JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

Iron-Catalyzed Intramolecular Allylic C−H Amination

Shauna M. Paradine and M. Christina White*

Roger Adams Laboratory, Department of Chemistry, University of Illinois, Urbana, Illinois 61801, United States

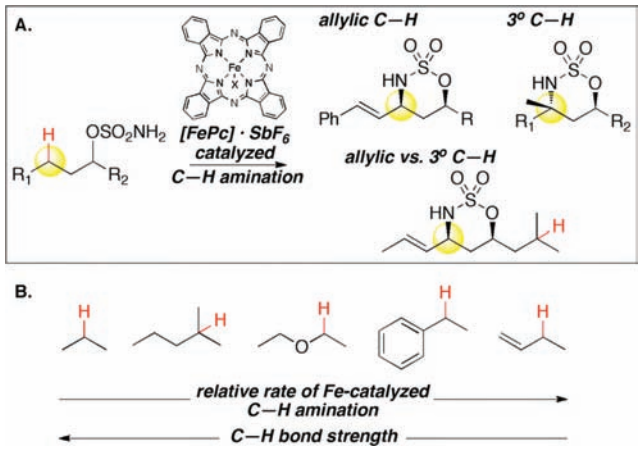
Supporting Information

ABSTRACT: A highly selective C−H amination reaction under iron catalysis has been developed. This novel system, which employs an inexpensive, nontoxic [Fe^{III}Pc] catalyst (typically used as an industrial ink additive), displays a strong preference for allylic C−H amination over aziridination and all other C−H bond types (i.e., allylic > benzylic > ethereal > 3° > 2° ≫ 1°). Moreover, in polyolefinic substrates, the site selectivity can be controlled by the electronic and steric character of the allylic C−H bond. Although this reaction is shown to proceed via a stepwise mechanism, the stereoretentive nature of C−H amination for 3° aliphatic C−H bonds suggests a very rapid radical rebound step.

Methods that enable the selective oxidation of C−H bonds are a powerful means of rapidly introducing functionality into complex molecules, obviating the need to carry sensitive groups through multiple manipulations and streamlining synthetic efforts.[1] C−H amination in particular is of interest because of the prevalence of nitrogen functionalities in biologically active molecules and the relative difficulty of incorporating nitrogen into molecular frameworks. The field of metal nitrenoid-based C−H amination was pioneered by Breslow, who demonstrated that Fe(TPP)Cl (TPP = tetraphenylporphyrinato) could aminate aliphatic and benzylic C−H bonds.[2] Despite the abundance and nontoxicity[3] of iron, the emerging use of selective iron catalysis,[4,5] and the possibility of orthogonal reactivity, very few C−H amination methods employing iron catalysts have been published since these seminal reports.[6] In this paper, we describe the first general and highly selective C−H amination reaction under iron catalysis.

Metal nitrenoid-based C−H amination methods have been most extensively studied with rhodium catalysts, which are thought to react via a concerted asynchronous mechanism.[7] The observed intramolecular reactivity trends indicate that C−H amination occurs preferentially at electron-rich C−H bonds (3° > ethereal ≈ benzylic > 2° ≫ 1°) and that alkene aziridination competes favorably with allylic C−H amination.[8] Conversely, nitrenoid-based catalysis with first-row metals such as copper, cobalt, manganese, and iron is thought to proceed via single-electron pathways.[9] We hypothesized that the reactivity trends with first-row metals should follow the trend in homolytic bond dissociation energies (BDEs), as in the case of ruthenium-based catalysis,[10] making orthogonal C−H amination reactivity possible. Under this type of reaction manifold, for example, allylic C−H amination should be strongly preferred (Scheme 1B).[11] The development of a general, highly selective allylic C−H amination reaction for internal olefins would be particularly significant.[12] Additionally, if the rebound rates of the iron amido species are tuned with the appropriate ligand environment, the resultant short-lived carbon radicals would allow for highly selective aminations.[13] We report herein the realization of these goals with an [Fe^{III}Pc]-catalyzed allylic C−H amination reaction, which demonstrates the highest chemo- and site-selectivities reported to date for nitrenoid-based amination. This reaction employs [FePc]Cl (Pc = phthalocyaninato), an inexpensive commercial compound that is typically used as an industrial additive for ink and rubber manufacturing. [Fe^{III}Pc] catalysis strongly favors allylic C−H amination over aziridination and amination of all other C−H bond types (Scheme 1A); moreover, high levels of site selectivity for polyolefins are demonstrated on the basis of electronics and sterics. Reactivity trends and mechanistic studies support a stepwise process for functionalization that occurs via initial homolytic C−H bond abstraction followed by a rapid radical rebound.

