Published in final edited form as:

Angew Chem Int Ed Engl. 2013 May 10; 52(20): . doi:10.1002/anie.201209599.

Effective Synthesis of Chiral *N*-Fluoroaryl Aziridines via Enantioselective Aziridination of Alkenes with Fluoroaryl Azides

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Keywords

aryl azides; enantioselective aziridination; *N*-fluoroaryl aziridines; metalloradical catalysis; cobalt porphyrin

Catalytic aziridination of alkenes with nitrene sources via “C2+N1” addition represents a general approach for the direct synthesis of aziridines, the smallest three-membered *N*-heterocycles.^[1] The enantioselective version of this catalytic process allows for efficient access to chiral nonracemic aziridines, which are versatile synthetic intermediates in asymmetric synthesis.^[1-2] Several classes of transition metal-based chiral catalysts, such as Mn, Fe, Cu, Rh and Co complexes, have been found effective in catalyzing asymmetric olefin aziridination with different nitrene sources.^[1,3] Besides iminoiodanes and haloamines, organic azides have been actively pursued as alternative nitrene sources for metal-catalyzed aziridination as they enjoy several advantages.^[3] While sulfonyl and phosphoryl azides have been effectively employed for metal-catalyzed asymmetric aziridination,^[4] catalytic processes based on the use of other types of azides, such as aryl azides, have been less developed. In addition to generating environmentally friendly nitrogen gas as the only byproduct, asymmetric catalytic aziridination with readily available aryl azides provides an attractive approach for the synthesis of valuable *N*-aryl aziridines through direct introduction of *N*-aryl groups concurrently with the ring formation.^[5,6] This would avoid two additional steps of deprotection and *N*-arylation when other types of nitrene sources are used for preparing *N*-aryl aziridines.^[7] However, few catalytic systems have been shown to be effective for asymmetric olefin aziridination with aryl azides.^[4d,6]

Fluoroaryl azides, which can be easily prepared from commercially available fluoroanilines, are a class of common aryl azides that have not been previously employed in catalytic aziridination of alkenes.^[8] A catalytic process for asymmetric aziridination with fluoroaryl azides would be particularly attractive as the resulting enantioenriched *N*-fluoroaryl aziridines could serve as effective chiral synthons for preparation of chiral fluoroarylamine-containing compounds via various ring-opening and ring-expansion transformations (Scheme 1).^[2] Chiral fluoroarylamine derivatives have been demonstrated to be useful in pharmaceutical and other important applications.^[9] To date, only a few metal complexes, including Ru, Co and Fe complexes, have been reported to catalyze the aziridination of alkenes with aryl azides.^[4d,6] None of them involved the use of fluoroaryl azides as nitrene

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sources. These existing catalytic aziridination systems typically required the use of excess olefins and relatively high reaction temperatures (70–90 °C) to achieve satisfactory yields. Furthermore, the majority of those are non-asymmetric systems, without addressing the issue of enantioselectivity. To the best of our knowledge, the only example of asymmetric aziridination with aryl azides was carried out for *p*-methylstyrene with 4-nitrophenyl azide by a Ru-based chiral catalyst, reaching only 10% enantiomeric excess in 35% yield.^[10] It is evident that asymmetric olefin aziridination with aryl azides, including fluoroaryl azides, is an unsolved problem and faces formidable challenges in both reactivity and enantioselectivity.

As stable metalloradicals with a well-defined open-shell doublet $d^{[7]}$ electronic structure, cobalt(II) complexes of D_2 -symmetric chiral amidoporphyrins, $[\text{Co}(D_2\text{-Por}^*)]$, have been shown to be effective catalysts for asymmetric aziridination of various olefin substrates with different classes of nitrene sources, particularly with sulfonyl and phosphoryl azides.^[4a,4b] Results from computational and experimental studies suggest a distinctive metalloradical mechanism for the Co(II)-catalyzed aziridination that involves an unprecedented Co(III)–nitrene radical intermediate proceeding a stepwise radical addition-substitution pathway.^[11] In addition to serving as rigid spacers to support and orient the chiral environments toward the cobalt center, the amide units of the D_2 -symmetric amidoporphyrins were shown to also function as potential donors to engage in hydrogen-bonding interaction with acceptors located at the nitrene moiety in the Co(III)–nitrene radical intermediate,^[12–13] lowering the energy barrier of the transition state and thus accelerating the reaction rate.^[11a] Given that the fluorine atom in organic fluorides can act as a potential hydrogen bond acceptor,^[14] we hypothesized the possibility of a similar hydrogen-bonding interaction in the corresponding Co(III)–nitrene radical intermediate from activation of fluoroaryl azides (Figure 1). Depending on the number of *ortho*-fluorine atoms in fluoroaryl azides, formation of single (Figure 1A) or double (Figure 1B) N–H...F hydrogen bonds between the amide N–H elements of amidoporphyrins and the *ortho*-F atoms of fluoroaryl groups would be attainable. On the basis of this hypothesis, we embarked on a research project studying catalytic asymmetric olefin aziridination with fluoroaryl azides by $[\text{Co}(D_2\text{-Por}^*)]$.

