CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201000581

[$Fe^{III}(F_{20}$-tpp)Cl] Is an Effective Catalyst for Nitrene Transfer Reactions and Amination of Saturated Hydrocarbons with Sulfonyl and Aryl Azides as Nitrogen Source under Thermal and Microwave-Assisted Conditions

Yungen Liu and Chi-Ming Che*[a]

Abstract: [$Fe^{III}(F_{20}$-tpp)Cl] (F_{20}-tpp = *meso*-tetrakis(pentafluorophenyl)porphyrinato dianion) is an effective catalyst for imido/nitrene insertion reactions using sulfonyl and aryl azides as nitrogen source. Under thermal conditions, aziridination of aryl and alkyl alkenes (16 examples, 60–95% yields), sulfimidation of sulfides (11 examples, 76–96% yields), allylic amidation/amination of α-methylstyrenes (15 examples, 68–83% yields), and amination of saturated C–H bonds including that of cycloalkanes and adamantane (eight examples, 64–80% yields) can be accomplished by using 2 mol% [$Fe^{III}(F_{20}$-tpp)Cl] as catalyst. Under microwave irradiation conditions, the reaction time of aziridination (four examples), allylic amination (five examples), sulfimidation (two examples), and amination of saturated C–H bonds (three examples) can be reduced by up to 16-fold (24–48 versus 1.5–6 h) without significantly affecting the product yield and substrate conversion.

Keywords: allylic compounds · azides · C–H activation · microwave chemistry · porphyrinoids

Introduction

Metal-catalyzed nitrene/imido transfer reactions, such as aziridination of alkenes, sulfimidation of sulfides, and amination/amidation of alkanes, have important applications in organic synthesis.[1] In particular, the amination of unactivated C–H bonds with acceptable product yields and selectivity remains a difficult challenge. Most of the reported nitrene/imido transfer and insertion reactions use *N*-arylsulfonyliminophenyliodinanes, bromamine-T or chloramine-T as nitrogen source.[2] In recent years, there has been a growing interest in the use of organic azides as nitrogen-transfer reagents because the by-product is nitrogen gas, which is nonhazardous to the environment.[3] Cenini,[4] Katsuki,[5] Zhang,[6] and their co-workers pioneered the development of nitrene transfer reactions with organic azides catalyzed by cobalt or ruthenium complexes.

Saturated C–H bonds are generally not regarded as functional groups in organic synthesis. After decades of efforts directed to C–H bond activation, direct functionalization of saturated C–H bonds by metal catalysis has become a viable approach and could be a useful tool for organic synthesis.[7] Up to now, most of the metal-catalyzed C–H bond activations have focused on activated C–H bonds (such as those at the allylic/benzylic position,[8] or adjacent to O or N atoms[9]) or intramolecular cyclization reactions.[10] Direct functionalization of unactivated saturated C–H bonds (e.g., aliphatic carbon chains) remains a formidable challenge and relatively few reports with practical applications have been published in this area.

In recent years, there has been a surge of interest in developing iron catalysts for atom- and group-transfer reactions for the construction of C–N bonds.[11] Compared with other transition-metal catalysts, iron complexes are inexpensive and biocompatible.[12] Among the iron complexes reported for this endeavor, iron porphyrins are commercially available, air and moisture stable, and can be easily prepared and modified. In the literature, iron porphyrins are known to catalyze C–N bond formation with *N*-(*p*-toluenesulfonyl)iminophenyliodinane (PhI=NTs) or bromamine-T as the nitrogen source.[1f,11c] Herein, we report that [$Fe^{III}(F_{20}$-tpp)Cl] (F_{20}-tpp = *meso*-tetrakis(pentafluorophenyl)porphyrinato dianion) is an effective catalyst for aziridination of alkenes, sulfimidation of both alkyl and aryl sul-

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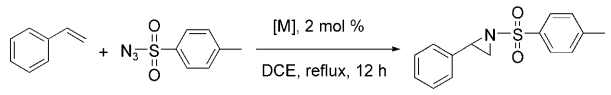
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201000581.

fides, direct allylic amidation/amination of α-methylstyrenes, and amination of saturated C–H bonds including that of cycloalkanes with sulfonyl and aryl azides as the nitrogen source.

Results and Discussion

At the outset, various metal complexes were evaluated by using aziridination of styrene by tosyl azide (TsN_3) as the test reaction (Table 1). [Mn^{III}(tdcpp)Cl], [Rh^{III}(F_{20}-tpp)I] (H_2F_{20}-tpp = *meso*-tetrakis(pentafluorophenyl)porphyrin), and [Ru^{II}(ttp)(CO)] (H_2ttp = *meso*-tetrakis(*p*-tolyl)porphyrin) were found to be inactive and in each case no product was detected with TsN_3 recovered quantitatively under the employed experimental conditions (Table 1, entries 1–3). [Fe^{III}(salen)Cl] (H_2salen = *N*,*N*′-bis(salicylidene)ethylenediamine) gave 2-phenyl-1-tosylaziridine in 60% yield with 40% azide consumption (Table 1, entry 4). When [Fe^{III}(tpp)Cl] was employed as the catalyst, the aziridine product was obtained in 80% yield with 60% azide consumption (Table 1, entry 5). The use of [Fe^{III}(F_{20}-tpp)Cl] bearing a fluorinated porphyrin ligand gave the aziridine product in 95% yield and with complete azide consumption in 12 h (Table 1, entry 6). The two iron(II) porphyrins [Fe^{II}(F_{20}-tpp)] and [Fe^{II}(tpp)], generated in situ by $NaBH_4$ reduction[13] of [Fe^{III}-(F_{20}-tpp)Cl] and [Fe^{III}(tpp)Cl], respectively, were found to be catalytically active although the activity in each case was lower than that displayed by their parent iron(III) porphyrin complexes (Table 1, entries 7 and 8).

Table 1. Aziridination of styrene catalyzed by various metal complexes.[a]

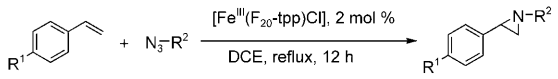


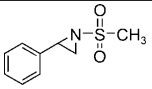
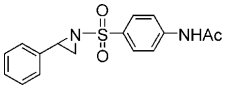
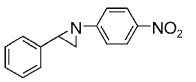
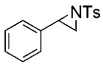
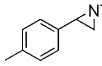
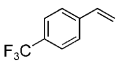
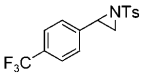
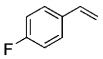
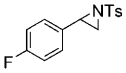
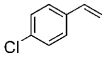
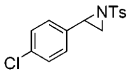
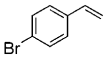
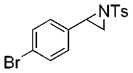
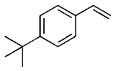
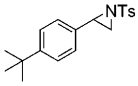
Entry	[M]	Conversion [%][b]	Yield [%][c]
1	[Mn^{III}(tdcpp)Cl]	0	0
2	[Rh^{III}(F_{20}-tpp)I]	0	0
3	[Ru^{II}(ttp)(CO)]	0	0
4	[Fe^{III}(salen)Cl]	40	60
5	[Fe^{III}(tpp)Cl]	60	80
6	[Fe^{III}(F_{20}-tpp)Cl]	100	95
7	[Fe^{II}(tpp)][d]	50	75
8	[Fe^{II}(F_{20}-tpp)][d]	80	85

[a] All reactions were performed with styrene (0.60 mmol), azide (0.20 mmol), metal complex (0.004 mmol), and 4 Å molecular sieves (60 mg) in anhydrous $ClCH_2CH_2Cl$ (1 mL) under N_2. [b] Determined by crude ^1H NMR spectroscopy. [c] Yield of isolated product based on conversion. [d] Formed in situ by $NaBH_4$ reduction. DCE: 1,2-dichloroethane.

