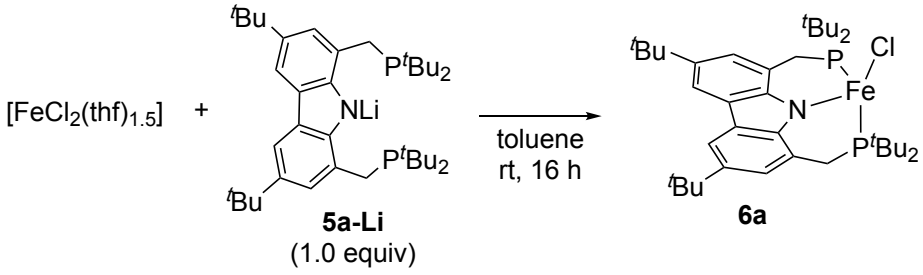
residue, the mixture was stirred at room temperature for 20 min. The mixture was extracted with Et_2O (4 mL, 3 times) and the combined extracts were dried over anhydrous $MgSO_4$. After filtration, the solvent was removed, and the residue was dried *in vacuo* to give **5b** as a white solid (146 mg, 0.161 mmol, 90%). ^{1}H NMR (C_6D_6) δ 10.27 (br s, N*H*, 1H), 8.16 (pseudo d, *J* = 1.6 Hz, Ar-*H*, 2H), 7.64 (s, Ar-*H*, 2H), 3.29 (s, ArCH_2P, 4H), 2.15-1.99 (m, Ad-C$H_{2(\gamma)}$, 24H), 1.88 (s, Ad-C$H_{(\beta)}$, 12H), 1.70 (s, Ad-C$H_{2(\alpha)}$, 24H), 1.55 (s, Ar^t*Bu*, 18H). ^{31}P{^{1}H} NMR (C_6D_6) δ 11.4 (s). Anal. Calcd. for $C_{62}H_{87}NP_2$: C, 81.98; H, 9.65; N, 1.54. Found: C, 81.63; H, 9.57; N, 1.88.

Preparation of lithium 3,6-di-*tert*-butyl-1,8-bis(di-*tert*-butylphosphinomethyl)carbazolide (5a-Li).



To a solution of **5a** (336 mg, 0.564 mmol) in THF (2 mL) was added dropwise ^{n}BuLi (1.55 M in hexane, 0.40 mL, 0.62 mmol) at 0 °C. After the reaction mixture was stirred at 0 °C for 1 h, the solvent was removed, and the residue was dried *in vacuo*. The obtained solid was washed with pentane and dried *in vacuo* to afford **5a**-Li as a yellow solid (268 mg, 0.445 mmol, 79%). The product was used for the subsequent reaction without further purification. ^{1}H NMR (THF-d_8) δ 7.75 (s, Ar-*H*, 2H), 7.30 (s, Ar-*H*, 2H), 3.39 (d, *J* = 3.0 Hz, ArCH_2P, 4H), 1.39 (s, Ar^t*Bu*, 18H), 1.18 (d, *J* = 10.5 Hz, ^{t}*Bu*$_2$P, 36H). ^{31}P{^{1}H} NMR (THF-d_8) δ 29.8 (s).

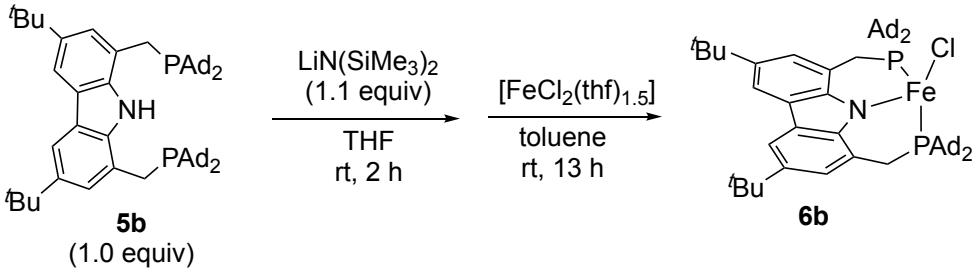
Preparation of 6a.



To a suspension of [$FeCl_2$(thf)$_{1.5}$] (332 mg, 1.41 mmol) in toluene (6 mL) was added a suspension

