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COMMUNICATION

Iron(III) tetrakis(pentafluorophenyl)porpholactone catalyzes nitrogen atom transfer to C=C and C–H bonds with organic azides†

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We have demonstrated that iron porpholactones could be effective catalysts for nitrogen atom transfer reactions such as aziridination of alkenes and amidation of alkanes using organic azides.

Porpholactones, as analogues of porphyrins, in which one pyrrole is replaced by an oxazolone ring, are regarded as "intermediates" to porphyrins and chlorins.[1] With lactone moiety replacement, partial saturation on porphyrin periphery results in restricted π-conjugation and lowered molecular symmetry on energies of the frontier molecular orbitals (MOs) predicted by an iterative extended Hückel (IEH) calculation.[1b] Compared with porphyrins, the energy of a porpholactone HOMO (the highest occupied molecular orbital) is slightly lower, supported by the anodic shift of the first oxidation potential of porpholactones relative to that of the corresponding porphyrins, indicating that porpholactones are better at stabilizing the high valent metal complexes than the corresponding porphyrins.[2] However, the effects of particular structures on catalysis remains unexplored, although "porphyrin-like" properties had been recognized for 20 years.[1b] In contrast to various kinds of metalloporphyrin catalyzed reactions, only two examples of oxidation of alkenes and sulfides by metalloporpholactones have been reported.[3] Thus, to expand the application of metalloporpholactones in catalysis is of importance. Herein, we report the first example of using iron porpholactone [Fe(F_{20}-TPPL)Cl] (F_{20}-TPPL = *meso*-tetrakis(pentafluorophenyl)porpholactonato dianion) (Fig. 1) as a catalyst for nitrogen atom transfer to C=C and C–H bonds with organic azides.

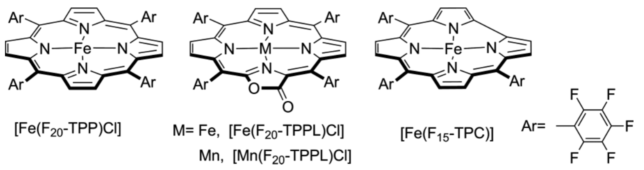

Fig. 1 Iron porphorinoid catalysts used in this work.

Nitrogen atom transfer reactions catalyzed by metalloporphyrins through metal nitrene intermediate(s) to C–H and C=C bonds attract much attention in organic synthesis.[4] For the choice of nitrogen source, there has been a growing interest in the use of organic azides, because the by-product is nitrogen gas whereas the other nitrogen sources such as PhINTs, bromamine-T or chloramine-T would lose PhI, NaCl and NaBr moieties. Cenini,[5] Che,[6] and Zhang[7] groups pioneered the development of nitrene transfer reactions such as inter- and intramolecular aziridination of alkenes, amidation of sulfides, and amidation of alkanes with organic azides catalyzed by ruthenium, cobalt and iron porphyrins. In this work, at the outset of the project, we aimed to identify a suitable azide as the "nitrogen source" using styrene and ethylbenzene as model substrates. Through optimization of reaction conditions (Table S1, ESI†), typical reactions were carried out in 1,2-dichloroethane at 80 °C in the presence of 4 Å molecule sieves for 12 h. We found that only *p*-toluenesulfonyl azide (TsN_3) and methylsulfonyl azide (MsN_3) allowed for aziridination of styrene and gave the corresponding aziridines in 87 and 61% yield (Table 1, entries 1 and 2, respectively). For ethylbenzene, only *p*-nitrophenyl azide is effective for amidation of a saturated C–H bond (Table 1, entry 10). Using PhINTs as the nitrogen source, [Fe(F_{20}-TPPL)Cl] shows no reactivity towards styrene and ethylbenzene (Table 1, entries 7 and 14). Control experiments in the absence of [Fe(F_{20}-TPPL)Cl] or only using $FeCl_3$ as catalysts were carried out.[8] As shown in Table S2,† for the aziridination of styrene, without metal salts or only using $FeCl_3$, we isolated styrene aziridine in yields of 30 and 52%, respectively, which are lower than that obtained by [Fe(F_{20}-TPPL)Cl]. For amidation of ethylbenzene, control experiments could not afford the amide product (Table S3, ESI†). In addition, we found sunlight to have a negligible effect on these reactions.