With [Fe^{III}(F_{20}-tpp)Cl] as catalyst, other azides, such as methanesulfonyl azide (MsN_3), *p*-acetamidobenzenesulfonyl azide (*p*-ABSA), and 4-nitrophenyl azide, were also examined as the nitrogen source (Table 2, entries 1–3). TsN_3 gave the best result when compared with MsN_3, *p*-ABSA, and 4-nitrophenyl azide. With TsN_3 as the nitrogen source, substituted styrenes, including those with electron-withdrawing or electron-donating substituents, gave the corresponding aziridines in excellent yields (92–95%, Table 2, entries 4–10) and with complete azide consumption.

Table 2. Aziridination of styrenes.[a]



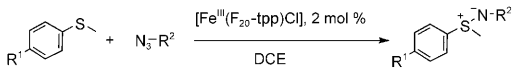
Entry	Substrates	Products	Yield [%][b]
1			75
2			85
3[c]			87
4			95
5			95
6			92
7			93
8			92
9			93
10			94

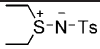
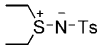
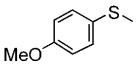
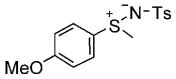
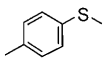
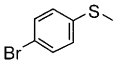
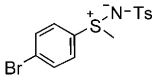
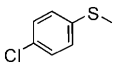
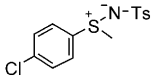
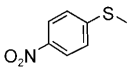
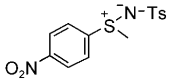
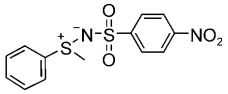
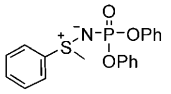
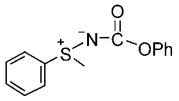
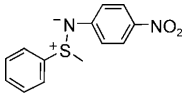
[a] All reactions were performed with styrene (0.60 mmol), azide (0.20 mmol), [Fe^{III}(F_{20}-tpp)Cl] (0.004 mmol), and 4 Å molecular sieves (60 mg) in anhydrous $ClCH_2CH_2Cl$ (1 mL) under N_2. [b] Yield of isolated product. [c] 1.00 mmol styrene was used.

Sulfimidation[14] is a useful nitrene/imido transfer reaction. In this work, both diethyl sulfide and thioanisoles were converted to sulfimides in high yields by TsN_3 and with [Fe^{III}-(F_{20}-tpp)Cl] as the catalyst (Table 3, entries 2–8). No sulfimidation was found in the absence of [Fe^{III}(F_{20}-tpp)Cl] (Table 3, entry 1). The sulfimidation of substituted thioanisoles is affected by the substituent group on the aryl ring. Strong electron-withdrawing groups such as NO_2 led to a longer reaction time (Table 3, entry 4 versus entry 8). With the other nitrogen sources, *p*-nitrobenzenesulfonyl azide (Table 3, entry 9), diphenyl phosphoryl azide (DPPA, Table 3, entry 10), phenyl carboxyl azide (Table 3, entry 11), and 4-nitrophenyl azide (Table 3, entry 12), the corresponding sulfimidation reactions also proceeded smoothly.

Aziridination of aliphatic alkenes could also be accomplished with the "[Fe^{III}(F_{20}-tpp)Cl] + sulfonyl or aryl azide" protocol. Compared with the reactions with styrenes, aziridination of aliphatic alkenes is conspicuously difficult due to

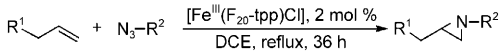
Table 3. Sulfimidation of sulfides.[a]

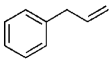
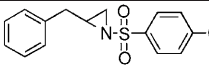
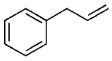
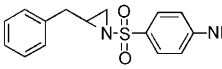
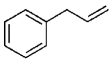
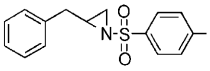
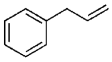
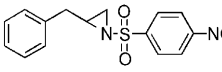
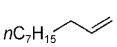
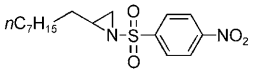
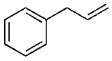
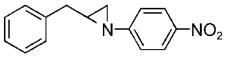
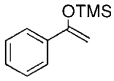
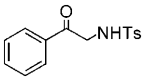


Entry	Substrates	Products	t [h]	Yield [%][b]
1[c]			12	0
2			12	96
3			24	94
4			24	95
5			24	95
6			24	93
7			24	92
8			48	90
9			24	95
10			24	91
11			24	76
12			36	78

[a] All reactions were performed with sulfide (0.60 mmol), azide (0.20 mmol), [$Fe^{III}(F_{20}$-tpp)Cl] (0.004 mmol), and 4 Å molecular sieves (60 mg) in anhydrous $ClCH_2CH_2Cl$ (1 mL) under N_2. [b] Yield of isolated product. [c] Without catalyst.

Table 4. Aziridination of aliphatic alkenes.[a]



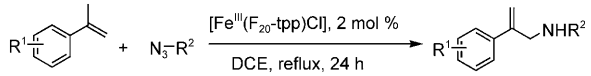
Entry	Substrates	Products	Yield [%][b]
1			60 (35 cvn[c])
2			70 (50 cvn[c])
3			75 (55 cvn[c])
4			85
5			83
6			75
7			90
8			80

[a] All reactions were performed with alkene (1.00 mmol), azide (0.20 mmol), [$Fe^{III}(F_{20}$-tpp)Cl] (0.004 mmol), and 4 Å molecular sieves (60 mg) in anhydrous $ClCH_2CH_2Cl$ (1 mL) under N_2. [b] Yield of isolated product based on conversion. [c] Conversion (cvn) was determined by crude ^1H NMR spectroscopy.

the low reactivity of aliphatic alkenes. For example, aziridination of styrene with MsN_3 could be accomplished in 75% yield with complete azide consumption (Table 2, entry 1), whereas under similar conditions the aziridination of allylbenzene can only be achieved in 60% yield with 35% azide consumption (Table 4, entry 1). With the other azides *p*-ABSA and TsN_3, both the azide consumption and product yield in each case were improved (Table 4, entries 2 and 3). The best result was obtained when *p*-nitrobenzenesulfonyl azide was used as the nitrogen source. The aziridination of allylbenzene and 1-decene by *p*-nitrobenzenesulfonyl azide was accomplished in product yields of 85 and 83%, respectively, and with complete azide consumption (Table 4, entries 4 and 5). 4-Nitrophenyl azide gave an aziridination product from allylbenzene in 75% yield with complete azide consumption (Table 4, entry 6). Although tosyl azide was found to give 2-(tosylamino)-1-phenylethanone from α-(trimethylsiloxy)styrene (Table 4, entry 7), the amidation of 2-(trimethylsiloxy)-1-decene could only be accomplished by using 4-nitrobenzenesulfonyl azide as the nitrogen source, which gave 1-(4-nitrobenzenesulfonylamino)-2-decanone in 80% yield and with complete azide consumption (Table 4, entry 8).