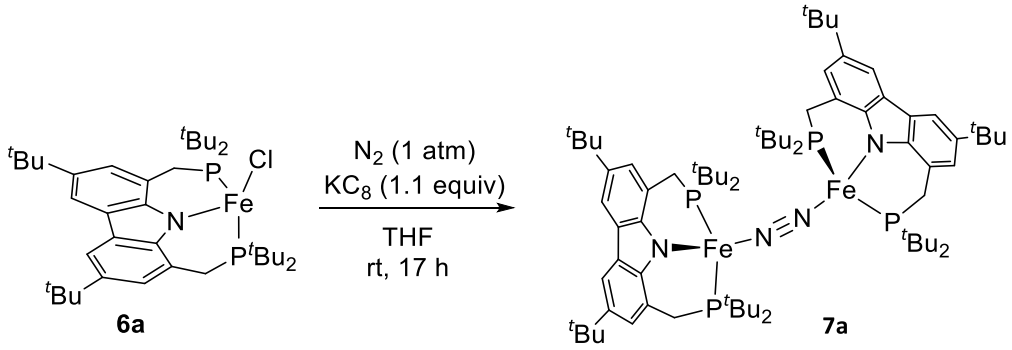
of **5a**-Li (850 mg, 1.41 mmol) in toluene (6 mL), and the resultant red mixture was stirred at room temperature for 16 h. Hexane (5 mL) was added to the red mixture, and the mixture was stirred at room temperature for several minutes. The mixture was filtered through Celite, and the filter cake was washed with hexane (3 mL, 3 times) and Et_2O (3 mL, 3 times). The combined filtrate was concentrated to *ca.* 5 mL to afford **6a** as an orange solid, which was collected by decantation, washed with a small amount of hexane and dried *in vacuo* (791 mg, 1.15 mmol, 82%). Single crystals of **6a**·0.5C_6H_{14} suitable for X-ray crystallography were obtained as orange crystals by recrystallization from hexane at -30 °C. ^{1}H NMR (C_6D_6) δ 47.0, 15.3, 9.1, 5.7, 1.9. Magnetic susceptibility (Evans' method): μ_{eff} = 4.9 ± 0.3 μ_B in C_6D_6 at 298 K. Anal. Calcd. for $C_{38}H_{62}ClFeNP_2$: C, 66.52; H, 9.11; N, 2.04. Found: C, 66.84; H, 9.41; N, 2.12.

Preparation of 6b·C_6H_6.



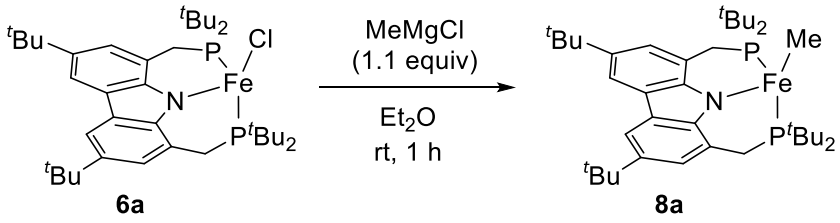
A solution of **5b** (454 mg, 0.500 mmol) and $LiN(SiMe_3)_2$ (87.4 mg, 0.522 mmol) in THF (5 mL) was stirred at room temperature for 2 h. After the solvent was removed, $[FeCl_2(thf)_{1.5}]$ (117 mg, 0.498 mmol) and toluene (7 mL) was added to the orange residue, and then the resultant red mixture was stirred at room temperature for 13 h. After the solvent was removed, the red residue was dissolved in benzene (10 mL). The solution was filtered through Celite, and the filter cake was washed with benzene (5 mL, 5 times). The product was recrystallized from benzene–hexane to afford **6b**·C_6H_6 as orange crystals, which were collected by decantation, washed with hexane and dried *in vacuo* (387 mg, 0.359 mmol, 72%). ^{1}H NMR (C_6D_6) δ 46.2, 9.3, 6.8, 5.6, 2.2, 1.9, 1.2, 0.1, -6.0. Magnetic susceptibility (Evans' method): μ_{eff} = 4.7 ± 0.3 μ_B in C_6D_6 at 298 K. Anal. Calcd. for $C_{68}H_{92}FeClNP_2$ (**6b**·C_6H_6): C, 75.85; H, 8.61; N, 1.30. Found: C, 75.51; H, 8.40; N, 1.41.

Preparation of 7a.



A suspension of **6a** (206 mg, 0.300 mmol) and KC_8 (44.5 mg, 0.329 mmol) in THF (6 mL) was stirred at room temperature for 17 h under N_2 (1 atm). After the solvent was removed, the dark yellow residue was dissolved in hexane (3 mL). The solution was filtered through Celite, and the filter cake was washed with hexane (2 mL, 3 times) and Et_2O (2 mL, 3 times). The combined filtrate was concentrated to *ca.* 3 mL, and the solution was kept at -17 °C to give **7a** as a dark brown solid, which was collected by decantation, washed with a small amount of hexane, and dried *in vacuo* (112 mg, 0.0842 mmol, 56%). Single crystals of **7a**·0.5C_6H_6 suitable for X-ray crystallography were obtained as dark green crystals by recrystallization from hexane-Et_2O-benzene at -30 °C. ^{1}H NMR (C_6D_6) δ 12.8, 11.5, 4.0, 3.2, 2.0, 1.5, 1.23, 1.15, 0.9, -0.4, -7.1, -9.7. Magnetic susceptibility (Evans' method): μ_{eff} = 7.5 ± 0.7 μ_B in C_6D_6 at 298 K. Anal. Calcd. for $C_{76}H_{124}Fe_2N_4P_4$: C, 68.66; H, 9.40; N, 4.21. Found: C, 68.61; H, 9.26; N, 3.03. It is considered that the low content of nitrogen is due to the labile property of the coordinated molecular dinitrogen in **7a**.

