

Iron-mediated Intermolecular *N*-Group Transfer Chemistry with Olefinic Substrates

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General Considerations

All manipulations of metal complexes were carried out in the absence of water and dioxygen using standard Schlenk techniques, or in an MBraun inert atmosphere drybox under a dinitrogen atmosphere. All glassware was oven dried for a minimum of 1 h and cooled in an evacuated antechamber prior to use in the drybox. Benzene and diethyl ether were dried and deoxygenated on a Glass Contour System (SG Water USA, Nashua, NH) and stored over 4 Å molecular sieves (Strem) prior to use. Chloroform-*d* was purchased from Cambridge Isotope Labs and used as received. Benzene-*d*₆ was purchased from Cambridge Isotope Labs and was degassed and stored over 4 Å molecular sieves prior to use. All reagents, unless otherwise specified, were purchased from Aldrich and used as received. *Cis*-β-deuterostyrene was synthesized according to literature procedure,¹ using Schwartz's reagent and freshly prepared d₁-phenylacetylene. Allylic amination substrates were distilled from CaH₂ and deoxygenated prior to use in the amination reactions. Celite® 545 (J. T. Baker) was dried in a Schlenk flask for 24 h under dynamic vacuum while heating to at least 150 °C prior to use in a drybox. Silica gel 32-63 μ (AIC, Framingham, MA) was used as received.

Characterization and Physical Measurements

¹H, ¹³C, and were recorded on Varian Mercury 400 MHz or Varian Unity/Inova 500 MHz spectrometers. ¹H and ¹³C NMR chemical shifts are reported relative to SiMe₄ using the chemical shift of residual solvent peaks as reference. Gas chromatography/mass spectrometry (GC/MS) was performed on an Agilent GC/MS 5975 Turbo system. Elemental analyses were carried out by Complete Analysis Laboratories, Inc. (Parsippany, NJ).

Catalysis and Competition Experiments

General Procedure for Amination and Aziridination Reactions. Under an inert N₂ atmosphere, 1-azidoadamantane (1–10 equiv.) was added to a stirring solution of (^{Ad}LCl₂)FeCl(OEt₂) (**1**) (20 mg, 0.028 mmol) or (^{tBu}LCl₂)FeCl(OEt₂) (**2**) (16 mg, 0.028 mmol) in 1 mL of substrate in a 20 mL scintillation vial. The resultant inky, dark red solution was stirred for 12 hours at 25 °C. The dark mixture was flash chromatographed through a short pipette of triethylamine-treated silica gel (10:1 hexanes:EtOAc) to yield a brightly colored solution. The

1. L. T. Ball, G. C. Lloyd-Jones and C. A. Russell, *Chem.-Eur. J.*, 2012, **18**, 2931.

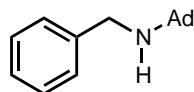
solvent was removed *in vacuo* to yield pure amine or aziridine product. The yields were determined by ^1H NMR *via* integration against ferrocene, averaging over three runs for each substrate. GC/MS yields for allylic amination reactions were also obtained after obtaining a calibration curve for the desired allylic amine products. Products were isolated for characterization via silica gel flash chromatography using 9:1 DCM:MeOH as eluent.

Determination of Substituent Effects for Amination and Aziridination Reactions via Competition Experiments. Under an inert N_2 atmosphere, 1 mL of an equimolar mixture of the two substrates was added to 1-azidoadamantane (6.1 mg, 0.028 mmol, 1 equiv) and ($^{\text{Ad}}\text{L}_{\text{Cl}_2}$)FeCl(OEt₂) (**1**) (10 mg, 0.014 mmol, 1 equiv.) in a 20 mL scintillation vial. The resultant inky, dark red solution was stirred for 12 hours at 25 °C. The dark mixture was flash chromatographed through a short pipette of silica gel (20:1 CH_2Cl_2 :MeOH) to yield a red solution. For the aziridination reactions, relative ratios were determined by ^1H NMR via integration of the benzylic resonance (dd, $\delta \sim 2.5\text{-}3$ ppm). For the amination reactions, relative ratios were determined by GC/MS. Yields were averaged over three runs. Table S-1 lists values and parameters used to plot the data.

