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Catalytic aziridination of olefins and amidation of thioanisole by a non-heme iron complex†

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A non-heme iron complex catalyses the aziridination of various olefins and the amidation of thioanisole in good yields at the expense of an aryl iodinane.

Biomimetic oxygen transfer has been thoroughly investigated over the past three decades both from heme and non-heme systems.[1,2] Consequently, the mechanism of the reaction has been largely deciphered and points to the occurrence of high-valent oxo-iron intermediates. In the early 80s, Mansuy *et al.*[3] reported that heme complexes were able to catalyse tosylamine transfer to olefins from aryl iodinanes. It was shown later that manganese[4] and ruthenium porphyrins,[5] as well as non-porphyrinic complexes of ruthenium[6] and copper[7,8] were similarly active. Very recently, Que *et al.* reported that a non-heme iron complex mediated the stoichiometric intramolecular insertion of a tosylamine group in the ligand.[9] In the course of our continuous study of biomimetic diiron complexes,[10,11] we reported[12] that the mixed-valent complex of the unsymmetrical hexadentate phenol ligand (HL, Scheme 1, X = H) is able to mediate the hydroxylation of the dangling benzyl group from oxygen donors such as *m*CPBA or ArIO[13] (ArIO = *o-tert*-butylsulfone iodosyl benzene). In this communication, we show that the analogous complex **1**$(CH_3OH)^{2+}$ obtained from the 2,6-dichlorobenzyl ligand (HL′, Scheme 1, X = Cl) is able to react with the tosylamine iodinane ArINTs[13] to produce an adduct **2**$^{2+}$ which catalyses the aziridination of various olefins in the presence of an excess of aryliodinane.

The synthesis and structural characterisation of complex **1**$(CH_3OH)^{2+}$ were described earlier.[11] When **1**$(CH_3OH)^{2+}$ was reacted with ArINTs in acetonitrile a new chromophore developed at 480 nm (Fig. 1) with an isosbestic point at *ca.* 610 nm.[14] This species was fully formed after addition of 1 eq. ArINTs and was moderately stable in these conditions. ESI-MS analyses of the corresponding solution in the negative mode (Fig. 2a) revealed a complex pattern of peaks for a monoanion at *m*/*z* = 1397. In the positive mode another pattern was observed at *m*/*z* = 549 for a dication (Fig. 2b). These peculiar isotopic distributions reflect the presence of different numbers of chlorine atoms in the two charged species. From comparison with theoretical isotopic distributions (Figure S1†), the dication and the monoanion could be assigned the respective formulas: Fe_2(L′)(mpdp)$(NHTs)^{2+}$, **2**$^{2+}$ and {Fe_2(L′)(mpdp)(NHTs) $(ClO_4)_3$}$^-$, {**2**$(ClO_4)_3$}$^-$. Complex **2**$^{2+}$ is therefore a diferric complex of the $TsNH^-$ group. The presence of an exchangeable hydrogen was confirmed by positive ESI-MS which showed the shift of the pattern of the dication by 0.5 unit (Fig. 2c) in the presence of D_2O. In addition, preliminary magnetic susceptibility and Mössbauer analyses confirmed the ferric nature of the two iron ions.

When **2**$^{2+}$ was prepared from 1 eq. ArINTs, it was unable to react with styrene. On the other hand, when **1**$^{2+}$ was treated with 20 eq. PhINTs, **2**$^{2+}$ formed rapidly, as judged from the 480 nm chromophore, and addition of 1000 eq. styrene caused a decrease of the intensity of the chromophore (Fig. 3) over 2 h. NMR analysis of the resulting solution showed the formation of the tosylaziridine of styrene in 88% yield (with respect to PhINTs).