Scheme 1. Reactivity Trends for Fe-Catalyzed Intramolecular C−H Amination

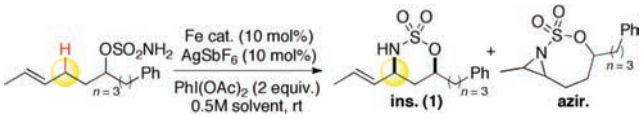


In initial reaction development, we tested several iron catalysts known to support high-valent metal oxidants for their efficacy in catalyzing the desired transformation (Table 1). The non-heme Fe(PDP) catalyst previously developed by our lab for aliphatic C−H hydroxylations[4e−h] was able to effect C−H amination with no observed aziridination, but the yields were poor (entry 1). The reactivity improved with the use of the heme iron catalyst Fe(TPP)Cl (entry 2). Interestingly, the iron complex of salen, known to be an effective heme ligand mimic for epoxidations,[14] showed no reactivity (entry 3). The iron

Received: December 12, 2011
Published: January 18, 2012

   dx.doi.org/10.1021/ja211600g | J. Am. Chem.Soc. 2012, 134, 2036−2039

Table 1. Development of the Fe-Catalyzed Intramolecular Allylic C−H Amination Reaction



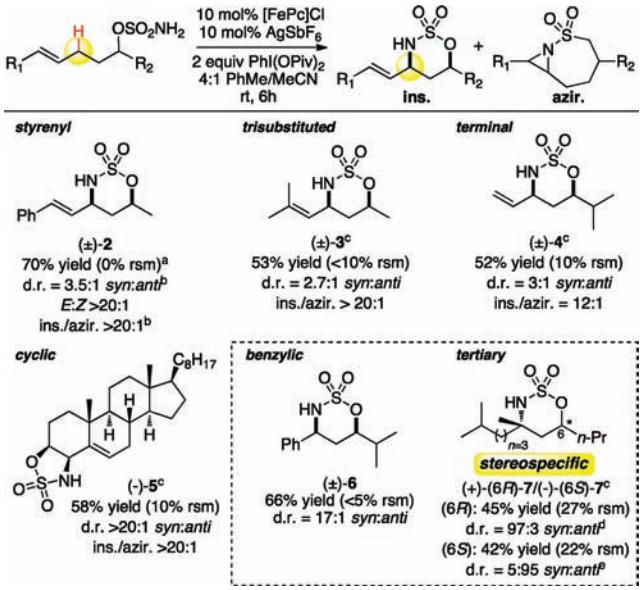
entry	catalyst	AgX	solvent	% yield[a]	ins./azir.[b]
1	Fe(*R,R*-PDP)	-	CH_3CN[c]	10 (58)[d]	>20:1
2	Fe(TPP)Cl	-	CH_3CN[c]	21 (41)[d]	>20:1
3	Fe(*R,R*-salen)Cl	-	CH_3CN[c]	0 (87)	-
4	[FePc]Cl	-	CH_3CN	34 (22)	15:1
5	[FePc]Cl	$AgSbF_6$	CH_3CN	39 (14)	16:1
6	[FePc]Cl	$AgSbF_6$	4:1 PhMe:CH_3CN	52 (7)	>20:1
7	[FePc]Cl[e]	$AgSbF_6$	4:1 PhMe:CH_3CN	68 (<5)	>20:1
8	[FePc]Cl[e]	-	4:1 PhMe:CH_3CN	58 (7)	>20:1
9	[FePc]Cl[e,f]	$AgSbF_6$	4:1 PhMe:CH_3CN	68 (<5)	>20:1