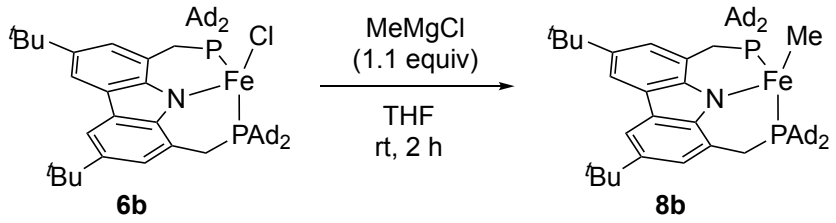
Preparation of 8a.



To a suspension of **6a** (207 mg, 0.302 mmol) in Et_2O (8 mL) was added MeMgCl (3.0 M in THF, 110 μL, 0.330 mmol) at room temperature, and resultant yellow mixture was stirred at room temperature for 1 h. After a small amount of 1,4-dioxane was added, the mixture was stirred at

room temperature for 10 min and the solvent was removed *in vacuo*. After addition of hexane (5 mL) to the yellow residue, the solution was filtered through Celite, and the filter cake was washed with hexane (2 mL, 3 times) and Et_2O (2 mL, 3 times). The combined filtrate was concentrated to *ca.* 3 mL and the solution was kept at -30 °C to give **8a** as a yellow solid, which was collected by decantation, washed with a small amount of hexane, and dried *in vacuo* (170 mg, 0.255 mmol, 85%). Single crystals of **8a**·0.5$C_4H_{10}O$ suitable for X-ray crystallography were obtained as yellow crystals by recrystallization of crude mixture from hexane at -30 °C. ^{1}H NMR (C_6D_6) δ 39.2, 27.9, 3.4, 1.5, 1.2, 0.9, 0.5, -4.1. Magnetic susceptibility (Evans' method): μ_{eff} = 4.7 ± 0.3 μ_B in C_6D_6 at 298 K. Anal. Calcd. for $C_{39}H_{65}FeNP_2$: C, 70.36; H, 9.84; N, 2.10. Found: C, 70.51; H, 9.77; N, 2.17.

Preparation of 8b.



To a solution of **6b**•C_6H_6 (108 mg, 0.100 mmol) in THF (4 mL) was added MeMgCl (3.0 M in THF, 37 μL, 0.11 mmol) at room temperature and the resultant yellowish-brown mixture was stirred at room temperature for 2 h. After a small amount of 1,4-dioxane was added, the mixture was stirred at room temperature for 20 min and the solvent was removed *in vacuo*. After the addition of benzene (2 mL) to the yellow residue, the suspension was filtered through Celite, and the filter cake was washed with benzene (2 mL, 4 times) and toluene (2 mL, 2 times). The product was recrystallized from benzene–toluene–hexane to afford **8b**•C_6H_6 as a yellow solid, which was collected by decantation, and dried *in vacuo* (67.5 mg, 0.0639 mmol, 64%). ^{1}H NMR (C_6D_6) δ 37.9, 12.5, 5.9, 4.9, 2.8, 0.5, 0.3, -0.7, -2.5. Magnetic susceptibility (Evans' method): μ_{eff} = 4.7 ± 0.3 μ_B in C_6D_6 at 298 K. Anal. Calcd. for $C_{69}H_{95}FeNP_2$ (**8b**•C_6H_6): C, 78.46; H, 9.07; N, 1.33. Found: C, 78.16; H, 8.98; N, 1.50.

X-ray crystallography.

Crystallographic data of **6a**, **6b**, **7a**, and **8a**·0.5$C_4H_{10}O$ are summarized in Tables S1–S2. The ORTEP drawings of **6a**, **6b**, **7a**, and **8a**·0.5$C_4H_{10}O$ are shown in Figures S2–S5 and selected bond lengths and angles of **6a**, **6b**, **7a**, and **8a**·0.5$C_4H_{10}O$ are shown in Tables S3–S6. Diffraction data for **6a**, **6b**, **7a**, and **8a**·0.5$C_4H_{10}O$ were collected for the 2θ range of 4° to 55° at –100 °C on a Rigaku RAXIS RAPID imaging plate area detector with graphite-monochromated Mo *K*α radiation (λ = 0.71075 Å), with VariMax optics. Intensity data were corrected for Lorenz-polarization effects and for empirical absorption (ABSCOR). The structure solution and refinements were carried out by using the *CrystalStructure* crystallographic software package.[S6] The positions of the non-hydrogen atoms were determined by direct methods (SIR 97[S7] for **6a**, **6b**, **8a**·0.5$C_4H_{10}O$, SHELXS97[S8] for **7a**) and subsequent Fourier syntheses (SHELXL Version 2016/6[S8]), and were refined on F_o^2 using all unique reflections by full-matrix least-squares with anisotropic thermal parameters except for some carbon atoms refined isotropically. All the hydrogen atoms were placed at the calculated positions with fixed isotropic parameters, while positions of some hydrogen atoms could not be refined.

