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Cationic Divalent Metal Sites (M = Mn, Fe, Co) Operating as Both Nitrene-Transfer Agents and Lewis Acids toward Mediating the Synthesis of Three- and Five-Membered N-Heterocycles

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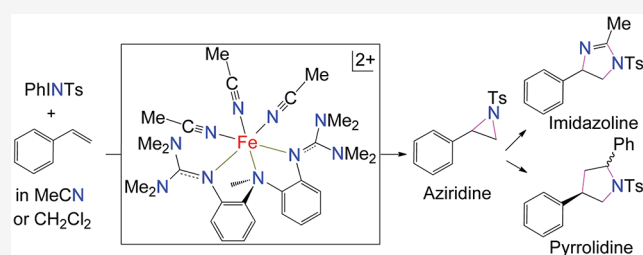
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ABSTRACT: The tripodal compounds $[(\text{TMG}_3\text{trphen})\text{M}^{\text{II}}\text{-solv}](\text{PF}_6)_2$ ($\text{M} = \text{Mn, Fe, Co}$; $\text{solv} = \text{MeCN, DMF}$) and bipodal analogues $[(\text{TMG}_2\text{biphen})\text{M}^{\text{II}}(\text{NCMe})_x](\text{PF}_6)_2$ ($x = 3$ for Mn, Fe; $x = 2$ for Co) and $[(\text{TMG}_2\text{biphen})\text{M}^{\text{II}}\text{Cl}_2]$ have been synthesized with ligands that feature a triaryl- or diarylmethyl-amine framework and superbasic tetramethylguanidyl residues (TMG). The dicationic M(II) sites mediate catalytic nitrene-transfer reactions between the imidoiodinane $\text{PhI}=\text{NTs}$ (Ts = tosyl) and a panel of styrenes in MeCN to afford aziridines and low yields of imidazolines (upon MeCN insertion) with an order of productivity that favors the bipodal over the tripodal reagents and a metal preference of $\text{Fe} > \text{Co} \geq \text{Mn}$. In CH_2Cl_2 , the more acidic Fe(II) sites favor formation of 2,4-diaryl-*N*-tosylpyrrolidines by means of an in situ (3 + 2) cycloaddition of the initially generated 2-aryl-*N*-tosylaziridine with residual styrene. In the presence of ketone, 1,3-oxazolidines can be formed in practicable yields, involving a single-pot cycloaddition reaction of alkene, nitrene, and ketone (2 + 1 + 2). Mechanistic studies indicate that the most productive bipodal Fe(II) site mediates stepwise addition of nitrene to olefins to generate aziridines with good retention of stereochemistry and further enables aziridine ring opening to unmask a 1,3-zwitterion that can undergo cycloaddition with dipolarophiles (MeCN, alkene, ketone) to afford five-membered *N*-heterocycles.



1. INTRODUCTION

Aziridines¹ are privileged synthetic targets and substrates for further derivatization given their presence in many natural (antineoplastic, antibacterial)² and value-added products (pharmaceuticals, fine chemicals, polymers).^{3,4} Their immense potential for structural elaboration (ring opening, expansion, or rearrangement)⁵ arises due to the rich stereochemical depository and high strain energy contained in the three-membered ring (ring strain for the parent aziridine: 27.1 (exp), 27.3 (calcd) kcal mol⁻¹; p*K*_a = 7.98 for the conjugate acid).⁶

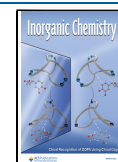
Among the common synthetic methods for synthesizing aziridines (cyclization of 1,2-amino precursors, addition of C₁ sources to imines, addition of N₁ sources to olefins),⁷ the “C₂ + N₁” methodology has received extensive attention and can be accomplished under a variety of organocatalytic⁸ or metal-dependent conditions,⁹ usually with the assistance of middle or late first-row transition elements,^{10–18} coinage metals,^{19,20} and platinum-group elements.^{21–23} The requisite N₁ donors are frequently sourced from a wide variety of nitrene- or nitrenoid-group (NR, NR(X)) precursors (e.g., organic azides,²⁴ iminoiodinanes,²⁵ haloamines,²⁶ *N*/*O*-substituted hydroxylamines,²⁷ *N*-tosyloxycarbamates²⁸), thus providing an enormous backdrop for the synthesis of both activated (EW nitrogen substituent, e.g., –SO₂R, –CO₂R, –C(O)R) and

nonactivated aziridines (ED nitrogen substituent, e.g., H, alkyl, aryl, silyl).²⁹

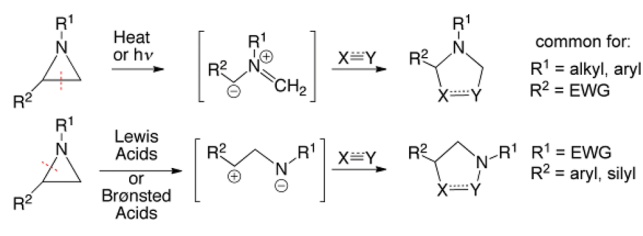
The type of nitrogen substituent plays a critical role in many aziridine ring expansion methodologies, chief among which is the formal (3 + 2) cycloaddition³⁰ of aziridines with several dipolarophiles (e.g., alkenes, alkynes, nitriles, carbonyls, imines, CO₂), affording a plethora of five-membered nitrogen heterocycles (e.g., pyrrolidines, pyrrolines, imidazolines, oxazolidines, imidazolidines, oxazolidinones; Scheme 1).³¹ Thermal/photochemical conditions³² or Lewis/Brønsted acids (in stoichiometric or catalytic amounts)³³ are frequently used to activate the aziridine ring toward unveiling the 1,3-dipole or zwitterion by means of C–C or C–N bond heterolytic cleavage, largely predicated on the electronic nature of the aziridine substitution pattern and reaction conditions. As a result of the guidance offered from the aziridine

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Scheme 1. Common (3 + 2) Cycloadditions of Aziridines with Dipolarophiles



substituents³⁴ and the existence of a plethora of dipolarophile partners that can be added in a concerted or a stepwise manner (two- or single-electron processes),³⁵ the (3 + 2) cycloaddition of a stereochemically endowed aziridine with an unsaturated substrate can provide numerous opportunities for chemo-, regio-, diastereo-, and enantioselective synthesis of five-membered nitrogen heterocycles.³⁶

In previous work, we have taken advantage of an $[N_3N]$ ligand scaffold^{37,38} that permits modular synthesis of an extensive family of tripodal $M(II)$ ($M = Mn, Fe, Co, Ni$) and $M(I)$ ($M = Cu, Ag$) reagents supported by an axial N_{amine} residue and equatorial N_{amido} or N_{imino} moieties. Both *anionic* divalent base-element (Mn, Fe, Co)³⁹ and *cationic* coinage-metal (Cu, Ag)⁴⁰ compounds have resulted from this synthetic effort and been employed as catalysts in nitrene- and chloro-transfer⁴¹ chemistry. The most successful anionic $M(II)$ reagents proved to transfer nitrene (NTs) to olefins (aziridination) in accordance with the anticipated electrophilicity of the putative $M^{III}-\bullet NR$ oxidant ($Co > Mn \geq Fe$),^{39b} although some exceptions in the preponderance of the electrophilicity criterion have been noted within the $Co(II)$ family of reagents.^{39a} The attenuated reactivity of these reagents, in line with their anionic character, provides instances of enhanced chemoselectivity in aziridination of olefins.^{39b} On the other hand, the structurally related *cationic* $Cu(I)$ reagents, bearing the strongly basic tetramethylguanidyl residues, offer superior reactivity for both aromatic and aliphatic olefin aziridinations and further mediate C–H bond aminations.⁴⁰

In the present publication, we extend the family of cationic reagents by exploring divalent base-metal analogues ($M = Mn, Fe, Co$) with the same tripodal ligand scaffold that provided the versatile $Cu(I)$ reagents⁴⁰ but also with a related bipodal congener that offers additional coordination sites for catalytic studies (Figure 1). These ligands provide phenylene-bridged analogues of metal reagents featuring the well-known TMG_3tren and TMG_2dien frameworks.⁴² Guanidynyl-supported ligands have been employed in numerous catalytic studies⁴³ and/or stoichiometric interactions between metal sites and small atoms or molecules (O, O_2, CN, NO), frequently giving rise to high-valent complexes with first-row transition-metal elements.⁴⁴

Certain members of the present family of dicationic reagents are capable of producing not only aziridines in catalytic nitrene transfer to olefins but also instances of five-membered N -heterocycles (imidazolines, pyrrolidines, oxazolidines)^{45,46} in the presence of nitrile, excess olefin, and ketones. Apparently, the dicationic charge of these reagents adds Lewis-acid characteristics to their operational capabilities; hence, the catalyst can potentially assume a dual role as a nitrene-transfer agent and an aziridine ring-opening facilitator. The combined result can provide avenues for synthesizing five-membered nitrogen heterocycles directly from (2 + 1 + 2) three-component systems (olefin, amine/oxidant, dipolarophile) for which only a handful of cases has been realized (see below). A similar approach has been implemented by Dauban and co-workers in oxyamination and diamination of olefins via rhodium-catalyzed nitrene transfer to generate an aziridine followed by in situ ring opening (mediated by the acidity of the dirhodium–nitrene) in the presence of suitable nucleophiles.⁴⁷

The present work also underscores the importance of dicationic iron(II) reagents as an alternative to monocationic $Cu(I)$ sites in nitrene-transfer chemistry, particularly when issues of selectivity associated with the product-determining steps are concerned. Starting with the introduction of iconic Fe porphyrinoid catalysts for the aziridination of olefins by Mansuy and co-workers,¹⁰ several other bioinspired Fe catalysts,^{14,48} engineered hemoprotein enzymes,¹² and even a single case of P450-mediated formation of an intermediate aziridine in benzastatin biosynthesis,⁴⁹ have paved the way to an iron age of highly selective nitrene-transfer transformations.⁵⁰ Yet, detailed investigations of in situ elaboration of amines or aziridines to other valuable heterocycles under iron nitrene-transfer catalysis have only recently started emerging.⁵¹ Notable are also efforts to generate disubstituted pyrrolidines by means of Fe -mediated intramolecular C–H bond amination⁵² or olefin hydroamination.⁵³ The current work further confirms the potential of iron compounds, especially those of acidic nature, in the generation of three- and five-membered N -heterocyclic products.

