Iron-Catalyzed Aziridination Reactions

Masafumi Nakanishi,^a Anne-Frederique Salit,^a and Carsten Bolm^{a,*}

^a Institute of Organic Chemistry, RWTH Aachen University, Landoltweg 1, 52056 Aachen, Germany Fax: (+49)-241-809-391; e-mail: Carsten.Bolm@oc.rwth-aachen.de

Received: October 31, 2007; Revised: June 3, 2008; Published online: July 10, 2008

Abstract: A small quantity of iron(II) triflate (2.5 to 5 mol%) catalyzes the aziridination reactions of enol silyl ethers with tosylimino(iodo)benzene (PhINTs) in acetonitrile to give α -N-tosylamido ketones by subsequent aziridine ring opening. Olefins are converted into aziridines by 5 mol% of this catalyst system. Both reactions afford the corresponding

Introduction

Aziridination reactions are among the most useful transformations in organic synthesis,^[1] since the resulting products are important building blocks for a variety of nitrogen-containing compounds.^[2] Of particular interest are α -amido ketones, which are accessible by ring opening of aziridines derived from enol ethers.^[3] During the last decades various aziridination catalysts have been developed,^[3c,4-10] but commonly they involve toxic metals, and their applicability is limited to a narrow substrate range. Consequently, further improvements in this area are desirable. In particular for industrial scale applications the use of environmentally benign oxidation catalysts is crucial, making low cost and non-toxic iron a prime element of choice.^[11]

Results and Discussion

In 2006 we reported on iron-catalyzed imination reactions of sulfides and sulfoxides leading to sulfilimines and sulfoximines, respectively. In this protocol, simple $Fe(acac)_3$ served as catalyst.^[12] With the goal to improve this preparatively important transformation, the application of iron(II) triflate, which is easily prepared from iron powder or iron(II) chloride and distilled trifluoromethanesulfonic acid,^[13] was investigated. To our delight we found that even as little as 2.5 mol% of $Fe(OTf)_2$ catalyzed the imination reaction of thioanisole methyl phenyl sulfoxide with PhINNs (**2a**) affording the corresponding sulfilimine and sulfoximine in 91% and 98% yields, respectively.^[14] This unexpected high activity led us to study the application products in moderate to good yields. In the presence of chiral ligands asymmetric aziridinations have been achieved.

Keywords: asymmetric catalysis; aziridination; iron; nitrogen transfer; sulfonamides

of the $Fe(OTf)_2$ -based catalyst system in other nitrogen transfer reactions.^[15] A recent paper by Halfen and co-workers on a related system^[16] prompted us to report our own findings.

Beginning with the aziridination of enol silvl ethers, we expected α -N-arylamido ketones to be the resulting products based on the observations by others.^[3] For the optimization of the protocol, styryloxytrimethylsilane (1a) was chosen as substrate. The best result was achieved by using 2.5 mol% of Fe(OTf)₂, 2 equiv. of 1a with respect to PhINTs (2b) and a small quantity of 4 Å molecular sieves (20 mg/0.5 mmol of substrate) in acetonitrile under argon at ambient temperature for 1 h affording α -N-tosylamido ketone **3a** in 72% yield (Table 1, entry 1). These optimized conditions were then applied for the conversion of other enol silyl ethers. β-Methyl-substituted styryloxytrimethylsilane (1b) gave the corresponding α -N-tosylamido ketone **3b** in 63% yield (Table 1, entry 2). Non-aromatic enol silvl ethers 1c and 1d led to aziridination products 3c and 3d in 63% and 46% yield, respectively (entries 3 and 4). Interestingly, aziridination of silyl ketene ketal 1e with PhINTs (2b) was also possible (Table 1, entry 5). Although the yield of N-tosyl-protected amino acid ester 3e was only 50%, this result is remarkable, since such a nitrogen transfer reaction under copper catalysis was considered as an impractical approach to the synthesis of α -amino esters.^[3c]

Next, the nitrogen transfer on to simple olefins was attempted. In this case, aziridines were formed (Table 2). The application of iminoiodianes formed *in situ* from mixtures of the corresponding sulfonamide and iodosylbenzene or iodobenzene diacetate in the presence of magnesium oxide was demonstrated by converting styrene **4a** into aziridines **5a** and **5b**. Yields