As an outcome of this effort, we report herein a highly effective catalytic system based on a new generation of chiral Co(II) metalloradical catalyst for asymmetric aziridination of alkenes with fluoroaryl azides. The Co(II)-catalyzed aziridination is suitable for a wide range of aromatic olefins and can also utilize different fluoroaryl azides, producing the corresponding *N*-fluoroaryl aziridines in high yields with excellent enantioselectivities. In addition to tolerance of a wide variety of fluoroaryl azides as nitrene sources, the new metalloradical aziridination process features a practical protocol that operates at room temperature without the need of excess olefin, generating N_2 as the only byproduct.

At the outset of our studies, we evaluated the catalytic capability of different D_2 -symmetric chiral amidoporphyrins $[\text{Co}(D_2\text{-Por}^*)]$ toward aziridination of styrene (**1a**) with 2-fluorophenyl azide (**2a**) (Table 1). Under the catalysis of 2 mol % of $[\text{Co}(\text{P1})]$ (**P1** = 3,5-Di^tBu-ChenPyrin),^[15] it was gratifying to find that the reaction went smoothly in benzene even at room temperature by using styrene as the limiting reagent, affording the desired aziridine product in 50% yield and 47% ee (Table 1, entry 1). Subsequent experiments showed that $[\text{Co}(\text{TPP})]$ (TPP = 5,10,15,20-tetraphenylporphyrin) was ineffective in catalyzing the reaction under the same conditions (Table 1, entry 2). The notable difference in catalytic capability between $[\text{Co}(\text{P1})]$ and $[\text{Co}(\text{TPP})]$ is in line with our assumption about the possible role of N–H...F hydrogen bonding interaction in activating the fluoroaryl azide (Figure 1A). Further studies showed 2,4,6-trifluorophenyl azide (**2b**) was also an effective aziridinating reagent for styrene by $[\text{Co}(\text{P1})]$, affording the corresponding aziridine in 95% yield and 66% ee (Table 1, entry 3). The observed improvement in reactivity and

stereoselectivity with azide **2b**, which contains two *ortho*-F atoms, is ascribed to potential formation of the double N–H...F hydrogen bonds in the postulated Co(III)–nitrene radical intermediate (Figure 1B). Further improvement in enantioselectivity was achieved for aziridination of styrene with azide **2b** when [Co(**P2**)] (**P2** = 3,5-Di^tBu-QingPhyrin), a second-generation metalloradical catalyst that was previously shown to be highly effective for asymmetric intramolecular cyclopropanation,^[16] was employed as a catalyst, reaching 73% ee with the same high yield (Table 1, entry 4). Successive studies resulted in the design and synthesis of a new *D*₂-symmetric chiral amidoporphyrin 3,5-Di^tBu-Xu(2-Naph)Phyrin (**P3**),^[17] whose Co(II) complex [Co(**P3**)] was shown to be the optimal catalyst for the process, giving the desired product in 94% yield and 90% ee even with only 1 mol % of catalyst loading (Table 1, entry 5). Among various solvents screened, fluorobenzene was found to be the solvent of choice, giving the aziridine product in high yield (94%) and excellent enantioselectivity (92% ee) at room temperature (Table 1, entries 5–8). As expected, control experiments in the absence of a catalyst gave no reaction (Table 1, entry 9).