Interestingly, allylic amidation/amination occurred with no aziridine detected when α-methylstyrenes were used as substrates. The results are listed in Table 5. In the literature, there are only a few reports on the direct allylic amidation of substituted α-methylstyrenes.[1a,4d,f] With TsN_3, substituted α-methylstyrenes gave the corresponding allylic sulfamides as the major products (Table 5, entries 1–8, 70–82% yields). The reaction of the structurally similar 2-isopropenylnaphthalene (Table 5, entry 9) gave the allylic amidation product in 78% yield. The reactions of α-methylstyrene with the other nitrogen sources, *p*-ABSA (Table 5, entry 10) and *p*-nitrobenzenesulfonyl azide (Table 5, entry 11), also gave the allylic amidation products in good yields. Allylic amination of 4-*tert*-butyl α-methylstyrene was accomplished in 83% product yield when 4-nitrophenyl azide was used as the nitrogen source (Table 5, entry 12). Both allylic amination and hydroxyamination products were obtained when α-methylstyrene (Table 5, entry 13) and 2-isopropenylnaphthalene (Table 5, entry 14) were employed as the substrates and by

Table 5. Allylic amidation of α-methylstyrenes.[a]



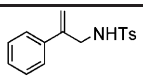
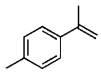
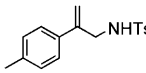
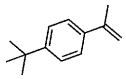
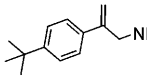
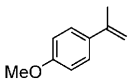
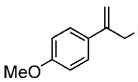
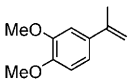
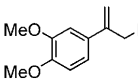
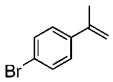
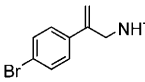
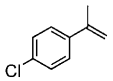
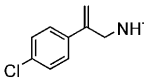
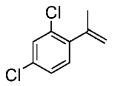
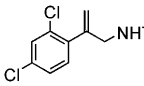
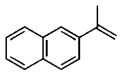
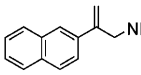
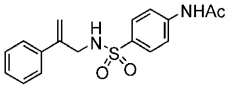
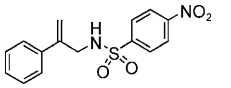
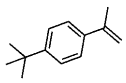
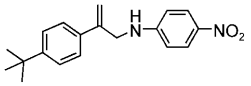
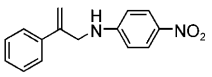
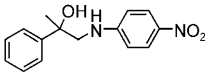
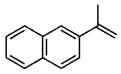
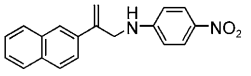
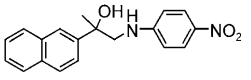
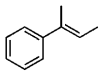
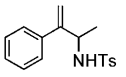
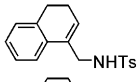
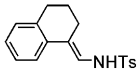
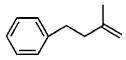
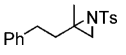
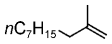
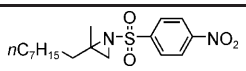
Entry	Substrates	Products	Yield [%][b]
1			80
2			81
3			82
4			72
5			70
6			78
7			74
8			70
9			78
10			72
11			83
12[c]			83
13[c]			32
			49
14[c]			26
			55
15			68
16			17
			67
17[c,d]			61

Table 5. (Continued)

Entry	Substrates	Products	Yield [%][b]
18[c,d]			83

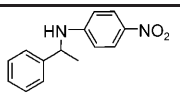
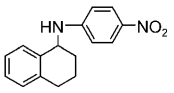
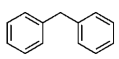
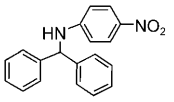
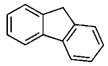
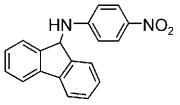
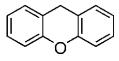
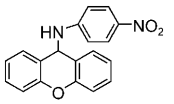
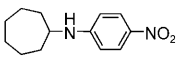
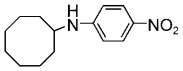
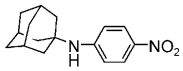
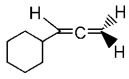
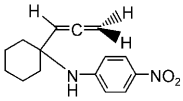
[a] Reactions were performed with α-methylstyrene (0.80 mmol), azide (0.20 mmol), $[Fe^{III}(F_{20}\text{-tpp})Cl]$ (0.004 mmol), and 4 Å molecular sieves (60 mg) in anhydrous $ClCH_2CH_2Cl$ (1 mL) under N_2. [b] Yield of isolated product. [c] 1.00 mmol olefin was used. [d] Heated to reflux for 48 h.

using 4-nitrophenyl azide as the nitrogen source. 2-Phenyl-2-butene (Table 5, entry 15) gave only one allylic amidation product in 68% yield without any amidation at the two terminal methyl groups. In addition, the amidation was exclusively found at the methylene group of α-methylenetetralin (Table 5, entry 16). Unfortunately, this reaction was found not to be applicable to 2-methyl-2-alkyl-substituted terminal alkenes. 2-Methyl-4-phenyl-1-butene (Table 5, entry 17) and 2-methyl-1-decene (Table 5, entry 18) gave aziridines as the major products and without any allylic amination product detected.

Direct functionalization of saturated C–H bonds is appealing in organic synthesis. At first, we examined the amidation of ethylbenzene by using sulfonyl azides (e.g., MsN_3, TsN_3, *p*-ABSA, and *p*-nitrobenzenesulfonyl azide) as the nitrogen source; however, no amidation product was obtained in each of the reactions studied. Eventually, amination of ethylbenzene was achieved to give 4-nitro-*N*-(1-phenylethyl)benzenamine in 71% yield and with complete azide consumption when 4-nitrophenyl azide was employed (Table 6, entry 1). Starting with 4-nitrophenyl azide, the benzylic C–H bonds of tetralin (Table 6, entry 2), diphenylmethane (Table 6, entry 3), fluorene (Table 6, entry 4), and xanthene (Table 6, entry 5) were successfully aminated in moderate to good yields. Importantly, amination of the unreactive saturated C–H bonds of cycloheptane (Table 6, entry 6), cyclooctane (Table 6, entry 7), and adamantane (Table 6, entry 8) was accomplished in moderate product yields. In the case of adamantane, the amination reaction occurred at 3° C–H bonds with no products derived from 2° C–H bonds detected. Similarly, the amination of 1-cyclohexylallene also occurred at the 3° C–H bond with the allene moiety and 2° C–H bonds remaining intact (Table 6, entry 9).