Entry

1

2

3

Table 1. Aziridinations of various enol silyl ethers.^[a]

OSiMe/





^[a] *Reaction conditions for a 0.25 mmol scale:* Fe(OTf)₂ (2.5 mol%), enol silyl ether **1** (2 equiv.), MeCN (1 mL), r.t., 1 h. ^[b] The known products were identified by comparison of their analytical data with those of previous reports.^[17]

Table 2. Iron triflate-catalyzed aziridinations of olefins with sulfonamides. $\ensuremath{^{[a]}}$



^[a] Reaction conditions for a 0.25 mmol scale: Fe(OTf)₂ (10 mol%), ArSO(X)NH₂ (1 equiv.), oxidant (2 equiv.), styrene (20 equiv.), MS 4 Å (400 mg), MeCN (2 mL), r.t., Ar, 24 h.

- ^[b] Use of 20 mol% of Fe(OTf)₂; no addition of MgO.
- ^[c] Value of the diastereometric mixture (dr = 7:3).
- ^[d] All products were identified by comparison of their analytical data with those of previous reports.^[3c,6c,e,19]

of up to 66% were achieved with 10 or 20 mol% of $Fe(OTf)_2$ as catalyst (Table 2). In the same manner, combinations of *N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidamide (**6c**), iodobenzene diacetate and MgO gave *N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidoaziridine (**5c**) in 58% yield.^[18]

Optimization studies allowed a reduction of both the catalyst loading and the amount of starting olefin. Thus, by using preformed iminoiodane PhINTs (2b), the addition of magnesium oxide could be avoided and less solvent had to be used (0.2 mL of acetonitrile for a 0.25 mmol scale reaction). Positive effects were also observed when the olefin concentration was increased and distilled styrene derivatives were used. Finally, moderate to good yields were achieved in all cases with only a 7-fold excess of olefin (Table 3). For example, with 5 mol% of Fe(OTf)₂ as catalyst the combination of styrene (4a) and PhINTs (2b) afforded the corresponding aziridine (5a) in 82% yield (entry 1).^[19] Other nitrogen carriers such PhINNs (2a), PhINSes (2c), and PhINSO₂[2-(5-methyl)pyridinyl] (2d) could also be applied leading to the corresponding aziridines 5b-5e in up to 90% yield (Table 3, entries 2-4). Conversions of methylstyrene derivatives 4b and 4c as well as cyclooctene afforded the products (5f, 5g and 5h) in reactions with PhINTs (2b) in yields of 45 and 35 and 61%, respectively (Table 3, entries 5–7). The two latter results were achieved with a catalyst loading of 10 mol%. Eventually, aziridination of *cis*-methylstyrene (4e) with

Table 3. Iron triflate-catalyzed aziridinations of olefins.^[a]

$$\begin{array}{c} R'' & Fe(OTf)_{2} (5 \text{ mol}\%) \\ R''' & PhINX (2), MS 4 \text{ Å}, \\ R''' & MeCN, r.t., 0.5 - 3 \text{ h} \\ 4 & Me \\ X = Ts, Ns, Ses, \\ N & SO_{2} - \end{array}$$

Entry	Substrate		Product		Yield [%] ^[b]
1	4 a		5a	NTs	82
2	4 a		5b	NNs	72
3	4 a		5d	NSes	74
4	4 a		5e		90
5	4b	Me	5f	Me_NTs	45
6	4c	Me	5g	NTs Me	35 ^[c,d]
7	4d		5h	NTs	61 ^[d]
8	4e	Me	5i	Me	56 ^[d]
9	4f		5j	Ts N N	$24^{[d,e]}$ (<i>cis/trans</i> = 57/43)

^[a] Reaction conditions for a 0.25 mmol scale: Fe(OTf)₂ (5 mol%), olefin (7 equiv.), MeCN (0.2 mL), r.t., 0.5-3 h.

^[b] All products were identified by comparison of their analytical data with those of previous reports.^[3c,4d,e,m,5d]

^[c] Only the *trans*-product was obtained selectively.

^[d] Use of 10 mol% of Fe(OTf)₂.

^[e] The yield reported is for the unseperable mixture of the *cis*- and the *trans*-aziridines.

