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COMMUNICATION

Unprecedented synthesis of iron–NHC complexes by C–H activation of imidazolium salts. Mild catalysts for reduction of sulfoxides[†]

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A direct synthesis of bidentate cyclopentadienyl-functionalised NHC–iron(II) complexes by using imidazolium salts and commercially available $Fe_3(CO)_{12}$ is developed. These well-defined iron–NHC complexes efficiently catalyse the reduction of sulfoxides under mild conditions. Radical scavenging experiments indicate the presence of free radicals in the catalytic reaction.

The development of homogeneous iron catalysts in organic synthesis has recently attracted much interest.¹ Iron is an interesting alternative to other metals used in catalysis because it is cheap, non-toxic, environmentally friendly and abundant. Despite the fast development of iron-based catalysts, catalytic applications with organometallic iron complexes containing N-heterocyclic carbene ligands (NHCs) are rare.² Notable exceptions are C–C bond formation reactions,³ cyclisation,⁴ polymerisation,⁵ arene borylation,⁶ and hydrosilylation.^{7–11}

Iron–NHC complexes are generally prepared *via* free carbenes (generated from deprotonation of imidazolium salts by a strong base)^{5a,12} or by using iron amides.¹³ Recently, Chen and co-workers described new approaches to Fe–NHC complexes: (i) electrochemical synthesis using imidazolium salts and metal plates,¹⁴ and (ii) direct reaction of metal powders with imidazolium salts or silver–NHC complexes.¹⁵

In this work we describe the unprecedented synthesis of iron N-heterocyclic carbene-functionalised cyclopentadienyl complexes by C–H activation of the corresponding imidazolium proligands with the commercially available iron carbonyl Fe₃(CO)₁₂. The direct reaction of the imidazolium proligands **1** and **2** with Fe₃(CO)₁₂ in refluxing toluene afforded the iron complexes $(\eta^5-Cp'-NHC)Fe(CO)I$ [Cp' = $\eta^5-C_5Me_4$ (Cp*), **3**; Cp' = $\eta^5-C_5H_4$ (Cp), **4**] in high yield (Scheme 1).

The formation of complexes **3** and **4** probably implies the oxidative addition of the C–H bond of imidazolium to Fe(0), followed by elimination of the Fe–H intermediate and the cyclopentadienyl proton. A similar reaction pathway has been recently reported by us^{16} and others¹⁷ for the synthesis of related ruthenium complexes. However, this type of C–H activation is unique in Fe–NHC chemistry.



Scheme 1 Synthesis of iron complexes 3 and 4.

Complexes 3 and 4 were recently prepared by our group by the *in situ* reaction at low temperature of proligands 1 and 2 with two equivalents of BuLi followed by addition of freshly prepared $FeI_2(CO)_4$.⁷ The generation of free carbenes requires harsh conditions such as strong base, and we noted that the presence of impurities in the deprotonated Cp-NHC proligand and/or in the carbonyl precursor FeI₂(CO)₄ seriously compromised this synthesis. The facile methodology described here afforded complexes 3 and 4 in high yield and purity. Moreover, the one-step reaction can be performed in a large scale (up to 3 grams) providing an easy access to these organometallic species. Related non-linked cyclopentadienyl Fe-NHC complexes have been prepared either by reaction of free carbene with CpFe(CO)₂I or by treatment of CpFe[N(SiMe₃)₂] with an imidazolium salt.¹⁸ To the best of our knowledge, this is the first report of an iron-NHC prepared by oxidative addition of imidazolium salts to iron carbonyl precursors. Remarkably, no base is required in this reaction.

The presence of the stereogenic centers at the aliphatic linker between the NHC and the cyclopentadienyl ring and at the metal center implies that a mixture of diastereomeric complexes is expected.¹⁹ However, NMR experiments (VT, and NMR carried out in different solvents, see ESI†) suggest that only one diastereomer has been formed.