[a]Isolated yields (sum of syn + anti; d.r. ~3:1 syn:anti); % recovered starting material (rsm) values are given parentheses. [b]Determined by ^{1}H NMR analysis of the crude reaction mixture. [c]Concentration = 0.1 M. [d]d.r. =1:1. [e]$PhI(OPiv)_2$ was used as the oxidant. [f][FePc]Cl and $AgSbF_6$ were added together in three 3.3 mol % portions at 2 h intervals.

phthalocyanine complex [FePc]Cl was superior to Fe(TPP)Cl in terms of reactivity (entry 4). This is likely due to the increased electron-withdrawing nature of phthalocyanine ligands relative to their porphyrin counterparts, which results in a more electrophilic metal center.[15] Addition of a noncoordinating silver salt (entry 5), the use of a mixed solvent system (entry 6), and switching to the more soluble $PhI(OPiv)_2$ oxidant (entry 7) all led to a significant improvement in the overall reactivity. Notably, the $AgSbF_6$ additive could be eliminated from the optimized conditions with only a slight decrease in reactivity (entry 8). A silver-free catalyst system could be particularly beneficial in large-scale applications where cost and procedural simplicity are key considerations. Iterative addition of a solid mixture of [FePc]Cl and $AgSbF_6$ (three or four 3.3 mol % portions) at 2 h intervals, although not always necessary (entry 9), was shown to improve the yields with poorly converting substrates, whereas simply increasing the catalyst loading was not beneficial (see below). Under the optimized conditions, good yields of allylic C−H amination product **1** were obtained with only trace aziridine (>20:1 ins./azir.).

This Fe-based system displays the highest chemoselectivities for intramolecular allylic C−H amination over aziridination reported to date. The selectivities are strong for allylic amination products with aliphatic (*E*)-olefins and styrenyl, trisubstituted, terminal, and cyclic olefins (Table 2) as well as *α,β*-unsaturated esters and allylic acetates (see Table 3, entries 9 and 10). In particular, the tolerance of terminal olefins is quite notable. When a terminal olefin is present in the bishomoallylic position, high selectivities are achieved for allylic C−H amination product **4** over the aziridination product (12:1 ins./azir.). This is in stark contrast to both rhodium- and ruthenium-catalyzed systems, where aziridination is generally competitive and in some cases preferred for terminal olefins, including those positioned remotely.[11c,16] Cyclic olefins are also viable substrates for C−H amination, even when the sulfamate ester is in the homoallylic position. *β*-Cholesterol was readily aminated via its sulfamate ester to afford a single diastereomer