PhINTs (2b) and 10 mol% of the iron catalyst produced exclusively *cis*-aziridine (5i) in 56% yield, while under the same reaction conditions *cis*-stilbene (4f) led to a mixture of the *cis*- and the *trans*-aziridine (5j) in a *cis/trans* = 43/57 ratio (24% yield) (Table 3, entries 8 and 9). The ¹H NMR analysis of the recovered *cis*-stilbene showed no isomerization of the double bond. Thus a concerted mechanism is unlikely, and the formation of a radical intermediate during the nitrogen transfer process can be suggested for the aziridination with Fe(OTf)₂ as a catalyst.^[20] Finally, the possibility of performing asymmetric aziridinations was evaluated. Among various tridentate ligands 7 tested in the iron(II) triflate-catalyzed conversion of styrene (4a) with PhINTs (2b) to give aziridine 5a, (S,S)-*i*-Pr-py-BOX (7a)^[21] was found to be the most effective leading to 5a with up to 40% *ee* in 72% yield (Table 4, entry 2). Interestingly, 2,6-bis(*N*-pyrazolyl)pyridines 7e and 7f could also be applied as chiral ligand (entries 6 and 7), which opens further options for ligand structure optimizations.

asc.wiley-vch.de

Table 4. Asymmetric aziridination of styrene.^[a]

Fe(OTf)₂ (2.5 mol%),



7 40 6

[a] Reaction conditions for a 0.25 mmol scale: Fe(OTf)₂ (2.5 mol%), ligand (5 mol%), styrene (20 equiv.), MeCN (1 mL), r.t., 1 h.

 $Fe(OTf)_2$ (5 mol%) and chiral ligand (30 mol%) were used.

Conclusions

In summary, we developed iron-catalyzed aziridination reactions of enol silvl ethers and olefins leading to a-N-tosylamido ketones and aziridines, respectively, in moderate to good yields. Both preformed imi-

noiodinanes as well as in situ-formed reagents of this type can serve as nitrogen sources. Finally, the potential of asymmetric reactions has been demonstrated.

Experimental Section

Materials

.NTs

Most starting materials were purchased from commercial suppliers and used without further purification. All enol silyl ethers,^[22] PhINNs (2a), PhINTs (2b), and PhINSes (2c) and [*N*-(5-methyl-2-pyridinesulfonyl)imino]phenyliodinane (2d) were prepared as reported previously or in analogy to known procedures.^[23] Fe(OTf)₂^[13a] and Fe(OTf)₂·2 MeCN^[13b] were prepared following published protocols. Dry acetonitrile was purchased from Fluka and Acros. Molecular sieves 4 Å (powder) was purchased from Fluka and activated by general procedures.

Representative Procedure for the Conversion of Silvl Enol Ethers (use of PhINTs)

Styryloxytrimethylsilane (1a, 96 mg, 0.5 mmol) and MS 4 Å (20 mg) were added to the solution of $Fe(OTf)_2$ (2.2 mg, 0.006 mmol) in acetonitrile (1 mL) at 0 °C. After the addition of PhINTs (2b, 93.3 mg, 0.25 mmol), the reaction mixture was stirred at ambient temperature for 1 h. Then, the solvents were evaporated (rotary evaporator), and the remaining mixture was separated by column chromatography (silica gel; ethyl acetate:pentane=2:3 as eluent) affording α -*N*-tosylamido ketone **3a**; yield: 52 mg (72%).

Representative Procedure for the Conversion of Olefins (use of PhINTs)

Freshly distilled styrene (4a, 182.0 mg, 0.20 mL, 1.75 mmol, 7 equiv.) and MS 4 Å powder (20 mg) were added to the solution of Fe(OTf)₂ (4.4 mg, 0.0125 mmol) in acetonitrile (0.2 mL). After the addition of PhINTs (2b, 93.3 mg, 0.25 mmol), the reaction mixture was stirred at ambient temperature for 0.5 h. After filtration of the reaction medium, the solvents were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; ethyl acetate:pentane=1:5 as eluent) affording aziridine 5a; yield: 56 mg (82%).