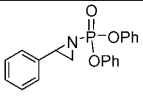
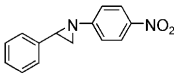
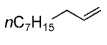
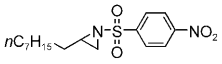
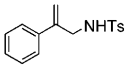
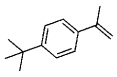
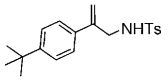
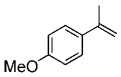
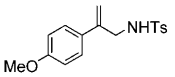
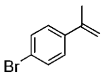
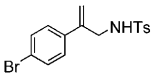
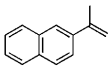
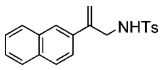
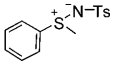
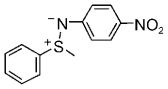
As reported in the literature, microwave irradiation could significantly shorten the time for completion of a reaction.[15] Thus, some of the sluggish substrates were selected for the catalysis under microwave irradiation and the results are depicted in Table 7. In this work, microwave irradiation was found to shorten the reaction time by up to 16-fold. As an example, the reaction of styrene with DPPA was slow under thermal conditions, as the conversion of DPPA was only 20% even after heating at reflux in $ClCH_2CH_2Cl$ for 24 h. Under microwave irradiation, this reaction could be completed in 2.5 h (Table 7, entry 1), and the time to complete the aziridination of both styrene and 1-decene was shortened greatly (Table 7, entries 2–4). Allylic amidation of α-

Table 6. Saturated C–H bond activation.[a]

Entry	Substrates	Products	t [h]	Conv. [%][b]	Yield [%][c]
1			36	100	71
2			36	100	73
3			48	100	72
4			24	100	80
5			24	100	78
6[d]			48	63	65
7[d]			48	65	64
8			48	60	68
9			24	100	64

[a] Reactions were performed with alkane (2.00 mmol), 4-nitrophenyl azide (0.20 mmol), [$Fe^{III}(F_{20}$-tpp)Cl] (0.004 mmol), and 4 Å molecular sieves (60 mg) in anhydrous $ClCH_2CH_2Cl$ (1 mL) under N_2. [b] Determined by crude ^1H NMR spectroscopy. [c] Yield of isolated product based on conversion. [d] 5.00 mmol cycloalkane was used.

Table 7. Microwave-accelerated nitrogen group transfer reactions.[a]

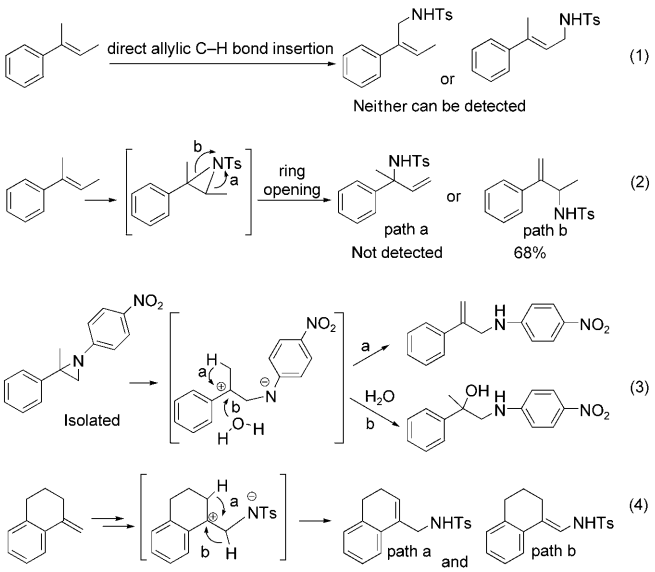
Entry	Substrates	Products	t [h]	Yield [%][b]
1			2.5	75
2			1	93
3[c]			3	82
4[c]			2	75
5[d]			1.5	75
6[d]			1.5	78
7[d]			1.5	70
8[d]			1.5	73
9[d]			1.5	74
10			2.5	76
11			3	75
12[e]			5	70
13[f]			3.5	64
14[e]			6	65

[a] Reactions were performed with alkene (0.30 mmol), azide (0.10 mmol), [Fe(F_{20}-tpp)Cl] (0.002 mmol), and 4 Å molecular sieves (40 mg) in anhydrous $ClCH_2CH_2Cl$ (1.0 mL). [b] Yield of isolated product. [c] 0.50 mmol olefin was used. [d] 0.40 mmol olefin was used. [e] 1.00 mmol alkane was used. [f] 2.5 mmol alkane was used.

methylstyrenes was finished in 1.5 h with TsN_3 as the nitrogen source (Table 7, entries 5–9). Compared with the reaction conducted under thermal conditions, microwave irradiation accelerated the reaction by nearly 16-fold (24 versus 1.5 h). Not surprisingly, sulfimidation of thioanisole was also accelerated under microwave irradiation conditions with TsN_3 or 4-nitrophenyl azide used as the nitrogen source (Table 7, entries 10 and 11). Notably, amination of the unreactive saturated C–H bonds of cycloheptane and adamantane can be accomplished in 64 and 65% yields, respectively (4-nitrophenyl azide as the limiting reagent) with complete azide conversion within a reaction time of 3.5 and 6 h, respectively. For all of the substrates, their reactions under microwave irradiation gave comparable product yields (slightly lower) to those obtained under thermal conditions within a reaction time shortened by up to 16-fold.

Compared with the reported nitrene/imido transfer reactions using iminophenyliodinanes (e.g., PhI=NTs) as the nitrogen source, the organic azides in our work have been found to give good results for both the aziridination and sulfimidation reactions described herein. In the context of green chemistry, organic azides only generate nitrogen gas as the by-product whereas iminophenyliodinanes release PhI as a side product. The drawbacks of organic azides include their difficulty in undergoing decomposition and their low oxidizing power, which is not favorable for the generation of highly active oxidative imido/nitrene reaction intermediates.

The reactions depicted in Table 5 might go through direct allylic C–H bond insertion or rearrangement of aziridines (Scheme 1). In this work, the allylic amidation product of 2-phenyl-2-butene (Table 5, entry 15) was obtained in 68% yield without any amidation at the two terminal methyl groups detected [Scheme 1, Eq. (1)]. This reveals that the product is derived from the ring opening of the aziridine intermediate [Scheme 1, Eq. (2)]. The reaction can be viewed



Scheme 1. Mechanistic study on direct allylic amidation.

as a formal direct allylic C–H bond insertion. When 4-nitrophenyl azide was employed as the nitrogen source, the aziridine intermediate could be isolated in the course of the reaction. Thus, the allylic amination/amidation and hydroxyamination products are derived from the ring opening and hydrolysis of the aziridine intermediate, respectively [Table 5, entry 13, and Scheme 1, Eq. (3)]. In addition, the result of the amination reaction of α-methylenetetralin (Table 5, entry 16) also supports the hypothesis depicted in Scheme 1 [Eq. (4)].