2. RESULTS AND DISCUSSION

2.1. Synthesis of Ligands and Compounds.

The synthesis of the tripodal ligand $TMG_3trphen$ (Figure 1) has been previously described⁴⁰ (ORTEP diagram, Figure S1). The bipodal ligand $TMG_2biphen$ is synthesized in an analogous manner (Scheme 2; ORTEP diagram, Figure S1) by coupling N -methyl-bis(2-aminophenyl)amine⁵⁴ and chlorotetramethylformamidinium chloride (prepared by chlorination of tetramethylurea with oxalyl chloride) in the presence of triethylamine in acetonitrile. The precursor methylated amine is prepared from bis(2-nitrophenyl)amine (synthesized according to a literature protocol)^{54b} by means of deprotonation ($NaOH$) and methylation with Me_2SO_4 followed by reduction of the nitro groups to the corresponding amines with the

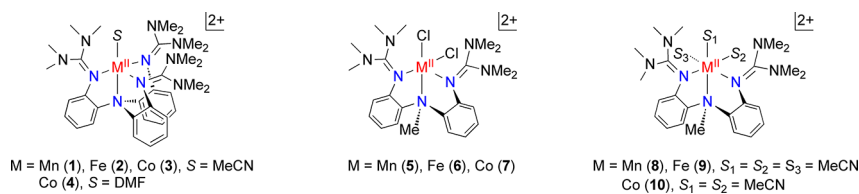


Figure 1. Tripodal $[N_3N]$ and bipodal $[N_2N]$ metal compounds used in this study.

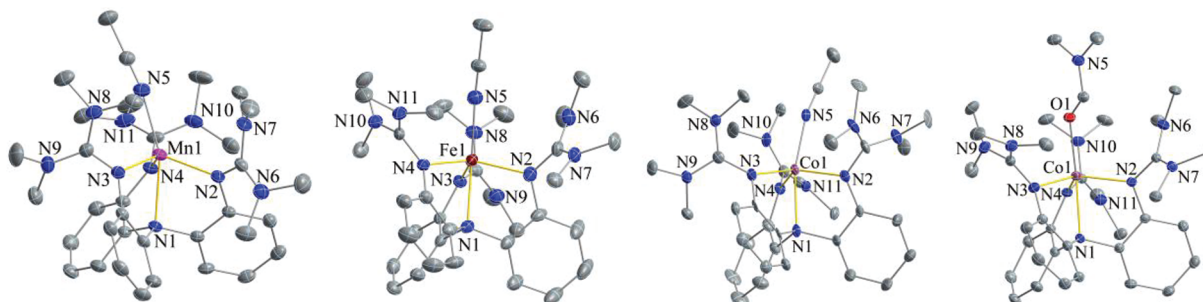
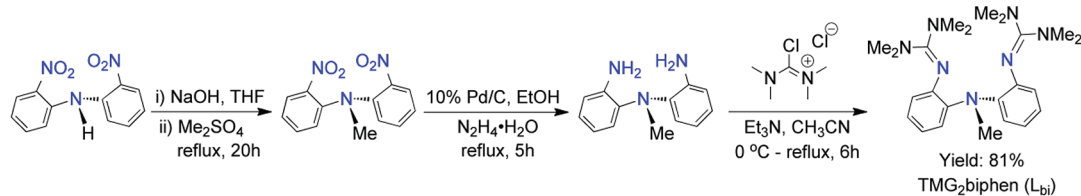
Scheme 2. Synthesis of the Bipodal Ligand TMG₂biphen

Figure 2. ORTEP diagrams of $[(\text{TMG}_3\text{trphen})\text{Mn}^{\text{II}}(\text{NCMe})](\text{PF}_6)_2 \cdot 2\text{MeCN} \cdot 0.5\text{Et}_2\text{O}$ (**1**), $[(\text{TMG}_3\text{trphen})\text{Fe}^{\text{II}}(\text{NCMe})](\text{PF}_6)_2 \cdot 1.25\text{CH}_2\text{Cl}_2$ (**2**), $[(\text{TMG}_3\text{trphen})\text{Co}^{\text{II}}(\text{MeCN})](\text{PF}_6)_2 \cdot \text{Et}_2\text{O}$ (**3**), and $[(\text{TMG}_3\text{trphen})\text{Co}^{\text{II}}(\text{DMF})](\text{PF}_6)_2 \cdot \text{DMF} \cdot \text{Et}_2\text{O}$ (**4**) (cations only) drawn with 40% thermal ellipsoids. Selective interatomic distances [Angstroms] and angles [degrees] for **1**: $\text{Mn}(1)-\text{N}(1) = 2.3408(19)$, $\text{Mn}(1)-\text{N}(2) = 2.122(2)$, $\text{Mn}(1)-\text{N}(3) = 2.131(2)$, $\text{Mn}(1)-\text{N}(4) = 2.170(2)$, $\text{Mn}(1)-\text{N}(5) = 2.190(2)$, $\text{N}(1)-\text{Mn}(1)-\text{N}(2) = 75.68(7)$, $\text{N}(1)-\text{Mn}(1)-\text{N}(5) = 156.98(8)$. For **2**: $\text{Fe}(1)-\text{N}(1) = 2.280(4)$, $\text{Fe}(1)-\text{N}(2) = 2.056(4)$, $\text{Fe}(1)-\text{N}(3) = 2.057(4)$, $\text{Fe}(1)-\text{N}(4) = 2.062(4)$, $\text{Fe}(1)-\text{N}(5) = 2.113(5)$, $\text{N}(1)-\text{Fe}(1)-\text{N}(2) = 78.53(16)$, $\text{N}(1)-\text{Fe}(1)-\text{N}(5) = 164.22(16)$. For **3**: $\text{Co}(1)-\text{N}(1) = 2.230(9)$, $\text{Co}(1)-\text{N}(2) = 2.045(9)$, $\text{Co}(1)-\text{N}(3) = 1.999(9)$, $\text{Co}(1)-\text{N}(4) = 2.007(10)$, $\text{Co}(1)-\text{N}(5) = 2.069(10)$, $\text{N}(1)-\text{Co}(1)-\text{N}(2) = 77.8(4)$, $\text{N}(1)-\text{Co}(1)-\text{N}(5) = 166.0(4)$. For **4**: $\text{Co}(1)-\text{N}(1) = 2.2334(14)$, $\text{Co}(1)-\text{N}(2) = 2.0160(13)$, $\text{Co}(1)-\text{N}(3) = 2.0538(14)$, $\text{Co}(1)-\text{N}(4) = 2.0283(13)$, $\text{Co}(1)-\text{O}(1) = 2.0906(13)$, $\text{N}(1)-\text{Co}(1)-\text{N}(2) = 79.17(4)$, $\text{N}(1)-\text{Co}(1)-\text{O}(1) = 167.75(4)$.

assistance of hydrazine over 10% Pd/C in ethanol.^{40,55} The last step of the ligand synthesis has been previously reported,⁵⁶ but the stated physical appearance of the product (dark colored) seems to be at variance with our observations (colorless).

The tripodal base-metal reagents $[(\text{TMG}_3\text{trphen})\text{M}^{\text{II}}-\text{NCMe}](\text{PF}_6)_2$ ($\text{M} = \text{Mn}$ (**1**), Fe (**2**), Co (**3**)) are best prepared from the reaction of the corresponding $[\text{M}^{\text{II}}(\text{NCMe})_6](\text{PF}_6)_2$ precursors and the tripodal ligand $\text{TMG}_3\text{trphen}$ in acetonitrile (Mn , Co) or dichloromethane (Fe). Specifically for cobalt, the DMF adduct (**4**) can be prepared in a similar manner in *N,N*-dimethylformamide. The starting $[\text{M}^{\text{II}}(\text{NCMe})_6](\text{PF}_6)_2$ adducts are synthesized from high-purity anhydrous MCl_2 beads and TlPF_6 in MeCN . The $\text{Fe}(\text{II})$ and $\text{Co}(\text{II})$ analogues are known compounds,^{57,58} but the $[\text{Mn}^{\text{II}}(\text{NCMe})_x]^{2+}$ congener has been reported with a host of other counteranions (e.g., BF_4^- , $x = 4$; $[\text{BAR}^{\text{F}}_4]^-$, MnI_4^- , $x = 6$)⁵⁹ as a tetrakis- or hexakis-acetonitrile adduct. The $[\text{Mn}^{\text{II}}(\text{NCMe})_6](\text{PF}_6)_2$ stoichiometry has been confirmed by X-ray diffraction analysis of single crystals obtained from MeCN (Figure S2; $\text{Mn}-\text{NCMe} = 2.215(3)$ Å for all acetonitrile moieties).

In contrast, the corresponding bipodal metal reagents are only obtained in low yields from the synthetic procedure noted above. These metal compounds are more reliably synthesized by an indirect protocol via the initial preparation of the chloride precursors $[(\text{TMG}_2\text{biphen})\text{M}^{\text{II}}\text{Cl}_2]$ ($\text{M} = \text{Mn}$ (**5**), Fe (**6**), Co (**7**)) from the reaction of the ligand and anhydrous MCl_2 in acetonitrile. The chlorides are then removed with the assistance of TlPF_6 in MeCN to afford $[(\text{TMG}_2\text{biphen})\text{M}^{\text{II}}-\text{NCMe}]_x(\text{PF}_6)_2$ ($\text{M} = \text{Mn}$ (**8**), Fe (**9**), $x = 3$; Co (**10**), $x = 2$). A similar procedure has been previously followed in the synthesis of $[(\text{TMG}_2\text{tren})\text{Fe}(\text{OTf})](\text{OTf})$.^{42b}

2.2. Structural Characterization. **2.2.1. Tripodal Metal Reagents.** The series of tripodal compounds $[(\text{TMG}_3\text{trphen})-\text{M}^{\text{II}}-\text{solv}](\text{PF}_6)_2$ ($\text{M} = \text{Mn}$ (**1**), Fe (**2**), Co (**3**), $\text{solv} = \text{MeCN}$; $\text{M} = \text{Co}$ (**4**), $\text{solv} = \text{DMF}$) has been characterized by X-ray diffraction analysis to reveal a distorted trigonal bipyramidal coordination geometry in all cases (Figure 2). The degree of distortion is best depicted by the τ_5 geometric index ($\tau_5 = 1$ or 0 for the ideal trigonal bipyramidal or square pyramidal geometries, respectively),⁶⁰ revealing that the sizable Mn^{2+} ion effects a larger deviation ($\tau_5 = 0.50$) from the trigonal bipyramidal geometry (at the boundary with square pyramidal geometry) by comparison to the smaller and more size-comparable Fe^{2+} ($\tau_5 = 0.60$) and Co^{2+} ions ($\tau_5 = 0.63$) of the MeCN adducts. The $\text{Co}-\text{DMF}$ analogue exhibits the least distorted trigonal bipyramidal geometry ($\tau_5 = 0.72$). Accordingly, the displacement of the Mn atom (0.569(2) Å) above the equatorial plane defined by atoms $\text{N}(2)$, $\text{N}(3)$, and $\text{N}(4)$ is more pronounced than that observed for the corresponding tripodal compounds of Fe (0.428(5) Å) and Co (0.381(3) Å). As expected, all $\text{M}-\text{N}$ bond distances for the acetonitrile residues are contracted by 0.08 (± 0.01) Å upon substituting Mn with Fe and further shortened by 0.040 (± 0.005) Å upon replacing Fe with Co . Otherwise, the ligand-related bond distances for the axial $\text{M}-\text{N}_{\text{amine}}$ (Mn , 2.341(2); Fe , 2.280(4); Co , 2.230(9) Å) and the equatorial $\text{M}-\text{N}_{\text{imine}}$ bonds (Mn , 2.141(± 0.021); Fe , 2.058(± 0.003); Co , 2.017(± 0.020) Å) are typical of high-spin, divalent base-metal sites.