Procedure for the Asymmetric Aziridination (use of **PhINTs)**

(*S*,*S*)-*i*-Pr-py-BOX (**7a**, 22.5 mg, 0.075 mmol, 30 mol%) was added to the solution of Fe(OTf)₂ (4.4 mg, 0.0125 mmol, 5 mol%) in acetonitrile (1 mL). After stirring for 15 min, styrene (260 mg, 0.29 mL, 5 mmol), MS 4 Å (20 mg) and PhINTs (2b, 93.3 mg, 0.25 mmol) were added. The reaction mixture was stirred at ambient temperature for 1 h, and then the solvents were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; ethyl acetate:pentane=1:5 as eluent) affording aziridine 5a; yield: 49 mg (72%, 40% ee).

The enantiomer ratio was determined by HPLC: (Chiralcel AS, heptane/2-propanol = 75:25 as eluent, 0.55 mLmin^{-1} , 254 nm); ret. time = 18 min (S) [minor] and 20 min (R) [major] (40% ee).^[4b,24]

Representative Procedure for the Conversion of Olefins [use of TsNH₂ (6b)]

Iodobenzene diacetate (161 mg, 0.5 mmol) was added to the solution of $TsNH_2$ (**6b**, 43 mg, 0.25 mmol), MgO (50 mg, 1.25 mmol) and MS 4 Å powder (400 mg) in acetonitrile (2 mL). After the addition of styrene (**4a**, 520 mg, 0.57 mL, 5 mmol, 20 equiv.) and Fe(OTf)₂ (8.8 mg, 0.025 mmol), the reaction mixture was stirred under argon for 24 h. The mixture was the filtrated and the solvent evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; ethyl acetate:pentane = 1:5 as eluent) affording aziridine **5a** as a white solid; yield: 41 mg (60%).

4-Methyl-N-(2-oxononyl)benzenesulfonamide (3d): mp 104–107 °C; ¹H NMR (400 MHz, CDCl₃): δ =0.71 (t, *J*= 6.6 Hz, 3 H), 0.90–1.13 (m, 8 H), 1.31–1.38 (m, 2 H), 2.16 (t, *J*=7.4 Hz, 2 H), 2.26 (s, 3 H), 3.66 (d, *J*=4.7 Hz, 2 H), 5.16 (broad t, *J*=4.7 Hz, 1 H), 7.14 (d, *J*=8.5 Hz, 2 H), 7.57 (d, *J*=8.5 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃): δ =203.8, 143.8, 136.0, 129.8, 127.2, 51.3, 40.1, 31.5, 28.9, 23.6, 22.6, 21.5, 14.0; MS (EI, 70 eV): *m*/*z* (%)=309 (M–2H)⁺; IR (KBr): v=3273, 2931, 2856, 1722, 1321, 1160, 691 cm⁻¹; anal. calcd. for C₁₆H₂₅NO₃S (311.44): C 61.70, H 8.09, N 4.50; found: C 61.94, H 8.19, N 4.44.

Preparation of PhINSO₂[2-(5-methyl)pyridinyl] (2d)

KOH (1.18 g, 21 mmol) was added to a solution of 5methyl-2-pyridinesulfonamide (1.72 g, 10 mmol) in methanol (30 mL). Then iodobenzene diacetate (3.22 g, 10 mmol) was added at 0°C. The reaction mixture was allowed to warm to room temperature and was stirred for 45 min. The reaction mixture was partially concentrated under reduced pressure and the white solid was filtered. The crystals were washed with distilled water affording PhINSO₂[2-(5-methyl)pyridinyl] (2d) as a white solid; yield: 2.2 g (61%); mp 144 °C (detonates); ¹H NMR (400 MHz, DMSO- d_6): $\delta = 2.28$ (s, 3 H), 7.39-7.45 (m, 2H), 7.48-7.54 (m, 1H), 7.59-7.62 (m, 1H), 7.65-7.70 (m, 1H), 7.87-7.90 (m, 2H), 8.31-8.32 (m, 1H); ¹³C NMR (75 MHz, DMSO- d_6): $\delta = 159.6$, 149.0, 138.7, 135.4, 133.1, 131.2, 131.0, 119.4, 119.3, 18.3; IR (KBr): v= 1567, 1465, 1444, 1271, 1132, 1099, 922, 898, 825, 736, 673, 629 cm $^{-1};$ anal. calcd. for $C_{12}H_{11}IN_2O2S$ (357.49): C 38.52, H 2.96, N 7.49; found: C 38.42, H 3.18, N 7.43.

