

Supporting Information for

**Catalytic Nitrene Transfer from an Imidoiron(III) Complex**

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<b>General Considerations</b>	<b>S-2</b>
<b>Synthetic Details</b>	<b>S-2 to S-4</b>
<b>EPR Spectroscopy</b>	<b>S-5</b>
<b>Figure S-1.</b> X-Band EPR spectrum of $L^{tBu}Fe(CNtBu)_3$	<b>S-5</b>
<b>Crystallographic Details</b>	<b>S-6</b>
<b>Table S-1.</b> Crystal data for $L^{tBu}Fe(CNtBu)_3$	<b>S-6</b>
<b>References</b>	<b>S-7</b>

## General Considerations

All air-sensitive manipulations were performed under a nitrogen atmosphere by standard Schlenk techniques or in an MBraun glovebox maintained at or below 1 ppm of O<sub>2</sub> and H<sub>2</sub>O. 1-Azidoadamantane (AdN<sub>3</sub>) was crystallized twice from pentane prior to use. Cyclohexylisocyanide and *tert*-butylisocyanide were purchased commercially and stored over 4 Å molecular sieves. The compound L<sup>tBu</sup>FeNNFeL<sup>tBu</sup> was prepared as previously described.<sup>1</sup> Pentane and toluene were purified by passage through activated alumina and “deoxygenizer” columns from Glass Contour Co. (Laguna Beach, CA, USA). C<sub>6</sub>D<sub>6</sub> was dried over CaH<sub>2</sub>, freeze-pump-thaw degassed, and vacuum transferred from a purple sodium benzophenone ketyl into a storage container. Before use, an aliquot of each solvent was tested with a drop of sodium benzophenone ketyl solution in THF. Celite was dried at 200 °C overnight under vacuum. All glassware was dried overnight at 150 °C. NMR data were collected on either a Bruker Avance 400 or Bruker Avance 500 spectrometer at 25 °C. <sup>1</sup>H NMR spectra are referenced to the residual protiated solvent (CHCl<sub>3</sub>, 7.26; C<sub>6</sub>D<sub>5</sub>H, 7.16 ppm). <sup>13</sup>C NMR spectra are referenced to TMS (0.00 ppm) or C<sub>6</sub>D<sub>5</sub>H (128.1 ppm). IR data were recorded on a Shimadzu 8400S spectrometer; samples were either thin films deposited on a NaCl plate, or obtained in a solution cell with CsF windows. UV-Vis spectra were recorded on a Cary 50 spectrometer using screw-cap cuvettes. Mass spectrometry analyses were performed on an HP 100 MSD with an APCI interface. Elemental analyses were determined by Desert Analytics, Tucson, AZ, USA.

### L<sup>tBu</sup>Fe=NAd

A general procedure for preparation of a solution of L<sup>tBu</sup>Fe=NAd is given: A J-Young NMR tube was charged with L<sup>tBu</sup>FeNNFeL<sup>tBu</sup> (12 mg, 10.5 μmol) and C<sub>6</sub>D<sub>6</sub> (0.4 mL). A 137 mM solution of N<sub>3</sub>Ad in C<sub>6</sub>D<sub>6</sub> was prepared, and the appropriate aliquot was added to the reaction (160 μL, 21.5 μmol, 2.05 eq). The solution immediately developed an orange-red color, concomitant with effervescence. <sup>1</sup>H NMR integration against an internal standard (sealed capillary of L<sup>tBu</sup>FeCl<sub>2</sub> in C<sub>6</sub>D<sub>6</sub>) after 3 minutes shows L<sup>tBu</sup>Fe=NAd is formed in 86% yield. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 77 (6H, Ad-α), 43 (1H, backbone α-H), 38 (3H, Ad-β or Ad-γ), 33 (3H, Ad-β or Ad-γ), 23 (3H, Ad-β or Ad-γ), 20 (18H, C(CH<sub>3</sub>)<sub>3</sub>), -9 (4H, *m*-Ar or CH(CH<sub>3</sub>)<sub>2</sub>), -13 (12H, CH(CH<sub>3</sub>)<sub>2</sub>), -38 (2H, *p*-Ar), -57 (12H, CH(CH<sub>3</sub>)<sub>2</sub>), -59 (4, *m*-Ar or CH(CH<sub>3</sub>)<sub>2</sub>). UV/vis (toluene, λ (nm), ε (mM<sup>-1</sup>cm<sup>-1</sup>)): 335 (18), 435 (3.5), 530(sh), 660(sh). IR (pentane): 3182(w), 2978(s), 2955(s), 2922(vs), 2870(m), 2858(m), 1456(s), 1379(m), 1342(w), 1327(w), 1308(w), 1263(w), 1138(m), 1014(w), 920(m), 908(m) cm<sup>-1</sup>.