2.2.2. Bipodal Metal Reagents. The two distinct series of metal compounds that bear the bipodal ligand, namely, $[(\text{TMG}_2\text{biphen})\text{M}^{\text{II}}\text{Cl}_2]$ ($\text{M} = \text{Mn}$ (**5**), Fe (**6**), Co (**7**)) and $[(\text{TMG}_2\text{biphen})\text{M}^{\text{II}}-\text{NCMe}]_x(\text{PF}_6)_2$ ($\text{M} = \text{Mn}$ (**8**), Fe (**9**), $x = 3$; Co (**10**), $x = 2$), have been crystallographically

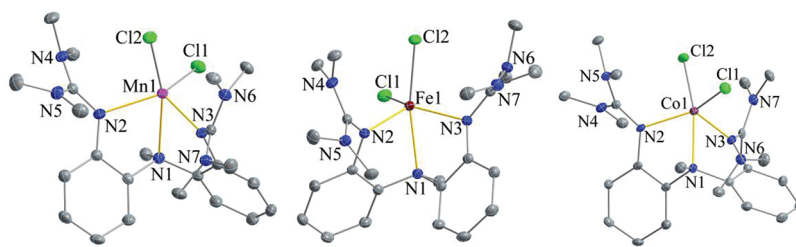


Figure 3. ORTEP diagrams of $[(\text{TMG}_2\text{biphen})\text{Mn}^{\text{II}}\text{Cl}_2]$ (**5**), $[(\text{TMG}_2\text{biphen})\text{Fe}^{\text{II}}\text{Cl}_2]$ (**6**), and $[(\text{TMG}_2\text{biphen})\text{Co}^{\text{II}}\text{Cl}_2]\cdot\text{MeCN}$ (**7**) drawn with 40% thermal ellipsoids. Selective interatomic distances [Angstroms] and angles [degrees] for **5**: Mn(1)–N(1) = 2.3980(16), Mn(1)–N(2) = 2.2214(18), Mn(1)–N(3) = 2.1751(16), Mn(1)–Cl(1) = 2.3542(6), Mn(1)–Cl(2) = 2.4012(6), N(1)–Mn(1)–N(2) = 71.55(6), N(1)–Mn(1)–Cl(1) = 92.15(4), N(1)–Mn(1)–Cl(2) = 161.98(4), Cl(1)–Mn(1)–Cl(2) = 105.15(2). For **6**: Fe(1)–N(1) = 2.3401(12), Fe(1)–N(2) = 2.1036(13), Fe(1)–N(3) = 2.1459(13), Fe(1)–Cl(1) = 2.3055(4), Fe(1)–Cl(2) = 2.3901(4), N(1)–Fe(1)–N(2) = 74.33(5), N(1)–Fe(1)–Cl(1) = 93.09(3), N(1)–Fe(1)–Cl(2) = 164.22(3), Cl(1)–Fe(1)–Cl(2) = 101.505(16). For **7**: Co(1)–N(1) = 2.320(2), Co(1)–N(2) = 2.068(2), Co(1)–N(3) = 2.041(2), Co(1)–Cl(1) = 2.2959(8), Co(1)–Cl(2) = 2.3617(8), N(1)–Co(1)–N(2) = 74.96(8), N(1)–Co(1)–Cl(1) = 90.62(6), N(1)–Co(1)–Cl(2) = 166.38(6), Cl(1)–Co(1)–Cl(2) = 102.13(3).

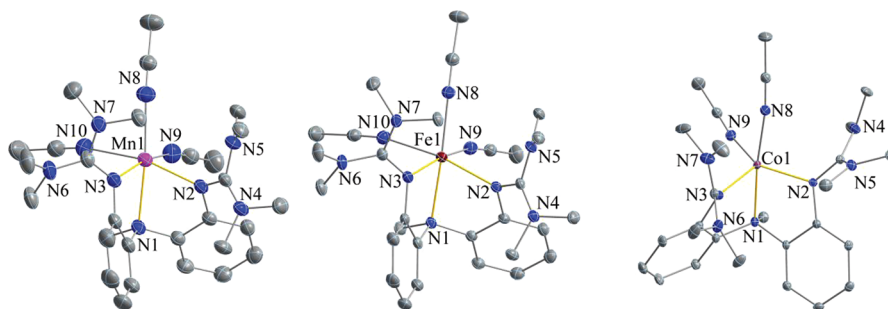


Figure 4. ORTEP diagrams of $[(\text{TMG}_2\text{biphen})\text{Mn}^{\text{II}}(\text{NCMe})_3](\text{PF}_6)_2\cdot\text{MeCN}$ (**8**), $[(\text{TMG}_2\text{biphen})\text{Fe}^{\text{II}}(\text{NCMe})_3](\text{PF}_6)_2\cdot\text{MeCN}$ (**9**), and $[(\text{TMG}_2\text{biphen})\text{Co}^{\text{II}}(\text{NCMe})_2](\text{PF}_6)_2\cdot\text{MeCN}$ (**10**) (cations only) drawn with 40% thermal ellipsoids. Selective interatomic distances [Angstroms] and angles [degrees] for **8**: Mn(1)–N(1) = 2.352(2), Mn(1)–N(2) = 2.202(2), Mn(1)–N(3) = 2.147(2), Mn(1)–N(8) = 2.232(3), Mn(1)–N(9) = 2.241(3), Mn(1)–N(10) = 2.351(3), N(1)–Mn(1)–N(2) = 74.18(8), N(1)–Mn(1)–N(8) = 170.75(10). For **9**: Fe(1)–N(1) = 2.2803(17), Fe(1)–N(2) = 2.1439(16), Fe(1)–N(3) = 2.0781(16), Fe(1)–N(8) = 2.1574(18), Fe(1)–N(9) = 2.1784(18), Fe(1)–N(10) = 2.2582(19), N(1)–Fe(1)–N(2) = 76.09(6), N(1)–Fe(1)–N(8) = 171.46(6). For **10**: Co(1)–N(1) = 2.2080(18), Co(1)–N(2) = 1.9912(18), Co(1)–N(3) = 2.0131(18), Co(1)–N(8) = 2.095(2), Co(1)–N(9) = 2.0396(18), N(1)–Co(1)–N(2) = 79.66(7), N(1)–Co(1)–N(8) = 174.30(7).

characterized for all divalent base metals examined in this study. The neutral, five-coordinate dichloro compounds exhibit distorted trigonal bipyramidal geometry (Figure 3) at the borderline with square pyramidal geometry ($\tau_5 = 0.56$ (Mn), 0.51 (Fe), 0.60 (Co)) featuring atoms N(1)_{amine} and Cl(2) along the axial ligand field (N(1)–M–Cl(2) = 161.98(4)° (Mn), 164.22(3)° (Fe), 166.38(6)° (Co)) and atoms N(2)_{imine}, N(5)_{imine}, and Cl(1) as equatorial residues. Metrical parameters for all bond distances associated with the metal center depict the same trend of metal-dependent contraction as that noted above for the tripodal metal reagents. As expected, the M–Cl_{ax} bond is significantly more elongated than the corresponding M–Cl_{eq} bond by 0.047 (Mn), 0.085 (Fe), and 0.066 (Co) Å.

The acetonitrile adducts of the bipodal reagents, $[(\text{TMG}_2\text{biphen})\text{M}^{\text{II}}(\text{NCMe})_x](\text{PF}_6)_2$ (M = Mn (**8**), Fe (**9**), $x = 3$; Co (**10**), $x = 2$), demonstrate two distinct geometric configurations: six-coordinate, distorted octahedral for the divalent Mn and Fe ions and five-coordinate, distorted trigonal bipyramidal for the Co(II) ion (Figure 4). The Mn(II) (**8**) and Fe(II) (**9**) analogues exhibit the usual facial coordination of the [N₂N] bipodal ligand accompanied by three MeCN molecules coordinated in trans positions versus the [N₂N] residues with small deviations from linearity (the least divergent angle is that for N(1)–M–N(8) (170.75(10)°, Mn; 171.46(6)°, Fe)). Although six coordinate, both Mn(II)

and Fe(II) demonstrate tighter [N₂N] coordination than the five-coordinate chloride precursors, presumably due to the cationic character of the acetonitrile adducts. By comparison to $[\text{M}(\text{NCMe})_6](\text{PF}_6)_2$ (M = Mn (Figure S1), Fe), the M–NCMe bond distances in **8** and **9** are appreciably longer, suggesting that the [N₂N] ligand field is stronger than that provided by three MeCN residues. One acetonitrile residue (N(10)) is significantly elongated (by 0.11 Å for Mn and 0.08 Å for Fe) versus the other two, most likely arising from steric interference with the methyl group of the [N₂NMe] ligand. Otherwise, the familiar contraction of all six M–N bonds is also observed in this series upon replacement of Mn by Fe, with all metrical parameters pinpointing toward high-spin metal sites (M–N_{amine} = 2.352(2) (Mn), 2.2803(17) (Fe) Å; av. M–N_{guanidine} = 2.175(±0.028) (Mn), 2.111(±0.033) (Fe) Å; av. M–N_{NCMe} = 2.275(±0.054) (Mn), 2.198(±0.043) (Fe) Å). Finally, the unique, five-coordinate $[(\text{TMG}_2\text{biphen})\text{Co}^{\text{II}}(\text{NCMe})_2](\text{PF}_6)_2$ (**10**, Figure 4) exhibits a trigonal bipyramidal geometry similar to that observed for the chloride precursor, albeit less distorted ($\tau_5 = 0.75$). The elongated axial ligand field is occupied by residues N(1)_{amine} of the ligand and N(8) of acetonitrile (N(1)–Co–N(8) (174.30(7)°). The two ligand-derived imino moieties and a second acetonitrile reside in the equatorial positions. As expected for a cationic, late transition metal, this Co(II) compound possesses the tightest [N₂N] ligand field among all other bipodal compounds