Under the optimized catalytic conditions, we then used styrene aziridination as a model reaction to investigate the scope and limitation of fluoroaryl azides as nitrene sources (Table 2). As in the case of aryl azide **2b** that has two *ortho*-F atoms (Table 1), use of the new metalloradical catalyst [Co(**P3**)] also led to significant improvement in enantioselectivity for the aziridination reaction with aryl azide **2a** containing one *ortho*-F atom (Table 2, entry 1 vs Table 1, entry 1). The [Co(**P3**)]-based catalytic aziridination system could effectively employ other mono-*ortho*-fluoro-substituted aryl azides as nitrene sources, as demonstrated by the use of 2,4,5-trifluorophenyl azide (**2c**) (Table 2, entry 2). In addition to azide **2b**, various other di-*ortho*-fluoro-substituted aryl azides, including 2,6-difluoro-, 2,3,5,6-tetrafluoro- and pentafluorophenyl azides (**2d–f**), were shown to be highly effective nitrene sources for the Co(II)-based aziridination process, yielding corresponding aziridines in high yields with excellent enantioselectivities (Table 2, entries 3–5). Presumably as a result of additional N–H...F hydrogen bonding interactions in the postulated Co(III)–nitrene radical intermediate (Figure 1), di-*ortho*-fluoro-substituted aryl azides were found to be more selective and effective aziridinating agents than mono-*ortho*-fluoro-substituted aryl azides. Similarly, 4-tetrafluoropyridinyl azide (**2g**) was found to be equally effective in aziridinating styrene, without complication from potential coordination of the pyridine unit to [Co(**P3**)] (Table 2, entry 6). Reactions with *para*-substituted fluoroaryl azides such as 4-bromotetrafluorophenyl azide (**2h**) and 4-trifluoromethyltetrafluorophenyl azide (**2i**) produced the desired products in excellent yields, albeit with slightly lower enantioselectivities (Table 2, entries 7–8). It is worth noting that 3,4,5-trifluorophenyl azide (**2j**), which contains three F-atoms but no *ortho*-F-atom, gave no reaction under the same conditions (Table 2, entry 9), again suggesting the important role that the N–H...F hydrogen bond plays in the Co(II)-based metalloradical aziridination process (Figure 1).^[18]

The [Co(**P3**)]-catalyzed asymmetric aziridination was found to be suitable for a wide spectrum of aromatic olefins with varied electronic and steric properties, as shown in Table 3 with 2,4,6-trifluorophenyl azide (**2b**) and pentafluorophenyl azide (**2f**) as representative fluoroaryl azides.^[19] Similar to styrene, styrene derivatives with electron-donating substituents at various positions, including Me, ^tBu, and MeO groups at the *para*-, *meta*- and *ortho*-positions, could be aziridinated smoothly, forming the corresponding *N*-fluoroaryl aziridines in high yields and high enantioselectivity (Table 3, entries 1–8). In addition, enantioenriched *N*-fluoroaryl aziridines could be readily formed from aziridination reactions of electron-deficient styrenes, such as *para*-CF₃- and *para*-CO₂Me-substituted styrenes (Table 3, entries 9–11). Moreover, [Co(**P3**)] could effect aziridination of various halogenated styrenes, such as fluorostyrenes and bromostyrenes, producing the corresponding aziridines with high enantiomeric excesses (Table 3, entries 12–16). The

Co(II)-based asymmetric aziridination could also be successfully applied to extended aromatic olefins, including 2-vinylnaphthalene and sterically demanding 1-vinylnaphthalene and 9-vinylnaphthalene (Table 3, entries 17–20). Notably, heteroaromatic alkenes such as *Boc*-protected 3-vinyndole could also be fruitfully aziridinated with fluoroaryl azides, generating the desired aziridinyndole **3ob** in high yield and excellent enantioselectivity (Table 3, entry 21).

The demonstrated asymmetric olefin aziridination with fluoroaryl azides by Co(II)-based metalloradical catalysis provides a practical method to access *N*-fluoroaryl-containing chiral compounds in high enantiomeric purity, which may find applications in asymmetric synthesis and pharmaceuticals.^[9] As an initial exploration of further transformations of these chiral *N*-fluoroaryl aziridines, it was found that the aziridine ring could be readily opened in the presence of a Lewis acid without apparent loss of the enantiomeric purity (Scheme 2, eqs 1–3).^[20] For instance, *N*-fluoroaryl-containing chiral aziridines **3ab** and **3af** readily underwent ring-opening reactions by MeOH in the presence of Cu(OTf)₂, generating chiral *N*-methoxy amine derivatives **4** and **5**, respectively, in high yields with high optical purity (eqs 1 and 2). X-ray structural analysis revealed the absolute configuration of the C-stereocenter in product **5** to be [*R*] (see Supp Info), indicating an S_N2-type ring-opening reaction at the original [*S*]-chiral center in **3af**. More significantly, even water could function as a nucleophile for the highly stereoselective ring-opening process, as demonstrated for chiral aziridine **3ab**, which resulted in the direct formation of chiral vicinal amino alcohol **6** (eq 3).

In summary, we have demonstrated that the metalloradical [Co(**P3**)] is an efficient catalyst for highly enantioselective aziridination of alkenes with fluoroaryl azides. This Co(II)-based process represents the first catalytic system for asymmetric olefin aziridination with aryl azides as the nitrene source. Among other attributes, the metalloradical aziridination can operate at room temperature using olefin as the limiting reagent without the need of any additives, generating nitrogen gas as the only byproduct. The resulting optically pure *N*-fluoroaryl aziridines should find useful applications in asymmetric synthesis. Efforts are underway to employ fluoroaryl azides as effective nitrene sources for developing other catalytic nitrene transfer processes via Co(II)-based metalloradical catalysis.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We are grateful for financial support by NSF (CHE-1152767) and NIH (R01-GM098777).