### AdN=C=NCy

To a stirring solution of L<sup>tBu</sup>FeNNFeL<sup>tBu</sup> (125 mg, 0.109 mmol) in toluene (20 mL) was added cyclohexylisocyanide (0.27 mL, 2.18 mmol, 20 equiv), followed by addition of a solution of 1-azidoadamantane (386 mg, 2.18 mmol, 20 equiv) in toluene (3 mL). The solution was heated at 60 °C for 22 h. The solution was cooled, and the volatile materials were removed under vacuum, affording a dark brown oil. The oil was exposed to air and taken up in a minimum of diethyl ether (~ 2 mL). This solution was passed through a column of silica (1 cm × 18 cm) using diethyl ether as eluent and the volatile materials were removed under vacuum. Kügelrohr distillation of the resulting yellow oil (0.02

mbar, ~110 °C) afforded 1-AdN=C=NCy as an off-white solid (512 mg, 91%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.19 (m, 1H, Cy-αH), 2.09 (s, 3H, Ad-β), 1.92 (m, 2H, Cy-H), 1.80 (s, 6H, Ad-α), 1.76 (m, 2H, Cy-H), 1.64 (m, 6H, Ad-γ), 1.32 – 1.05 (m, 6H, Cy-H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 140, 55.9, 55.0, 44.8, 36.0, 35.0, 29.9, 25.5, 24.8 ppm. FTIR (thin film): 2925 (s), 2905 (s), 2850 (m), 2112 (vs), 2049 (w), 1436 (w), 1353 (w), 1302 (w), 1260 (w), 1101 (w), 1074 (m), 1015 (w), 937 (w), 890 (w), 665 (m) cm<sup>-1</sup>. GC/MS (APCI<sup>+</sup>): *m/z* 259 (MH<sup>+</sup>). Anal. Calcd. for C<sub>17</sub>H<sub>26</sub>N<sub>2</sub> (FW = 258.4): C, 79.02; H, 10.14; N, 10.84. Found: C, 79.57; H, 10.29; N, 10.84.

### AdN=C=N<sup>t</sup>Bu

To a stirring solution of L<sup>tBu</sup>FeNNFeL<sup>tBu</sup> (125 mg, 0.109 mmol) in toluene (20 mL) was added *tert*-butylisocyanide (0.25 mL, 2.18 mmol, 20 equiv), followed by addition of a solution of 1-azidoadamantane (386 mg, 2.18 mmol, 20 equiv) in toluene (3 mL). The solution was heated at 60 °C for 18 h. The solution was cooled, and the volatile materials were removed under vacuum, affording a dark brown oil. The oil was exposed to air and taken up in a minimum of diethyl ether (~ 2 mL). This solution was passed through a column of silica (1 cm × 18 cm) using diethyl ether as eluent and the volatile materials were removed under vacuum. Kugelrohr distillation of the resulting dark yellow oil (0.9 mbar, ~100 °C) afforded AdN=C=N<sup>t</sup>Bu as a waxy off-white solid (461 mg, 91%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.08 (s, 3H, Ad-β), 1.78 (s, 6H, Ad-α), 1.62 (m, 6H, Ad-γ), 1.28 (s, 9H, <sup>t</sup>Bu). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 139, 55.0, 54.9, 44.9, 36.1, 31.3, 29.9 ppm. FTIR (thin film): 2967 (m), 2907 (s), 2851 (m), 2124 (vs), 2103 (vs), 2042 (w), 1452 (w), 1391 (w), 1364 (m), 1353 (m), 1306 (w), 1236 (m), 1187 (s), 1102 (m), 1069 (s), 934 (w), 906 (m), 848 (w), 813 (w), 733 (w), 665 (s), 612 (m) cm<sup>-1</sup>. GC/MS (APCI<sup>+</sup>): *m/z* 233 (MH<sup>+</sup>). Anal. Calcd. for C<sub>15</sub>H<sub>24</sub>N<sub>2</sub> (FW = 232.4): C, 77.53; H, 10.41; N, 12.06. Found: C, 77.21; H, 10.12; N, 11.84.