General remark: In the literature, there are many reports on metal-catalyzed nitrene/imido group transfer and insertion reactions using organic azides as the nitrogen source, but the majority of the reported reactions focus on aziridination of alkenes and sulfimidation of sulfides. Over the past few decades, functionalization of unactivated C–H bonds through metal-catalyzed nitrene/imido group insertion has been realized and a number of metal catalysts were reported to give good results. In the 1980s, Breslow,[16a] Mansuy[16b] and co-workers reported nitrene transfer reactions catalyzed by Mn^{III} and Fe^{III} complexes of tpp with PhI=NTs as the nitrogen source. In recent years, Du Bois and co-workers developed dirhodium(II,II) complexes as effective catalysts for the functionalization of saturated C–H bonds with practical interest.[10b,17] In our group, ruthenium porphyrin complexes have been demonstrated to catalyze aziridination of alkenes and amidation of saturated C–H bonds with iminophenyliodinanes as nitrogen source.[1d,18] Other metal complexes, such as those of Cu,[19] Ag,[20] and Au,[21] have also been revealed to display potent activity toward functionalization of unactivated C–H bonds by nitrene insertion reactions. Cenini, Katsuki, and their co-workers reported intermolecular amination of saturated C–H bonds with organic azides catalyzed by ruthenium[4a,g,5e] or cobalt[4a–c,e] complexes. Very recently, Zhang and co-workers[6b,f,g] reported inter- and intramolecular amination of saturated C–H bonds with Co^{II}-porphyrin as the catalyst and with organic azides as the nitrogen source. However, iron complex-catalyzed nitrene/imido group insertions into saturated C–H bonds are sparse in the literature.[11d,g,h] In addition, most of the reported reactions use iminophenyliodinanes (e.g., PhI=NTs) as the nitrogen source. Up to now, there have only been a few reports on the use of organic azides as the nitrogen source for the activation of unactivated C–H bonds.[4c,6b,19d] Also, lower product yields are usually encountered in the aziridination of aliphatic alkenes by organic azides using metal complexes as catalysts.[4–6] Thus, the protocol "[Fe^{III}(F_{20}-tpp)Cl]+4-nitrophenyl azide" described in this work is useful in that it is a simple system and yet can realize intermolecular amination of saturated C–H bonds, even the unreactive ones of cycloalkanes and adamantane, with acceptable product yields.

Based on the similar results obtained for the aziridination of styrene catalyzed by iron(III) porphyrin and its iron(II) counterpart with tosyl azide as the nitrogen source, the nitrene/imido insertion and transfer reactions described in this work might go through a reactive iron-imido/nitrene intermediate generated by the reaction of organic azide with [Fe(F_{20}-tpp)]$^{n+}$ ($n=0,1$) generated in situ. As suggested by Mansuy and co-workers, the Fe(V) imido species containing a porphyrin ligand, if it exists, should be highly reactive and able to rapidly react with saturated C–H bonds.[22] In this work, this kind of Fe(V)-imido intermediate is unlikely as the nitrene insertion into the C–H bonds of ethylbenzene cannot be accomplished with TsN_3 as the nitrogen source. Thus, the iron(IV) imido/iron(II) nitrene species is a more reasonable reaction intermediate for the catalysis described in this work. In our previous studies on nitrene transfer reactions with [Fe^{II}(Cl_3terpy)$_2$]$^{2+}$ (Cl_3terpy=4,4′,4″-trichloro-2,2′:6′,2″-terpyridine) as the catalyst and PhI=NTs as the nitrogen source, the [Fe(Cl_3terpy)$_2$(NTs)]$^{2+}$ reactive intermediate was characterized by ESIMS analysis.[11h] Aryl imidoiron(IV)/aryl nitrene iron(II) might have enough activity to undergo nitrene insertion into saturated C–H bonds. This hypothesis has support from the recent work by King and Betley,[23] which revealed that amination of the primary C–H bond of coordinated trimesityldipyrromethene can occur via an aryl imidoiron(IV) intermediate.

Conclusion

The commercially available and air stable [Fe^{III}(F_{20}-tpp)Cl] complex is a useful catalyst for imido/nitrene transfer reactions with sulfonyl and aryl azides as the nitrogen source. Aziridination of alkenes, sulfimidation of sulfides, allylic amination of α-methylstyrenes, and amination of unactivated saturated C–H bonds can all be accomplished in good to excellent product yields. In addition, the reactions can be significantly accelerated by up to 16-fold under microwave irradiation conditions.

Experimental Section

General: Reagents were obtained commercially and used without further purification unless otherwise indicated. 1,2-Dichloroethane (DCE) was freshly distilled from calcium hydride under a nitrogen atmosphere. Molecular sieves (4 Å) were dried at 300 °C for 3 h prior to use. Flash column chromatography (silica gel, 230–400 mesh) was performed with a gradient solvent system (EtOAc/*n*-hexane as eluent unless specified otherwise). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-500 or DPX-400 spectrometer. Chemical shifts (δ ppm) were determined with tetramethylsilane (TMS) as internal reference. Mass spectra were recorded on a Finnigan MAT 95 mass spectrometer. Microwave irradiation experiments were conducted with a CEM Discover Synthesis Unit (CEM Corp., Matthews, NC). ***Caution!*** *Organic azides are potentially explosive and should be handled with great care.*

General procedure for aziridination of styrenes: 1,2-Dichloroethane (1 mL) was added to a mixture of styrene (0.60 mmol), azide (0.20 mmol), catalyst (0.004 mmol), and 4 Å molecular sieves (60 mg). Then the reaction mixture was heated to reflux and kept at this temperature under nitrogen. After complete consumption of the azide as monitored by TLC, the mixture was concentrated under reduced pressure and the residue was purified by flash column chromatography. In some cases, the consumption of azide was determined by crude ^{1}H NMR spectroscopy with 1,1-dipenylethene as the internal standard.

General procedure for sulfimidation of sulfides: 1,2-Dichloroethane (1 mL) was added to a mixture of sulfide (0.60 mmol), azide (0.20 mmol), catalyst (0.004 mmol), and 4 Å molecular sieves (60 mg). Then the reaction mixture was heated to reflux and kept at this temperature under nitrogen. After complete consumption of the azide as monitored by TLC, the mixture was concentrated under reduced pressure and the residue was purified by flash column chromatography.

General procedure for aziridination of aliphatic alkenes: 1,2-Dichloroethane (1 mL) was added to a mixture of alkene (1.00 mmol), azide (0.20 mmol), catalyst (0.004 mmol), and 4 Å molecular sieves (60 mg). Then the reaction mixture was heated to reflux and kept at this temperature under nitrogen. After complete consumption of the azide as monitored by TLC, the mixture was concentrated under reduced pressure and the residue was purified by flash column chromatography. In some cases, the consumption of azide was determined by crude ^{1}H NMR spectroscopy with 1,1-dipenylethene as the internal standard.