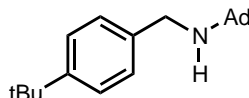
Table S-1. Competition Experiment Details. Variation of $\log k_R$ with σ^+ , σ_{mb} , σ_{JJ}^\bullet scales for the aziridination and amination of *para*-substituted styrenes and toluenes.

Substrate (para substituent)	Product Ratio	$\log k$ (exptl_avg)	$\log k_{avg}$ (std dev)	σ^+	σ_{mb}	σ_{JJ}^\bullet	$\log k_R$ (calcd) ^b
Aziridination							
Cl	1.15	0.06070	0.0311	0.11	0.11	0.18	0.0324
	1.09	0.03742	(0.014)				
	1.08	0.03342					
Br	1.13	0.05308	0.0452	0.15	0.13	0.26	0.0459
	1.07	0.02938	(0.015)				
	1.06	0.02531					
OMe	1.21	0.08279	0.0801	-0.78	-0.77	0.42	0.0793
	1.19	0.07555	(0.004)				
	1.21	0.08278					
Amination							
Cl	1.09	0.03743	0.0559	0.11	0.11	0.18	0.0521
	1.25	0.09691	(0.036)				
	1.08	0.03342					
Br	1.17	0.06819	0.0703	0.15	0.13	0.26	0.0725
	1.12	0.04922	(0.022)				
	1.24	0.09342					
OMe	1.09	0.03743	0.0334	-0.78	-0.77	0.42	0.0333
	1.09	0.03743	(0.007)				
	1.06	0.02531					
<i>t</i> Bu	1.2	0.07918	0.0426	-0.26	-0.22	0.26	0.0427
	1.05	0.02119	(0.032)				
	1.06	0.02531					

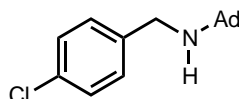
Characterization Data



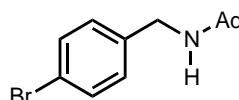
***N*-benzyladamantan-1-amine**²



***N*-(4-(*tert*-butyl)benzyl)adamantan-1-amine:** ¹H NMR (500 MHz, CDCl₃) δ/ppm 7.34 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 3.73 (s, 3H), 2.10 (m, 3H), 1.77–1.59 (m, 12H), 1.30 (m, 9H). ¹³C NMR (100 MHz, CDCl₃) δ: 149.6, 138.3, 128.0, 125.3, 51.1, 44.7, 42.7, 36.7, 34.4, 31.4, 29.6. IR (thin film) n_{\max} = 2966, 2908, 2852, 1718, 1516, 1454, 1362, 1311, 1265, 1136, 1097 cm⁻¹. HRMS (ESI⁺) *m/z* Calc. 298.2564 [C₂₁H₃₁N+H]⁺, Found 298.2571 [M+H]⁺.



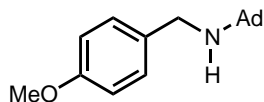
***N*-(4-chlorobenzyl)adamantan-1-amine:** ¹H NMR (500 MHz, CDCl₃) δ: 7.32–7.21 (m, 4H), 3.72 (s, 3H), 2.11–2.05 (m, 3H), 1.71–1.56 (m, 12H). ¹³C NMR (125 MHz, CDCl₃) δ: 140.0, 132.3, 129.6, 128.4, 51.0, 44.4, 42.7, 36.6, 31.4, 29.7. IR (thin film) n_{\max} = 2931, 2852, 1723, 1493, 1451, 1359, 1312, 1265, 1137, 1097. HRMS (ESI⁺) *m/z* Calc. 276.1549 [C₁₇H₂₂ClN+H]⁺, Found 276.1544 [M+H]⁺.



