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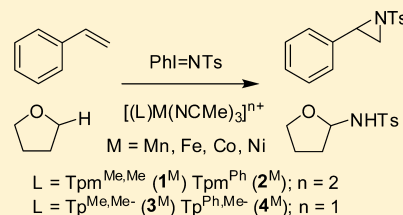
Half-Sandwich Scorpionates as Nitrene Transfer Catalysts

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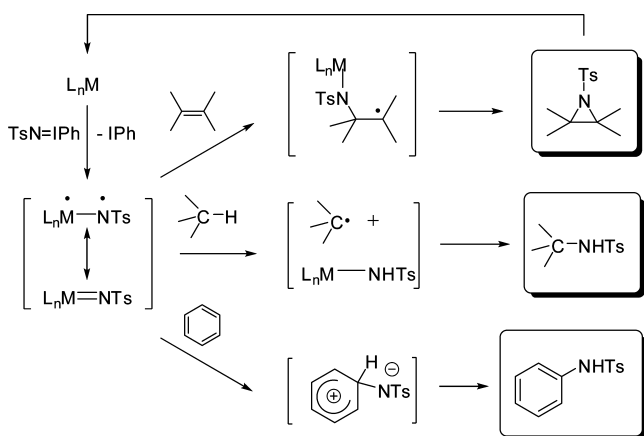
Supporting Information

ABSTRACT: Scorpionate complexes of the middle to late 3d transition metals $[(L)M(NCMe)_3](BF_4)_n$ ($M = Mn, Fe, Co, Ni$; 1^M , $L = \text{tris}(3,5\text{-dimethylpyrazol-1-yl})\text{methane}$, $Tpm^{Me,Me}$, $n = 2$; 2^M , $L = \text{tris}(3\text{-phenylpyrazol-1-yl})\text{methane}$, Tpm^{Ph} , $n = 2$; 3^M except 3^{Mn} , $L = \text{hydrotris}(3,5\text{-dimethylpyrazol-1-yl})\text{borate}$, $[Tp^{Me,Me}]^-$, $n = 1$; 4^M , $L = \text{hydrotris}(3\text{-phenyl-5-methylpyrazol-1-yl})\text{borate}$, $[Tp^{Ph,Me}]^-$, $n = 1$) were examined as catalysts for styrene aziridination and THF amination using phenyl-*N*-tosyliodinane as a nitrene donor. $[(Tpm^{Me,Me})Fe(NCMe)_3](BF_4)_2$ (1^{Fe}) was identified as the most active catalyst, giving nearly quantitative nitrene transfer yields at 5 mol % loadings. The reactivity of 1^{Fe} with a wider range of organic substrates was also explored, and a striking observation was strong selectivity for aromatic rather than benzylic amination for alkylaromatic substrates.



Nitrene transfer catalysis is a means to elaborate hydrocarbons into valuable heteroatomic products, through olefin C=C bond aziridination or C–H bond amination (Scheme 1).¹ Prototypical examples utilizing the earth-

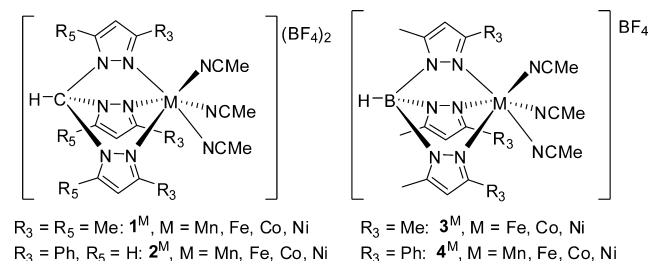
Scheme 1



abundant first-row transition metals manganese,^{2–4} iron,^{2,3,5} cobalt,^{2,6} and copper^{2,7,8} have been reported. This study was motivated by copper scorpionate complexes, with either tris(pyrazol-1-yl)methane (i.e., Tpm)⁹ or hydrotris(pyrazol-1-yl)borate (i.e., Tp)¹⁰ ligands, that catalyze nitrene transfer from phenyl-*N*-tosyliodinane (i.e., $PhI=NTs$)¹¹ to a diverse range of organic substrates.⁸ The discovery of new catalysts and reaction mechanisms may increase the scope and viability of this chemistry. We examined analogous complexes of the other first-row transition metals for nitrene transfer from $PhI=NTs$ and report a new Fe(II) catalyst exhibiting unusual propensity for aromatic amination.