In a preliminary study, we reported the catalytic activity of the iron complexes **3** and **4** in the catalytic transfer hydrogenation of ketones, and the activity of the unsaturated 16-electron species (Cp*-NHC)FeCl in the hydrosilylation of aldehydes.⁷ A year later, Sortais, Darcel and co-workers described the activity of related non-linked NHC cyclopentadienyl iron complexes [CpFe(IMes)(CO)₂]I in the hydrosilylation of aldehydes and ketones,⁸ and more recently, they extended to the reduction of amides,⁹ nitriles⁹ and imines.¹⁰

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Selective hydrosilylation of ketones catalysed by *in situ* generated iron(II)–NHC complexes has also been recently reported by Adolfsson and co-workers.¹¹

We present here a novel catalyst system based on iron(II) complex **4** combined with $AgBF_4/PhSiH_3$ which resulted to be highly efficient and selective in the reduction of sulfoxides to sulfides.[‡] The catalytic activity of **4** was tested using methyl phenyl sulfoxide and phenylsilane with a reaction ratio of 1 : 2 in the presence of 1 mol% catalyst (treated *in situ* with 1 equiv. of AgBF_4). The reaction was carried out in toluene at 100 °C over 3 h to yield the corresponding sulfide in quantitative yield (>99% determined by GC).

As shown in Table 1, the catalytic reaction is suitable for a variety of sulfoxides, including aromatic (Table 1, entries 1–6)

Table 1Reduction of sulfoxides catalysed by iron complex 4^a

 $R^{O}_{R}^{II} \xrightarrow{\text{cat. 4/AgBF}_{4}} R^{S}_{R'}$

Entry	Substrate	$\operatorname{Yield}^{b}(\%)$
1	O S S	> 99
2	O S S	71
3		53
4	H ₃ C	> 99°
5		96 ^e
6	O O O O O O O O O O O O O O O O O O O	No reaction
7	O II S	> 99
8	Dodecyl CH3	> 99
9	0 Н ₃ С ^{_S} СН ₃	66

^{*a*} Reaction conditions: sulfoxide (1 mmol), catalyst **4** (1 mol%), AgBF₄ (1 mol%, ratio 1 : 1 *vs.* catalyst **4**), PhSiH₃ (2 mmol), toluene (2 mL), 3 h, 100 °C. ^{*b*} Determined by GC methods using biphenyl as an internal standard. ^{*c*} 6 h at 100 °C.

Table 2 Effect of the temperature and different silanes in the reduction of methyl phenyl sulfoxide catalysed by 4^{α}

Entry	Silane (equiv.)	$T/^{\circ}\mathrm{C}$	$\operatorname{Yield}^{b}(\%)$
1	PhSiH ₃ (2.0)	100	< 99
2	$PhSiH_3$ (2.0)	75	88
3	$PhSiH_3(2.0)$	50	57
4	$PhSiH_3$ (2.0)	25	0
5	$PhSiH_3$ (1.2)	100	71
6	PhMe ₂ SiH (2.0)	100	15
7	$(EtO)_2$ MeSiH (2.0)	100	69
8	$(EtO)_2$ MeSiH (1.2)	100	24
9	PMHS (3.0)	100	61

^{*a*} Reaction conditions: sulfoxide (1 mmol), catalyst **4** (1 mol%), AgBF₄ (1 mol%, ratio 1 : 1 *vs.* catalyst **4**), silane (2 mmol), toluene (2 mL), 3 h, 100 °C. ^{*b*} Determined by GC methods using biphenyl as an internal standard.

and aliphatic (Table 1, entries 7–9). In some cases excellent yields (>99%) and selectivities were obtained after 3 h of reaction (Table 1, entries 1, 4, 7, and 8). Sulfoxides containing functional groups such as halogens and alkenyls were reduced, although the latter with lower yield (Table 1, entries 5 and 3, respectively). Noteworthily, methyl 2-phenylsulfinylacetate was not reduced under similar reaction conditions (Table 1, entry 6).