Acknowledgements

We are grateful to the Fonds der Chemischen Industrie and to the Deutsche Forschungsgemeinschaft (DFG) within the SPP 1118 for continuous support of our research program.

References

[1] For reviews on aziridination reactions, see: a) D. Tanner, *Angew. Chem.* **1994**, *106*, 625; *Angew. Chem.*

Int. Ed. Engl. 1994, 33, 599; b) J. B. Sweeney, Chem. Soc. Rev. 2002, 31, 247; c) W. McCoull, F. A. Davies, Synthesis 2000, 1347; d) P. Duban, R. H. Dodd, Synlett 2003, 1571; e) P. Müller, C. Fruit, Chem. Rev. 2003, 103, 2905; f) C. Moessner, C. Bolm, in: Transition Metals For Organic Chemistry: Building Blocks and Fine Chemicals, 2nd edn., (Eds.: M. Beller, C. Bolm), Vol. II, Wiley/VCH, Weinheim, 2004, p 389; g) Aziridines and Epoxides in Organic Synthesis, (Ed.: A. K. Yudin), Wiley-VCH, Weinheim, 2006, p 1.

- [2] For overviews focusing on aziridine transformations, see: a) I. D. G. Watson, L. Yu, A. K. Yudin, *Acc. Chem. Res.* 2006, *39*, 194; b) B. Zwanenburg, P. ten Holte, *Top. Curr. Chem.* 2001, *216*, 93; c) W. McCoull, F. A. Davis, *Synthesis* 2000, 1347.
- [3] a) S. Lociuro, L. Pellacani, P. A. Tardella, *Tetrahedron Lett.* 1983, 24, 593; b) S. Fioravanti, M. A. Loreto, L. Pellacani, P. A. Tardella, J. Org. Chem. 1985, 50, 5365; c) D. A. Evans, M. M. Faul, M. T. Bilodeau, J. Am. Chem. Soc. 1994, 116, 2742; for the synthesis of α-N-to-sylamido ketones by oxidative ring opening of aziridines, see: d) K. Surendra, N. S. Krishnaveni, K. R. Rao, *Tetrahedron Lett.* 2005, 46, 4111; e) M. S. Reddy, M. Narender, K. R. Rao, *Tetrahedron Lett.* 2005, 46, 1299.
- [4] For Cu-catalyzed aziridinations, see: a) D. A. Evans, M. A. Faul, M. T. Bilodeau, J. Org. Chem. 1991, 56, 6744; b) D. A. Evans, M. A. Faul, M. T. Bilodeau, B. A. Andersson, D. M. Barnes, J. Am. Chem. Soc. 1993, 115, 5328; c) Z. Li, K. R. Conser, E. N. Jacobsen, J. Am. Chem. Soc. 1993, 115, 5326; d) M. J. Södergren, D. A. Alonso, P. G. Anderson, Tetrahedron: Asymmetry 1997, 8, 3563; e) P. Dauban, R. H. Dodd, J. Org. Chem. 1999, 64, 5304; f) D. B. Llewellyn, D. Adamson, B. A. Arndtsen, Org. Lett. 2000, 2, 4165; g) W. Adam, K. J. Roschmann, C. R. Saha-Möller, Eur. J. Org. Chem. 2000, 557; h) P. Dauban, L. Sanière, L. Tarrade, R. H. Dodd, J. Am. Chem. Soc. 2001, 123, 7707; i) M. Shi, C.-J. Wang, A. S. C. Chan, Tetrahedron: Asymmetry 2001, 12, 3105; j) S. L. Jain, B. Sain, Tetrahedron Lett. 2003, 44, 575; k) P. Comba, M. Merz, H. Pritzkow, Eur. J. Inorg. Chem. 2003, 1711; l) H. L. Kwong, D. Liu, K.-Y. Chan, C.-S. Lee, K.-H. Hung, C.-M. Che, Tetrahedron Lett. 2004, 45, 3965; m) H. Han, I, Bae, E. J. Yoo, J. Lee, Y. Do, S. Chang, Org. Lett. 2004, 6, 4109; n) T. C. H. Lam, W.-L. Mak, W.-L. Wong, H.-L. Kwong, H. H. Y. Sung, S. M. F. Lo, I. D. Williams, W.-H. Leung, Organometallics 2004, 23, 1247; o) S. L. Jain, V. B. Sharma, B. Sain, Synth. Commun. 2005, 35, 9; p) S. L. Jain, B. Sain, J. Mol. Catal. A 2003, 195, 283; q) P. Dauban, R. H. Dodd, Org. Lett. 2000, 2, 2327; r) D. Leca, A. Toussaint, C. Mereau, L. Fensterbank, E. Lacôte, M. Malarcria, Org. Lett. 2004, 6, 3573; s) K. M. Gillespie, E. J. Crust, R. J. Deeth, P. Scott, Chem. Commun. 2001, 785.
- [5] For Rh-catalyzed aziridinations, see: a) G. F. Keaney, J. L. Wood, *Tetrahedron Lett.* 2005, 46, 4031; b) A. J. Catino, J. M. Nichols, R. E. Forslund, M. P. Doyle, *Org. Lett.* 2005, 7, 2787; c) K. Guthikonda, J. Du Bois, *J. Am. Chem. Soc.* 2002, 124, 13672; d) P. Müller, C. Baud, Y. Jacquier, *Tetrahedron Lett.* 1996, 37, 1543; e) I. Nägeli, C. Baud, G. Bernardinelli, Y. Jacquier, M. Moran, P Müller, *Helv. Chim. Acta* 1997, 80, 1087.