### Catalytic formation of *p*-TolylN=C=N<sup>t</sup>Bu

A J-Young NMR tube was loaded with L<sup>tBu</sup>FeNNFeL<sup>tBu</sup> (8.0 mg, 7.0 μmol) and C<sub>6</sub>D<sub>6</sub> (0.7 mL) to give a wine-red solution. *tert*-Butylisocyanide (16 μL, 140 μmol) was added, followed by *p*-tolyl azide (18 μL, 140 μmol). The solution immediately effervesced, and the <sup>1</sup>H NMR spectrum recorded within 3 min indicated complete consumption of both starting materials and *p*-tolylN=C=N<sup>t</sup>Bu formed in >95% yield versus an integration standard (1,3,5-trimethoxybenzene). A similarly prepared control reaction in the absence of iron catalyst showed <0.5% conversion to *p*-tolylN=C=N<sup>t</sup>Bu, even after heating for 3 days at 60 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.15 (d, 2H, *J* = 7.6 Hz), 6.89 (d, 2H, *J* = 7.6 Hz), 2.05 (s, 3H), 1.15 (s, 9H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 139, 137, 134, 130, 124, 56.9, 31.5, 20.9 ppm. GC/MS (EI<sup>+</sup>): *m/z* 188 (M<sup>+</sup>), 132 (M – <sup>t</sup>Bu + H)<sup>+</sup>.

### Catalytic Formation of AdN=C=O

A 50-mL Schlenk flask was loaded with N<sub>3</sub>Ad (200 mg, 1.13 mmol) and toluene (20 mL) and sealed with a rubber septum. The flask was freeze-pump degassed and back-filled with 1 atm CO<sub>(g)</sub>. The solution was warmed to room temperature, and a solution of L<sup>tBu</sup>FeNNFeL<sup>tBu</sup> (64 mg, 0.056 mmol) in toluene (5 mL) was added via syringe. The flask was heated in a 60 °C oil bath, and the reaction was monitored by periodically removing 1-mL aliquots via syringe, removing the solvent under vacuum, and observing

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. The aliquot taken after 185 min showed  $\text{AdN}=\text{C}=\text{O}$  was formed in >95% yield based on  $^1\text{H}$  NMR integration against a standard. A similarly prepared control reaction in the absence of iron catalyst (200 mg  $\text{N}_3\text{Ad}$  in 25 mL toluene under 1 atm  $\text{CO}_{(\text{g})}$ ) showed no conversion to  $\text{AdN}=\text{C}=\text{O}$  even after 2 d at 60 °C. Spectral data for  $\text{AdN}=\text{C}=\text{O}$ :  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  124, 55.2, 44.8, 35.4, 29.6 ppm.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.68 (s, 3H), 1.55 (m, 6H), 1.28 (m, 6H) ppm. This compound has been previously reported.<sup>3</sup>