To investigate the ligand effect on the reactivity of N atom transfer to alkenes and alkanes, we chose [Fe(F_{20}-TPP)Cl] and [Fe(F_{15}-TPC)] (F_{20}-TPP = *meso*-tetrakis(pentafluorophenyl)porphyrino dianion and F_{15}-TPC = *meso*-tris(pentafluoro-phenyl)corrolato trianion) as the catalysts and styrene, *p*-chlorostyrene and ethylbenzene as the substrates. As shown in Table S4,† [Fe(F_{20}-TPPL)Cl] exhibited higher reactivity (88, 80 and 88%, entries 1, 5 and 8, respectively) than [Fe(F_{20}-TPP)Cl] and [Fe(F_{15}-TPC)] (entries 2, 3, 6, 7, 9 and 10). Replacing iron with manganese resulted in a decrease of the reactivity of aziridination of styrene to 53% yield (entry 4, Table S4, ESI†). A time course plot (Fig. S1, ESI†) for the aziridination of styrene by [Fe(F_{20}-TPPL)Cl] and

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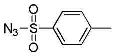
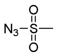
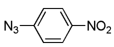
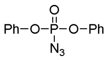
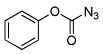
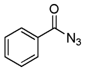
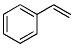
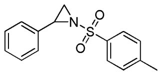
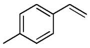
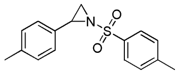
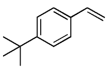
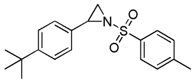
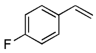
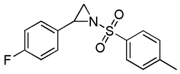
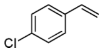
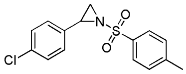
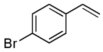
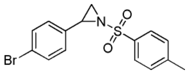
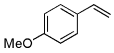
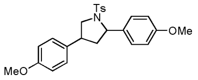
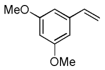
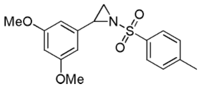
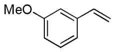
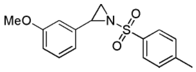
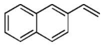
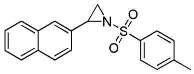
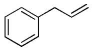
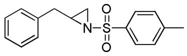
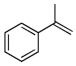
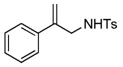
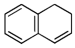
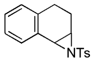
† Electronic supplementary information (ESI) available: Experimental procedures and characterization and spectral reproduction for new compounds. See DOI: 10.1039/c2dt11995a

Table 1 Organic azides for catalytic aziridination of styrene and amidation of ethylbenzene by [Fe(F_{20}-TPPL)Cl][a]

Entry	Azide	Sub.	Yield (%)[b]	Entry	Sub.	Yield (%)[b]
1		styrene	87	8	ethylbenzene	0
2		styrene	61	9	ethylbenzene	0
3		styrene	n.d[c]	10	ethylbenzene	88
4	 $\mathrm{Ph{-}O{-}\overset{O}{\underset{N_3}{P}}{-}O{-}Ph}$	styrene	0	11	ethylbenzene	0
5		styrene	0	12	ethylbenzene	0
6		styrene	0	13	ethylbenzene	0
7	PhINTs	styrene	0	14	ethylbenzene	0

[a] Performed under N_2 in the presence of 4 Å molecule sieves: [substrate] = 1 mmol mL^{-1}; 1 mol% catalyst based on azide; styrene/azide = 3 : 1, ethylbenzene/azide = 5 : 1 in 1,2-dichloroethane at 80 °C. [b] Isolated yields based on the conversion of azides. [c] n.d. is not determined.