For the crystal of **6a** (**6a**·0.5C_6H_{14}, actually), one of the two crystallographically independent molecules contains whole molecule disorder where the central iron atom and its surrounding ligands may be disordered among more than two positions, but was solved modeling over two positions (Fe(2)–Cl(2) and Fe(3)–Cl(3)) with atom occupancies of 0.85 and 0.15, respectively, without solving minor disorders further, while positions of six hydrogen atoms bonded to two carbon atoms (C(67) and C(74)) close to the Cl(3) atom could not be refined (Figure S1). There is also one heavily disordered *tert*-butyl group rotating around a C–C bond, and was solved over two sets of three methyl groups (C(14A), C(15A), C(16A), and C(14B), C(15B), C(16B)) with atom occupancies of 0.6 and 0.4, respectively. The unit cell of **6a** contains a solvent accessible void of 982 Å^3. The ^{1}H NMR of the crystals suggested that the void was occupied by one hexane molecule per asymmetric unit, which could not be located appropriately. The diffused electron density associated with the solvent molecule was removed by SQUEEZE routine in PLATON.[S9]

For the crystal of **6b** (**6b**·C_6H_6, actually), the unit cell contains a solvent accessible void of 872 Å^3. The ^{1}H NMR and the elemental analysis of the crystals suggested that the void was

occupied with one benzene molecule, which could not be located appropriately. The diffused electron density associated with the solvent molecule was removed by SQUEEZE routine in PLATON.[S9]

For the crystal of **7a** (**7a**·0.5C_6H_6, actually), the unit cell contains a solvent accessible void of 568 Å^3. The ^{1}H NMR and the elemental analysis of the crystals suggested that the void was occupied with a half benzene molecule, which could not be located appropriately. The diffused electron density associated with the solvent molecule was removed by SQUEEZE routine in PLATON.[S9]

For the crystal of **8a**·0.5$C_4H_{10}O$, there is one heavily disordered *tert*-butyl group rotating around a C–C bond, and was solved over two sets of three methyl groups (C(14A), C(15A), C(16A), and C(14B), C(15B), C(16B)) with atom occupancies of 0.6 and 0.4, respectively.

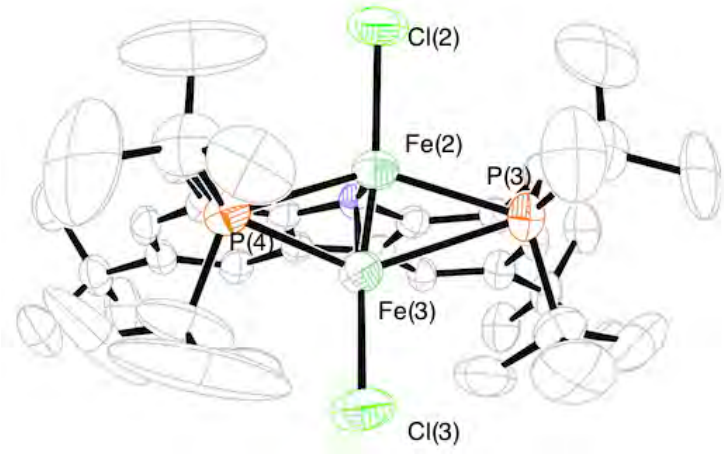


Figure S1. An ORTEP drawing of one of the crystallographically independent molecule of **6a**. The whole molecule disorder was solved over two positions (Fe(2)–Cl(2) and Fe(3)–Cl(3)).

Table S1 | X-ray crystallographic data for **6a** and **6b**

	6a	**6b**
chemical formula	$C_{38}H_{62}FeNP_2$	$C_{62}H_{86}ClFeNP_2$
CCDC number	1546201	1546204
formula weight	686.16	998.62
dimensions of crystals	0.40 × 0.30 × 0.15	0.30 × 0.15 × 0.05
crystal color, habit	orange, block	orange, block
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a, Å	23.0868(5)	11.7043(3)
b, Å	14.8066(4)	25.1225(5)
c, Å	24.7743(5)	19.9855(4)
α, deg	90	90
β, deg	93.479(7)	93.203(7)
γ, deg	90	90
V, Å^3	8453.2(3)	5867.4(2)
Z	8	4
ρ_{calcd}, g cm^{-3}	1.078	1.130
F(000)	2960.00	2152.00
μ, cm^{-1}	5.185	3.933
trans. factors range	0.622 – 0.925	0.686–0.981
no. reflections measured	72868	56900
no. unique reflections	19229 (R_{int} = 0.0726)	13427 (R_{int} = 0.0614)
no. parameters refined	828	604
$R1$ ($I > 2\ \sigma(I)$)[a]	0.1168	0.0590
$wR2$ (all data)[b]	0.2535	0.1368
GOF (all data)[c]	1.217	1.029
max diff peak / hole, e Å^{-3}	0.82 / –1.24	0.86/–0.27

[a] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (qP)^2 + rP]$, $P = (\mathrm{Max}(F_o^2, 0) + 2\ F_c^2)/3$ [q = 0.0798 (**6a**), 0.0578 (**6b**); r = 22.3708 (**6a**), 5.0383 (**6b**)]. [c] GOF = $[\Sigma w(F_o^2-F_c^2)^2/(N_o-N_{params})]^{1/2}$.