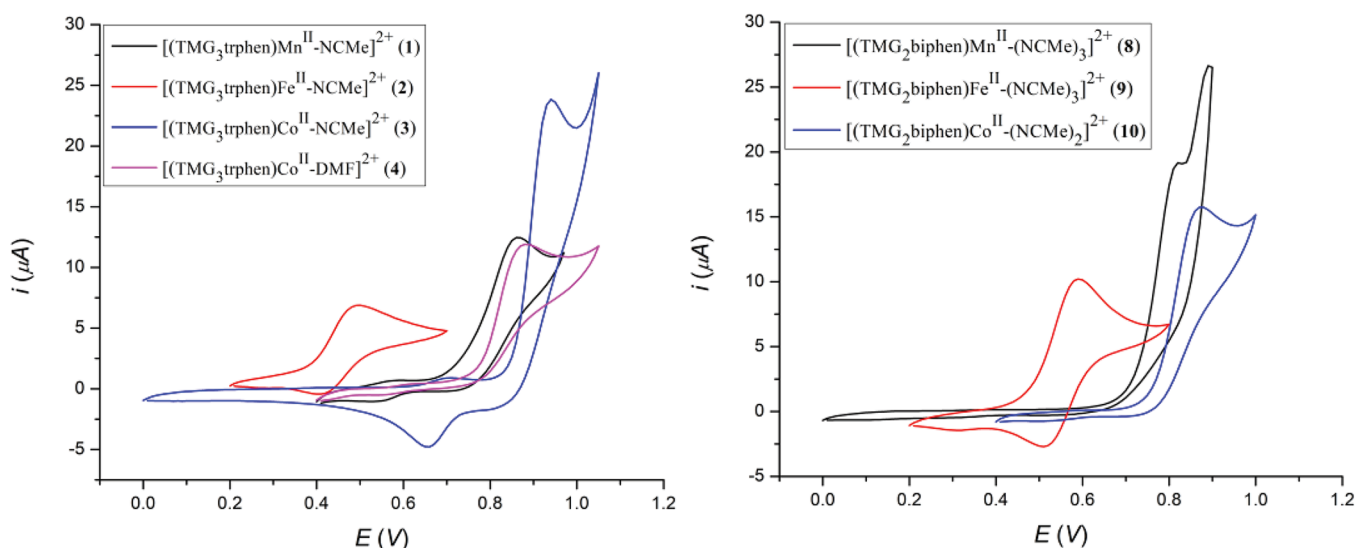


Figure 5. Cyclic voltammograms of tripodal compounds $[(\text{TMG}_3\text{trphen})\text{M}^{\text{II}}-\text{solv}](\text{PF}_6)_2$ ($\text{M} = \text{Mn}$ (1), Fe (2), Co (3), $\text{solv} = \text{MeCN}$; Co (4), $\text{solv} = \text{DMF}$) and bipodal analogues $[(\text{TMG}_2\text{biphen})\text{M}^{\text{II}}-(\text{NCMe})_x](\text{PF}_6)_2$ ($\text{M} = \text{Mn}$ (8), Fe (9), $x = 3$; Co (10), $x = 2$) in $\text{MeCN}/\text{Bu}_4\text{NPF}_6$ (1–3, 8–10) or $\text{DMF}/\text{Bu}_4\text{NPF}_6$ (4) with a Au disk electrode (1.6 mm in diameter); scan rate 0.2 V/s.

Table 1. Product Yields in Catalytic Nitrene Transfer to Styrene Mediated by $\text{M}(\text{II})$ Reagents^a

entry	catalyst	MeCN			DCM		DCE		PhCl	
		A	I	P	A	P	A	P	A	P
1	$[(\text{TMG}_2\text{diphen})\text{Mn}^{\text{II}}(\text{NCMe})_3](\text{PF}_6)_2$	25	trace	trace	20	2 (1:0.7) ^b	22	2 (1:0.7) ^b	4	trace
2	$[(\text{TMG}_3\text{trphen})\text{Mn}^{\text{II}}(\text{NCMe})](\text{PF}_6)_2$	15	n.d.	n.d.	10	n.d.	7	n.d.	9	trace
3	$[\text{Mn}^{\text{II}}(\text{NCMe})_6](\text{PF}_6)_2$	14	trace	2 (1:0.6) ^b	n.d.	7 (1:0.7) ^b	10	12 (1:0.7) ^b	3	6 (1:0.8) ^b
4	$[(\text{TMG}_2\text{diphen})\text{Fe}^{\text{II}}(\text{NCMe})_3](\text{PF}_6)_2$	65	3	2 (0.7:1) ^b	1	33 (1:0.8) ^b	5	25 (1:0.7) ^b	4	22 (1:0.7) ^b
5	$[(\text{TMG}_3\text{trphen})\text{Fe}^{\text{II}}(\text{NCMe})](\text{PF}_6)_2$	20	trace	trace	10	2 (1:0.9) ^b	8	trace	13	trace
6	$[\text{Fe}^{\text{II}}(\text{NCMe})_6](\text{PF}_6)_2$	66	6	2 (1:0.7) ^b	n.d.	33 (1:0.7) ^b	n.d.	28 (1:0.7) ^b	n.d.	30 (1:0.7) ^b
7	$[(\text{TMG}_2\text{diphen})\text{Co}^{\text{II}}(\text{NCMe})_2](\text{PF}_6)_2$	27	n.d.	trace	18	trace	29	trace	10	trace
8	$[(\text{TMG}_3\text{trphen})\text{Co}^{\text{II}}(\text{NCMe})](\text{PF}_6)_2$	21	n.d.	3 (1:0.6) ^b	23	trace	13	trace	14	trace
9	$[\text{Co}^{\text{II}}(\text{NCMe})_6](\text{PF}_6)_2$	32	n.d.	trace	9	trace	14	trace	trace	trace

^aYields are obtained from ^1H NMR experiments of purified products using internal standard. ^bDiastereomeric ratio (cis:trans)

examined in this study as well as two unequal acetonitrile moieties ($\text{Co}-\text{N}(8)_{\text{ax}} = 2.095(2)$, $\text{Co}-\text{N}(9)_{\text{eq}} = 2.0396(18)$ Å). Structural similarities with relevant literature compounds are discussed in the SI.

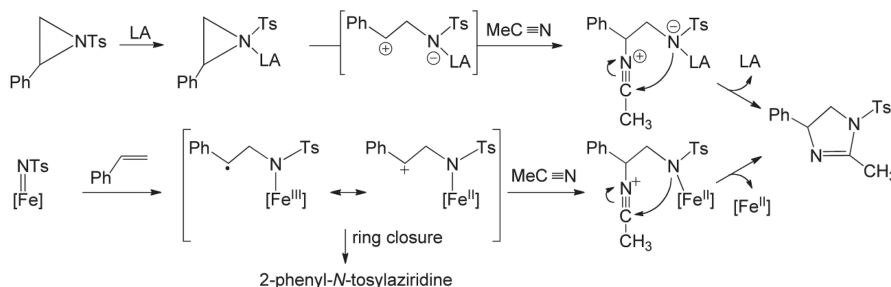
The strong donor character of the superbasic TMG residue upon metalation can be evaluated by the degree of charge delocalization over the CN_3 triangle as depicted by the structural parameter $\rho = 2a/(b+c)$, where a is the $\text{C}=\text{N}$ bond distance and b and c are the two $\text{C}-\text{NMe}_2$ bond distances.⁶¹ Indeed, whereas for the tripodal ($\text{TMG}_3\text{trphen}$) and bipodal ligands ($\text{TMG}_2\text{biphen}$) the length of the $\text{C}=\text{N}$ bond is 94% of the average $\text{C}-\text{NMe}_2$ bonds ($\rho = 0.94$), for all metal compounds that are supported by these ligands the corresponding bond lengths are essentially equivalent ($\rho = 0.99$ (1, 5, 8, 9), 1.00 (2, 3, 4, 6, 7, 10)).

2.3. Magnetic Susceptibility Measurements and Electrochemistry. Magnetic susceptibility data for the tripodal (1–4) and bipodal (8–10) metal compounds were obtained by the Evans ^1H NMR method.⁶² The effective magnetic moments (μ_{eff}) calculated are within experimental

values of high-spin configurations⁶³ for all compounds (Mn : $S = 5/2$ ($\mu_{\text{eff}} = 5.9$ (1), 6.1 (8) μ_{B}); Fe : $S = 2$ ($\mu_{\text{eff}} = 5.7$ (2), 5.7 (9) μ_{B}); Co : $S = 3/2$ ($\mu_{\text{eff}} = 4.2$ (3), 4.3 (4), 4.3 (10) μ_{B}), in agreement with metrical parameters noted above (Table S5).

Cyclic voltammograms of the tripodal compounds 1–4 and bipodal analogues 8–10 (Figure 5) were obtained in MeCN, with the exception of 4 (in DMF). Table S6 summarizes relevant electrochemical data (potentials are referenced versus the Fc^+/Fc couple). Among all compounds studied, only the Fe tripodal (2) and bipodal (9) congeners are associated with semireversible waves, which can reasonably be assigned to $\text{Fe}(\text{II})/\text{Fe}(\text{III})$ couples. The corresponding $E_{1/2}$ values for these species (0.45 (2), 0.55 (9) V) are consistent in view of the supporting ligand fields and also in line with the reported $E_{1/2}$ value (0.52 V in MeCN) for the tripodal $[(\text{TMG}_3\text{tren})\text{Fe}(\text{NCMe})](\text{ClO}_4)_2$.^{42a} On the other hand, the Mn tripodal (1) and bipodal analogues (8) give rise to essentially only anodic waves at higher voltages ($E_{\text{p,a}} = 0.86$ (1), 0.82 (8) V) given the stability of high-spin Mn(II) sites. These anodic waves are also associated with sizable currents, presumably

Scheme 3. Possible Pathways for the Insertion of Nitrile in Aziridination Processes



denoting ligand contributions to the oxidation events. Interestingly, the corresponding tripodal compound [(TMG₃tren)Mn(NCMe)](ClO₄)₂ features a reversible Mn(II)/Mn(III) couple at a similar voltage ($E_{1/2}$ (MeCN) = 0.88 V), which shifts to more accessible potentials when Cl⁻ is present in the coordination sphere ($E_{1/2}$ = 0.47 V for [(TMG₃tren)MnCl]Cl).^{42a} Similar results are obtained with the Co(II) analogues, for which only anodic waves are obtained at slightly higher potentials vs the Mn(II) compounds (E_{pa} = 0.94 (3), 0.88 (4), 0.87 (10) V). Specifically, for the tripodal compounds of Mn(II) and Co(II), small reductive waves denote possible decomposition of high-valent species generated at high voltages.

2.4. Catalytic Nitrene Transfer to Olefins. 2.4.1. Styrene.

To start evaluating the atom/group-transfer chemistry facilitated by the tripodal and bipodal divalent base reagents in hand, we conducted a study of nitrene addition (PhINTs, 1 equiv) to styrene (8 equiv) in the presence of 5 mol % of catalyst and molecular sieves (5 Å) in various solvents (MeCN, CH₂Cl₂, DCE, PhCl) at 30 °C (drybox temperature) over 24 h. The requirement for 8.0 equiv of styrene over PhINTs (limiting reagent) has been confirmed in styrene aziridinations in MeCN mediated by the bipodal Fe(II) reagent **9** (aziridine yields 45%, 2 equiv of styrene; 55%, 4 equiv of styrene; 61%, 8 equiv of styrene; 63%, 16 equiv of styrene).