Table 2. Scope of Fe-Catalyzed C−H Amination



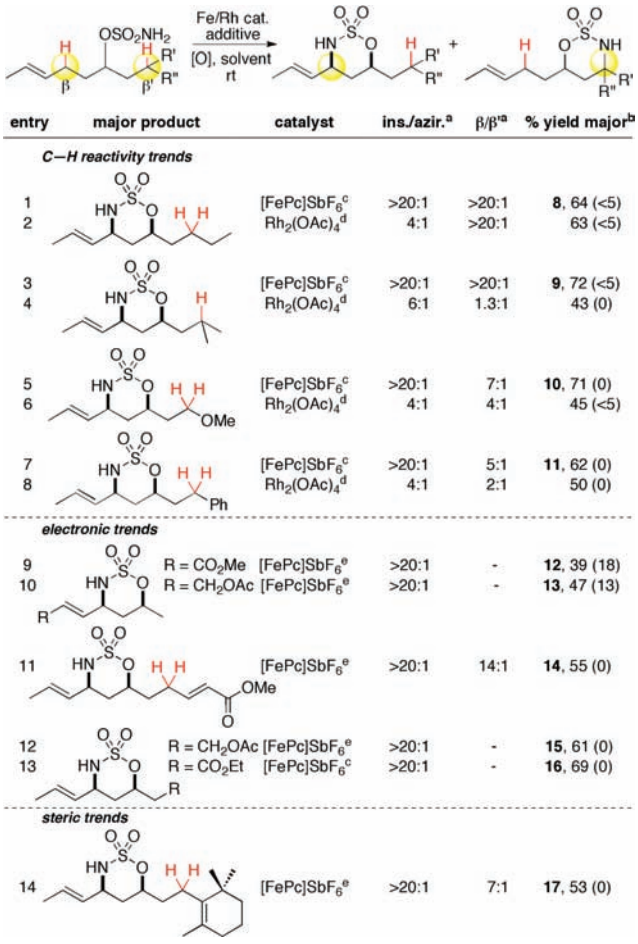
[a]Isolated yields (syn + anti); % rsm in parentheses. [b]All product ratios were determined by ^{1}H NMR analysis of the crude reaction mixture. [c]Conditions: 4 × (0.03 equiv of [FePc]Cl, 0.03 equiv of $AgSbF_6$), 2 equiv of $PhI(OPiv)_2$, 4:1 PhMe/MeCN, rt, 8 h. [d]Determined by GC analysis of the crude mixture; starting d.r. = 97:3. [e]Determined by GC analysis of the crude mixture; starting d.r. = 5:95.

of the 1,2-difunctionalized product **5** in 58% yield. [Fe^{III}Pc] is also a competent catalyst for benzylic and 3° aliphatic C−H aminations. It is significant to note that the aliphatic C−H amination of a substrate containing a stereochemically defined 3° C−H center was stereospecific, affording (+)-(6*R*)-**7** or (−)-(6*S*)-**7** with no loss of chiral information.

We next sought to determine the reactivity trends for [Fe^{III}Pc]-catalyzed amination of allylic C−H bonds relative to other C−H bond types (Table 3). Accordingly, intramolecular competition experiments were performed on sulfamate ester compounds having an allylic C−H bond and a second, energetically distinct type of C−H bond positioned at the *β* and *β′* carbons, respectively. Upon comparison of the [Fe^{III}Pc]-catalyzed method with the traditional $Rh_2(OAc)_4$-catalyzed system, it is clear that the competing olefin aziridination pathway is strongly suppressed in the iron system relative to rhodium catalysis (entries 1−8). Additionally, the [Fe^{III}Pc]-catalyzed system is generally more selective in discriminating between energetically distinct C−H bonds than the $Rh_2(OAc)_4$-catalyzed system. For the iron-catalyzed reaction, allylic C−H amination is exclusively preferred over both aliphatic 2° and 3° C−H amination (*β*/*β′* >20:1; entries 1 and 3). Although the same selectivity is observed for 2° C−H bonds, rhodium nitrenes show essentially no preference for allylic versus 3° C−H bond insertion (*β*/*β′* = 1.3:1; entries 2 and 4). Ruthenium nitrenes have also been reported to have a much lower preference (*β*/*β′* = 5:1).[11c] Moreover, while iron nitrenes demonstrate synthetically useful levels of selectivity for allylic versus ethereal and benzylic C−H bond aminations (*β*/*β′* = 7:1 and 5:1, respectively; entries 5 and 7), rhodium nitrenes show only a slight preference for allylic versus ethereal and benzylic C−H aminations (*β*/*β′* = 4:1 and 2:1; entries 6 and 8). In general, the following reactivity trend is observed for the iron-catalyzed C−H amination: allylic > benzylic > ethereal >