Table S2 | X-ray crystallographic data for **7a** and **8a**·0.5$C_4H_{10}O$

	7a	**8a**·0.5$C_4H_{10}O$
chemical formula	$C_{76}H_{124}Fe_2N_4P_4$	$C_{41}H_{70}FeNO_{0.5}P_2$
CCDC number	1546202	1546203
formula weight	1329.43	702.81
dimensions of crystals	0.15 × 0.10 × 0.02	0.15 × 0.10 × 0.03
crystal color, habit	brown, platelet	yellow, platelet
crystal system	monoclinic	monoclinic
space group	$P2_1/a$	$P2_1/n$
a, Å	25.4160(5)	23.1407(4)
b, Å	13.1322(3)	14.8928(3)
c, Å	24.3186(6)	24.4042(4)
α, deg	90	90
β, deg	102.791(7)	92.8868(7)
γ, deg	90	90
V, Å^3	7915.4(4)	8399.8(3)
Z	4	8
ρ_{calcd}, g cm^{-3}	1.116	1.111
F(000)	2880.00	3064.00
μ, cm^{-1}	4.872	4.626
trans. factors range	0.595–0.990	0.680–0.986
no. reflections measured	74187	79684
no. unique reflections	17614 (R_{int} = 0.0937)	19147 (R_{int} = 0.0858)
no. parameters refined	810	853
$R1$ ($I > 2\ \sigma(I)$)[a]	0.0649	0.0523
$wR2$ (all data)[b]	0.1603	0.1212
GOF (all data)[c]	1.021	1.012
max diff peak / hole, e Å^{-3}	0.70/–0.58	0.74/–0.55

[a] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (qP)^2 + rP]$, $P = (\mathrm{Max}(F_o^2, 0) + 2\ F_c^2)/3$ [q = 0.0755 (**7a**), 0.0592 (**8a**·0.5$C_4H_{10}O$); r = 3.2458 (**7a**), 0 (**8a**·0.5$C_4H_{10}O$)]. [c] GOF = $[\Sigma w(F_o^2-F_c^2)^2/(N_o-N_{params})]^{1/2}$.

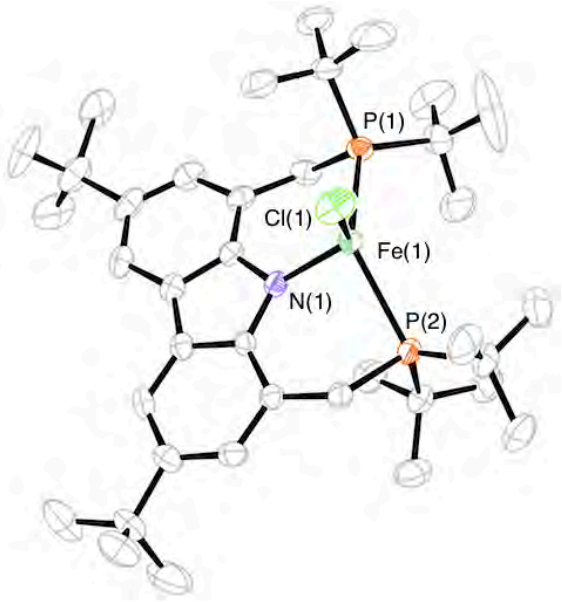


Figure S2. ORTEP drawing of **6a**. Thermal ellipsoids are shown at the 50% probability level. Only one of the two crystallographically independent molecules is shown, while minor disorder components and hydrogen atoms are omitted for clarity.

Table S3. Selected Bond Lengths (Å) and Angles (deg) for **6a**.

Fe(1)—N(1)	1.973(4)	Fe(2)—N(2)	1.958(4)
Fe(1)—P(1)	2.4349(13)	Fe(2)—P(3)	2.4637(18)
Fe(1)—P(2)	2.5015(13)	Fe(2)—P(4)	2.5031(19)
Fe(1)—Cl(1)	2.2853(14)	Fe(2)—Cl(2)	2.252(2)
P(1)—Fe(1)—P(2)	130.67(5)	P(3)—Fe(2)—P(4)	139.80(7)
N(1)—Fe(1)—P(1)	97.17(11)	N(2)—Fe(2)—P(3)	97.65(13)
N(1)—Fe(1)—P(2)	88.40(11)	N(2)—Fe(2)—P(4)	95.53(13)
N(1)—Fe(1)—Cl(1)	118.30(12)	N(2)—Fe(2)—Cl(2)	105.02(15)
P(1)—Fe(1)—Cl(1)	111.54(5)	P(3)—Fe(2)—Cl(2)	106.43(8)
P(2)—Fe(1)—Cl(1)	108.30(5)	P(4)—Fe(2)—Cl(2)	106.47(9)

