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Probing the role of an Fe^{IV} tetrazene in catalytic aziridination

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Experimental Section

All reactions were performed under a dry nitrogen atmosphere with the use of either a drybox or standard Schlenk techniques. Solvents were dried on an Innovative Technologies (Newburgport, MA, USA) Pure Solv MD-7 Solvent Purification System and degassed by three freeze-pump-thaw cycles on a Schlenk line to remove O_2 prior to use. Acetonitrile-d_3, and chloroform-*d* were degassed by three freeze-pump-thaw cycles prior to drying over activated molecular sieves. These NMR solvents were then stored under N_2 in a glovebox. $[\{(^{Me,Et}TC^{Ph})Fe(NCCH_3)_2](PF_6)_2$ and tolyl azide were prepared as described previously.[1, 2] All reagents were purchased from commercial vendors and used without purification. ^1H, $^{13}C\{^1H\}$, and ^{19}F NMR spectra were recorded at ambient temperature on a Varian VNMRS 500 MHz narrow-bore broadband system. ^1H and ^{13}C NMR chemical shifts were referenced to the residual solvent. ^{19}F NMR chemical shifts are reported relative to an external standard of neat $CFCl_3$. All mass spectrometry analyses were conducted at the Mass Spectrometry Center located in the Department of Chemistry at the University of Tennessee. The DART analyses were performed using a JEOL AccuTOF-D time-of-flight (TOF) mass spectrometer with a DART (direct analysis in real time) ionization source from JEOL USA, Inc. (Peabody, MA, USA). The ESI/MS analyses were performed using a QSTAR Elite quadrupole time-of-flight (QTOF) mass spectrometer with an electrospray ionization source from AB Sciex (Concord, Ontario, Canada). Mass spectrometry sample solutions of metal complexes were prepared in acetonitrile. Infrared spectra were collected on a Thermo Scientific Nicolet iS10 with a Smart iTR accessory for attenuated total reflectance. UV-vis measurements were taken inside a dry glovebox on an Ocean Optics USB4000 UV-Vis system with 1 cm path length quartz crystal cell. Cyclic voltammetry measurements were made inside a dry glovebox using a BASi Epsilon electrochemical analyzer with a platinum working electrode, platinum wire counter electrode, and $Ag/AgNO_3$ reference electrode. All potentials were measured versus an external standard of ferrocene. Carbon, hydrogen, and nitrogen analyses were obtained from Atlantic Microlab, Norcross, GA, USA.

Synthesis of $[(^{Me,Et}TC^{Ph})Fe((p\text{-tolyl})N_4(p\text{-tolyl}))](PF_6)_2$, (2). $[(^{Me,Et}TC^{Ph})Fe(CH_3CN)_2](PF_6)_2$ (**1**) (0.0154 g, 0.0112 mmol) was added to a 20 mL vial with acetonitrile (10 mL) and stirred (450 rpm) with heating at 40 °C for 20 minutes. Tolyl azide (50 µL) was then added to the reaction mixture and heated and stirred overnight. The volatiles were then removed under reduced pressure. The residue was then washed with diethyl ether (3x10 mL) and residual solvent was removed under reduced pressure. The remaining solids were dissolved in acetonitrile (4 mL) and filtered over Celite and the filtrate was collected. The pure product was collected as red crystals by vapor diffusion of diethyl ether into the acetonitrile solution (0.0127 g, 74.1%). ^1H NMR (CD_3CN, 499.74 MHz): δ 7.35 (m, 28H), 7.16 (m, 12H), 6.97 (d, *J* = 7.4 Hz, 8H), 6.06 (d, *J* = 12.6 Hz, 2H), 5.15 (d, *J* = 13.4 Hz, 2H), 3.52 (m, 4H), 2.41 (m, 4H), 2.40 (s, 6H). ^{13}C NMR (CD_3CN, 125.66 MHz): δ 169.79, 154.89, 139.16, 136.41, 134.35, 131.09, 131.00, 130.72, 130.70, 130.67, 129.76, 129.56, 126.52, 125.95, 124.56, 57.56, 44.85, 20.61. ^{19}F NMR (CD_3CN, 470.23 MHz): δ -72.42 (d, *J* = 706 Hz). IR (neat): 3061, 1594, 1500, 1489, 1444, 1414, 1375, 1338, 1225, 1184, 1100, 1077, 1008, 926, 829, 788, 764, 696 cm^{-1}. UV-vis (CH_3CN) λ_{max}, nm (ε): 420 (9300). Zero-field ^{57}Fe Mössbauer (90 K) (δ, $|\Delta E_Q|$ (mm/s)): -0.01, 0.62 (γ = 0.27 mm/s). ESI/MS (*m*/*z*): $[M\text{-}PF_6]^+$ 1395.43, $[M\text{-}2PF_6]^{2+}$ 625.68. Electrochemistry (vs ferrocene in CH_3CN with (TBA)(PF_6) as supporting electrolyte): Fe^{IV}/Fe^{III}, -1055 mV. Anal. Calcd for $C_{80}H_{66}F_{12}FeN_{12}P_2$: C, 62.34; H, 4.32; N, 10.91. Found: C, 61.43; H, 4.67; N, 11.62.