General procedure for allylic amidation of α-methylstyrenes: 1,2-Dichloroethane (1 mL) was added to a mixture of styrene (0.80 mmol), azide (0.20 mmol), catalyst (0.004 mmol), and 4 Å molecular sieves (60 mg). Then the reaction mixture was heated to reflux and kept at this temperature under nitrogen. After complete consumption of the azide as monitored by TLC, the mixture was concentrated under reduced pressure and the residue was purified by flash column chromatography.

General procedure for amination of saturated C–H bonds: 1,2-Dichloroethane (1 mL) was added to a mixture of saturated hydrocarbon (2.00 mmol), azide (0.20 mmol), catalyst (0.004 mmol), and 4 Å molecular sieves (60 mg). Then the reaction mixture was heated to reflux and kept at this temperature under nitrogen. After complete consumption of the azide as monitored by TLC, the mixture was concentrated under reduced pressure and the residue was purified by flash column chromatography. In some cases, the consumption of azide was determined by crude ^{1}H NMR spectroscopy with 1,1-dipenylethene as the internal standard.

General procedure for nitrogen transfer reactions under microwave irradiation conditions: (***Caution!*** *All of the reactions were conducted by using 16 mg organic azide in 1 mL 1,2-dichloroethane in a 10 mL glass vial.*) A mixture of alkene, sulfide or alkane (0.30, 0.30, or 1.00–2.50 mmol), azide (0.10 mmol), catalyst (0.002 mmol), and 4 Å molecular sieves (40 mg) was suspended in 1,2-dichloroethane (1.0 mL) in a 10 mL glass vial equipped with a small magnetic stirring bar. The mixture was irradiated with microwaves at 100 °C at an irradiation power of 200 W. The reaction was monitored by TLC. The mixture was then concentrated under reduced pressure and the residue was purified by flash column chromatography.

Acknowledgements

This work was supported by the Hong Kong Research Grants Council (HKU1/CRF/08 and HKU700708) and the Areas of Excellence Scheme established under the University Grants Committee of the Hong Kong Special Administrative Region, China (AoE/P-10/01).

[1] a) D. A. Evans, M. M. Faul, M. T. Bilodeau, *J. Org. Chem.* **1991**, *56*, 6744–6746; b) H. Takada, Y. Nishibayashi, K. Ohe, S. Uemura, C. P. Baird, T. J. Sparey, P. C. Taylor, *J. Org. Chem.* **1997**, *62*, 6512–6518; c) S. Minakata, T. Ando, M. Nishimura, I. Ryu, M. Komatsu, *Angew. Chem.* **1998**, *110*, 3596–3598; *Angew. Chem. Int. Ed.* **1998**, *37*, 3392–3394; d) S. M. Au, J. S. Huang, W. Y. Yu, W. H. Fung, C. M. Che, *J. Am. Chem. Soc.* **1999**, *121*, 9120–9132; e) J. L. Liang, X. Q. Yu, C. M. Che, *Chem. Commun.* **2002**, 124–125; f) P. Müller, C. Fruit, *Chem. Rev.* **2003**, *103*, 2905–2919; g) J. A. Halfen, *Curr. Org. Chem.* **2005**, *9*, 657–669; h) H. M. L. Davies, M. S. Long, *Angew. Chem.* **2005**, *117*, 3584–3586; *Angew. Chem. Int. Ed.* **2005**, *44*, 3518–3520; i) O. G. Mancheño, C. Bolm, *Chem. Eur. J.* **2007**, *13*, 6674–6681.

[2] a) B. M. Chanda, R. Vyas, A. V. Bedekar, *J. Org. Chem.* **2001**, *66*, 30–34; b) M. Anada, M. Tanaka, N. Shimada, H. Nambu, M. Yamawaki, S. Hashimoto, *Tetrahedron* **2009**, *65*, 3069–3077.

[3] a) H. Kwart, A. A. Khan, *J. Am. Chem. Soc.* **1967**, *89*, 1951–1953; b) S. Bräse, C. Gil, K. Knepper, V. Zimmermann, *Angew. Chem.* **2005**, *117*, 5320–5374; *Angew. Chem. Int. Ed.* **2005**, *44*, 5188–5240; c) T. Bach, C. Körber, *Tetrahedron Lett.* **1998**, *39*, 5015–5016; d) T. Bach, C. Körber, *Eur. J. Org. Chem.* **1999**, 1033–1039; e) T. Bach, C. Körber, *J. Org. Chem.* **2000**, *65*, 2358–2367; f) T. Bach, B. Schlummer, K. Harms, *Chem. Eur. J.* **2001**, *7*, 2581–2594; g) B. J. Stokes, H. Dong, B. E. Leslie, A. L. Pumphrey, T. G. Driver, *J. Am. Chem. Soc.* **2007**, *129*, 7500–7501; h) H. Dong, M. Shen, J. E. Redford, B. J. Stokes, A. L. Pumphrey, T. G. Driver, *Org. Lett.* **2007**, *9*, 5191–5194; i) M. Shen, B. E. Leslie, T. G. Driver, *Angew. Chem.* **2008**, *120*, 5134–5137; *Angew. Chem. Int. Ed.* **2008**, *47*, 5056–5059; j) B. J. Stokes, B. Jovanović, H. Dong, K. J. Richert, R. D. Riell, T. G. Driver, *J. Org. Chem.* **2009**, *74*, 3225–3228; k) B. J. Stokes, K. J. Richert, T. G. Driver, *J. Org. Chem.* **2009**, *74*, 6442–6451; l) K. Sun, R. Sachwani, K. J. Richert, T. G. Driver, *Org. Lett.* **2009**, *11*, 3598–3601.

[4] a) S. Cenini, S. Tollari, A. Penoni, C. Cereda, *J. Mol. Catal. A* **1999**, *137*, 135–146; b) S. Cenini, E. Gallo, A. Penoni, F. Ragaini, S. Tollari, *Chem. Commun.* **2000**, 2265–2266; c) F. Ragaini, A. Penoni, E. Gallo, S. Tollari, C. L. Gotti, M. Lapadula, E. Mangioni, S. Cenini, *Chem. Eur. J.* **2003**, *9*, 249–259; d) S. Cenini, E. Gallo, A. Caselli, F. Ragaini, S. Fantauzzi, C. Piangiolino, *Coord. Chem. Rev.* **2006**, *250*, 1234–1253; e) A. Caselli, E. Gallo, S. Fantauzzi, S. Morlacchi, F. Ragaini, S. Cenini, *Eur. J. Inorg. Chem.* **2008**, 3009–3019; f) S. Fantauzzi, E. Gallo, A. Caselli, C. Piangiolino, F. Ragaini, N. Re, S. Cenini, *Chem. Eur. J.* **2009**, *15*, 1241–1251; g) S. Fantauzzi, E. Gallo, A. Caselli, F. Ragaini, N. Casati, P. Macchic, S. Cenini, *Chem. Commun.* **2009**, 3952–3954.