dx.doi.org/10.1021/ja211600g | J. Am. Chem.Soc. 2012, 134, 2036−2039

Table 3. Reactivity Trends for Allylic C−H Amination

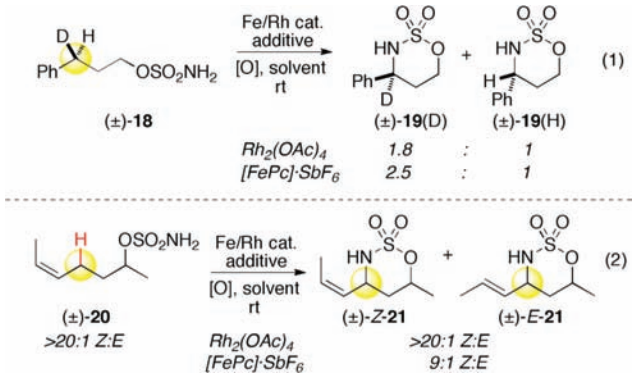


[a]Determined by ^{1}H NMR analysis of the crude reaction mixture (d.r. ≈ 3:1 unless otherwise noted). [b]Isolated yields (syn + anti; E/Z > 20:1 in all cases); % rsm in parentheses. [c]Conditions: 0.10 equiv of [FePc]Cl, 0.10 equiv of $PhI(OPiv)_2$, 4:1 PhMe/MeCN, rt, 6 h. [d]Conditions: 0.02 equiv of $Rh_2(OAc)_4$, 1.1 equiv of $PhI(OAc)_2$, 2.3 equiv of MgO, CH_2Cl_2, rt, 4 h. [e]Conditions: 4 × (0.03 equiv of [FePc]Cl, 0.03 equiv of $AgSbF_6$), 2 equiv of $PhI(OPiv)_2$, 4:1 PhMe/MeCN, rt, 8 h.

3° > 2° ≫ 1°. Notably, this trend is in agreement with the C−H bond dissociation energies (Scheme 1B).[17]

Similar to what has been shown with Fe(PDP)-catalyzed aliphatic C−H oxidations, we hypothesized that allylic C−H bonds in polyolefin compounds could be differentiated and selectively functionalized by the bulky, electrophilic iron nitrene oxidant on the basis of their electronic and steric characters. We observed that electron-withdrawing groups proximal to the allylic C−H bond, such as an α,β-unsaturated ester, substantially decreased its reactivity toward C−H amination (Table 3, entries 9 and 10). Consistent with this, amination of a polyolefin-containing substrate occurred with high selectivity at the more electron-rich allylic C−H bond (β/β' = 14:1; entry 11) to afford monoaminated product **14** in a preparatively useful yield (55%). Electron-withdrawing functionality remote from the allylic C−H bond had no effect on the reactivity, allowing acetoxy and ester moieties β to the sulfamate tether to be well tolerated under the reaction conditions (entries 12 and 13). We next evaluated whether we could also differentiate allylic C−H bonds in a polyolefinic substrate on the basis of their steric environment. Gratifyingly, using the [Fe^{III}Pc] catalyst, the less sterically hindered allylic C−H bond of a citral-derived substrate was functionalized with useful selectivity (β/β' = 7:1; entry 14), affording product **17** in good yield (53%).