Synthesis of [(^{Me,Et}TC^{Ph})Fe((*p*-tolyl)N_4(*p*-tolyl))](PF_6), (3). [(^{Me,Et}TC^{Ph})Fe((*p*-tolyl)N_4(*p*-tolyl))]$(PF_6)_2$ (**2**) (0.0616 g, 0.0400 mmol) was added to a 20 mL vial with acetonitrile (5 mL) and stirred (450 rpm) for 20 min. Cobaltocene (0.0076 g, 0.040 mmol) was then added to the reaction mixture which was stirred overnight. The pure product was collected as purple crystals by vapor diffusion of diethyl ether into the acetonitrile solution (0.0394 g, 70.6%). IR (neat): 3062, 1602, 1497, 1443, 1395, 1348, 1325, 1252, 1223, 1185, 1076, 1047, 1002, 960, 835, 786, 762, 736, 698 cm^{-1}. UV-vis (CH_3CN) λ_{max}, nm (ε): 350 (11100), 543 (2200). Zero-field ^{57}Fe Mössbauer (90 K) (δ, $|\Delta E_Q|$ (mm/s)): 0.10, 1.13 (γ_L = 0.43 mm/s; γ_R = 0.55 mm/s). EPR (2-methyltetrahydrofuran:acetonitrile (1:1), 77 K): $g_{||}$ = 2.094(1), $g_\perp$ = 1.997(1). Anal. Calcd for $C_{80}H_{66}F_6FeN_{12}P$: C, 68.82; H, 4.76; N, 12.04. Found: C, 67.85; H, 4.64; N, 12.13.

Thermal Decomposition of 2. [($^{Me,Et}TC^{Ph}$)Fe((*p*-tolyl)N$_4$(*p*-tolyl))](PF$_6$)$_2$ (**2**) was dissolved in CD$_3$CN and placed into an NMR tube which was sealed with Parafilm. ^{1}H NMR was taken initially and then heated to 75 °C overnight. ^{1}H NMR was then taken at 12 hour intervals at which time the heat was raised by 5 °C until all **2** was converted back to complex **1** (Figure S1). At 85 °C all of **2** had been converted back to **1** as evidenced by ^{1}H NMR and DART/MS confirmed the presence of 4,4'-dimethylazobenzene as an additional product of the decomposition.