### **$\text{L}^{\text{tBu}}\text{Fe}(\text{CNtBu})_3$**

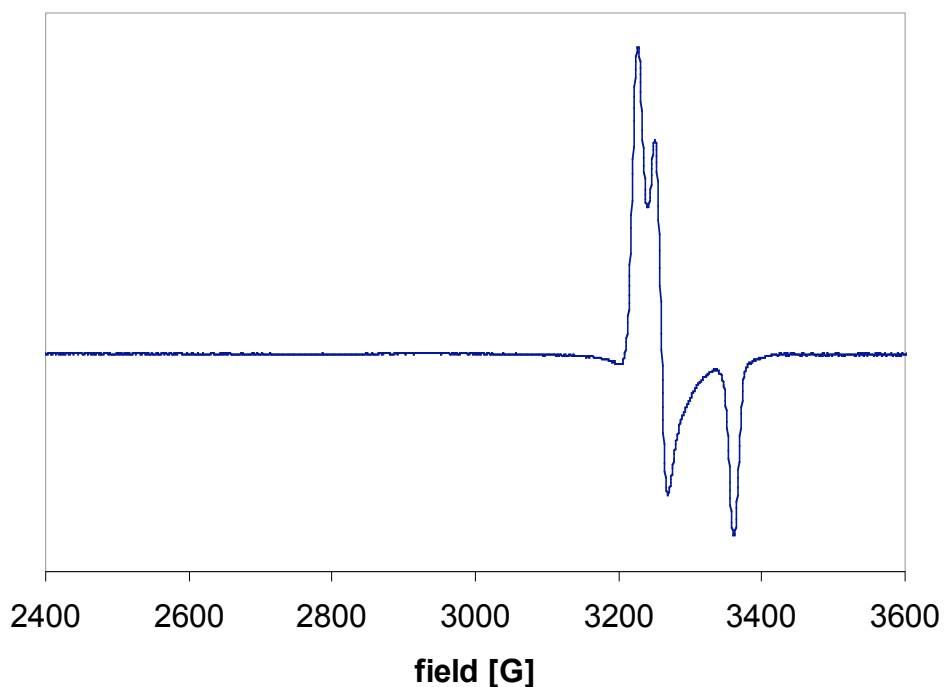
This compound is most conveniently prepared directly from  $\text{L}^{\text{tBu}}\text{FeNNFeL}^{\text{tBu}}$ . A 20-mL scintillation vial is loaded with  $\text{L}^{\text{tBu}}\text{FeNNFeL}^{\text{tBu}}$  (34.6 mg, 30.3  $\mu\text{mol}$ ) and pentane (3 mL) to give a dark wine-red solution. *tert*-Butylisocyanide (20.6  $\mu\text{L}$ , 182  $\mu\text{mol}$ , 6 equiv) is added, resulting in vigorous effervescence and a color change to yellow-brown. The solution is stirred for 5 min and then chilled to -45 °C. Large, dark crystalline plates were collected by decanting the supernatant solution and were dried under vacuum (42 mg, 86%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): silent.  $\mu_{\text{eff}} = 2.0(2) \mu_{\text{B}}$ . IR (KBr): 2961 (s), 2928 (m), 2906 (m), 2868 (m), 2096 (m), 2068 (m), 2012 (s), 1448 (m), 1431 (m), 1391 (s), 1364 (s), 1313 (m), 1213 (m), 1157 (m), 1097 (m)  $\text{cm}^{-1}$ . EPR (toluene, 77K):  $g_{\text{eff}} = 2.087, 2.066, 2.004$ . Anal. Found: C, 72.59; H, 9.33; N, 8.27.  $\text{C}_{50}\text{H}_{80}\text{FeN}_5$  requires C, 74.41; H, 9.99; N, 8.68%.