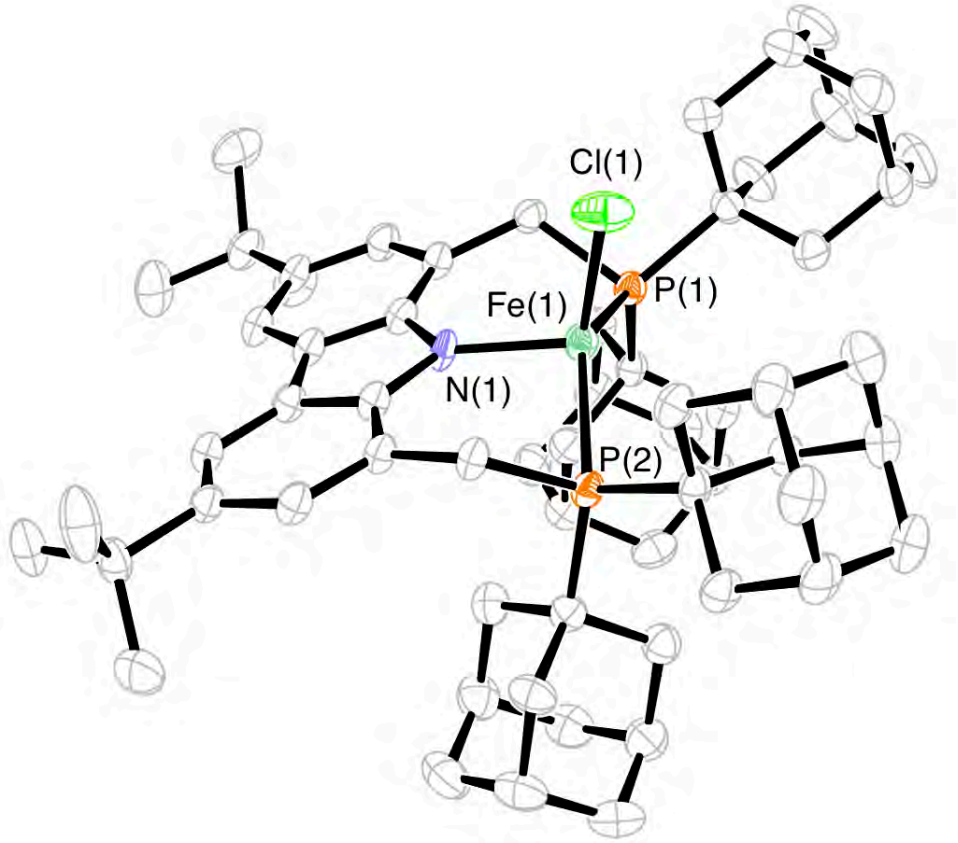


Figure S3. ORTEP drawing of **6b**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table S4. Selected Bond Lengths (Å) and Angles (deg) for **6b**.

Fe(1)—N(1)	2.000(2)
Fe(1)—P(1)	2.4471(7)
Fe(1)—P(2)	2.4459(7)
Fe(1)—Cl(1)	2.2716(8)
P(1)—Fe(1)—P(2)	139.87(3)
N(1)—Fe(1)—P(1)	96.72(6)
N(1)—Fe(1)—P(2)	95.85(6)
N(1)—Fe(1)—Cl(1)	107.55(7)
P(1)—Fe(1)—Cl(1)	106.04(3)
P(2)—Fe(1)—Cl(1)	106.11(3)