Half-sandwich scorpionate complexes incorporating first-row transition metals $[(L)M(NCMe)_3](BF_4)_n$ (Scheme 2, $M = Mn$ except 3^{Mn} , Fe, Co, Ni ; 1^M , $L = \text{tris}(3,5\text{-dimethylpyrazol-1-yl})\text{methane}$, $Tpm^{Me,Me}$, $n = 2$; 2^M , $L = \text{tris}(3\text{-phenylpyrazol-1-yl})\text{methane}$, Tpm^{Ph} , $n = 2$; 3^M , $L = \text{hydrotris}(3,5\text{-dimethylpyrazol-1-yl})\text{borate}$, $[Tp^{Me,Me}]^-$, $n = 1$; 4^M , $L = \text{hydrotris}(3\text{-phenyl-5-methylpyrazol-1-yl})\text{borate}$, $[Tp^{Ph,Me}]^-$, $n = 1$) were reported previously.¹² In this work, the complexes were screened for catalysis in two reactions using $PhI=NTs$ as a nitrene donor: aziridination of styrene and α -amination of THF. The highest transfer yields were observed for $[(Tpm^{Me,Me})Fe(NCMe)_3](BF_4)_2$ (1^{Fe}), which were nearly quantitative. Conditions were subsequently optimized for 1^{Fe} and extended to a variety of organic substrates, including olefins as well as aliphatic, benzylic, and aromatic hydrocarbons. A remarkable result is selectivity for aromatic over benzylic amination, yielding *N*-tosylanilines in preference to benzylic amines, exactly the reverse of copper scorpionate catalysts.^{8b}

Scheme 2



The scorpionate complexes 1^M – 4^M were screened initially as catalysts for styrene aziridination. Reactions were carried out under typical conditions for catalyst evaluation (experimental procedures and NMR product characterizations are given in the Supporting Information).² 1^{Fe} and 3^{Fe} were the most effective (Table 1), catalyzing aziridine formation in nearly quantitative transfer yields, with complete dissolution of solid $PhI=NTs$

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Table 1. Catalyst Activity Screen

complex	styrene aziridination ^a		THF α -amination ^c	
	time (h)	yield (%) ^b	time (h)	yield (%) ^d
1 ^{Mn}	2.0	18	1.0	32
1 ^{Fe}	0.5	94	0.5	99
1 ^{Co}	1.0	19	0.5	69
1 ^{Ni}	2.0	16	0.5	74
2 ^{Mn}	1.7	17	1.0	33
2 ^{Fe}	0.5	63	0.5	68
2 ^{Co}	0.7	30	0.5	60
2 ^{Ni}	1.7	16	0.5	65
3 ^{Fe}	0.5	89	0.5	67
3 ^{Co}	1.0	42	0.5	64
3 ^{Ni}	2.3	30	0.8	66
4 ^{Mn}	2.0	18	1.0	38
4 ^{Fe}	0.5	51	0.5	36
4 ^{Co}	1.0	42	0.5	29
4 ^{Ni}	2.0	15	0.7	60

^aConditions: 5 mol % catalyst, 5:1 styrene:PhI=NTs in CH₂Cl₂ at 293 K. ^bDetermined by isolated product mass. ^cConditions: 20 vol % THF in CH₃CN at 293 K. ^dDetermined by ¹H NMR integration.

observed within 5 min. Irrespective of the actual scorpionate ligand, other metals gave lower activities in the order Fe(II) > Co(II) > Ni(II) \approx Mn(II), as indicated by increased reaction times and decreased transfer yields.

The complexes were also examined as catalysts (5 mol %) for α -amination of THF. Conversion of THF to *N*-(tetrahydro-2-furanyl)-4-toluenesulfonamide was obtained with transfer yields ranging from 29% to 99% (Table 1). 1^{Fe} again supported nearly quantitative transfer, but 3^{Fe} was less active. The Co(II) and Ni(II) complexes gave moderate yields, with Mn(II) complexes exhibiting relatively low activity.

We varied the reaction conditions for styrene aziridination by 1^{Fe} (Table S1, Supporting Information). The initial screening was optimal, as implied by near-quantitative yields. Lower catalyst loadings resulted in decreased yields and longer reaction times, yet a 62% transfer yield was obtained within 1 h using only 0.5 mol % 1^{Fe}. However, the aziridine yield dropped precipitously when the styrene was reduced to 1.0 equiv vs PhI=NTs.

Despite the generally high activity of Fe(II) catalysts, lower yields were obtained using 2^{Fe} and 4^{Fe}, having 3-phenylpyrazole substituents proximal to the metal, rather than methyls. Reaction of 4^{Fe} with PhI=NTs without a substrate generated an intense optical chromophore (Figure S1, Supporting Information), consistent with intramolecular ortho aminations previously observed in aryl-appended ligand complexes.¹³ This modification would increase the denticity, bulk, and anionic charge of the scorpionate, which may decrease reactivity with PhI=NTs. The apparent lack of 3-methyl amination through mechanistically distinct hydrogen atom abstraction is reflected in the intermolecular reactivity of alkylaromatics (vide infra).