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17. Chiral porphyrin P3 was developed using an iterative approach based on Co(II)-catalyzed asymmetric cyclopropanation (ref. 16). For details on its synthesis and X-ray crystal structure, see supporting information.
18. a) no reactions were observed with phenyl azide and 2,6-dichlorophenyl azide. b) Inverse kinetic isotope effect was observed with deuterated catalyst.

19. The current catalytic system was found to be ineffective for disubstituted alkenes. For substrates containing secondary and allylic C–H bonds, catalytic C–H amination was observed instead of olefin aziridination.
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Figure 1.
H-Bonding in Postulated Nitrene Radical Complex.

Scheme 1. Synthesis and Transformations of *N*-Fluoroaryl Aziridines

Scheme 2. Nucleophilic Ring-Opening of *N*-Fluoroaryl Aziridines

Table 1

Enantioselective Aziridination by Different [Co(*D*₂-Por*)]^a

entry	catalyst	Ar	solvent	yield(%) ^b	ee(%) ^c
1 ^d	[Co(P1)]	o-FC ₆ H ₄ (2a)	PhH	50 ^e	-47
2 ^d	[Co(TPP)]	o-FC ₆ H ₄ (2a)	PhH	trace	----
3 ^d	[Co(P1)]	2,4,6-F ₃ C ₆ H ₂ (2b)	PhH	95	-66
4 ^d	[Co(P2)]	2,4,6-F ₃ C ₆ H ₂ (2b)	PhH	95	73
5	[Co(P3)]	2,4,6-F ₃ C ₆ H ₂ (2b)	PhH	94	90
6	[Co(P3)]	2,4,6-F ₃ C ₆ H ₂ (2b)	PhCl	80	91
7	[Co(P3)]	2,4,6-F ₃ C ₆ H ₂ (2b)	PhF	94	92
8	[Co(P3)]	2,4,6-F ₃ C ₆ H ₂ (2b)	hexane	72	90
9	----	2,4,6-F ₃ C ₆ H ₂ (2b)	PhH	NR	----

^aCarried out with 1 equiv of olefin (0.2 M) and 1.2 equiv of azide with [Co(Por)] (1 mol %).

^bIsolated yields.

^cDetermined by chiral HPLC.

^d2 mol %.

^e¹⁹F-NMR yield. Contained **2a** (10%), azo fluorobenzene (15%), fluoroaniline (10%) and unknowns (15%).

Table 2
[Co(P3)]-Catalyzed Enantioselective Aziridination of Styrene with Various Fluoroaryl Azides^a

entry 1 ^e : 3aa ; 52% y, 75% ee	entry 2: 3ac ; 64% y, 80% ee	entry 3 ^d : 3ad ; 80% y, 96% ee
entry 4: 3ae ; 95% y, 89% ee	entry 5: 3af ; 99% y, 92% ee	entry 6: 3ag ; 96% y, 90% ee
entry 7: 3ah ; 95% y, 80% ee	entry 8: 3ai ; 99% y, 68% ee	entry 9: 3aj ; no reaction

See Table 1 for [a], [b], [c] & [e]. [d] Determined by X-ray diffraction.

Table 3
Enantioselective Aziridination of Different Combinations of Olefins with Azides
 Catalyzed by [Co(P3)]^{a, b, c}

entry 1: 3ab ; 99% y, 94% ee	entry 2: 3af ; 99% y, 92% ee	entry 3: 3bf ; 99% y, 96% ee
entry 4: 3cb ; 99% y, 92% ee	entry 5: 3cf ; 95% y, 94% ee	entry 6: 3df ; 99% y, 87% ee
entry 7: 3eb ; 85% y, 92% ee	entry 8: 3fb ; 99% y, 87% ee	entry 9: 3gb ; 77% y, 92% ee
entry 10 ^d : 3gf ; 91% y, 85% ee	entry 11: 3hb ; 80% y, 92% ee	entry 12: 3ib ; 93% y, 95% ee
entry 13 ^d : 3if ; 90% y, 91% ee	entry 14 ^d : 3jb ; 81% y, 92% ee	entry 15: 3kb ; 82% y, 93% ee
entry 16: 3kf ; 95% y, 89% ee	entry 17: 3lb ; 80% y, 90% ee	entry 18: 3lf ; 73% y, 98% ee
entry 19: 3mb ; 74% y, 86% ee	entry 20: 3nf ; 90% y, 85% ee	entry 21: 3ob ; 80% y, 96% ee

See Table 1 for [a], [b] & [c]. [d] Determined by X-ray diffraction.