Aziridination of styrene, cyclooctene and 1-hexene was studied in conditions used recently by Halfen *et al.*[7] for copper complexes:

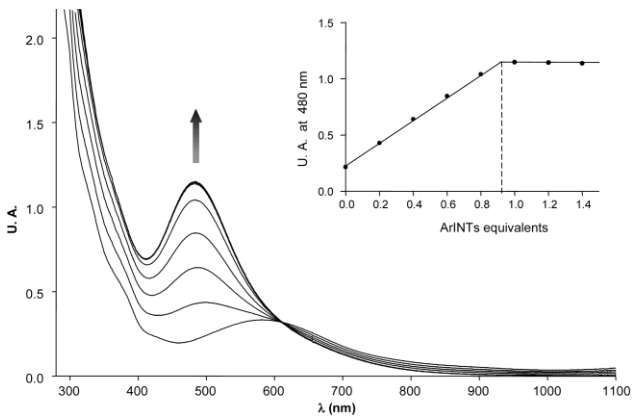


Fig. 1 UV-visible titration of **1**$(CH_3OH)^{2+}$ in acetonitrile by ArINTs. Insert: titration curve.

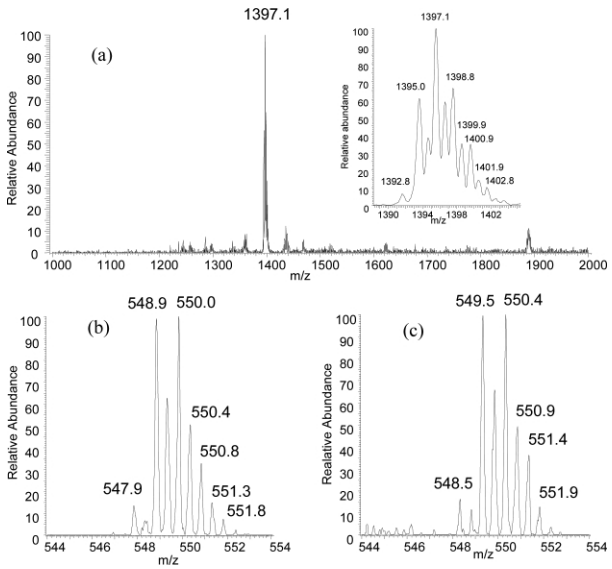
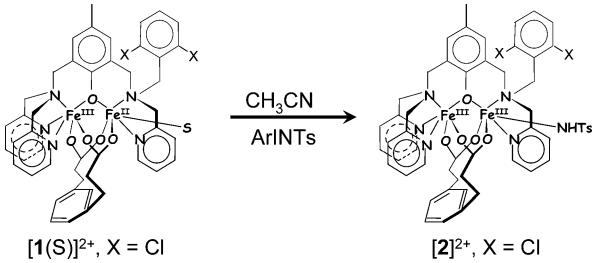


Fig. 2 ESI-MS spectra of **2**$^{2+}$ (a) in the negative mode with a zoom on the molecular peak in the insert, (b) in the positive mode and (c) as (b) in the presence of D_2O.



Scheme 1 (S = acetonitrile.)

† Electronic supplementary information (ESI) available: Fig. S1 illustrates the theoretical isotopic patterns for the respective formulae. See http://www.rsc.org/suppdata/cc/b4/b404561k/

DOI: 10.1039/b404561k

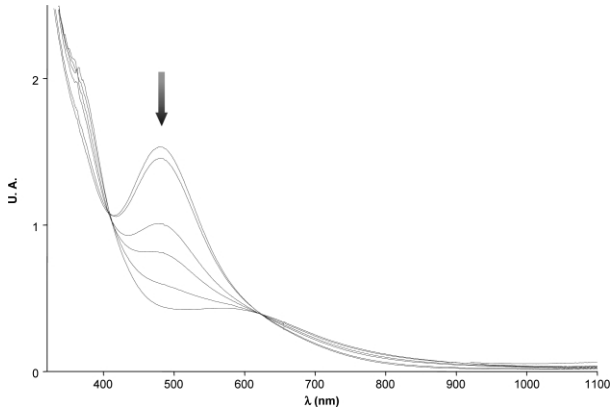


Fig. 3 UV-visible monitoring of the reaction of $\mathbf{2}^{2+}$ with styrene in acetonitrile. Spectra were recorded 0, 1, 10, 15, 30, 60 min. after styrene addition.