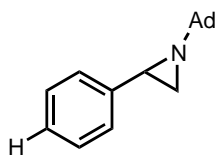
***N*-(4-bromobenzyl)adamantan-1-amine:** ¹H NMR (500 MHz, CDCl₃) δ: 7.30 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 3.76 (s, 3H), 3.71 (s, 3H), 2.08 (m, 3H), 1.75 (m, 6H), 1.65 (q, *J* = 12.1 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ: 158.7, 131.8, 130.0, 113.8, 55.2, 53.4, 44.3, 42.0,

2. For physical and spectroscopic characterization data, see: S. Calet, F. Urso and H. Alper, *J. Am. Chem. Soc.*, 1989, **111**, 931.

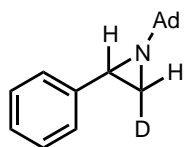
36.5, 31.6, 29.5. **IR** (thin film) $n_{\max} = 2960, 2932, 2912, 1720, 1613, 1513, 1458, 1252, 1248, 1137, 1037 \text{ cm}^{-1}$. **HRMS** (ESI⁺) m/z Calc. 272.2014 [C₁₈H₂₅NO+H]⁺, Found 272.2005 [M+H]⁺.



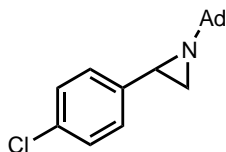
N-(4-methoxybenzyl)adamantan-1-amine: ¹H NMR (400 MHz, CDCl₃) δ : 7.42 (d, $J = 8.4$ Hz, 2H), 7.23 (d, $J = 8.4$ Hz, 2H), 3.71 (s, 2H), 2.09 (m, 3H), 1.73–1.63 (m, 12H). ¹³C NMR (100 MHz, CDCl₃) δ /ppm 140.8, 131.6, 130.2, 120.7, 53.7, 44.7, 43.0, 36.8, 29.9. **IR** (thin film) $n_{\max} = 2911, 2851, 1702, 1591, 1488, 1450, 1358, 1098, 1070 \text{ cm}^{-1}$. **HRMS** (ESI⁺) m/z Calc. 320.0954 [C₁₆H₂₂NBr+H]⁺, Found 320.0968 [M+H]⁺.



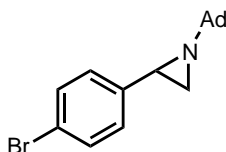
1-(adamantan-1-yl)-2-phenylaziridine: ¹H NMR (600 MHz, CDCl₃) δ /ppm 7.34–7.30 (m, 2 H), 7.28 (t, $J = 7.6$ Hz, 2 H), 7.22 - 7.18 (m, 1 H), 2.81 (dd, $J = 3.2, 6.2$ Hz, 1 H), 2.10 (br. s., 3 H), 2.07 (d, $J = 6.2$ Hz, 1 H), 1.72–1.66 (m, 3 H), 1.64 (m, 6 H), 1.62 (d, $J = 3.2$ Hz, 1 H). ¹³C NMR (125 MHz, CDCl₃) δ /ppm 141.5, 128.1, 126.7, 126.5, 52.8, 40.4, 39.8, 31.7, 29.5, 28.4. **HRMS** (ESI⁺) m/z Calc. 254.1909 [C₁₈H₂₃N+H]⁺, Found 254.1940 [M+H]⁺.



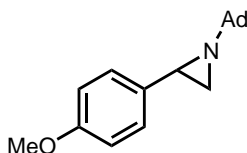
1-(adamantan-1-yl)-3-deutero-2-phenylaziridine: ¹H NMR (500 MHz, CDCl₃) δ : 7.33–7.25 (m, 4 H), 7.23 - 7.17 (m, 1 H), 2.81 (d, $J = 6.4$ Hz, 1 H), 2.09 (br. s., 3 H), 2.06 (d, $J = 6.4$ Hz, 1 H), 1.72–1.66 (m, 3 H), 1.62 (br. s., 6 H).