[5] a) M. Murakami, T. Uchida, T. Katsuki, *Tetrahedron Lett.* **2001**, *42*, 7071–7074; b) M. Murakami, T. Katsuki, *Tetrahedron Lett.* **2002**, *43*, 3947–3949; c) Y. Tamura, T. Uchida, T. Katsuki, *Tetrahedron Lett.* **2003**, *44*, 3301–3303; d) T. Uchida, Y. Tamura, M. Ohba, T. Katsuki, *Tetrahedron Lett.* **2003**, *44*, 7965–7968; e) K. Omura, M. Murakami, T. Uchida, R. Irie, T. Katsuki, *Chem. Lett.* **2003**, *32*, 354–355; f) K. Omura, T. Uchida, R. Irie, T. Katsuki, *Chem. Commun.* **2004**, 2060–2061; g) T. Katsuki, *Chem. Lett.* **2005**, *34*, 1304–1309; h) H. Kawabata, K. Omura, T. Katsuki, *Tetrahedron Lett.* **2006**, *47*, 1571–1574; i) H. Kawabata, K. Omura, T. Uchida, T. Katsuki, *Chem. Asian J.* **2007**, *2*, 248–256; j) H. Fujita, T. Uchida, R. Irie, T. Katsuki, *Chem. Lett.* **2007**, *36*, 1092–1093.

[6] a) G. Y. Gao, J. E. Jones, R. Vyas, J. D. Harden, X. P. Zhang, *J. Org. Chem.* **2006**, *71*, 6655–6658; b) J. V. Ruppel, R. M. Kamble, X. P. Zhang, *Org. Lett.* **2007**, *9*, 4889–4892; c) J. V. Ruppel, J. E. Jones, C. A. Huff, R. M. Kamble, Y. Chen, X. P. Zhang, *Org. Lett.* **2008**, *10*, 1995–1998; d) J. E. Jones, J. V. Ruppel, G. Y. Gao, T. M. Moore,

X. P. Zhang, *J. Org. Chem.* **2008**, *73*, 7260–7265; e) V. Subbarayan, J. V. Ruppel, S. Zhu, J. A. Perman, X. P. Zhang, *Chem. Commun.* **2009**, 4266–4268; f) H. Lu, V. Subbarayan, J. Tao, X. P. Zhang, *Organometallics* **2010**, *29*, 389–393; g) H. Lu, J. Tao, J. E. Jones, L. Wojtas, X. P. Zhang, *Org. Lett.* **2010**, *12*, 1248–1251.

[7] a) M. P. Doyle, D. C. Forbes, *Chem. Rev.* **1998**, *98*, 911–935; b) G. Dyker, *Angew. Chem.* **1999**, *111*, 1808–1822; *Angew. Chem. Int. Ed.* **1999**, *38*, 1698–1712; c) J. A. Labinger, J. E. Bercaw, *Nature* **2002**, *417*, 507–514; d) F. Kakiuchi, N. Chatani, *Adv. Synth. Catal.* **2003**, *345*, 1077–1101; e) J. A. Johnson, D. Sames, *J. Am. Chem. Soc.* **2000**, *122*, 6321–6322; f) J. A. Johnson, N. Li, D. Sames, *J. Am. Chem. Soc.* **2002**, *124*, 6900–6903; g) H. M. L. Davies, R. E. J. Beckwith, *Chem. Rev.* **2003**, *103*, 2861–2903; h) K. Godula, D. Sames, *Science* **2006**, *312*, 67–72; i) A. R. Dick, M. S. Sanford, *Tetrahedron* **2006**, *62*, 2439–2463; j) M. Christmann, *Angew. Chem.* **2008**, *120*, 2780–2783; *Angew. Chem. Int. Ed.* **2008**, *47*, 2740–2742; k) H. M. L. Davies, J. R. Manning, *Nature* **2008**, *451*, 417–424.

[8] a) M. Johannsen, K. A. Jørgensen, *Chem. Rev.* **1998**, *98*, 1689–1708; b) M. S. Chen, M. C. White, *Science* **2007**, *318*, 783–787; c) S. A. Reed, M. C. White, *J. Am. Chem. Soc.* **2008**, *130*, 3316–3318; d) D. J. Covell, M. C. White, *Angew. Chem.* **2008**, *120*, 6548–6551; *Angew. Chem. Int. Ed.* **2008**, *47*, 6448–6451.

[9] a) P. Wang, J. Adams, *J. Am. Chem. Soc.* **1994**, *116*, 3296–3305; b) D. F. Taber, K. K. You, A. L. Rheingold, *J. Am. Chem. Soc.* **1996**, *118*, 547–556; c) D. F. Berndt, P. Norris, *Tetrahedron Lett.* **2002**, *43*, 3961–3962.

[10] a) J. L. Liang, S. X. Yuan, J. S. Huang, W. Y. Yu, C. M. Che, *Angew. Chem.* **2002**, *114*, 3615–3618; *Angew. Chem. Int. Ed.* **2002**, *41*, 3465–3468; b) D. N. Zalatan, J. Du Bois, *J. Am. Chem. Soc.* **2008**, *130*, 9220–9221.

[11] a) L. Simkhovich, Z. Gross, *Tetrahedron Lett.* **2001**, *42*, 8089–8092; b) B. D. Heuss, M. F. Mayer, S. Dennis, M. M. Hossain, *Inorg. Chim. Acta* **2003**, *342*, 301–304; c) R. Vyas, G. Y. Gao, J. D. Harden, X. P. Zhang, *Org. Lett.* **2004**, *6*, 1907–1910; d) S. Y. Yan, Y. Wang, Y. J. Shu, H. H. Liu, X. G. Zhou, *J. Mol. Catal. A* **2006**, *248*, 148–151; e) A. C. Mayer, A. F. Salit, C. Bolm, *Chem. Commun.* **2008**, 5975–5977; f) M. Nakanishi, A. F. Salit, C. Bolm, *Adv. Synth. Catal.* **2008**, *350*, 1835–1840; g) Z. Wang, Y. Zhang, H. Fu, Y. Jiang, Y. Zhao, *Org. Lett.* **2008**, *10*, 1863–1866; h) P. Liu, E. L. M. Wong, A. W. H. Yuen, C. M. Che, *Org. Lett.* **2008**, *10*, 3275–3278; i) M. Shen, T. G. Driver, *Org. Lett.* **2008**, *10*, 3367–3370; j) K. L. Klotz, L. M. Slominski, M. E. Riemer, J. A. Phillips, J. A. Halfen, *Inorg. Chem.* **2009**, *48*, 801–803.

[12] a) C. Bolm, J. Legros, J. Le Paih, L. Zani, *Chem. Rev.* **2004**, *104*, 6217–6254; b) A. A. O. Sarhan, C. Bolm, *Chem. Soc. Rev.* **2009**, *38*, 2730–2744.

[13] D. V. Konarev, S. S. Khasanov, A. Otsuka, G. Saito, R. N. Lyubovskaya, *Inorg. Chem.* **2007**, *46*, 2261–2271.