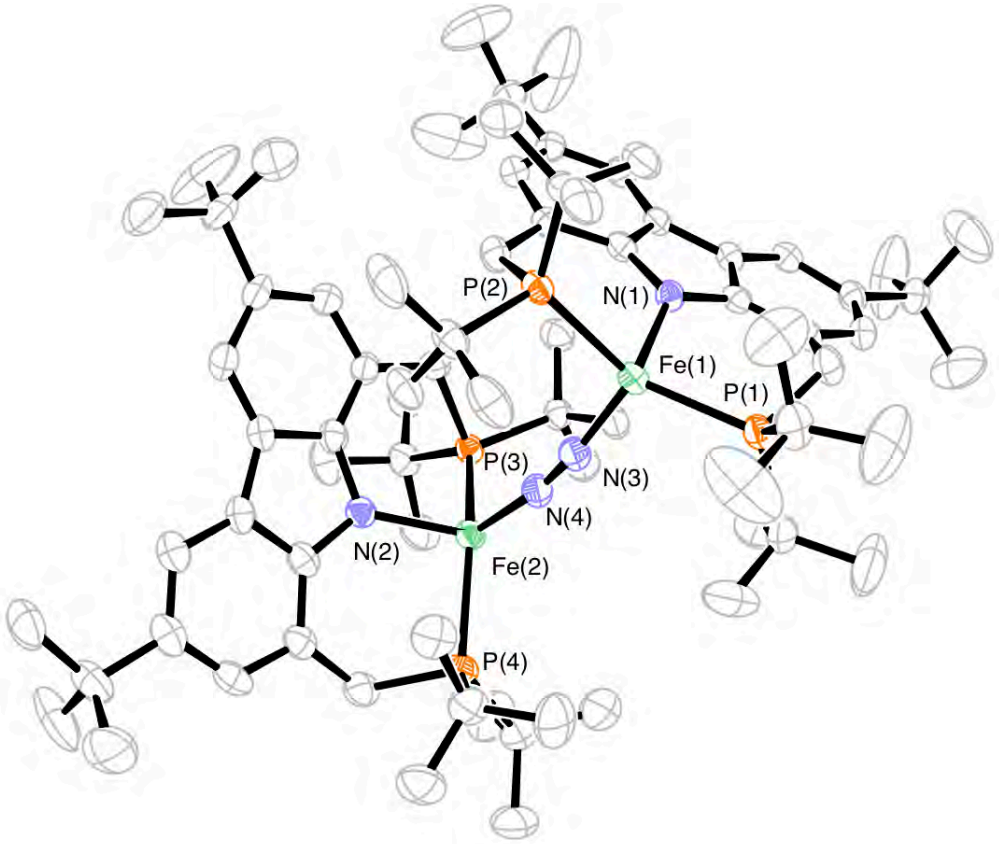


Figure S4. ORTEP drawing of **7a**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table S5. Selected Bond Lengths (Å) and Angles (deg) for **7a**.

Fe(1)—N(1)	2.055(3)	Fe(2)—N(2)	1.959(3)
Fe(1)—P(1)	2.3449(10)	Fe(2)—P(3)	2.5396(10)
Fe(1)—P(2)	2.3922(9)	Fe(2)—P(4)	2.4122(10)
Fe(1)—N(3)	1.746(3)	Fe(2)—N(4)	1.743(3)
N(3)—N(4)	1.106(4)		
P(1)—Fe(1)—P(2)	135.63(4)	P(3)—Fe(2)—P(4)	141.67(4)
N(1)—Fe(1)—P(1)	99.36(7)	N(2)—Fe(2)—P(3)	89.34(8)
N(1)—Fe(1)—P(2)	92.60(7)	N(2)—Fe(2)—P(4)	95.29(8)
N(1)—Fe(1)—N(3)	115.61(12)	N(2)—Fe(2)—N(4)	117.62(12)
P(1)—Fe(1)—N(3)	108.70(9)	P(3)—Fe(2)—N(4)	103.50(10)
P(2)—Fe(1)—N(3)	103.95(9)	P(4)—Fe(2)—N(4)	107.74(10)
Fe(1)—N(3)—N(4)	166.3(3)	Fe(2)—N(4)—N(3)	170.9(3)

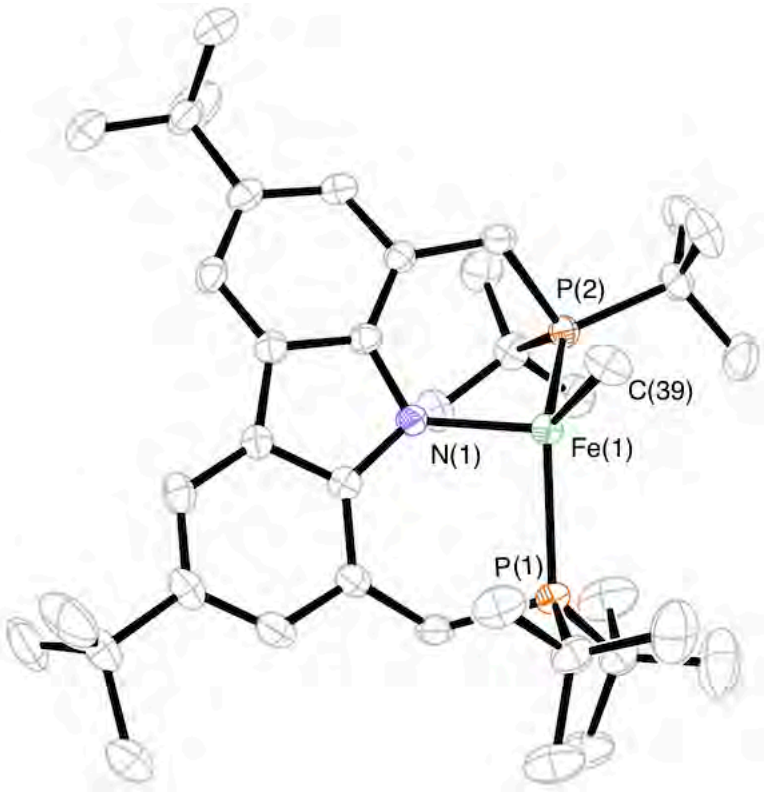
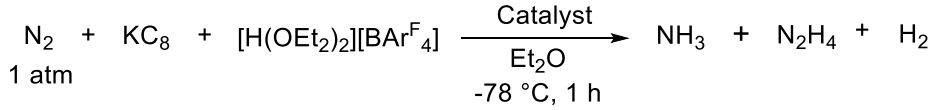


Figure S5. ORTEP drawing of **8a**·0.5$C_4H_{10}O$. Thermal ellipsoids are shown at the 50% probability level. Only one of the two crystallographically independent molecules is shown, while minor disorder components, hydrogen atoms, and solvated molecules are omitted for clarity.