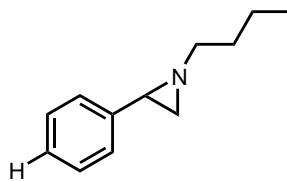
1-(adamantan-1-yl)-2-(4-chlorophenyl)aziridine: ^1H NMR (500 MHz, CDCl_3) δ /ppm 7.24 (m, 4H), 2.76 (dd, $J = 6.3, 3.0$ Hz, 1H), 2.12–2.01 (m, 5H), 1.79–1.47 (m, 12H). ^{13}C NMR (125 MHz, CDCl_3) δ /ppm 140.4, 132.3, 128.4, 128.2, 53.1, 40.6, 37.0, 34.9, 31.8, 29.7. IR (thin film) $n_{\text{max}} = 2955, 2852, 1722, 1492, 1456, 1356, 1311, 1265, 1136, 1076$ cm^{-1} . HRMS (ESI^+) m/z Calc. 288.1514 [$\text{C}_{18}\text{H}_{22}\text{NCl}+\text{H}$] $^+$, Found 288.1508 [$\text{M}+\text{H}$] $^+$.



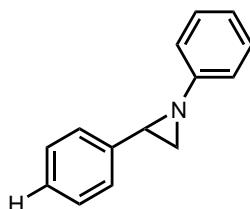
1-(adamantan-1-yl)-2-(4-bromophenyl)aziridine: ^1H NMR (500 MHz, CDCl_3) δ /ppm 7.38 (d, $J = 8.4$ Hz, 2H), 7.18 (d, $J = 8.5$ Hz, 2H), 2.74 (dd, $J = 6.4, 3.0$ Hz, 1H), 2.11–2.02 (m, 5H), 1.76–1.37 (m, 12H). ^{13}C NMR (125 MHz, CDCl_3) δ /ppm 144.7, 140.9, 131.4, 128.6, 53.1, 45.7, 40.6, 37.0, 31.8, 29.7. IR (thin film) $n_{\text{max}} = 2910, 2899, 1488, 1450, 1358, 1289, 1136, 1012$ cm^{-1} . HRMS (ESI^+) m/z Calc. 332.1008 [$\text{C}_{18}\text{H}_{22}\text{NBr}+\text{H}$] $^+$, Found 332.1000 [$\text{M}+\text{H}$] $^+$.



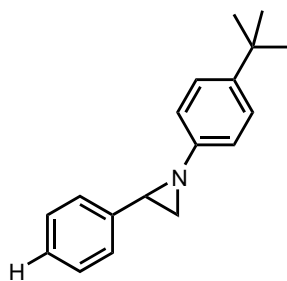
1-(adamantan-1-yl)-2-(4-methoxyphenyl)aziridine: ^1H NMR (600 MHz, CDCl_3) δ 7.29 (d, $J = 8.6$ Hz, 2H), 6.89 (d, $J = 8.6$ Hz, 2H), 3.84 (s, 3H), 2.17–2.13 (m, 5H), 1.71–1.30 (m, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ /ppm 164.3, 131.4, 127.8, 113.7, 55.4, 52.8, 40.5, 37.0, 31.8, 29.9. IR (thin film) = 2959, 2913, 2855, 1613, 1513, 1300, 1248, 1036 cm^{-1} . HRMS (ESI^+) m/z Calc. 284.2009 [$\text{C}_{19}\text{H}_{25}\text{NO}+\text{H}$] $^+$, Found 284.2012 [$\text{M}+\text{H}$] $^+$.



1-butyl-2-phenylaziridine³



1,2-diphenylaziridine⁴



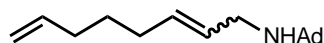
1-(4-(*tert*-butyl)phenyl)-2-phenylaziridine³



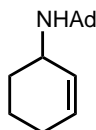
***N*-(hex-2-en-1-yl)adamantan-1-amine:** ¹H NMR (600 MHz, C₆D₆) δ (mixture of *E* and *Z* isomers): 6.26–6.34 (m, 0.3 H), 6.12–6.21 (m, 0.7 H), 5.58–5.72 (m, 2 H), 3.46 (d, *J* = 7.0 Hz, 0.6 H), 3.30 (d, *J* = 7.0 Hz, 1.4 H), 2.07–2.14 (m, 6 H), 1.97–2.05 (m, 2 H), 1.84–1.90 (m, 3 H),

3. For physical and spectroscopic characterization, see: S. Fantauzzi, E. Gallo, A. Caselli, C. Piangiolo, F. Ragaini and S. Cenini, *Eur. J. Org. Chem.*, 2007, **36**, 6053.
4. For physical and spectroscopic characterization, see: W. Chamchaang and A. R. Pinhas, *J. Org. Chem.*, 1990, **55**, 2943.