Table 1 summarizes product yields for the three base metals examined (M = Mn, Fe, Co), each represented by three reagents, featuring bipodal (TMG₂biphen), tripodal (TMG₃trphen), and ligand-free coordination ([M(NCMe)₆](PF₆)₂). In addition to aziridine (**A**), two additional insertion products are rather unexpectedly observed, albeit in moderate amounts in most cases. Further analysis uncovered that in reactions conducted in MeCN, the major product (aziridine) is accompanied by low yields (<10%) of imidazoline (**I**), largely in Fe-catalyzed reactions (entries 4–6), presumably arising from formal insertion of MeCN into the corresponding aziridine. Moreover, 2,4-diphenyl-1-tosyl-pyrrolidines (**P**, *cis* and *trans* diastereomers) are detected in very low amounts, a likely result of formal (3 + 2) cycloaddition of aziridine and styrene.³¹ The diastereomeric pyrrolidines are more prominently represented in the product profile of Fe(II)-catalyzed reactions carried out in chlorinated solvents. Indeed, for the [(TMG₂biphen)Fe(NCMe)₃](PF₆)₂- and [Fe(NCMe)₆](PF₆)₂-mediated reactions in CH₂Cl₂, DCE, or chlorobenzene (entries 4 and 6), the pyrrolidines are almost exclusively observed in lieu of aziridine, albeit in modest overall yields (for yield optimization, see below). A similar observation has been previously made by Liang and Jensen with [Fe(NCMe)₆](BF₄)₂ in CH₂Cl₂.⁶⁴ On the other hand, the tripodal [(TMG₃trphen)Fe(NCMe)](PF₆)₂ exhibits low conversion

of aziridine to pyrrolidine in chlorinated solvents (entry 5). Finally, the Mn and Co reagents (entries 1–3 and 7–9) are significantly less productive than the corresponding Fe reagents in terms of both aziridine formation (in MeCN) and aziridine conversion to pyrrolidines (in chlorinated solvents). It is plausible that the instability of the Mn and Co sites upon oxidation, as indicated by the electrochemical studies, may be responsible for the low catalytic activity of these metals.

With respect to aziridine formation, this initial assessment indicates that (i) acetonitrile is a more productive solvent than the chlorinated solvents tested, (ii) divalent reagents supported by the bipodal framework are more high yielding than the corresponding tripodal catalysts in MeCN and on par with the ligand-free acetonitrile adducts, and (iii) the observed reactivity trend (Fe > Co ≥ Mn) favors Fe reagents by a considerable margin.

Given the comparable yields afforded by [(TMG₂biphen)-Fe(NCMe)₃](PF₆)₂ and [Fe(NCMe)₆](PF₆)₂, we investigated whether any bipodal ligand is released in MeCN upon catalytic turnover. The aforementioned catalytic aziridination of styrene was repeated on a larger scale (triple) in the presence of [(TMG₂biphen)Fe(NCMe)₃](PF₆)₂ (5 mol %), and the residue, after removal of volatiles, was analyzed by ¹H NMR in CD₃CN (aziridination yield 62%). Although broad paramagnetic features are observed due to the metal, those do not impede us from concluding that no free ligand (or any aminated derivative) is generated, as judged with the assistance of an authentic ligand sample. Moreover, additional product profile data provide divergent yields and selectivities in aziridination/amination of substrates by the two catalysts, as detailed below.

2.5. Provenance of Five-Membered N-Heterocycles.

Latour and co-workers have recently observed imidazolines as byproducts of iron-catalyzed aziridinations of styrene and para-substituted congeners in the presence of nitriles.^{14g,51b} As opposed to the well-established Lewis- or Brønsted-acid-catalyzed imidazoline generation by means of ring opening of aziridine (C–N bond cleavage) and nitrile insertion (formal (3 + 2) cycloaddition via an incipient 1,3-dipole intermediate; Scheme 3, top),³³ these workers propose a new mechanistic path that is intimately connected to the aziridine formation route by way of a competitive insertion of nitrile (Scheme 3, bottom; adapted from ref 51b). Among the isomeric styrenyl radical and carbocation intermediates, the carboradical was deemed exclusively responsible for nucleophilic attack by the nitrile, since electronically diverse nitriles provided the same aziridine/imidazoline distribution.^{51b} On the other hand, in a related study involving photocatalytically generated nitrene radicals (*NHSO₂Ar), styrenes, and nitriles, RCN is deemed to

preferably attack the carbocationic intermediate toward imidazoline formation.⁶⁵

To start assessing these potential pathways, we performed a reaction between 2-phenyl-*N*-tosylaziridine (0.15 mmol) and excess MeCN (5.0 mmol) in the presence of [(TMG₂biphen)Fe(NCMe)₃](PF₆)₂ (**9**) or [Fe(NCMe)₆](PF₆)₂ (10 mol %) at 30 °C. Very low yields of imidazoline (1%) were detected with the former catalyst after 24 h (aziridine recovery 86%) and slightly higher (8%) with the latter more acidic reagent (aziridine recovery 70%), thus suggesting that the imidazoline noticed in the catalytic reactions of Table 1 might be the product of a subsequent reaction between preformed aziridine and MeCN. Decomposition of some aziridine is noted in these experiments to unaccounted products. These initial observations suggest that the two Fe(II) compounds may engage in Lewis-acid-catalyzed imidazoline generation in the nitrene-transfer reactions (Table 1), but this proposition is tentative given the very low yields of imidazoline observed in the catalytic reactions.

To further evaluate the origin of pyrrolidines in the aziridination reactions of styrene catalyzed by [(TMG₂biphen)Fe(NCMe)₃](PF₆)₂ and [Fe(NCMe)₆](PF₆)₂, a series of catalytic reactions was conducted in CH₂Cl₂ at 20 and 30 °C, quenched at different time intervals. The product profiles (Table 2) indicate that the highest

Table 2. Time-Dependent Product Yields in Fe(II)-Mediated Nitrene Transfer to Styrene

time (h)	[Fe ^{II} (NCMe) ₆](PF ₆) ₂ (20/30 °C)		[(TMG ₂ biphen)Fe ^{II} (NCMe) ₃] (PF ₆) ₂ (20/30 °C)	
	aziridine (%)	pyrrolidine (%)	aziridine (%)	pyrrolidine (%)
0.5	32/28	2/6	43/42	3/12
1	30/27	2/9	45/36	6/16
2	22/7	8/27	37/32	10/20
4	8/4	18/28	21/15	15/26
24	0/0	27/33	15/5	19/31

combined product yield (mostly aziridine) is already achieved in 0.5–1.0 h, followed by progressive conversion of aziridine to pyrrolidine. As expected, the conversion is faster at 30 °C. A moderate total yield erosion is also observed over time, potentially by means of aziridine decomposition as noted above. The presence of even small amounts of MeCN (CH₂Cl₂/MeCN, 20:1 w/w) yields aziridine (58%) and only minimal amounts of pyrrolidine (2%) in reactions catalyzed by [(TMG₂biphen)Fe(NCMe)₃](PF₆)₂. These experiments indicate that the pyrrolidine obtained in the catalytic reactions is most likely the product of a secondary reaction between preformed aziridine and excess styrene, with Fe(II) (or a

higher oxidation-state derivative) acting as a Lewis acid (Scheme 4) in the absence of acetonitrile.

Mixtures of isomeric pyrrolidines have been first reported, and similarly interpreted, by nitrene-chemistry pioneer Paul Müller and co-workers,^{22d,66} generated in the Rh₂(OAc)₄-catalyzed aziridination of α -methylstyrene, 4-methoxystyrene, or ethyl vinyl ether by PhI=NNs in CH₂Cl₂. In our hands, the aziridination of styrene (2.0 mmol) by PhI=NTs (0.25 mmol) in the presence of Rh₂(OAc)₄ (2.5 mol %) in CH₂Cl₂ (24 h) affords 48% of 2-phenyl-*N*-tosylaziridine and 10% of pyrrolidines. In olefin aziridinations (TsN₃) mediated by Fe(III) porpholactone catalysts, low yields of pyrrolidines were observed for 4- and 3-methoxystyrene, rationalized via a mechanism that favors styrene addition to an intermediate α -styrenyl radical.⁶⁷ As noted above, Liang and Jensen were the first to realize the role of [Fe(NCMe)₆](BF₄)₂ in mediating catalytic reactions of styrenes and PhINTs to afford pyrrolidines (via aziridine formation) as well as (3 + 2) cycloadditions involving 2-phenyl-*N*-tosylaziridine and dipolarophiles.⁶⁴ More recently, low yields (1–2%) of the two *cis/trans* pyrrolidine diastereomers have also been observed by means of catalytic nitrene transfer (PhI(OAc)₂/TsNH₂) to styrene, mediated by a host of Ag(I) triflate reagents supported by nitrogen-confused C-scorpionates in MeCN at 80 °C.⁶⁸ Naturally, several pyrrolidines have been previously obtained in the presence of various Lewis or Brønsted acids by means of (3 + 2) cycloaddition of aziridines with alkenes.^{31–36,69}

2.5.1. Para-Substituted Styrenes. We have subsequently extended the investigation to encompass a wider range of substrates, starting with a panel of para-substituted styrenes (Table 3) for which aziridination reactions were performed in MeCN at 30 °C. Once again, [(TMG₂biphen)Fe(NCMe)₃](PF₆)₂ (**9**) and [Fe(NCMe)₆](PF₆)₂ demonstrated superior efficacy over the tripodal Fe(II) congener (**2**) as well as all other Mn(II) and Co(II) reagents (Fe > Co \geq Mn) for the entire substrate panel. A similar reactivity pattern has been observed with base-metal scorpionate complexes.⁷⁰ The highest aziridination yields ($\geq 80\%$) for the two most productive Fe(II) reagents were obtained for the least electron-rich olefin (4-nitrostyrene), presumably because the 1,3-zwitterion resulting from aziridine ring opening is destabilized by EW substituents. Low yields of imidazolines (<10%) are observed with these two Fe(II) catalysts, especially with the more electron-rich olefins, in agreement with the proposed Lewis-acid role of the dicationic reagents.