A drop in yield of methy phenyl sulfide has been observed by decreasing the temperature (88% yield at 75 °C, and 57% at 50 °C, Table 2, entries 2 and 3) and no reaction was observed at room temperature (Table 2, entry 4). The use of other solvents such as acetonitrile and tetrahydrofuran resulted in poorer conversions (39% in NCMe and 80% in THF of methyl phenyl sulfide). We have also explored the use of different silanes as reducing agents. As shown in Table 2, PhSiH₃ displayed the best performance (Table 2, entry 1). Under similar reaction conditions, dimethylphenylsilane and methyldiethoxysilane were substantially less effective (Table 2, entries 6 and 7). The cheap and convenient silane polymethylhydrosiloxane (PMHS) could be employed; however, only 61% yield of the corresponding methyl phenyl sulfide was obtained (Table 2, entry 9). When the amount of silane was reduced to 1.2 equiv., a detrimental effect on the yield of sulfide was observed (Table 2, entries 5 and 8).

For comparison, we studied the catalytic activity of the tetramethylcyclopentadienyl-NHC iron complex (Cp*-NHC)Fe-(CO)I (3). Its catalytic activity in the reduction of methyl phenyl sulfoxide with phenylsilane was comparable, affording a 90% yield of the corresponding sulfide (in 3 h at 100 °C with 2 equiv. of PhSiH₃). It seems that the replacement of the Cp ligand by the stronger electron-donating Cp* is not improving the catalytic activity of the iron complex.

In order to get an insight into the mechanism of the catalytic reaction, we performed radical trapping experiments. The experiments were performed by carrying out the catalytic reaction in the presence of radical scavengers (3 : 1 ratio radical scavenger : catalyst) under exclusion of air.²⁰ The addition of both carbon- and oxygen-centered spin traps²¹ such as TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) and BHT (2,6-di-*tert*-butyl-4-methylphenol) inhibited the reaction during the first hours, after which catalysis resumed; however a significant detrimental effect on the yield of methyl phenyl sulfoxide was obtained (28% and 22% yield after 6 hours of

reaction in the presence of TEMPO and BHT, respectively). Addition of the carbon-radical trap BrCCl₃²² slowed down the reaction (quantitative conversion to methyl phenyl sulfide was obtained in 6 h compared to the 3 h needed in the absence of spin trap). These findings indicate the presence of free radicals in the catalytic reaction, and suggest a radical-based mechanism.²³ To the best of our knowledge, the only example of an iron species catalysing the reduction of sulfoxides was recently reported by Enthaler.²⁴

For a further mechanistic insight, the stoichiometric reaction of **4** with $AgBF_4$ was monitored by NMR spectroscopy in C_6D_6 using a J Young-valve tube. However, we could not observe any intermediate species. Probably, the insolubility of the formed species in benzene hampers their observation.²⁵

The reaction of **4** with 1 equivalent of AgBF₄ was also monitored by IR spectroscopy. The IR spectrum showed that the ν_{CO} band corresponding to the CO ligand in complex **4** (at 1932 cm⁻¹) completely disappeared after 30 min of reaction. The IR spectrum of the new species formed in the reaction did not show any bands in the region 1700–2200 cm⁻¹, indicating that under the reaction conditions, **4** loses the carbonyl ligand.²⁶

In conclusion, we have set up a simpler protocol for the synthesis of Fe(II) complexes bearing a cyclopentadienylfunctionalised NHC ligand by direct reaction of the imidazolium proligands and $Fe_3(CO)_{12}$. We have proved the catalytic efficiency of these well-defined iron species in the deoxygenation of sulfoxides. Excellent performance of the catalytic system (Cp-NHC)Fe(CO)I/AgBF₄ using PhSiH₃ as a reducing agent is demonstrated for both aliphatic and aromatic substrates. The presence of radicals in the catalytic reactions has been proved by radical trap experiments. Further investigation into the mechanism of the hydrosilylation reaction and reactivity of iron complexes containing the Cp-NHC fragment is currently underway in our laboratories.

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‡ Typical experimental procedure for the reduction of sulfoxides: all operations were carried out under nitrogen. In a small flask, a mixture of sulfoxide (1 mmol), silane (2 mmol), catalyst/AgBF₄ (ratio 1 : 1, 1 mol%), toluene (2 mL) was stirred at 100 °C and the reaction was monitored by gas chromatography.

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