Supporting Information for

Mechanism of the iron-mediated alkene aziridination reaction: experimental and computational investigations

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Synthetic details and aziridination procedure

**Synthesis of Et₅dien.** *N,N,N′*-Triethylethylenediamine (1.20 g, 7.10 mmol), 2-chloro-*N,N*-diethylethylamine hydrochloride (1.62 g, 9.42 mmol, 1.1 eq), K₂CO₃ (3.0 g, 22 mmol) and Bu₄NI (tr.) were combined in CH₃CN (20 mL) and heated at reflux overnight. After cooling to room temperature, K₂CO₃ was removed by filtration from the reaction mixture, and the solvent was evaporated to produce an oil. This oil was dissolved in CH₂Cl₂ (20 mL) and washed with 6 M NaOH (20 mL). The organic phase was dried (MgSO₄) and the solvent removed to provide a yellow oil, which was purified by Kugelrohr distillation. The pure ligand was isolated as a colorless oil (0.40 g, 1.6 mmol, 24%). ¹H NMR (400 MHz, CDCl₃): δ 2.58-2.51 (m, 18H), 1.03 (t, *J*=7.2 Hz, 3H), 1.02 (t, *J*=7.2 Hz, 12H) ppm; LREIMS (m/z) 242 ([M-H]).

**Synthesis of [(Et₅dien)Fe(CF₃SO₃)₂]** (2). In an inert atmosphere glovebox, Et₅dien (0.208 g, 0.855 mmol) dissolved in THF (1 mL) was added to a solution of Fe(CF₃SO₃)₂·2CH₃CN (0.377 g, 0.631 mmol) in THF (1 mL). After stirring for 45 min, Et₂O (15 mL) was added and the solution was cooled to -25°C to precipitate the product as a white solid. The solvent was removed, and the product was dried under vacuum (0.34 g, 0.57 mmol, 85%). Recrystalization from THF/CH₃CN/Et₂O provided 2 as a colorless crystalline solid. µₑffective (solid, 25 °C) = 4.91 µₜ. Anal. Calcd for C₁₆H₃₃F₆FeN₃O₆S₂: C, 32.17; H, 5.57; N, 7.03. Found: C, 32.19; H, 5.53; N, 7.01.

**Standard procedure for the aziridination of alkenes.** In an inert atmosphere glovebox, PhINTs (0.130 g, 0.349 mmol),³ styrene (0.20 mL, 1.7 mmol) or cis-1-phenylpropene (1.00 mL, 8.73 mmol) and solid 1 (0.0092 g, 0.017 mmol), 2 (0.0103 g, 0.0173 mmol), or 3 (0.0105 g, 0.0173 mmol) were combined in CH₂Cl₂ or CH₃CN (3 mL). The mixtures turned golden brown in color, and the reactions were completed when the insoluble iodinane dissolved completely. At this time, the clear brown solution was passed through a column of alumina (to remove iron salts) and eluted with EtOAc (10 mL). The combined eluates were evaporated, the resulting residue was dissolved in CDCl₃, and 2,4-di-tert-butylphenol was added as an internal standard for quantitation. Products were identified by their ¹H NMR spectra. A representative NMR spectrum used to quantify both syn and anti aziridines, is provided on the next page.

Representative $^1$H NMR spectrum of a crude reaction mixture containing both syn and anti 2-methyl-3-phenyl-N-tosyl aziriridines (as well as 2,4-di-tert-butylphenol (2,4-DTBP) for quantitation).
Computational details


Unrestricted DFT calculations were performed using the mPWPW91 functional. In all cases, only the triplet (high spin Fe$^{4+}$) state was considered. Reported results are for the 6-31G(d) basis set and optimizations were obtained within standard convergence criteria. The standard default integration grid, which is a pruned (75,302) grid having 75 radial shells and 302 angular points per shell, was used. Solvation energies for these geometries were calculated using the polarized continuum model (PCM) with default parameters for CH$_2$Cl$_2$ as the solvent. These consist of the gas phase electronic energies plus the solvation contribution to the free energy but do not include vibrational contributions.
Energy minimized structures for alternative formulations of intermediate A. The energies of each intermediate (gas phase electronic energy plus free energy of solvation in CH₂Cl₂) relative to that of the lowest energy structure (page S7) are provided in units of kcal/mol. The energies include contributions from any non-coordinated triflate counterions that are part of the formula (i.e., the energy of structure #1, below, is the energy of the dication plus the energies of two non-coordinated triflate anions).

1. Imidoiron(IV) complex without bound triflate ions, [(Me₅dien)Fe(NTs)]²⁺. The iron complex was constructed with a square-planar geometry, but during the energy minimization process, the initially monodentate =NTs group became bidentate. The minimized structure features an iron center in a distorted 5-coordinate geometry.

![Image 1]

Fe=N(Ts): 1.740 Å
Fe-O(Ts): 1.956 Å
Fe-N(amine): 2.082-2.121 Å
N(Ts)-Fe-O(Ts): 79.6°

Relative energies of [(Me₅dien)Fe(NTs)](CF₃SO₃)₂:
Gas-phase electronic energy (ESCF): + 258.1 kcal/mol
ESCF + Solvation free energy: + 54.5 kcal/mol

2. Imidoiron(IV) complex with one bound triflate ion, [(Me₅dien)Fe(NTs)(O₃SCF₃)]⁺. This formulation has two energy minimized structures, in which the monodentate =NTs and –O₃SCF₃ groups exchange positions (equatorial and axial) within the square-pyramidal coordination sphere of the iron(IV) center.

![Image 2]

“NTs equatorial”

Fe=N(Ts): 1.666 Å
Fe-O(triflate): 1.887 Å
Fe-N(amine): 2.088-2.180 Å

Relative energies of “NTs equatorial”
[(Me₅dien)Fe(NTs)(O₃SCF₃)]CF₃SO₃:
Gas-phase electronic energy (ESCF): + 85.6 kcal/mol
ESCF + Solvation free energy: +15.6 kcal/mol

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3. Imidoiron(IV) complex with two bound triflate ions, [(Me₅dien)Fe(NTs)(O₃SCF₃)₂]. This formulation has three energy minimized octahedral structures. One of these isomers features a facial Me₅dien ligand. The other two feature a meridional Me₅dien ligand, and differ by the location of the =NTs group (either in the equatorial plane or in an axial coordination site).

Relative energy of “Me₅dien facial” [(Me₅dien)Fe(NTs)(O₃SCF₃)₂]:
Gas-phase electronic energy (ESCF): + 10.1 kcal/mol
ESCF + Solvation free energy: + 13.0 kcal/mol
“Me₅dien meridional, =NTs equatorial”

Fe=N(Ts): 1.726 Å
Fe-O(triflate): 1.932, 2.038 Å
Fe-N(amine): 2.126-2.150 Å

Relative energies of “Me₅dien meridional, =NTs equatorial”, [(Me₅dien)Fe(NTs)(O₃SCF₂)$_2$]:
Gas-phase electronic energy (ESCF): + 2.3 kcal/mol
ESCF + Solvation free energy: + 4.8 kcal/mol

“Me₅dien equatorial, =NTs axial” (lowest energy structure; intermediate A in manuscript)

Fe=N(Ts): 1.739 Å
Fe-O(triflate): 1.942, 1.993 Å
Fe-N(amine): 2.062-2.234 Å