2.5.2. Other Alkenes. The two most productive Fe(II) catalysts were subsequently evaluated as mediators of nitrene transfer to a panel of aromatic and aliphatic alkenes in MeCN (Tables 4 and S7). Styrenes with ortho substitution (entry 1) proved to give modest yields of aziridine, especially in the presence of [Fe(NCMe)₆]²⁺ as catalyst, hinting to a steric but also an electronic hampering factor (orthogonal orientation of the aromatic/olefinic planes).⁷¹ Trace amounts of benzylic amination are also observed. Nitrene transfer to the α -substituted styrenes (Me and Ph; entries 2 and 3) is also

Scheme 4. Proposed Pathway for Pyrrolidine Formation in Aziridination Catalysis

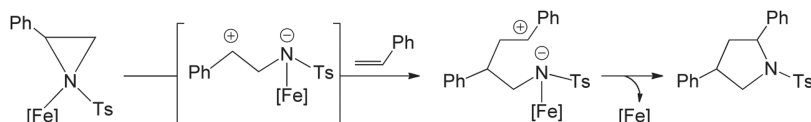
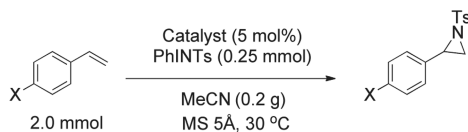


Table 3. Yields of Aziridines from Para-Substituted Styrenes in MeCN^{a,b,c}

entry	substrate	[L _{bi} Mn] ²⁺	[L _{tri} Mn] ²⁺	[Mn(NCMe) ₆] ²⁺	[L _{bi} Fe] ²⁺	[L _{tri} Fe] ²⁺	[Fe(NCMe) ₆] ²⁺	[L _{bi} Co] ²⁺	[L _{tri} Co] ²⁺	[Co(NCMe) ₆] ²⁺
1	X = H	25	15	14	61(3)	20	62(6)	29	24	32
2	X = Me	20	18	18	62(2)	21	69(4)	20	13	34
3	X = ^t Bu	23	19	21	63(3)	23	71(4)	21	15	37
4	X = Cl	19	12	13	58(tr)	15	55(3)	20	14	32
5	X = F	18	12	11	54(tr)	13	53(4)	15	13	33
6	X = CF ₃	15	10	10	62(nd)	13	75(tr)	14	10	36
7	X = NO ₂	8	9	5	80(nd)	12	84(tr)	18	12	20

^aL_{bi} = TMG₂biphen, L_{tri} = TMG₃trphen. ^bYields of imidazolines in parentheses. ^cThe counteranion for all catalysts is hexafluorophosphate (PF₆⁻).

Table 4. Yields of Aziridination and Amination Products Generated in Fe(II)-Mediated Nitrene Transfer to Various Olefins^a

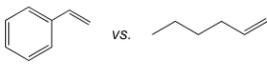
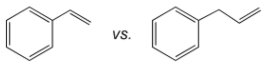
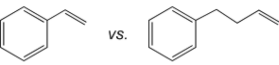
Entry No.	Substrate	Products	Yield (%) [(TMG ₂ biphen)Fe(NCMe) ₃] ²⁺	Yield (%) [Fe(NCMe) ₆] ²⁺
1.			26, trace	7, trace
2.			5, 8, 20	4, 9, 22
3.			trace, 27	trace, 40
4.			50, 4	38, 6
5.			13	10
6.			4, 4, 6	6, 3, 16
7.			3, 11	trace, 28
8.			8, 16 (trace, 28) ^b	22, 16 (trace, 22) ^b
9.			30, 3	18, trace
10.			4, 25	5, 20
11.			9, 4	7, 6
12.			56, trace	47, 3
13.			24, 6	43, 8

^aCatalyst, 0.0125 mmol (5 mol %); PhINTs, 0.25 mmol; olefin, 2.0 mmol; MS 5 Å, 20 mg; MeCN 0.250 g; 30 °C; 24 h. ^bA 0.25 mmol amount of substrate and 0.50 mmol of PhINTs were used.

affected by steric effects. The α -methylstyrene is susceptible to allylic amination but also gives rise to a major imidazoline product, presumably arising from formal insertion of MeCN into the corresponding aziridine. Only trace aziridine is observed for the α -Ph congener (entry 3) since it is known to undergo facile ring opening and rearrangement to afford the enamine in good yields.⁷² The mechanistically significant *cis*-

and *trans*- β -methylstyrenes (entries 4 and 5) indicate that the usually more productive *cis* congener provides better yields for the bipodal Fe(II)-supported reactions and also retains stereochemistry to a great extent upon aziridination (93% and 86% retention for the reactions mediated by [(TMG₂biphen)Fe(NCMe)₃]²⁺ and [Fe(NCMe)₆]²⁺, respectively). The case of *cis*- and *trans*-stilbene (entries 6 and 7) is

Table 5. Competitive Aziridination of Styrene vs 1-Hexene, Allylbenzene, and 4-Phenyl-1-butene

Compound			
$[(\text{TMG}_2\text{biphen})\text{Fe}(\text{NCMe})_3](\text{PF}_6)_2$ (9)	8.3:1	6.8:1	6.9:1
$[\text{Fe}(\text{NCMe})_6](\text{PF}_6)_2$	6.0:1	4.1:1	7.2:1

more complicated because the corresponding aziridine undergoes ring opening and phenyl migration to afford the enamine noted in entry 3.⁶⁶ Overall, for both the α - and the β -substituted styrenes (entries 2–7), the bipodal Fe(II) reagent **9** is more productive in conjunction with the smaller Me substituent, whereas $[\text{Fe}(\text{NCMe})_6]^{2+}$ is more suitable for the bulkier Ph congener. For styrenyl substrates that may also possess allylic/benzylic sites (entries 8 and 9), C–H aminations are competitive with aziridinations, especially when trans substrates (entry 8) restrict aziridination yields. As a matter of fact, the allylic/benzylic amination is essentially dominant if the trans substrate (entry 8) is used as the limiting reagent (substrate/PhINTs 1:2). The effect of the bulkier $[(\text{TMG}_2\text{biphen})\text{Fe}(\text{NCMe})_3](\text{PF}_6)_2$ (**9**) versus $[\text{Fe}(\text{NCMe})_6](\text{PF}_6)_2$ is also evident in conjunction with the less encumbered cis substrate (entry 9).

Further experimentation with aliphatic olefins (entries 10–13) furnished moderate yields of nitrene-transfer products in reactions catalyzed by the bipodal Fe(II) reagent **9** or $[\text{Fe}(\text{NCMe})_6]^{2+}$, in sharp contrast to high-yielding reactions by analogous Cu(I) reagents.⁴⁰ Among cycloalkenes (entries 10–12), the more electron-rich *cis*-cyclooctene undergoes aziridination almost exclusively, whereas cyclopentene favors allylic amination. Reportedly, the barrier for H-atom abstraction from allylic C–H bonds is substantial for cyclooctene by comparison to cyclopentene or cyclohexene as a result of poor $\sigma_{\text{C-H}}/\pi_{\text{C=C}}$ orbital overlap (orthogonality).⁷³ Methylene cyclohexane (entry 13) affords good aziridination yields, especially with the less encumbered $[\text{Fe}(\text{NCMe})_6]^{2+}$, accompanied by limited amounts of allylic amination (single isomer). Other terminal aliphatic olefins (entries 14–19, Table S7) provide low aziridination yields, especially for those reactions catalyzed by the bipodal Fe(II) reagent **9**.


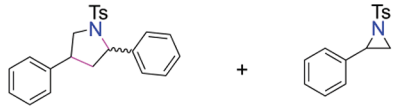
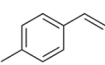
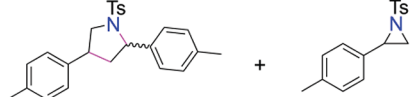
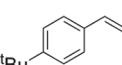
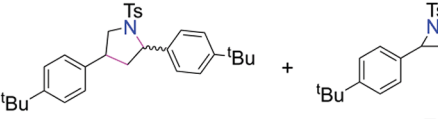
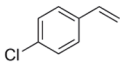
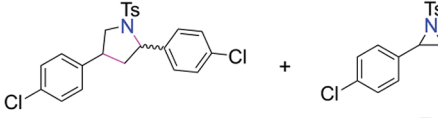
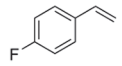
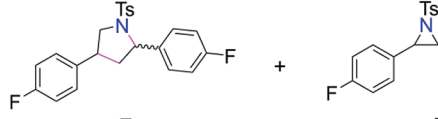
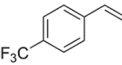
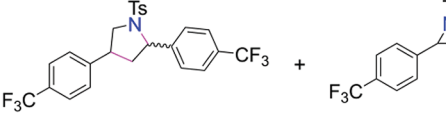
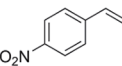
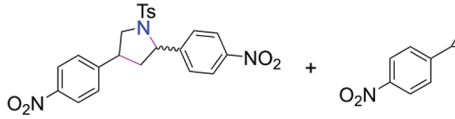
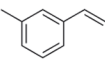
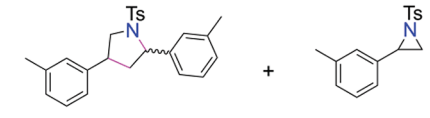

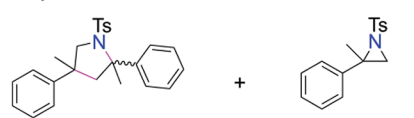
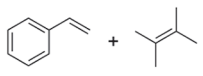
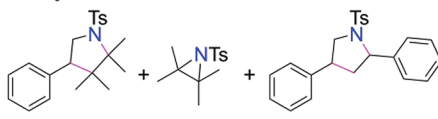
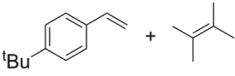
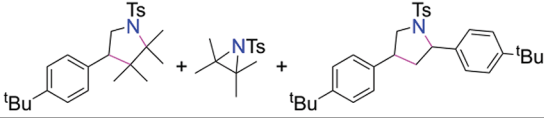
Competitive aziridinations of a mixture of styrene (1.0 mmol) with equimolar amounts of a second olefin (1-hexene, allylbenzene, 4-phenyl-1-butene; Table 5) by PhINTs (0.25 mmol) in the presence of the bipodal Fe(II) reagent **9** or $[\text{Fe}(\text{NCMe})_6](\text{PF}_6)_2$ (5 mol %) in MeCN at 20 °C reveals a preponderance of aromatic over aliphatic alkene aziridination by a factor ranging from 4.1 to 8.3. The observed chemoselectivity of **9** exceeds that of $[\text{Fe}(\text{NCMe})_6](\text{PF}_6)_2$, save for the styrene/4-phenyl-1-butene competition, but is somewhat inferior to that previously encountered for the same competition experiments mediated by similar anionic Fe(II) reagents,^{39b} the latter being significantly slower in converting alkenes to aziridines.