Table S6. Selected Bond Lengths (Å) and Angles (deg) for **8a**·0.5$C_4H_{10}O$.

Fe(1)—N(1)	1.9986(19)	Fe(2)—N(2)	2.0037(19)
Fe(1)—P(1)	2.4530(7)	Fe(2)—P(3)	2.4400(8)
Fe(1)—P(2)	2.5181(7)	Fe(2)—P(4)	2.4404(7)
Fe(1)—C(39)	2.064(2)	Fe(2)—C(78)	2.050(3)
P(1)—Fe(1)—P(2)	126.39(2)	P(3)—Fe(2)—P(4)	135.61(3)
N(1)—Fe(1)—P(1)	95.90(6)	N(2)—Fe(2)—P(3)	95.05(6)
N(1)—Fe(1)—P(2)	86.92(6)	N(2)—Fe(2)—P(4)	95.07(6)
N(1)—Fe(1)—C(39)	120.04(10)	N(2)—Fe(2)—C(78)	105.64(10)
P(1)—Fe(1)—C(39)	114.14(8)	P(3)—Fe(2)—C(78)	109.88(9)
P(2)—Fe(1)—C(39)	110.01(8)	P(4)—Fe(2)—C(78)	108.65(8)

Catalytic Reduction of Dinitrogen to Ammonia and Hydrazine under N_2 (1 atm).



Catalytic reduction of dinitrogen into ammonia and hydrazine was carried out according to a method similar to the Peters' procedure.[S10] A typical experimental procedure using **7a** is described below.

In a 50 mL Schlenk flask were placed **7a** (5.9 mg, 0.0050 mmol), KC_8 (54.1 mg, 0.400 mmol), and $[H(OEt_2)_2]BAr^F{}_4$ (385 mg, 0.380 mmol). After the mixture was cooled to -196 °C, Et_2O (5 mL) was added to the mixture by trap-to-trap distillation. The Schlenk flask was warmed to -78 °C and then was filled with N_2 (1 atm). After stirring at -78 °C for 1 h, the mixture was warmed to room temperature and further stirred at room temperature for 20 min. The amount of dihydrogen evolved in the reaction was determined by GC analysis. The reaction mixture was evaporated under reduced pressure, and the distillate was trapped in dilute H_2SO_4 solution (0.5 M, 10 mL). Aqueous solution of potassium hydroxide (30 wt%, 5 mL) was added to the residue, and the mixture was distilled into another dilute H_2SO_4 solution (0.5 M, 10 mL). The amount of NH_3 present in each of the H_2SO_4 solutions was determined by the indophenol method.[S11] The amount of NH_2NH_2 present in each of the H_2SO_4 solutions was determined by the *p*-(dimethylamino)benzaldehyde method.[S12]

References.

S1. (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. (b) Live, D. H.; Chan, S. I. *Anal. Chem.* **1970**, *42*, 791. (c) Bain, G. A.; Berry, J. F. *J. Chem. Educ.* **2008**, *85*, 532.

S2. (a) Gibson, V. C.; Spitzmesser, S. K.; White, A. J. P.; Williams, D. J. *Dalton Trans.* **2003**, 2718. (b) Grüger, N.; Rodríguez, L.-I.; Wadepohl, H.; Gade, L. H. *Inorg. Chem.* **2013**, *52*, 2050.

S3. Kern, R. J. *J. Inorg. Nucl. Chem.* **1962**, *24*, 1105.

S4. Wietz, I. S.; Rabinovitz, M. *J. Chem. Soc., Perkin Trans.* **1993**, *1*, 117.

S5. Brookhart, M.; Grant, B.; Volpe, Jr., A. F. *Organometallics* **1992**, *11*, 3920.

S6. *CrystalStructure 4.0*: *Single Crystal Structure Analysis Software*; Rigaku Corp: Tokyo, Japan, and MSC: The Woodlands, TX, 2010.

S7. Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidorib, G.; Spagnac, R. *J. Appl. Crystallogr.* **1999**, *32*, 115–119.

S8. Sheldrick, G. M. *Acta crystallogr.* **2008**, *A64*, 112-122.

S9. Spek, A. L. *PLATON: A Multipurpose Crystallographic Tool.* Utrecht University: Utrecht, The Netherlands, 1998.

S10. (a) Anderson, J. S.; Rittle, J.; Peters, J. C. *Nature* **2013**, *501*, 84. (b) Creutz, S. E.; Peters, J. C. *J. Am. Chem. Soc.* **2014**, *136*, 1105. (c) Ung, G.; Peters, J. C. *Angew. Chem. Int. Ed.* **2015**, *54*, 532.

S11. Weatherburn, M. W. *Anal. Chem.* **1967**, *39*, 971.

S12. Watt, G. W.; Chrisp, J. D. *Anal. Chem.* **1952**, *24*, 2006.