[14] a) D. A. Evans, M. M. Faul, M. T. Bilodeau, B. A. Anderson, D. M. Barnes, *J. Am. Chem. Soc.* **1993**, *115*, 5328–5329; b) C. P. Baird, P. C. Taylor, *J. Chem. Soc. Chem. Commun.* **1995**, 893–894; c) H. Takada, K. Ohe, S. Uemura, *Angew. Chem.* **1999**, *111*, 1367–1369; *Angew. Chem. Int. Ed.* **1999**, *38*, 1288–1289; d) C. Bolm, D. Müller, C. P. R. Hackenberger, *Org. Lett.* **2002**, *4*, 893–896; e) C. Bolm, M. Martin, G. Gescheidt, C. Palivan, D. Neshchadin, H. Bertagnolli, M. Feth, A. Schweiger, G. Mitrikas, J. Harmer, *J. Am. Chem. Soc.* **2003**, *125*, 6222–6227; f) M. Langner, C. Bolm, *Angew. Chem.* **2004**, *116*, 6110–6113; *Angew. Chem. Int. Ed.* **2004**, *43*, 5984–5987; g) C. Moessner, C. Bolm, *Angew. Chem.* **2005**, *117*, 7736–7739; *Angew. Chem. Int. Ed.* **2005**, *44*, 7564–7567; h) O. G. Mancheño, C. Bolm, *Org. Lett.* **2006**, *8*, 2349–2352; i) O. G. Mancheño, J. Dallimore, A. Plant, C. Bolm, *Org. Lett.* **2009**, *11*, 2429–2432; j) O. G. Mancheño, J. Dallimore, A. Plant, C. Bolm, *Adv. Synth. Catal.* **2010**, *352*, 309–316; k) R. Bentley, *Chem. Soc. Rev.* **2005**, *34*, 609–624.

[15] a) M. Larhed, C. Moberg, A. Hallberg, *Acc. Chem. Res.* **2002**, *35*, 717–727; b) B. A. Roberts, C. R. Strauss, *Acc. Chem. Res.* **2005**, *38*, 653–661; c) X. Y. Liu, C. H. Li, C. M. Che, *Org. Lett.* **2006**, *8*, 2707–2710; d) X. Y. Liu, P. Ding, J. S. Huang, C. M. Che, *Org. Lett.* **2007**, *9*, 2645–2648.

[16] a) R. Breslow, S. H. Gellman, *J. Am. Chem. Soc.* **1983**, *105*, 6728–6729; b) D. Mansuy, J. P. Mahy, A. Dureault, G. Bedi, P. Battioni, *J. Chem. Soc. Chem. Commun.* **1984**, 1161–1163.

[17] a) C. G. Espino, J. Du Bois, *Angew. Chem.* **2001**, *113*, 618–620; *Angew. Chem. Int. Ed.* **2001**, *40*, 598–600; b) P. M. Wehn, J. Du Bois, *J. Am. Chem. Soc.* **2002**, *124*, 12950–12951; c) A. Hinman, J. Du Bois, *J. Am. Chem. Soc.* **2003**, *125*, 11510–11511; d) K. W. Fiori, J. J. Fleming, J. Du Bois, *Angew. Chem.* **2004**, *116*, 4449–4452; *Angew. Chem. Int. Ed.* **2004**, *43*, 4349–4352; e) J. J. Fleming, J. Du Bois, *J. Am. Chem. Soc.* **2006**, *128*, 3926–3927; f) K. W. Fiori, J. Du Bois, *J. Am. Chem. Soc.* **2007**, *129*, 562–568; g) J. J. Fleming, M. D. McReynolds, J. Du Bois, *J. Am. Chem. Soc.* **2007**, *129*, 9964–9975; h) J. V. Mulcahy, J. Du Bois, *J. Am. Chem. Soc.* **2008**, *130*, 12630–12631; i) D. N. Zalatan, J. Du Bois, *J. Am. Chem. Soc.* **2009**, *131*, 7558–7559; j) B. M. Andresen, J. Du Bois, *J. Am. Chem. Soc.* **2009**, *131*, 12524–12525; k) T. Kurokawa, M. Kim, J. Du Bois, *Angew. Chem.* **2009**, *121*, 2815–2817; *Angew. Chem. Int. Ed.* **2009**, *48*, 2777–2779; l) P. M. Wehn, J. Du Bois, *Angew. Chem.* **2009**, *121*, 3860–3863; *Angew. Chem. Int. Ed.* **2009**, *48*, 3802–3805.

[18] a) X. G. Zhou, X. Q. Yu, J. S. Huang, C. M. Che, *Chem. Commun.* **1999**, 2377–2378; b) J. L. Zhang, C. M. Che, *Org. Lett.* **2002**, *4*, 1911–1914; c) J. L. Liang, J. S. Huang, X. Q. Yu, N. Zhu, C. M. Che, *Chem. Eur. J.* **2002**, *8*, 1563–1572; d) S. K. Y. Leung, W. M. Tsui, J. S. Huang, C. M. Che, J. L. Liang, N. Zhu, *J. Am. Chem. Soc.* **2005**, *127*, 16629–16640.

[19] a) M. M. Díaz-Requejo, T. R. Belderraín, M. C. Nicasio, S. Trofimenko, P. J. Pérez, *J. Am. Chem. Soc.* **2003**, *125*, 12078–12079; b) M. R. Fructos, S. Trofimenko, M. M. Días-Requejo, P. J. Pérez, *J. Am. Chem. Soc.* **2006**, *128*, 11784–11791; c) R. Bhuyan, K. M. Nicholas, *Org. Lett.* **2007**, *9*, 3957–3959; d) Y. M. Badiei, A. Dinescu, X. Dai, R. M. Palomino, F. W. Heinemann, T. R. Cundari, T. H. Warren, *Angew. Chem.* **2008**, *120*, 10109–10112; *Angew. Chem. Int. Ed.* **2008**, *47*, 9961–9964.

[20] a) Y. Cui, C. He, *Angew. Chem.* **2004**, *116*, 4306–4308; *Angew. Chem. Int. Ed.* **2004**, *43*, 4210–4212; b) Z. Li, D. A. Capretto, R. Rahaman, C. He, *Angew. Chem.* **2007**, *119*, 5276–5278; *Angew. Chem. Int. Ed.* **2007**, *46*, 5184–5186.

[21] Z. Li, D. A. Capretto, R. O. Rahaman, C. He, *J. Am. Chem. Soc.* **2007**, *129*, 12058–12059.

[22] a) J. P. Mahy, P. Battioni, D. Mansuy, *J. Am. Chem. Soc.* **1986**, *108*, 1079–1080; b) J. P. Mahy, P. Battioni, G. Bedi, D. Mansuy, J. Fischer, R. Weiss, I. Morgenstern-Badarau, *Inorg. Chem.* **1988**, *27*, 353–359.

[23] E. R. King, T. A. Betley, *Inorg. Chem.* **2009**, *48*, 2361–2363.

Received: March 5, 2010
Published online: July 20, 2010