Aziridine yields for para-substituted styrenes (i.e., CH₂=C(H)C₆H₄-4-X; X = CH₃, Cl, CF₃, NO₂) were determined in competition with styrene using 1^{Fe} (5 mol %). Relative yields of aziridines obtained from 1:1 mixtures in CH₃CN were determined by ¹H NMR spectroscopy. A logarithmic plot of the yield quotients against σ_p^+ values exhibited a linear relationship ($r^2 = 0.98$), and $\rho^+ = -0.58(5)$ was obtained from the slope (Figure 1). This ρ^+ value is intermediate between those obtained for reaction of PhI=NTs and styrenes

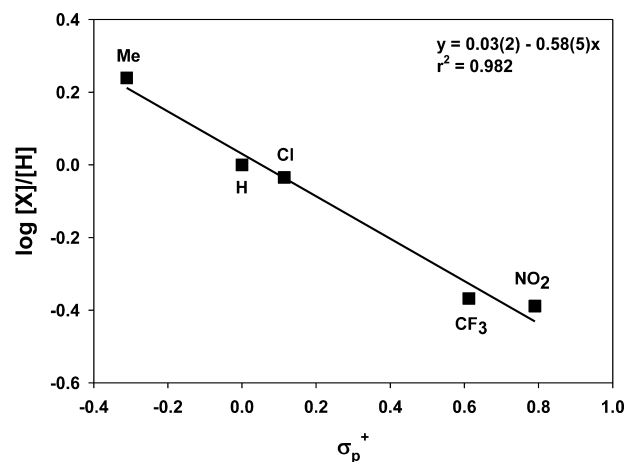


Figure 1. Hammett plot for competitive aziridination of para-substituted styrenes catalyzed by 1^{Fe}.

catalyzed by [Tp^{Me,Me}Cu(C₂H₄)] ($\rho^+ = -0.28(6)$, also by competition),^{8a} and for reaction of styrenes with the bis(imido) Ru(VI) complex [Ru(TPP)(NTs)₂] (TPP = tetraphenylporphyrinato; $\rho^+ = -1.1(1)$ by direct kinetics).¹⁴ Negative ρ^+ values are consistent with an electrophilic intermediate, plausibly an adduct of the iodine or an imidoiron(IV) complex derived from subsequent loss of iodobenzene; nonetheless, stepwise addition to styrene would likely generate an α -radicaloid intermediate (Scheme 1), as proposed for the ruthenium complexes.¹⁴

To probe the amination mechanism, an experiment using a 1:1 mixture of THF and THF-*d*₈ as substrate was performed with 5 mol % 1^{Fe}. The ratio of product isotopologues observed by ¹H NMR (Figure S14, Supporting Information) indicates the isotope effect, $k_H/k_D = 1.4$, is much less than the classical value for hydrogen atom abstraction.¹⁴ The C–H bond cleavage is kinetically masked, consistent with prior coordination of THF within a substitution-inert intermediate, such as an imidoiron(IV) complex.

Other olefins utilized as substrates included cyclohexene, norbornene, *trans*-methyl cinnamate, and *cis*- and *trans*-stilbenes; moderate transfer yields were obtained using 5 mol % 1^{Fe} (Table 2). Cyclohexene yielded a mixture of aziridination and allylic C–H bond amination, while norbornene and *trans*-methyl cinnamate gave the *exo*- and *trans*-aziridines, respectively. Reaction of *cis*-stilbene gave *cis*-aziridine as a major product, but a minor product was observed that was not the *trans*-aziridine or a ring-opened product. This was also obtained as the sole product from *trans*-stilbene. NMR spectra reveal loss of phenyl ring equivalence (Figures S21–S25, Supporting Information), indicating the product arises from aromatic or olefinic C–H bond amination. To our knowledge, the latter would be unprecedented, yet the reactivity is competitive with aziridination. The ¹H NMR spectrum contains two doublets at 6.79 and 6.26 ppm ($J = 11.6$ Hz); the latter is broad, consistent with attachment to a quadrupolar ¹⁴N nucleus, and the product was tentatively assigned as *trans*-*N*-(1,2-diphenylvinyl)-4-toluene sulfonamide, the olefinic C–H amination product.

We examined 1^{Fe} (5 mol %) as an amination catalyst for the cyclic alkane substrates cyclopentane and cyclohexane (33 vol % in CH₂Cl₂). Low yields of cyclopentyl- and cyclohexyl-*N*-tosylamines (30% and 40%, respectively) were obtained after 5 h. These results presumably reflect the higher C–H bond strengths of these substrates.^{1b,8b}

Table 2. Nitrene Transfer to Olefins Catalyzed by 1^{Fea}

Entry	Substrate	Product(s)	Yield ^b	Ratio
1			83	1.00:
2			51	0.69 ^b
3			46	
4			79	1.00:
5			51	0.39 ^c

^aConditions: 5 mol % 1^{Fe} , 5:1 substrate:PhI=NTs in CH_2Cl_2 at 293 K. ^bDetermined by total mass of isolated products. ^cDetermined by ^1H NMR integration against an internal standard.