### ***p*-Tolyl azide**

A 500-mL flask was loaded with *p*-toluidene·HCl (3.70 g, 25.8 mmol), and 1M HCl (~200 mL), and the solution was chilled to 0 °C. A solution of  $\text{NaNO}_2$  (1.87 g, 27 mmol) in water (~20 mL) was added, and after 20 min the reaction was warmed to room temperature and quenched with aqueous  $\text{NaHCO}_3$  until the pH was neutral. A solution of  $\text{NaN}_3$  (1.76 g, 27 mmol) in water (~20 mL) was added, and the reaction was stirred 2 h. The product was extracted into  $\text{Et}_2\text{O}$  (~200 mL), washed with water ( $2 \times 200$  mL), dried over  $\text{MgSO}_4$ , and concentrated to a reddish oil. The product was recovered as a very light yellow oil after vacuum distillation (~10 mbar, 42 °C) (3.05 g, 89 %). *p*-Tolyl azide was stored in the freezer until use.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  6.76 (m, 2H), 6.70 (m, 2H), 1.98 (s, 3H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  138, 135, 131, 119, 21.0 ppm.

### EPR Spectroscopy

Electron Paramagnetic Resonance spectroscopy used a Bruker ER200D spectrometer interfaced to an IBM PC for data recording. Data acquisition used a locally written program by Prof. Robert Kreilick at the University of Rochester. Field measurements were calibrated using samples of known compounds. A field modulation of 15 G and 100 kHz was used. For  $L^{\text{tBu}}\text{FeNAd}$ , the sample was cooled to  $8 \pm 3$  K using a liquid helium cryostat, and the temperature was calibrated by a thermocouple placed in a sample tube in the cavity. For  $L^{\text{tBu}}\text{FeNAd}$  (Figure 1b), the following parameters were used: frequency 9.415 GHz; power 1.06 mW; modulation 15 G, time constant 100 ms.



**Figure S-1.** X-Band EPR spectrum of  $L^{\text{tBu}}\text{Fe}(\text{CNtBu})_3$  in toluene recorded at 77 K. Parameters: frequency 9.426 GHz; power 0.1 mW; modulation 10.3 G/100 kHz; time constant 81.92  $\mu\text{s}$

### Crystallographic Details

Crystals were mounted onto the tip of a ~0.1 mm diameter glass capillary using Krytox oil (GPL-105) and mounted on a Bruker SMART APEX II CCD Platform diffractometer<sup>4</sup> for a data collection at 100.0(1) K using MoK $\alpha$  radiation (graphite monochromator). A randomly oriented region of reciprocal space was surveyed: three major sections of frames were collected with 0.50° steps in  $\omega$  at four different  $\phi$  settings and a detector position of -38° in  $2\theta$ . The intensity data were corrected for absorption.<sup>5</sup> Final cell constants were calculated from the xyz centroids of 3358 strong reflections from the actual data collection. The structure was solved using SHELXS-97<sup>6</sup> and refined using SHELXL-97.<sup>6</sup> The space groups  $P2_1/c$  was determined based on systematic absences and intensity statistics. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. One *tert*-butyl group was modeled as rotationally disordered over two positions (83:17). The final full matrix least squares refinement for **1** converged to  $R_1 = 0.0528$  ( $F^2$ ,  $I > 2\sigma(I)$ ) and  $wR_2 = 0.1312$  ( $F^2$ , all data).

	$L^{tBu}Fe(CNtBu)_3$
Empirical formula	$C_{50} H_{80} Fe N_5$
Formula weight	807.04
Crystal system	monoclinic
Space group	$P2_1/c$
$a$ (Å)	13.1565(17)
$b$ (Å)	19.524(2)
$c$ (Å)	18.978(2)
$\beta$ (°)	117.244(2)
$V$ (Å <sup>3</sup> )	4790.0(10)
$Z$	4
$\theta$ range for data collection (°)	2.32 to 24.34
crystal size (mm <sup>3</sup> )	0.20 × 0.12 × 0.10
$\rho$ (calcd) (g/cm <sup>3</sup> )	1.119
$\mu$ (mm <sup>-1</sup> )	0.352
R(int)	0.1720
$R_1$ ( $I > 2\sigma(I)$ )	0.0609
$wR_2$ (all data)	0.1244
GOF	0.965
largest residual density (e Å <sup>-3</sup> )	0.338 and -0.323

**Table S-1.** Crystal data for  $L^{tBu}Fe(CNtBu)_3$

## References

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