2.5.3. Single-Pot Cycloadditions for the Synthesis of Pyrrolidines. To further evaluate the scope of 2,4-disubstituted pyrrolidine synthesis, we investigated the reaction of several styrenes (2.0 mmol) with PhINTs (0.25 mmol) mediated by

$[(\text{TMG}_2\text{biphen})\text{Fe}(\text{NCMe})_3](\text{PF}_6)_2$ (**9**) in dichloromethane (Table 6). An initial optimization process indicated that maximum yields (pyrrolidine, aziridine) are obtained in most cases with 10 mol % catalyst and in dilute solutions. Notably, styrenes with electron-donating para substituents (entries 1–3) are significantly more productive in the synthesis of pyrrolidines at the expense of aziridines, presumably because the electron-donating residue stabilizes the incipient 1,3-dipole upon aziridine ring opening. Conversely, electron-withdrawing substituents can only partially, if at all, facilitate aziridine to pyrrolidine conversion (entries 4–7). 3-Methyl- and α -methylstyrene (entries 8 and 9) can also provide pyrrolidines almost exclusively, albeit in lower yields. In a preliminary attempt to use two distinct olefins (entries 10 and 11), one aromatic and one aliphatic (in 4-fold excess over the aromatic), the aryl/alkyl-substituted pyrrolidine can be obtained at the expense of the aryl/aryl-substituted congener, but yields are undercut by the presence of the inert aziridine of the aliphatic olefin. In a control experiment, 1 equiv of 2-phenyl-*N*-tosylaziridine and equimolar amounts of styrene and 2,3-dimethyl-2-butene (4 equiv each) provide the corresponding pyrrolidines in 27% and 25% yields, respectively, in the presence of **9** (15 mol %) in CH_2Cl_2 . Hence, both olefins are equally effective in (3 + 2) cycloaddition with the aziridine. Further optimization of the conditions for generating pyrrolidines from two distinct olefins as well as pyrrolidines from alkene/alkyne combinations will be addressed in future investigations.

2.5.4. (2 + 1 + 2) Cycloadditions for the Synthesis of Oxazolidines. In the presence of carbonyl substrates, styrenes can undergo nitrene transfer (NTs) that results in incorporation of the carbonyl component to generate the corresponding 1,3-oxazolidine in situ (Table 7).⁷⁴ In the majority of cases, a 4-fold excess of carbonyl substrate over the aromatic olefin is needed to achieve maximum yields in the presence of **9** (10 mol %) in CH_2Cl_2 at ambient temperatures. Cycloaddition of styrene, NTs, and acetone (2 + 1+2) provides practicable yields (70%) of the 1,3-oxazolidine as the sole product. As anticipated, a small increase in the yields of the corresponding oxazolidines is observed with the electron-rich 4-Me- and 4-*t*-Bu-styrene. Conversely, use of the electron-deficient 4-Cl-styrene results in decreased oxazolidine yields accompanied by low amounts of 4-Cl-styrene-derived pyrrolidine (7%). Higher homologues of acetone, such as 2-butanone and 3-pentanone, also provide good yields of oxazolidines, although somewhat lower than those of acetone, presumably due to steric reasons. This is further confirmed with the sterically demanding diisopropyl ketone and di-*tert*-butyl ketone (not shown) that proved to be inert to the reaction conditions; only 2,4-diphenyl-*N*-tosyl pyrrolidine and residual aziridine are observed. On the other hand, cyclohexanone, acetophenone, and benzophenone offer clean reactions with good yields of the

Table 6. Yields of Pyrrolidines and Aziridines Derived from Nitrene Transfer to Styrenes Mediated by [(TMG₂biphen)Fe(NCMe)₃](PF₆)₂ (9)^a

Entry	Substrate	Products	Yields
1.			50 (d.r. 1:1), 2
2.			60 (d.r. 1:1), trace
3.			72 (d.r. 1:1), n.d.
4.			10 (d.r. 1:1), 32
5.			9 (d.r. 1:1), 34
6.			n.d., 39
7.			n.d., 40
8.			38 (d.r. 1:1), n.d.
9.			37 (d.r. 1:1), n.d.
10.			16, 10, 4 (d.r. 1:1) ^b
11.			18, 14, 3 (d.r. 1:1) ^b

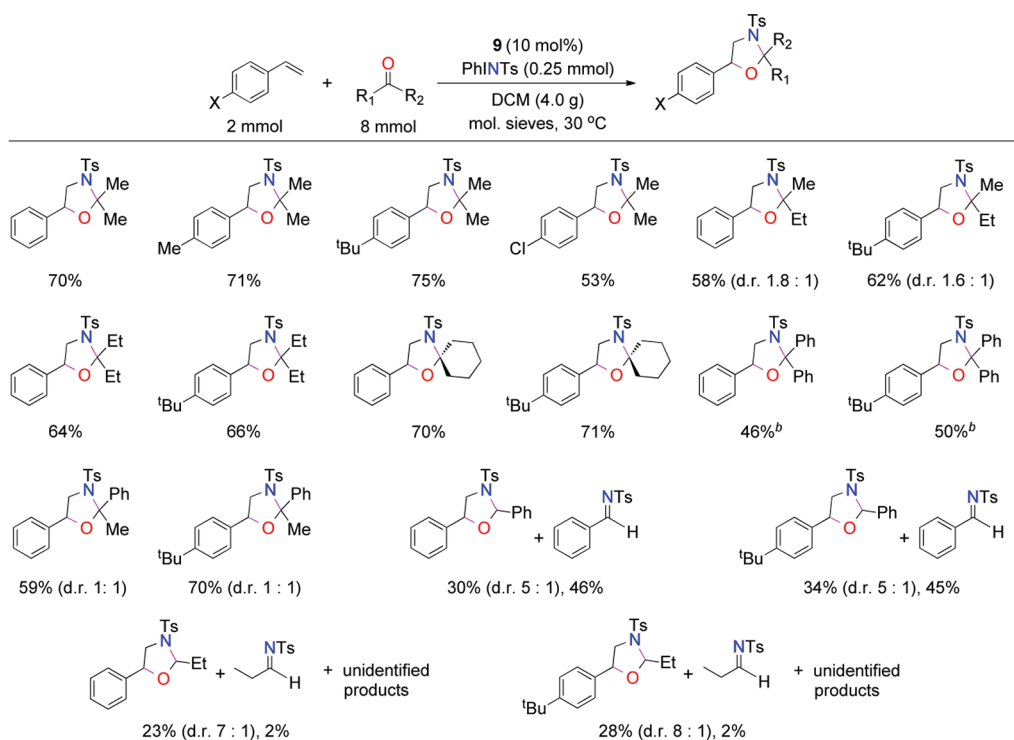
^aCatalyst **9**, 0.025 mmol (10 mol %); PhINTs, 0.25 mmol; olefin, 2.0 mmol; MS 5 Å, 20 mg; CH₂Cl₂, 4.0 g; 30 °C; 24 h. ^b2,3-Dimethyl-2-butene, 8.0 mmol.

corresponding oxazolidine (either as a single product or as two diastereomers). Benzaldehyde can also be converted to the corresponding 1,3-oxazolidine with promising diastereoselection but at more modest yields, presumably because the nitrene is consumed in a parallel catalytic reaction between PhCHO and PhINTs, to generate the aldimine (PhC(=NTs)H).⁷⁵ The latter has been confirmed in a control experiment in the absence of styrene (51% of aldimine obtained). Interestingly, no amidation of the aldehyde (PhCONHTs) was observed.⁷⁶ However, aldimine was only detected in low yields with propionaldehyde, but other

unidentified products affect the yield of the 1,3-oxazolidine. Suitable protocols for the incorporation of aldehydes and imines as dipolarophiles will be explored in future studies.

2.6. Mechanistic Studies. **2.6.1. Hammett Plots.** Competitive aziridinations by PhINTs (1.0 equiv) involving styrene (4.0 equiv) and a 4-X-substituted styrene (4.0 equiv; X = ^tBu, Me, Cl, F, CF₃, NO₂) with the bipodal Fe(II) catalyst **9** (5 mol %) in MeCN at 20 °C provided k_X/k_H data (Table S8) from the ratio of the corresponding aziridines, as determined by ¹H NMR. Linear free energy correlations of log(k_X/k_H) as a function of the polar substituent parameters σ_p (Figure S3)

Table 7. Yields of Oxazolidines and Related Products Derived from Nitrene Transfer to Styrenes in the Presence of Carbonyls As Mediated by [(TMG₂biphen)Fe(NCMe)₃](PF₆)₂ (9)^a



^aCatalyst 9, 0.025 mmol (10 mol %); PhINTs, 0.25 mmol; olefin, 2.0 mmol; dipolarophile, 8.0 mmol; MS 5 Å, 20 mg; CH₂Cl₂, 4.0 g; 30 °C; 24 h.
^bDipolarophile, 12.0 mmol.

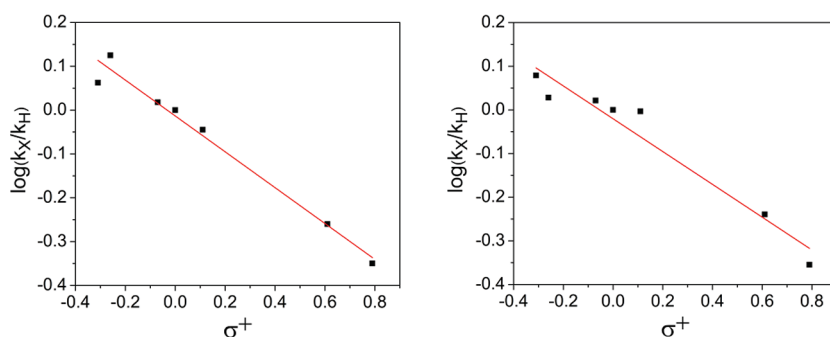


Figure 6. Linear free energy correlation of $\log(k_X/k_H)$ as a function of σ^+ for the competitive aziridination of para-substituted styrenes versus styrene catalyzed by [(TMG₂biphen)Fe(NCMe)₃](PF₆)₂ (9) (left) and [Fe(NCMe)₆](PF₆)₂ (right).