To probe the mechanism of the [Fe^{III}Pc]-catalyzed C−H amination, we determined the effect of deuterium substitution on the rate of benzylic amination. The measured kinetic isotope effect (KIE) of 2.5 ± 0.2 for the C−H amination of **18** under iron-based catalysis is higher and statistically different from that measured for the same substrate under rhodium-based catalysis (k_H/k_D = 1.8 ± 0.2) (eq 1).[8a] However, this value is much



lower than what has been previously measured for reactions proceeding via a C−H abstraction/rebound amination mechanism (k_H/k_D = 6−12).[7c] Given the modest KIE values and the observed stereoretention in amination of tertiary C−H centers, we performed an additional study on Z-olefins to determine if scrambling of the double bond geometry occurred during allylic C−H amination When sulfamate ester **20** (>20:1 Z/E) was subjected to [Fe^{III}Pc]-catalyzed C−H amination, the allylic-functionalized product **21** was obtained as a 9:1 Z/E mixture, likely through the intermediacy of a stabilized carbon-centered radical (eq 2). No isomerization was observed under $Rh_2(OAc)_4$ catalysis, suggesting that different functionalization mechanisms are operative in these two cases.

In conclusion, we have reported the first highly selective and general C−H amination via iron catalysis. In addition to using an economical and nontoxic metal source, [Fe^{III}Pc]-catalyzed intramolecular C−H amination exhibits the highest chemo- and site selectivities reported to date for allylic C−H amination of internal olefins. Allylic C−H amination is strongly preferred over aziridination as well as over amination of stronger C−H bonds (i.e., 3° and 2° aliphatic, ethereal, or benzylic). Additionally, for polyolefin-containing substrates, allylic C−H amination with this electrophilic, bulky oxidant occurs with high selectivity at the most electron-rich, least sterically hindered site. We anticipate that this reaction will find widespread use in streamlining the synthesis of nitrogen-containing complex molecules.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, compound characterization data, and NMR spectra for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

white@scs.illinois.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

M.C.W. gratefully acknowledges Pfizer and Bristol-Myers Squibb for generous gifts. S.M.P. is a recipient of the University of Illinois Sylvia Stoesser and NSF Graduate Research Fellowships. We thank Mr. Jeffrey Sayler for synthesizing the alcohol starting material for Table 3, entry 11, and Dr. Tobias Thaler for confirming the experimental procedure in entries 3, 4, 6, and 8 of Table 3.

■ REFERENCES

(1) For examples of C−H functionalization in streamlining complex molecule derivatizations and synthesis, see: (a) Hinman, A.; Du Bois, J. *J. Am. Chem. Soc.* **2003**, *125*, 11510. (b) Wender, P. A.; Hilinski, M. K.; Mayweg, A. V. W. *Org. Lett.* **2005**, *7*, 79. (c) Fraunhoffer, K. J.; Bachovchin, D. A.; White, M. C. *Org. Lett.* **2005**, *7*, 223. (d) Davies, H. M. L.; Long, M. S. *J. Am. Chem. Soc.* **2006**, *128*, 2485. (e) Covell, D. J.; Vermeulen, N. A.; Labenz, N. A.; White, M. C. *Angew. Chem., Int. Ed.* **2006**, *45*, 8217. (f) Stang, E. M.; White, M. C. *Nat. Chem* **2009**, *1*, 547. (g) Vermeulen, N. A.; Delcamp, J. H.; White, M. C. *J. Am. Chem. Soc.* **2010**, *132*, 11323. (h) Quasdorf, K. W.; Huters, A. D.; Lodewyk, M. W.; Tantillo, D. J.; Garg, N. K. *J. Am. Chem. Soc.* **2012**, DOI: 10.1021/ja210837b.

(2) (a) Breslow, R.; Gellman, S. H. *J. Chem. Soc., Chem. Commun.* **1982**, 1400. (b) Breslow, R.; Gellman, S. H. *J. Am. Chem. Soc.* **1983**, *105*, 6728.

(3) Enthaler, S.; Junge, K.; Beller, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 3317.