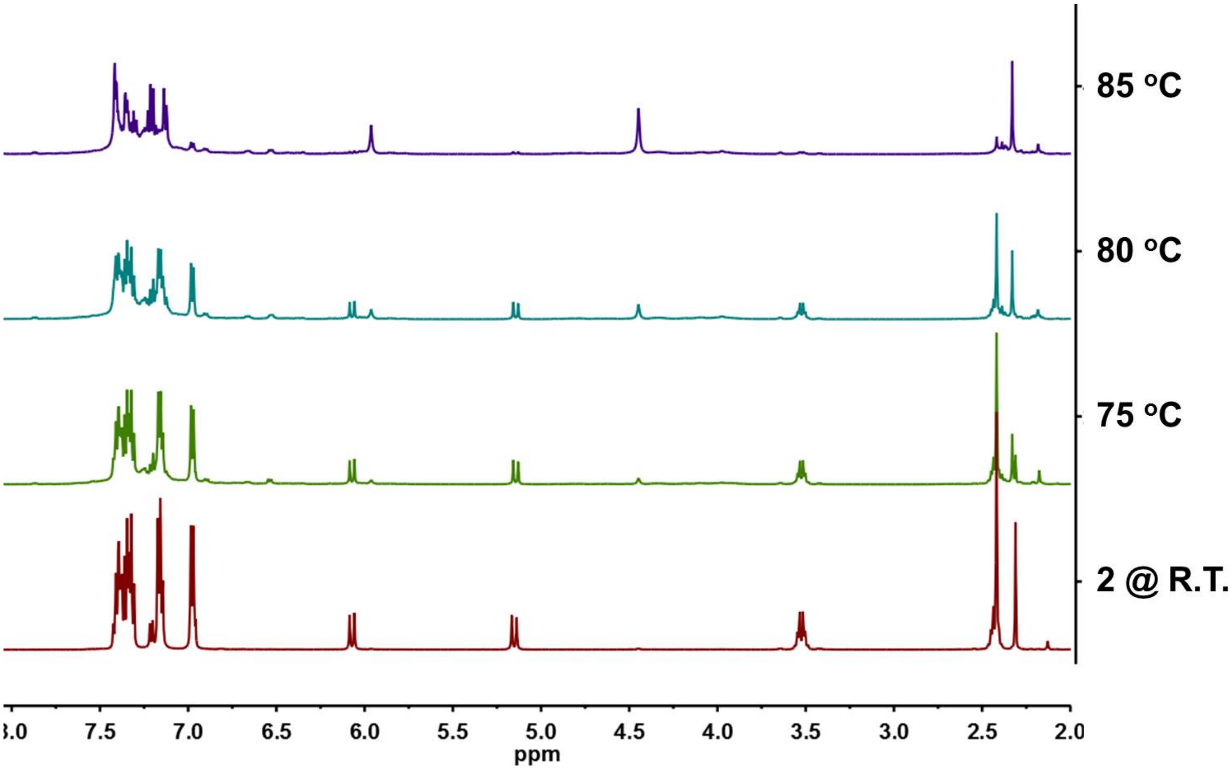

Figure S1. Decomposition of **2** as followed by ^{1}H NMR at room temperature (red), 75 °C (green), 80 °C (blue), and 85 °C (purple).

To quantify the amount of 4,4'-dimethylazobenzene produced from decomposition, **2** (0.0122g, 7.92 μmol) was added to a 20 mL vial and heated to 85 °C overnight in heptane (2 mL). The sample was allowed to cool to room temperature and was filtered over Celite. All volatiles were removed from the filtrate en vacuo. The remaining solid was dissolved in CDCl$_3$ and a 45 μL of stock solution of 1,2,4,5-tetrachlorobenzene (43.5 mM) in CDCl$_3$ was added. ^{1}H NMR revealed an integration ratio of 1.72:1.00 of 4,4'-dimethylazobenzene to 1,2,4,5-tetrachlorobenzene (43% yield).