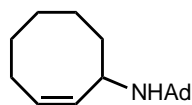
1.34–1.49 (m, 8 H), 0.87 - 0.93 (m, 3 H). ^{13}C NMR (125 MHz, C_6D_6) δ (Z-olefin in parentheses): 137.7(135.2), 122.8(122.5), 57.3, 42.4, 36.7(37.2), 35.8, 34.7, 29.5, 22.4(22.7), 13.9. HRMS (ESI⁺) m/z Calc. 234.4017 [$\text{C}_{16}\text{H}_{27}\text{N}+\text{H}$]⁺, Found 234.4012 [$\text{M}+\text{H}$]⁺.



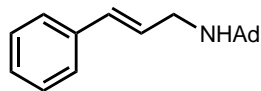
N-(octa-2,7-dien-1-yl)adamantan-1-amine: ^1H NMR (600 MHz, C_6D_6) δ : 5.72 (ddt, $J = 16.7$, 9.9, 6.7 Hz, 2 H), 5.61–5.49 (m, 1 H), 5.03–4.90 (m, 2 H), 3.26 (d, $J = 6.8$ Hz, 0.3 H), 3.17 (d, $J = 6.8$ Hz, 1.7 H), 1.99–1.85 (m, 7 H), 1.62 (br. s., 6 H), 1.55–1.43 (m, 6 H), 1.38 (p, $J = 7.5$ Hz, 2 H). ^{13}C NMR (125 MHz, C_6D_6) δ : 138.9, 131.5, 130.2, 114.8, 51.3, 43.1, 42.7, 36.9, 33.6, 32.2, 30.0, 29.0. HRMS (ESI⁺) m/z Calc. 260.4392 [$\text{C}_{18}\text{H}_{29}\text{N}+\text{H}$]⁺, Found 260.4388 [$\text{M}+\text{H}$]⁺.



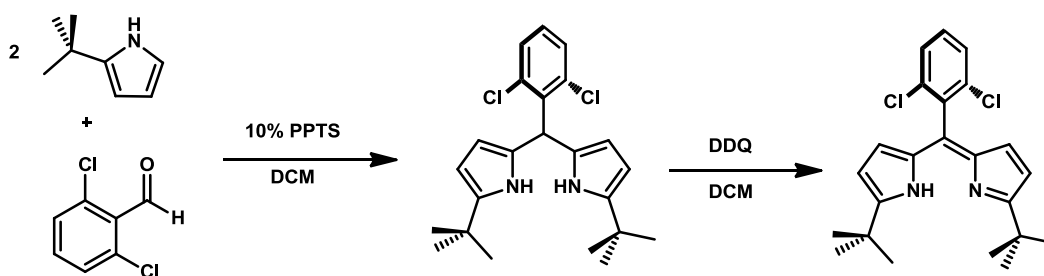
N-(cyclohex-2-en-1-yl)adamantan-1-amine: ^1H NMR (600 MHz, C_6D_6) δ : 6.21 (d, $J = 10.0$ Hz, 1 H), 5.81–5.87 (m, 1 H), 3.48–3.56 (m, 1 H), 2.32–2.45 (m, 2 H), 2.13 (br. s., 6 H), 1.90 (br. s., 5 H), 1.79–1.87 (m, 1 H), 1.68–1.77 (m, 1 H), 1.31–1.56 (m, 6 H). ^{13}C NMR (125 MHz, C_6D_6) δ : 132.1, 126.8, 59.1, 49.2, 39.1, 36.2, 30.0, 29.3, 24.9, 21.1. HRMS (ESI⁺) m/z Calc. 234.4017 [$\text{C}_{15}\text{H}_{23}\text{N}+\text{H}$]⁺, Found 234.4018 [$\text{M}+\text{H}$]⁺.