(4) For oxidative transformations, see: (a) White, M. C.; Doyle, A. G.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2001**, *123*, 7194. (b) Legros, J.; Bolm, C. *Angew. Chem., Int. Ed.* **2003**, *42*, 5487. (c) Suzuki, K.; Oldenberg, P. D.; Que, L. Jr. *Angew. Chem., Int. Ed.* **2008**, *47*, 1887. (d) Nishikawa, Y.; Yamamoto, H. *J. Am. Chem. Soc.* **2011**, *133*, 8432. (e) Chen, M. S.; White, M. C. *Science* **2007**, *318*, 783. (f) Vermeulen, N. A.; Chen, M. S.; White, M. C. *Tetrahedron* **2009**, *65*, 3078. (g) Chen, M. S.; White, M. C. *Science* **2010**, *327*, 566. (h) Bigi, M. A.; Reed, S. A.; White, M. C. *Nat. Chem.* **2011**, *3*, 218.

(5) For reductive transformations, see: (a) Nakamura, M.; Matsuo, K.; Ito, S.; Nakamura, E. *J. Am. Chem. Soc.* **2004**, *126*, 3686. (b) Sapountzis, I.; Lin, W.; Kofink, C. C.; Despotopoulou, C.; Knochel, P. *Angew. Chem., Int. Ed.* **2005**, *44*, 1654. (c) Enthaler, S.; Erre, G.; Tse, M. K.; Junge, K.; Beller, M. *Tetrahedron Lett.* **2006**, *47*, 8095. (d) Sherry, B. D.; Fürstner, A. *Acc. Chem. Res.* **2008**, *41*, 1500. (e) Wu, J. Y.; Stanzi, B. N.; Ritter, T. *J. Am. Chem. Soc.* **2010**, *132*, 13214.

(6) For iron salts, see: (a) Barton, D. H. R.; Hay-Motherwell, R. S.; Motherwell, W. B. *J. Chem. Soc., Perkin Trans.* **1983**, 445. (b) Wang, Z.; Zhang, Y.; Fu, H.; Jiang, Y.; Zhao, Y. *Org. Lett.* **2008**, *10*, 1863. For stoichiometric ligand C−H amination, see: (c) Jensen, M. P.; Mehn, M. P.; Que, L. *Angew. Chem., Int. Ed.* **2003**, *42*, 4357. (d) King, E. R.; Betley, T. A. *Inorg. Chem.* **2009**, *48*, 2361. For catalytic C−H amination, see: (e) Yan, S.-Y.; Wang, Y.; Shu, Y.-J.; Liu, H.-H.; Zhou, X.-G. *J. Mol. Catal. A: Chem.* **2006**, *248*, 148. (f) King, E. R.; Hennessy, E. T.; Betley, T. A. *J. Am. Chem. Soc.* **2011**, *133*, 4917.

(7) For selected reviews, see: (a) Müller, P.; Fruit, C. *Chem. Rev.* **2003**, *103*, 2905. (b) Espino, C. G.; Du Bois, J. In *Modern Rhodium-Catalyzed Organic Reactions*; Evans, P. A., Ed.; Wiley-VCH: Weinheim, Germany, 2005; pp 379−416. (c) Huard, K.; Lebel, H. *Chem.—Eur. J.* **2008**, *14*, 6222. (d) Zalatan, D. N.; Du Bois, J. *Top. Curr. Chem.* **2010**, *292*, 347.

(8) (a) Fiori, K. W.; Espino, C. G.; Brodsky, B. H.; Du Bois, J. *Tetrahedron* **2009**, *65*, 3042. For a rare intermolecular allylic C−H amination requiring a matched chiral dirhodium catalyst and chiral nitrene source, see: (b) Liang, C.; Collet, F.; Robert-Peillard, F.; Müller, P.; Dodd, R. H.; Dauban, P. *J. Am. Chem. Soc.* **2008**, *130*, 343. For a chiral dirhodium catalyst showing a preference for intramolecular allylic C−H amination vs aziridination with reduced reactivity, see: (c) Zalatan, D. N.; Du Bois, J. *J. Am. Chem. Soc.* **2008**, *130*, 9220.