Table 2 Aziridination of alkenes with TsN_3 by [Fe(F_{20}-TPPL)Cl][a]

Entry	Alkene	Product	Yield (%)[b]
1			87
2			81
3			87
4			88
5			80
6			89
7			<20
8			75
9			<20[c]
10			81
11			84
12			82
13			58

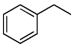
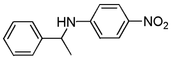
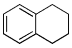
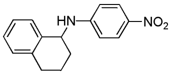
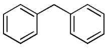
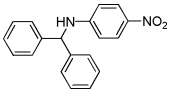
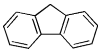
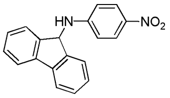
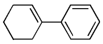
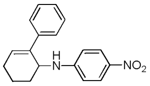
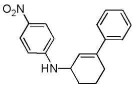
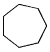
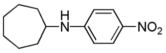
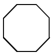
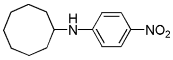
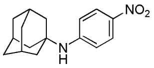
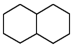
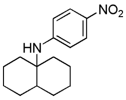
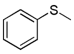
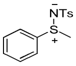
[a] Performed under N_2 in the presence of 4 Å molecule sieves: alkenes/azide = 3 : 1, 0.5 mol% catalyst (based on azide). [b] Isolated yields based on the conversion of azides. [c] Tetrahydropyrrole(<10%) was detected.

[Fe(F_{20}-TPP)Cl] shows a higher reaction rate (TOFs: 0.83 *vs.* 0.16 min^{-1}) obtained by [Fe(F_{20}-TPPL)Cl].

The scope of alkenes for a [Fe(F_{20}-TPPL)Cl]/TsN_3-based catalytic system was investigated and the results are summarized in Table 2. For *p*-substituted styrene, except for *p*-methoxystyrene, the corresponding aziridines were obtained in isolated yields of 75–89% (Table 2, entries 1–6). When *p*-methoxystyrene was employed as the substrate, we could not isolate the aziridine product but instead a tetrahydropyrrole product was isolated in low yield (<20%, Table 2, entry 7), which was first observed in metal catalyzed aziridination of alkenes using organic azides. We attempted to use *p*-*N*,*N*-dimethyl styrene as the substrate, but only observed a polymeric product. Using 3,5-dimethoxystyrene and *m*-methoxystyrene as the substrate gave the corresponding aziridines in moderate to low yield (75% to less than 20%, Table 2, entries 8 and 9), indicating the electron donating group and steric effect on styrene affects the formation of aziridines and consequent reactions. The other terminal alkenes such as 2-vinylnaphthalene and allylbenzene gave the aziridines in good yields (Table 2, entries 10 and 11), whereas α-methylstyrene give the allylic amidation product and no aziridine was detected (82% yield, Table 2, entry 12), which is in accord with previously reported literature using [Fe(F_{20}-TPP)Cl] as the catalyst.[6a] In addition, dihydronaphthalene with an intramolecular double bond was used and the aziridine product was isolated in moderate yield (58%, Table 2, entry 13).

The catalytic amidation of saturated C–H bonds was also investigated. As described above, *p*-nitrophenyl azide was used as the nitrogen source reagent and *p*-nitro-*N*-(1-phenylthyl) benzenamine was obtained in 88% yield with complete azide consumption. Using 4-nitrophenyl azide, the benzylic C–H bonds of tetralin, diphenylmethane and fluorene were successfully aminated in good yields (85–91%, Table 3, entries 2–4). Chemoselective allylic amidation of 1-phenyl cyclohexene was observed (the ratio of 3- to 6-amines is 1.7 : 1, Table 3, entry 5) and [Fe(F_{20}-TPPL)Cl] prefers to catalyze the amidation of the 3-position of cyclohexene.[6a] Furthermore, amidation of the unfunctionalized saturated C–H bonds such as cycloheptane, cyclooctane, adamantane and decalin were accomplished in moderate to good yields (71–80%, Table 3, entries 6–9). For adamatane and decalin with both of 2° and 3° C–H bonds, only amidation of 3° C–H bond products were obtained, which is similar to the previous observation in amidation of alkanes using metalloporphyrins.[5,6,7a] It is noteworthy that [Fe(F_{20}-TPPL)Cl] is also competent in the amidation of thioanisole with high yield (Table 3, entry 10).