Group Transfer from 2 to form aziridine. Complex **2** was added to a 20 mL vial and 5 mL of cyclooctene was added. The mixture was heated to 90 °C and stirred for 12 h. After 12 h the reaction was cooled to room temperature and all volatiles were removed under reduced pressure. Benzene was then added to the vial (4 mL), stirred for ten minutes, and filtered over Celite. The volatiles of the filtrate were again removed and dissolved in $CDCl_3$. The chemical shifts of 9-(p-tolyl)-9-azabicyclo[6.1.0]nonane were previously reported and an external standard revealed the shifts of 4,4'-dimethylazobenzene in $CDCl_3$. Direct integration of the doublets in the aryl region of the ^1H NMR spectra determined a 2.30:1.00 ratio of 4,4'-dimethylazobenzene to 9-(p-tolyl)-9-azabicyclo[6.1.0]nonane (Figure S2).

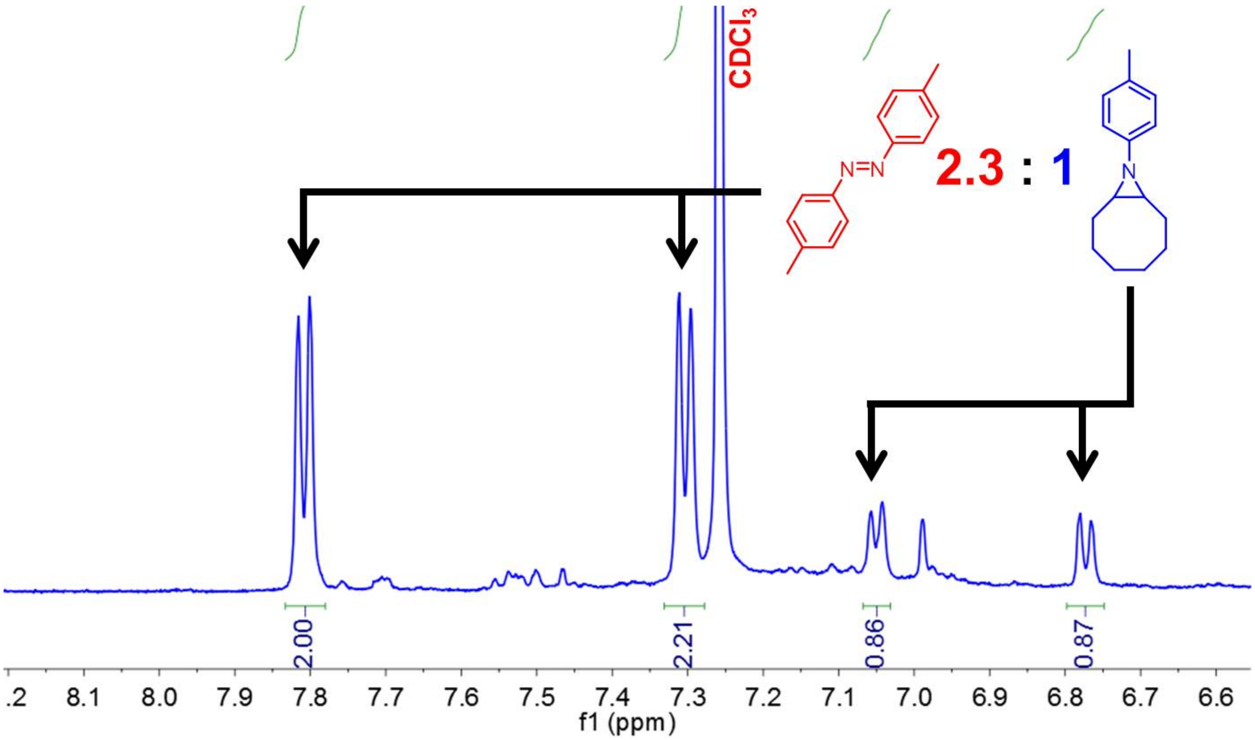

Figure S2. ^1H NMR of the extracted organic products from the decomposition of $[(^{Me,Et}TC^{Ph})Fe(ArN_4Ar)](PF_6)_2$ in the presence of excess cyclooctene.