- [6] For Mn-catalyzed aziridinations, see: a) D. Mansuy, J.-P. Mahy, A. Dureault, G. Bedi, P. Battioni, J. Chem. Soc. Chem. Commun. 1984, 1161; b) T.-S. Lai, H.-L. Kwong, C.-M. Che, S.-M. Peng, Chem. Commun. 1997, 2373; c) M. Nishimura, S. Minakata, T. Takahashi, Y. Oderaotoshi, M. Komatsu, J. Org. Chem. 2002, 67, 2101; d) H. Nishikori, T. Katsuki, Tetrahedron Lett. 1996, 37, 9245; e) M. J. Zdilla, M. M. Abu-Omar, J. Am. Chem. Soc. 2006, 128, 16971; f) K. J. O'Connor, S.-J. Wey, C. J. Burrows, Tetrahedron Lett. 1992, 33, 1001.
- [7] For Ru-catalyzed aziridinations, see: a) K. Omura, T. Uchida, R. Irie, T. Katsuki, *Chem. Commun.* 2004, 2060; b) H. Kawabata, K. Omura, T. Katsuki, *Tetrahedron Lett.* 2006, 47, 1571; c) K. Omura, M. Murakami, T. Uchida, R. Irie, T. Katsuki, *Chem. Lett.* 2003, 32, 354; d) J.-L. Zhang, J.-S. Huang, C.-M. Che, *Chem. Eur. J.* 2006, 12, 3020; e) S. K.-Y. Leung, W.-M. Tsui, J.-S. Huang, C.-M. Che, J.-L. Liang, N. Zhu, J. Am. Chem. Soc. 2005, 127, 16629; f) J.-L. Zhang, C.-M. Che, Org. Lett. 2002, 4, 1911.
- [8] For Ag-catalyzed aziridinations, see: a) Y. Cui, C. He, *J. Am. Chem. Soc.* 2003, *125*, 16202; b) K. A. Kumar, K. M. Lokanatha Rai, K. B. Umesha, *Tetrahedron Lett.* 2001, *42*, 6993; c) review: Z. Li, C. He, *Eur. J. Org. Chem.* 2006, 4313.
- [9] For Au-catalyzed aziridinations, see: Z. Li, X. Ding, C. He, J. Org. Chem. 2006, 71, 5876.
- [10] For Co-catalyzed aziridinations, see: a) G.-Y. Gao, J. E. Jones, J. D. Harden, X. P. Zhang, J. Org. Chem. 2006, 71, 6655; b) G.-Y. Gao, J. D. Harden, X. P. Zhang, Org. Lett. 2005, 7, 3191.
- [11] For general overviews on iron catalysis in organic chemistry, see: a) C. Bolm, J. Legros, J. Le Paih, L. Zani, *Chem. Rev.* 2004, 104, 6217; b) A. Fürstner, R. Martin, *Chem. Lett.* 2005, 624; c) A. Correa, O. García Mancheño, C. Bolm, *Chem. Soc. Rev.* 2008, 37, 1108.
- [12] a) O. García Mancheño, C. Bolm, Org. Lett. 2006, 8, 2349; b) O. García Mancheño, C. Bolm, Chem. Eur. J. 2007, 13, 6674.
- [13] a) J. S. Haynes, J. R. Sams, R. C. Thomson, *Can. J. Chem.* 1981, *59*, 669; b) K. S. Hagen, *Inorg. Chem.* 2000, *39*, 5867.
- [14] M. Nakanishi, *Dissertation*, RWTH Aachen University, 2007.
- [15] For the use of other iron catalysts in syntheses of aziridines, see: a) M. F. Mayer, M. M. Hossain, J. Org. Chem. 1998, 63, 6839; b) J.-C. Simonato, J. Pécant, J.-C. Marchon, R. W. Scheidt, Chem. Commun. 1999, 989;