N-(cyclooct-2-en-1-yl)adamantan-1-amine: ^1H NMR (500 MHz, CDCl_3) δ 5.50–5.58 (m, 1 H), 5.30–5.38 (m, 1 H), 3.79–3.92 (m, 1 H), 2.13–2.24 (m, 1 H), 1.99–2.12 (m, 4 H), 1.51–1.76 (m, 16 H), 1.30–1.44 (m, 4 H). ^{13}C NMR (125 MHz, CDCl_3) δ 138.3, 127.1, 51.6, 47.3, 44.1, 39.0, 36.8, 29.9, 29.8, 27.5, 27.3, 24.9, 22.8. HRMS (ESI⁺) m/z Calc. 260.2382 [$\text{C}_{18}\text{H}_{29}\text{NO}+\text{H}$]⁺, Found 260.2373 [$\text{M}+\text{H}$]⁺.



N-cinnamyladamantan-1-amine: $^1\text{H NMR}$ (500 MHz, CDCl_3) δ /ppm 7.23–7.15 (m, 3H), 7.12 (d, $J = 7.2$ Hz, 2H), 6.48–6.41 (m, 1H), 6.29 (d, $J = 13.0$ Hz, 1H), 3.35 (d, $J = 6.3$ Hz, 1H), 1.97 (m, 3H), 1.64 (m, 6H), 1.55 (m, 6H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ /ppm 137.3, 128.7, 127.6, 126.6, 52.0, 43.2, 42.5, 36.8, 29.9. **HRMS** (ESI^+) m/z . Calc. 268.2065 [$\text{C}_{19}\text{H}_{25}\text{N}+\text{H}$] $^+$, Found 268.2069 [$\text{M}+\text{H}$] $^+$.



1,9-di(*tert*-butyl)-5-(2,6-dichloro)benzene-dipyrrromethane ($^{\text{tBu}}\text{L}_{\text{Cl}_2}\text{H}$): A 500 mL round-bottom flask was charged with 2-*tert*-butylpyrrole (7.5 g, 60.9 mmol), 2,6-dichlorobenzaldehyde (5.3 g, 30.3 mmol, 0.5 equiv.) and 200 mL of dry CH_2Cl_2 . After stirring until all materials were dissolved, pyridinium *p*-toluenesulfonate (1.5 g, 5.98 mmol, 0.1 equiv.) was added. The reaction was refluxed at 40 °C for 12 h. The solution was concentrated *in vacuo* and filtered through a plug of silica gel in a medium porosity frit (150 mL) with CH_2Cl_2 to give an orange filtrate. Solvent was removed *in vacuo* affording 1,9-di(*tert*-butyl)-5-(2,6-dichloro)benzene-dipyrrromethane (12.2 g, 99%) as an orange oil. $^1\text{H NMR}$ (500 MHz, CDCl_3): 8.00 (br. s, 2 H), 7.28–7.35 (m, 2 H), 7.11 (d, $J = 0.76$ Hz, 1 H), 6.40 (s, 1 H), 5.82–5.91 (m, 4 H), 1.25 (s, 18 H). The product (12.2 g, 30.4 mmol) was dissolved in 300 mL CH_2Cl_2 . The oxidant, 2,3-dichloro-5,6-dicyanoquinone (DDQ) (7.1 g, 31.3 mmol, 1 equiv.), was added to immediately give a dark red solution which was stirred overnight. The solution was concentrated *in vacuo* and residue was dissolved in ethyl acetate (350 mL) and was washed with saturated aqueous sodium bicarbonate, water and brine, dried over magnesium sulfate, filtered and concentrated *in vacuo* to give a brown solid. The product was loaded onto an alumina plug and eluted with 10:1 hexanes:ethyl acetate to give a red filtrate. Solvent was removed *in vacuo* and resulting solid was