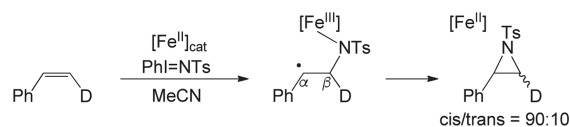
and σ^+ (Figure 6, left) provide satisfactory fits ($\rho_p = -0.47$, $R^2 = 0.97$; $\rho^+ = -0.41$, $R^2 = 0.98$) that are not improved by invoking spin-responsive radical parameters, presumably because the polar contribution is dominant with these dicationic catalysts (Figure S4). Less satisfactory fits are obtained for the analogous styrene/*p*-X-styrene competition reactions in the presence of 5.0 mol % [Fe(NCMe)₆](PF₆)₂ ($\rho_p = -0.42$, $R^2 = 0.89$ (Figure S3); $\rho^+ = -0.38$, $R^2 = 0.93$ (Figure 6, right)), possibly because of the coproduction of low yields of imidazolines. The negative ρ_p and ρ^+ slope values are indicative of an electrophilic oxidant operating and a small positive charge evolving at the benzylic carbon en route to the transition state. The ρ^+ values are particularly close to those reported by Latour and co-workers ($\rho^+ = -0.38$, -0.42) for styrene aziridinations (PhI=NTs) in MeCN mediated by catalysts [L^{NO₂}Fe^{II}(NCMe)₂] (L^{NO₂} is a tripodal ligand with an axial N_{amine} residue along with two 2,4-NO₂-substituted

phenolate arms and a pyridine moiety)⁷⁷ and [(^{Me,Me}TC^H)-Fe^{II}(NCMe)₂](PF₆)₂ (^{Me,Me}TC^H is a tetracarbene macrocycle).⁷⁸ Other more prominent ρ^+ slope values for similar aziridinations mediated by cationic Fe(II) catalysts have been reported by Che ($\rho^+ = -0.72$),⁷⁹ Jensen ($\rho^+ = -0.58$, -0.61),⁷⁰ and Latour ($\rho^+ = -0.71$, -0.83 , -0.94).^{14g,80}

2.6.2. Secondary Kinetic Isotope Effect and Retention of Stereochemistry upon Aziridination. To further assess the site of the initial nitrene (NTs) attack on styrene, we evaluated the secondary KIE upon aziridination of styrene with the assistance of α -*d*₁-styrene and *cis*- β -*d*₁-styrene. A mixture of styrene (1.0 mmol) and α -*d*₁-styrene (1.0 mmol) was reacted with PhINTs (0.25 mmol) in the presence of [(TMG₂biphen)-Fe(NCMe)₃](PF₆)₂ (5 mol %) in MeCN at 20 °C, and the reaction was quenched after 30 min (to avoid secondary products) to afford KIE values (by ¹H NMR) in the vicinity of 1.0(±0.01) (yield 40%). The same KIE value is essentially

obtained at $-20\text{ }^{\circ}\text{C}$ for reactions quenched after 2.0 h (yield 35%). On the other hand, the analogous competition reaction between styrene and *cis*- β - d_1 -styrene provides a small inverse kinetic isotope effect $0.97(\pm 0.02)$ at $20\text{ }^{\circ}\text{C}$ (30 min) and a more significant one, $0.81(\pm 0.01)$, at $-20\text{ }^{\circ}\text{C}$ (2.0 h). These results suggest that only the C_{β} carbon of styrene is largely engaged in the initial nitrene attack, most likely with an early transition state (Scheme 5). Aziridination of *cis*- β - d_1 -styrene

Scheme 5. Proposed Mechanism for Nitrene Addition to Styrene and Aziridine Ring Closure



(single substrate) by PhINTs under the same conditions provides *cis*- and *trans*-aziridine with good levels of stereo-retention (*cis/trans* = 90:10; evaluated by ^2H NMR), hence indicating that the aziridine ring closure ($\text{N}-\text{C}_{\alpha}$ bond formation) is fast in comparison with $\text{C}_{\alpha}-\text{C}_{\beta}$ bond rotation. This level of stereocontrol is considerably higher than that previously achieved by the anionic $[\text{K}(\text{MeCN})(\text{L}^8)\text{Fe}^{\text{II}}-\text{NCMe}]^{39\text{b}}$ or the cationic $[(\text{TMG}_3\text{trphen})\text{Cu}^{\text{I}}](\text{PF}_6)^{40}$ nitrene-transfer catalysts.

3. FURTHER DISCUSSION AND CONCLUSIONS

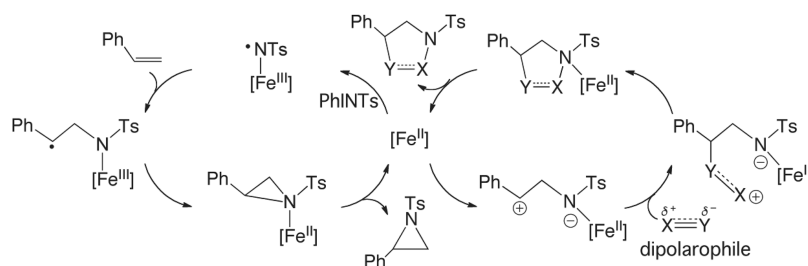
The following are the most significant findings and insights garnered from this investigation.

- A series of cationic bipodal and tripodal compounds of high-spin Mn(II), Fe(II), and Co(II) sites has been synthesized, featuring $[\text{N}_2\text{N}]$ and $[\text{N}_3\text{N}]$ coordination composed of an apical amine residue and two or three superbasic TMG arms. The general stoichiometry of $[(\text{TMG}_2\text{biphen})\text{M}^{\text{II}}(\text{NCMe})_x](\text{PF}_6)_2$ ($x = 3$ for Mn, Fe; $x = 2$ for Co) and $[(\text{TMG}_3\text{trphen})\text{M}^{\text{II}}-\text{solv}](\text{PF}_6)_2$ (solv = MeCN, DMF) is confirmed by single-crystal X-ray diffraction analysis, revealing distorted trigonal bipyramidal and octahedral geometries for the 5- and 6-coordinate compounds, respectively.
- The reaction of styrene and *para*-substituted styrenes with $\text{PhI}=\text{NTs}$ in the presence of catalytic amounts (5 mol %) of the newly synthesized bipodal and tripodal compounds as well as their ligand-free precursors $[\text{M}(\text{NCMe})_6]^{2+}$ affords both three-membered (aziridines) and five-membered *N*-heterocycles (imidazolines, pyrrolidines) depending on metal complex and reaction conditions. The formation of aziridines is favored in MeCN with a reactivity trend in the order

$\text{Fe} > \text{Co} \geq \text{Mn}$, applying individually to $[(\text{TMG}_2\text{biphen})\text{M}]^{2+}$, $[(\text{TMG}_3\text{trphen})\text{M}]^{2+}$, and $[\text{M}(\text{NCMe})_6]^{2+}$. Among these three types of reagents, the observed reactivity trend is as follows: $[(\text{TMG}_2\text{biphen})\text{M}]^{2+} \approx [\text{M}(\text{NCMe})_6]^{2+} > [(\text{TMG}_3\text{trphen})\text{M}]^{2+}$, suggesting that the availability of ample coordination space offers reactivity advantages. Interestingly, similar anionic tripodal compounds of the three divalent base metals^{39b} reveal rates of aziridine production which are in the order $\text{Co} > \text{Mn} \geq \text{Fe}$, although slower than those for the present cationic catalysts. Apparently, for these anionic catalysts, the electrophilicity of the putative $[(\text{L})\text{M}^{\text{III}}-\bullet\text{NTs}]^-$ is the main driver of reactivity,⁸⁰ whereas for the present cationic sites, the ease of formation (Fe) and/or decomposition (Mn, Co) of high-valent metal–nitrene species may be contributing factors, in tentative agreement with the electrochemical data.

- In addition to or in lieu of aziridines, five-membered *N*-heterocycles, namely, imidazolines and pyrrolidines, are observed in catalytic nitrene-transfer reactions, signifying the potential for in situ (3 + 2) cycloaddition reactions of aziridines with nitriles (MeCN) and olefins (excess substrate), respectively. The *N*-heterocycles can also be generated separately from the reaction of aziridine with MeCN (imidazolines) or olefin (pyrrolidines) in the presence of catalytic amounts of the divalent metal reagents. Notably, these insertion reactions occur largely with Fe(II) catalysts, in agreement with the higher acidity of Fe^{2+} over Mn^{2+} and to a lesser extent Co^{2+} ⁸¹ to effect ring opening of the aziridine ($\text{C}-\text{N}$ bond cleavage). The importance of metal acidity is also highlighted by the fact that the formation of five-membered *N*-heterocycles is facilitated in the order $[\text{Fe}(\text{NCMe})_6]^{2+} > [(\text{TMG}_2\text{biphen})\text{Fe}(\text{NCMe})_3]^{2+} \gg [(\text{TMG}_3\text{trphen})\text{Fe}(\text{NCMe})]^{2+}$ and in noncoordinating chlorinated solvents such as CH_2Cl_2 rather than in MeCN. The evolution of the product profile confirms a quick initial generation of the aziridine followed by slower conversion of the aziridine to the corresponding pyrrolidine. Upon further optimization of conditions, practicable yields of 2,4-substituted-pyrrolidines and 1,3-oxazolidines (in the presence of carbonyl cosubstrates) can be obtained in one-pot operations with electron-rich styrenes, provided that the reactivity of the nitrene vis-à-vis the dipolarophile can be minimized.
- Initial mechanistic data suggest that the most successful catalyst in this family of reagents, $[(\text{TMG}_2\text{biphen})\text{Fe}(\text{NCMe})_3]^{2+}$, may first generate a putative electrophilic $[\text{Fe}]=\text{NTs}$ oxidant, whose geometric and electronic attributes have yet to be defined, that performs nitrene

Scheme 6. Working Mechanism for the Catalytic Generation of *N*-Heterocycles



transfer to the substrate in a stepwise process (Scheme 6). According to KIE data and Hammett analysis, the first step consists of nitrene addition to the C_b carbon of styrene and concomitant generation of a C_a radical, characterized by an early transition state and a rather modest positive charge developing on the benzylic carbon. The second, ring-closing step is characterized by significant retention of stereochemistry ($\geq 90\%$ for *cis*- β -*d*-styrene and *cis*- β -methylstyrene). As previously noted,⁸² ring closing is a three-electron redox process that incorporates a formal one-electron oxidation of the carboradical and one-electron reduction of the metal; hence, the relative ease of reduction (Fe(III) \rightarrow Fe(II)) of the dicationic reagent **9** ($E_{1/2} = 0.55$ V vs Fc⁺/Fc) facilitates ring closure. Although no detailed mechanistic studies have been undertaken with regard to the formation of the extended 5-membered rings, the (3 + 2) cycloaddition of the aziridine with a dipolarophile (nitrile, olefin, carbonyl) is most likely the result of an independent catalytic cycle (Scheme 6) that involves Lewis-acid-mediated loosening of the ring toward an incipient 1,3-dipole, which then undergoes stepwise insertion of the dipolarophile. This interpretation is consistent with the time-dependent generation of aziridines/pyrrolidines and the favorable role of electron-rich styrenes in support of the zwitterion formation. The two-step addition of the dipolarophile is suggested by the loss of stereospecificity in product formation. Although the Fe(II) catalyst precursor can act as a Lewis acid, other, potentially high-valent, intermediates of the aziridination cycle cannot be excluded.

Future studies will explore conditions that permit the exclusive generation of five-membered *N*-heterocycles from the (2 + 1 + 2) cycloaddition of aromatic olefins, nitrenes, and a host of dipolarophiles (aliphatic olefins, alkynes, aldehydes, imines) for the generation of diverse five-membered heterocycles (e.g., pyrrolidines, pyrrolines, oxazolidines, imidazolidines). In addition, studies will be directed toward a more precise definition of the role of metal sites in the present multicomponent synthesis of *N*-heterocycles.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.3c01209>.

Experimental details: synthetic protocols, NMR, X-ray crystallography data, and additional figures and tables as noted in the text (PDF)

Accession Codes

CCDC 2229390–2229402 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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