c) L. Simkhovich, Z. Gross, *Tetrahedron Lett.* **2001**, *42*, 8089; d) B. D. Heuss, M. F. Mayer, S. Dennis, M. M. Hossain, *Inorg. Chim. Acta* **2003**, *342*, 301; e) R. Vyas, G.-Y. Gao, J. D. Harden, X. P. Zhang, *Org. Lett.* **2004**, *6*, 1907; f) F. Avenier, J.-M. Latour, *Chem. Commun.* **2004**, 1544.

- [16] a) Here, the preparation of Fe(OTf)₂·2 MeCN triamine complexes and their use in aziridinations of styrene and 1-hexene with PhINTs (applying catalyst:PhINT-S:olefin ratios of 1:20:100–500) in CH₂Cl₂ was reported: Klotz, L. M. Slominski, A. V. Hull, V. M. Gottsacker, R. Mas-Ballesté, L. Que, Jr., J. A. Halfen, *Chem. Commun.* 2007, 2063; b) for a summary of our preliminary results, see ref.^[14]
- [17] D. J. Wallace, J. M. Goodman, D. J. Kennedy, A. J. Davies, C. J. Cowden, M. S. Ashwood, I. F. Cottrell, U.-H. Dolling, P. J. Reider, *Org. Lett.* **2001**, *3*, 671.
- [18] For analogous reactions with Cu and Rh catalysts, see:
 a) P. H. Di Chenna, F. Robert-Peillard, P. Dauban, R. H. Dodd, Org. Lett. 2004, 6, 4503; b) C. Fruit, F. Robert-Peillard, G. Bernardinelli, P. Müller, R. H. Dodd, P. Dauban, Tetrahedron: Asymmetry 2005, 16, 3484.
- [19] In ref.^[3c] the Fe(OTf)₂-catalyzed nitrogen transfer from PhINTs onto styrene (5 equiv.) has already been described. With 5 mol% of catalyst, a yield of 63% of the corresponding aziridine was reported (as single example in a Table summarizing the results obtained in catalyses with various metal salts).
- [20] For a recent theoretical study of Fe-catalyzed nitrogen transfer reactions, see: Y. Moreau, H. Chen, E. Derat, H. Hirao, C. Bolm, S. Shaik, *J. Phys. Chem. B* 2007, *111*, 10288.
- [21] For a review on py-BOX ligands, see: G. Desimoni, G. Faita, R. Quadrelli, *Chem. Rev.* **2003**, *103*, 3119.
- [22] J. Eames, G. S. Coumbarides, M. J. Suggatte, N. Weerasooriya, *Eur. J. Org. Chem.* 2003, 634.
- [23] a) Y. Yamada, T. Yamada, M. Okawara, Chem. Lett.
 1975, 361; b) H. Takada, H. Nishibayashi, K. Ohe, S. Uemura, C. P. Baird, T. J. Sparey, P. C. Taylor, J. Org. Chem. 1997, 62, 6512; c) B. V. Meprathu, S. Diltz, P. J. Walsh, J. D. Protasiewicz, Tetrahedron Lett. 1999, 40, 5459; d) J. Gullick, D. Ryan, P. McMorn, D. Bethell, F. King, F. Hancock, G. Hutchings, New J. Chem. 2004, 28, 1470.
- [24] A. Toshimitsu, H. Abe, C. Hirosawa, K. Tamao, J. Chem. Soc. Perkin Trans. 1 1994, 3465.

1840