catalyst (0.05), PhINTs (1), olefin (2000). The yields of aziridine (isolated after crystallisation) with respect to the iodinane are given in the Table and compared to the copper systems used by Halfen *et al.*[7] and Dodd *et al.*[8] It can be seen (entry 1) that our system is less active toward styrene than the copper systems, although it exhibits notable activity (entry 2) even at a low catalyst/reagent ratio of 1%. Also worth noting is the fact that the present system works equally well (entry 3) when the reagent consists of a mixture of PhIO and $TsNH_2$. In the latter case, no product from oxygen transfer was found indicating a far stronger tosylamine transfer ability of the system. In the case of less active olefins such as cyclooctene (entry 4) and 1-hexene (entry 5), the present system appears more efficient than the copper-based ones. This is also the case in the amination of thioanisole (entry 6). Indeed, a yield of 96% of Ph(Me)SNTs (isolated product) is obtained after 4 h while 63% is reached after 24 h with a copper catalyst.[15]

The present observations that a tosylamido Fe(III) species catalyse tosylamine transfer in the presence of an excess tosylaminoiodinane is reminiscent of the behaviour of non-porphyrinic ruthenium complexes.[16] Indeed, a bistosylamidoruthenium(III) complex was isolated and shown to become active in the amine transfer upon oxidation. A high-valent metal imino species Ru = NTs was proposed to be the active species,[6] as in the case of metalloporphyrins.[3–5] In the present system, the tosylamidoiron(III) complex inactive in stoichiometric tosylamine transfer appears a precursor of the catalytic species (Fig. 3) in presence of excess ArINTs. Therefore, all available evidence suggests that the present non-heme iron system behaves as the above ruthenium complexes.[16] Therefore, it is reasonable to envisage that the actual aziridination and sulfamidation catalyst is a high-valent iron-imino species formed upon oxidation of $\mathbf{2}^{2+}$ by excess ArINTs.

To summarize, we have reported the first tosylamine transfer catalysed by a non-heme iron complex. This reaction applies efficiently to the aziridination of olefins and amidation of thioethers. Its scope and mechanism are presently being investigated and isolation of putative intermediates is being actively pursued.

Table 1 Catalytic tosylamine transfer to olefins and thioanisole[a]

Entry	Substrate	Reaction	Amine yield (%)	
		Time (h)	Halfen	This work
1	Styrene	3	80–96	69
2	Styrene	16	99[b]	46[b]
3	Styrene	18	75[c]	42[c]
4	Cyclooctene	24	25–35	50
5	1-Hexene	24	25–30	51
6	Thioanisole[d]	4	63	96

[a] Conditions: catalyst/reagent/substrate = 0.05/1/2000 [b] catalyst/reagent/substrate = 0.01/1/2000 [c] reagent = PhIO+$TsNH_2$[8] [d] catalyst/reagent/substrate = 1/20/20, reaction time 24 h[15]

Notes and references

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14 $\mathbf{1}(CH_3OH)(ClO_4)_2$ was prepared as already described.[11] $\mathbf{2}(ClO_4)_2$ was obtained by addition of 1.5 eq. of ArINTs[13] (17.5 mg) to an acetonitrile solution of $\mathbf{1}(CH_3OH)(ClO_4)_2$ (40 mg in 200 mL), 2 min stirring, concentration to $\frac{1}{4}$ of the volume and careful precipitation with diethyl ether (all operations performed in a glove box under argon). In a typical catalytic experiment, 120 mg (0.03 mmol) of tosyliminoiodobenzene PhINTs were suspended in 2 mL acetonitrile with 1 mL of styrene. 16.9 mg of $\mathbf{1}(CH_3OH)(ClO_4)_2$ in solution in 100 μL acetonitrile were then added. The reaction mixture was vigorously stirred for 3 h, filtered on alumina which was then washed with acetonitrile and ethyl acetate (10 mL each). After evaporation of the combined fractions, the resulting oil was treated with hexane to precipitate a white solid which was recrystallised in hexane/diethyl ether at −20 °C. All other substrates were treated similarly.
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