trituated with acetonitrile to give (^tBuLCl₂)H (8.2 g, 68%) as a brown-orange solid. ¹H NMR (500 MHz, C₆D₆): δ 13.35 (br. s, 1 H), 6.96 (dd, *J* = 8.01, 0.76 Hz, 2 H), 6.55 (m, 1 H), 6.47 (d, *J* = 4.20 Hz, 2 H), 6.24 (d, *J* = 4.20 Hz, 2 H), 1.28 (s, 18 H). ¹³C NMR (125 MHz, C₆D₆): δ 167.0, 139.1, 136.5, 135.9, 132.8, 129.8, 127.6, 126.9, 115.2, 33.6, 29.8. HRMS (ESI⁺) *m/z*. Calc. 401.1546 [C₂₃H₂₇Cl₂N₂+H]⁺, Found. 401.1562 [M+H]⁺.

^tBuLCl₂FeCl(OEt₂) (**2**): Complex was prepared following literature precedent⁵ from the corresponding ligand ^tBuLCl₂(H). ¹H NMR: (500 MHz, C₆D₆): δ 59.54. (s), 21.42 (br. s), 10.65 (br. s), 6.82 (br. s), 1.61 (br. s), -5.68 (br. s). Elemental Anal. Calc. for C₂₇H₃₅Cl₃FeN₂O: C 57.32, H 6.24, N 4.95; Found: C 57.37, H 6.27, N 4.89. Single crystals of **2** were obtained by storing a concentrated diethyl ether solution at room temperature (Figure S-1).

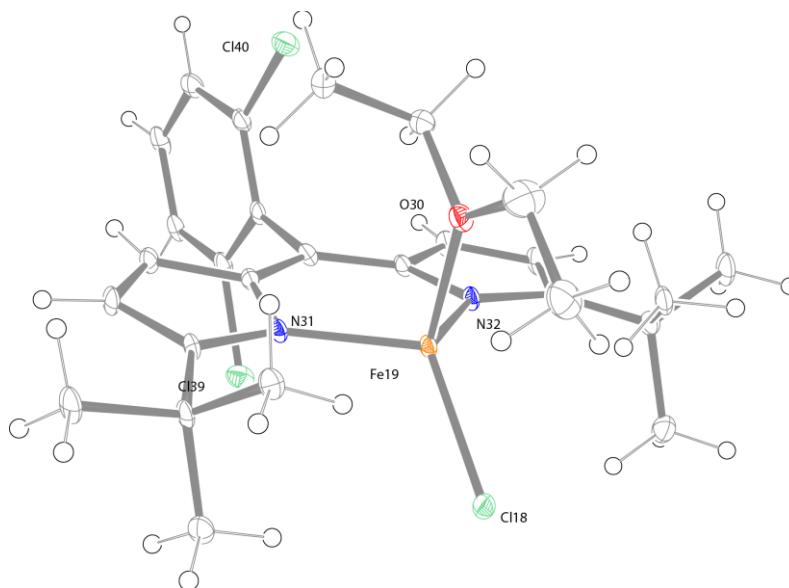


Figure S-1. Solid-state structure for **2** with the thermal ellipsoids set at 50% probability level (Fe orange, N blue, O red, C gray, H white).

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Table S-2. X-ray crystallographic experimental details for **2**.

2	
Formula	C ₂₇ H ₃₅ FeN ₂ O
FW	565.77
Crystal System	Orthorhombic
Space Group (Z)	Pbca (8)
a (Å)	15.980(3)
b (Å)	14.393(2)
c (Å)	24.368(4)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
Volume (Å³)	5604.7(16)
Calc. ρ (g/cm³)	1.341
μ (mm⁻¹)	0.846
Reflections	5371
Compl. (to 2θ)	99.4
GOF on F²	0.984
R1, wR2^c	0.0594
[I>2σ(I)]	0.1665

^a λ = 0.71073 Å; ^b T = 100(2) K; ^c R1 = $\Sigma||F_o| - |F_c|| / \Sigma|F_o|$, wR2 = $\{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)]\}^{1/2}$