(9) (a) Mansuy, D.; Mahy, J.-P.; Dureault, A.; Bedi, G.; Battioni, P. *J. Chem. Soc., Chem. Commun.* **1984**, 1161. (b) Mahy, J. P.; Bedi, G.; Battioni, P.; Mansuy, D. *Tetrahedron Lett.* **1988**, *29*, 1927. (c) Moreau, Y.; Chen, H.; Derat, E.; Hirao, H.; Bolm, C.; Shaik, S. *J. Phys. Chem. B* **2007**, *111*, 10288. (d) Lu, H.; Subbarayan, V.; Tao, J.; Zhang, X. P. *Organometallics* **2010**, *29*, 389. (e) Lu, H.; Jiang, H.; Wojtas, L.; Zhang, X. P. *Angew. Chem., Int. Ed.* **2010**, *49*, 10192. (f) Badiei, Y. M.; Dinescu, A.; Dai, X.; Palomino, R. M.; Heinemann, F. W.; Cundari, T. R.; Warren, T. H. *Angew. Chem., Int. Ed.* **2008**, *47*, 9961.

(10) Leung, S. K.-Y.; Tsui, W.-M.; Huang, J.-S.; Che, C.-M.; Liang, J.-L.; Zhu, N. *J. Am. Chem. Soc.* **2005**, *127*, 16629.

(11) For allylic C−H amination with ruthenium, see: (a) Liang, J.-L.; Yuan, S.-X.; Huang, J.-S.; Che, C.-M. *J. Org. Chem.* **2004**, *69*, 3610. (b) Milczek, E.; Boudet, N.; Blakey, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 6825. (c) Harvey, M. E.; Musaev, D. G.; Du Bois, J. *J. Am. Chem. Soc.* **2011**, *133*, 17207. For cobalt catalysis, see: (d) Lu, H.; Tao, J.; Jones, J. E.; Wojtas, L.; Zhang, X. P. *Org. Lett.* **2010**, *12*, 1248.

(12) For Pd(II)/bis-sulfoxide-catalyzed allylic aminations of terminal olefins, see: (a) Fraunhoffer, K. J.; White, M. C. *J. Am. Chem. Soc.* **2007**, *129*, 7274. (b) Rice, G. T.; White, M. C. *J. Am. Chem. Soc.* **2009**, *131*, 11707. (c) Qi, X.; Rice, G. T.; Lall, M. S.; Plummer, M. S.; White, M. C. *Tetrahedron* **2010**, *66*, 4816. (d) Nahra, F.; Liron, F.; Prestat, G.; Mealli, C.; Messaoudi, A.; Poli, G. *Chem.—Eur. J.* **2009**, *15*, 11701. (e) Reed, S. A.; White, M. C. *J. Am. Chem. Soc.* **2008**, *130*, 3316. (f) Reed, S. A.; Mazzotti, A. R.; White, M. C. *J. Am. Chem. Soc.* **2009**, *131*, 11701. (g) Liu, G.; Yin, G.; Wu, L. *Angew. Chem., Int. Ed.* **2008**, *47*, 4733.

(13) Iron porphyrin complexes can be electronically tuned at the ligand and counterion to alter the aziridination stereospecificity. See: Mahy, J. P.; Bedi, G.; Battioni, P.; Mansuy, D. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1517.

(14) Jacobsen, E. N. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 1993; pp 159−202.

(15) Löbbert, G. Phthalocyanines. In *Ullman's Encylopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, Germany, 2000.

(16) For example, when reacted with tris-homoallylic sulfamates, $Rh_2(OAc)_4$ and $Rh_2(esp)_2$ catalysts gave 1:1 mixtures of seven-membered allylic C−H insertion products with 8,3-bicyclic aziridine products (see ref 8a).

(17) *CRC Handbook of Chemistry and Physics*, 91st ed.; Haynes, W. M., Ed.; CRC Press: Boca Raton, FL, 2010; pp 9−65.