Aminations of aromatic hydrocarbons were examined using 5 mol % 1^{Fe} (Table 3). Benzene was converted into *N*-tosylaniline in 45% isolated yield within 30 min, comparable to the activity of $[\text{Tp}^{\text{Br}_3}\text{Cu}(\text{NCMe})]$.^{8b} This copper complex also catalyzes benzylic amination of toluene and mesitylene, forming benzylamines in >95% yields.^{8b} In marked contrast, 1^{Fe} favors aromatic over benzylic amination, giving significant yields of aniline derivatives. Nitrene transfer yields were enhanced for electron-rich aromatic substrates, increasing in the order benzene (45%) < toluene (60%) < *m*-xylene (74%) <

mesitylene (81%); anilines dominated the isolated products, with benzylic amines comprising <5% of a given product mixture. Consistent with the trend toward weaker benzylic C–H bonds,^{1b} higher mole fractions of benzylic insertion were obtained for ethylbenzene (51%) and cumene (45%); normalization of the yields to reflect the number of unique C–H bonds gives the expected series toluene (2%) < ethylbenzene (37%) < cumene (47%). Competing aromatic amination produced a mixture of aniline isomers, with the normalized ortho:para ratio increasing in the series toluene (3:1) < ethylbenzene (7:1) < cumene (9:1), likely resulting from a modest yet increasing steric effect of the alkyl substituents on ortho amination. For this reason, benzylic amination was also slightly more competitive on *o*- and *p*-xylenes. Hence, the overall nitrene transfer yields remain nearly constant.

Although 1^{Fe} and $[\text{Tp}^{\text{Br}_3}\text{Cu}(\text{NCMe})]$ exhibit comparable activities for benzene amination, the latter catalyzes benzylic amination of toluene and mesitylene,^{8b} whereas 1^{Fe} exhibits selectivity toward aromatic amination. Aromatic amination of mesitylene was obtained using PhI=NNs (Ns = $\text{S}(\text{O})_2\text{C}_6\text{H}_4\text{-4-NO}_2$) and AuCl_3 as a catalyst, in which a proposed arylgold intermediate undergoes nitrene insertion; less substituted aromatics, including benzene, gave only minor aromatic insertion yields, and competitive amination of tertiary benzylic C–H bonds was observed.¹⁵ In pioneering work, Barton reported aromatic halogenation of mesitylene using chloramine-T with FeCl_2 or FeBr_2 , as well as competitive halogenation and diamination of naphthalene.^{5a} Intramolecular aromatic ligand amination was reported for iron complexes,¹³ and such reactivity was observed herein for the aryl-substituted complex 4^{Fe} without substrate. Chelation-assisted ortho aminations were reported for palladium and rhodium, the latter being catalytic.¹⁶

Table 3. Nitrene Transfer to Aromatic Substrates Catalyzed by 1^{Fea}

Entry	Substrate	Product(s)	Yield ^b	Product ratio ^c	Normalized ^d
1			45		
2			60	1.00:0.73:0.08	1.00:0.37:0.03
3			62	1.00:0.29:1.34	1.00:0.15:0.67
4			57	1.00:0.22:1.00	1.00:0.11:1.00
5			63	1.00:0.30:0.10	1.00:0.30:0.03
6			74	1.00:0.18:0.04	1.00:0.36:0.01
7			66	1.00:0.18	1.00:0.12
8			81	1.00:0.04	1.00:0.01

^aConditions: 5 mol % 1^{Fe} , 0.2 mmol PhI=NTs, 20–33 vol % substrate in CH_2Cl_2 at 293 K. ^bDetermined by total mass of isolated product(s).

^cDetermined by ^1H NMR integration. ^dProduct ratio divided by relative numbers of unique C–H bonds.

Having identified active Fe(II) catalysts, future work will probe mechanistic details. The electrophilic intermediate derived from I^{Fe} may be an imidoiron(IV) complex. Authentic imidoiron(IV) complexes are known; however, these were not shown to effect $\text{C}\equiv\text{C}$ aziridination or $\text{C}\text{--}\text{H}$ aminations.¹⁷ One unique example, a spin- and valence-isomeric Fe(III)-imido radical formed by *p*-*t*Bu-C₆H₄N₃ activation at a three-coordinate Fe(II) complex, reacts with toluene to yield the benzylamine.^{5h} Of particular interest are factors that discriminate between radicaloid and electrophilic substrate additions (Scheme 1), leading to the unique reactivity of I^{Fe} .

■ ASSOCIATED CONTENT

■ Supporting Information

Text, tables, and figures giving experimental details and NMR characterization data for the organic products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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