Catalytic Aziridination with 2 as catalyst. $[(^{Me,Et}TC^{Ph})Fe((p\text{-tolyl})N_4(p\text{-tolyl}))](PF_6)_2$ (**2**) (0.0065 g, 0.0042 mmol) was added to a 20 mL vial followed by the addition of cyclooctene (4.23 g, 0.0384 mol). The reaction mixture was heated to 90 °C while stirring for 10 min. *p*-Tolyl azide (0.281 g, 2.11 mmol) was added to the reaction and the reaction continued for 16 hours. The reaction mixture was cooled to room temperature and the filtered over Celite. The volatiles of the filtrate were removed en vacuo to give a crude product (0.4526 g). A small fraction of this crude product (0.0150 g) and 1,2,4,5-tetrachlorobenzene (0.0113 g, 0.0523 mmol) were added to a 4 mL vial and dissolved in 2 mL of $CDCl_3$. ^1H NMR integration revealed 9-(*p*-tolyl)-9-azabicyclo[6.1.0]nonane (0.0116 g, 0.0539 mmol) was present in a ratio of 1.03:1.00 (aziridine:standard). This result was then extrapolated to determine the total amount of 9-(*p*-tolyl)-

9-azabicyclo[6.1.0]nonane in the reaction mixture (0.350 g, 1.63 mmol, 77.2% yield). By NMR integration, 4,4'-dimethylazobenzene was less than 5% yield, but it was clearly detected in GC/MS.

Electron Paramagnetic Resonance (EPR) Spectroscopy. An EPR spectrum of **3** was collected at 77 K on a Bruker ElexSys E500 EPR spectrometer. Complex **3** was dissolved in a 1:1 mixture of 2-methyltetrahydrofuran and acetonitrile. Mw power = 0.6325 mW. No other transitions were found at lower fields that could be ascribed to intermediate (or high) spin Fe(III). Data was simulated using EasySpin in Matlab.[3]

Zero field ^{57}Fe Mössbauer Spectroscopy. Spectra were collected at 90 K on samples immobilized in Paratone oil with a constant acceleration spectrometer (SEE Co., Minneapolis, MN, USA). All samples were prepared in a dry box under N_2 atmosphere. These samples were subsequently covered with Paratone oil. Isomer shifts are given relative to α–Fe metal at 298 K. Data were analyzed using an in-house package written by E. R. King in Igor Pro (Wavemetrics) based on procedures outlined previously.[4]

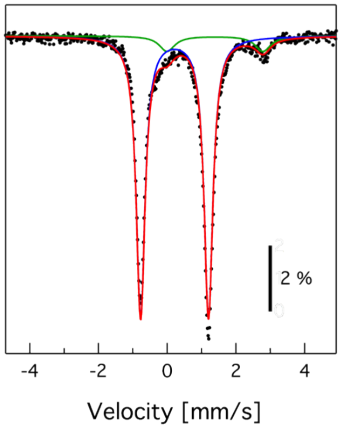

Figure S3. Mössbauer spectrum of powder **1** after drying (blue line is a fit to the experimental data in black dots): δ, $|\Delta E_Q|$ (mm/s): 0.21, 1.95 mm/s. Green line corresponds to a minor unidentified component (< 5%).

X-ray Structure Determinations. X-ray diffraction measurements were performed on single crystals coated with Paratone oil and mounted on glass fibers. Each crystal was frozen under a stream of N_2 while data were collected on a Bruker APEX diffractometer. A matrix scan using at least 12 centered reflections was used to determine initial lattice parameters. Reflections were merged and corrected for Lorenz and polarization effects, scan speed, and background using SAINT 4.05. Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS, if necessary. Space group assignments were based upon systematic absences, *E* statistics, and successful refinement of the structure. The structures were solved by direct methods with the aid of successive difference Fourier maps, and were refined against all data using the SHELXTL 5.0 software package.

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