Table 3 Amidation of saturated C–H bonds by [Fe(F_{20}-TPPL)Cl][a]

Entry	Alkane	Product	Yield (%)[b]
1			88
2			91
3			85
4			90
5			28
			51
6			71
7			78
8			80
9			72
10			85

[a] Performed under N_2 in the presence of 4 Å molecule sieves: substrate = 0.5 mmol mL^{-1}; substrate/azide = 5 : 1, 0.5 mol% catalyst (based on azide). [b] Isolated yields based on the conversion of azides.

To demonstrate the potential application of [Fe(F_{20}-TPPL)Cl] in organic synthesis, we used fullerene as the substrate to examine the ability to produce C_{60} aziridine, which is an important intermediate for further functionalization of fullerenes as useful optical and electromaterials. Under the catalytic reaction conditions described in Fig. 2, we isolated C_{60} aziridine in 43% yield, which was comparable to that obtained with CuCl as catalyst (10 mol% loading) and using PhINTs as the nitrogen source.[9]

In general, metalloporphyrins which catalyze N atom transfer to C=C and C–H bonds are associated with a reactive metal-imido/nitrene key intermediate.[4] The lower energy of the porpholactone HOMO and the better stability of high valent Fe than porphyrin,[10] which imposes a radical-type reactivity to the "nitrene" moiety, led to the different reactivity for iron porpholactone and porphyrin. For the formation of tetrahydropyrrole products (Table 2, entries 7 and 9), two possible mechanisms shown in Fig. 3 are proposed: 1) ring-opening of the aziridine catalyzed by [Fe(F_{20}-TPPL)Cl] followed by nucleophilic attack with activated sp^2 C–H bond, which is known for Lewis acids such as Ag or Cu complexes;[11] 2) generating the "NR′–CH_2–CHR•" radical before formation of the aziridine, which then reacts with another styrene and then ring closure occurs to form tetrahydropyrrole. For route 1, direct reaction of aziridine and styrene in the presence of iron porpholactone results in the tetrahydropyrrole in trace yield (<5%), indicating route 1 might not be the mechanism. According to our experiments, only *p*- and *m*-methoxystyrene as substrates form tetrahydropyrrole and *p*- and *m*-methoxy substituents might stabilize the possible radicals such as the (NR′–CH_2–CHR•). In addition, TEMPO was added as a radical quencher and no product is detected, indicating the formation of radicals for this reaction is important.

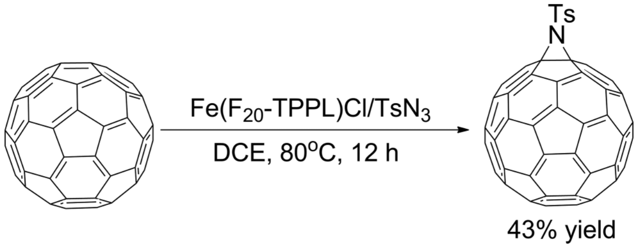


Fig. 2 [Fe(F_{20}-TPPL)Cl] catalyzed aziridination of C_{60}.

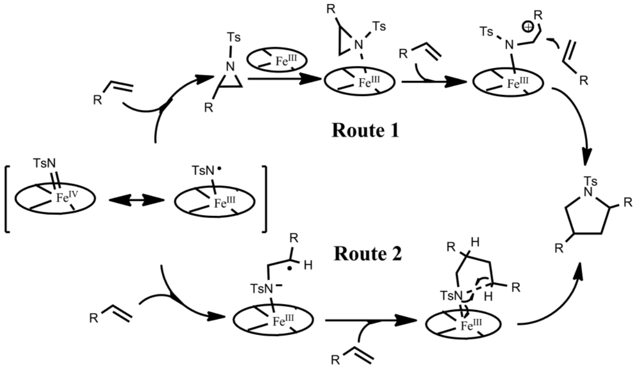


Fig. 3 Possible mechanisms for tetrahydropyrrole formation in the presence of [Fe(F_{20}-TPPL)Cl].

Thus, we propose route 2 might be the possible mechanism. Further investigations for the catalytic tetrahydropyrrole formations and mechanistic study are undergoing.

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