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Chelating bis-N-heterocyclic carbene complexes of iron(II) containing bipyridyl ligands as catalyst precursors for oxidation of alcohols

Mara F. Pinto,^a Bernardo de P. Cardoso,^a Sonia Barroso,^b Ana M. Martins,^b and Beatriz Royo^{a*}

Chelating bis-N-heterocyclic carbene (bis-NHC) complexes of iron(II) containing pyridyl ligands have been prepared by the reaction of [FeCl₂L] [L = bipy (**1**), phen (**2**)] with [LiN(SiMe₃)₂] and a bis(imidazolium) salt. The [Fe(bis-NHC)L(I)₂] complexes were active pre-catalysts in the oxidation of 1-phenylethanol with *tert*-butyl hydroperoxide in neat conditions, affording quantitative yield of acetophenone in 4.5 h. The catalyst could be reused up to six cycles giving a turnover number (TON) of 1500. Various secondary alcohols, both aromatic and aliphatic were selectivity oxidised to the corresponding ketones in excellent yields. Compound **1** is stable in acetonitrile solution for ca. 4 h, although after 16 h, it evolves to a mixture of [Fe(bis-NHC)(bipy)₂]₁, (**3**), [Fe(bipy)₃]²⁺ and bis-imidazolium salt. The molecular structure of **3** has been determined by X-ray diffraction studies.

Introduction

The low price, high abundance, and non-toxicity of iron, along with the great popularity of NHC ligands in catalysis have triggered the growing interest in the development of iron-NHC chemistry.¹ Several iron complexes supported by chelating bis-NHC ligands have been described in the literature,² but their use as catalysts is still rather rare. To the best of our knowledge, only three reports on catalytic applications of iron bis-NHCs can be found in the literature. In 2011, Meyer described the activity of four-coordinate iron(II) complexes Fe(bis-NHC)X₂ in cross-coupling catalysis,^{2a} and later Hazari reported their use in homocoupling of Grignard reagents.^{2d} Same year, Driess described the catalytic activity of the iron(0) Fe(η^6 -arene)(bis-NHC) complex in the reduction of amides to amines with silanes.^{2e}

We recently became interested in exploring complexes containing the "Fe-bis-NHC" fragment combined with 2,2-bipyridine (bipy) and 1,10-phenanthroline (phen) aiming to explore reactivity in oxidation reactions. Phenanthroline and bipyridine are classical ligands that play important role in coordination chemistry.³ Their related transition metal complexes often show interesting properties that can be

applied in catalysis, artificial photosynthesis, molecular electronics, and metallasupramolecular chemistry, among others.⁴ Iron complexes bearing NHCs and polypyridines independently bound to the metal center are very rare. The first heteroleptic tetrakis(NHC) Fe(II) complex containing a mesoionic bis(1,2,3-triazol-5-ylidene) and a bipyridine ligand was recently described by Sundström.⁵ In contrast, iron-NHCs containing polypyridine ligands as part of multidentate frameworks have been intensively studied in the last years.⁶ Recently, Herrmann and Kühn reported exciting results describing the catalytic activity of iron(II) complexes bearing tetradentate NHC-pyridine ligands in the epoxidation of olefins, and in hydroxylation of toluene and benzene with H_2O_2 .^{6d,e} Based on these precedents, and on our own experience on the preparation of iron-NHC based complexes,⁷ we now report the synthesis of a series of chelating bis-NHC iron(II) pyridyl complexes and their application as catalysts for the oxidation of alcohols.

Results and discussion

The iron bis-NHC complex [Fe(bis-NHC)(bipy)I₂] (**1**) (NHC = 1,1'methylene-3,3'-di-benzylimidazole-2-ylidene) was prepared as shown in Scheme 1, by the reaction of [FeCl₂(bipy)] with two equivalents of [LiN(SiMe₃)₂] followed by addition of 1,1'methylene-3,3'-di-benzylimidazolium diiodide in THF. This procedure is based on the method disclosed by Danopoulos for the preparation of Fe bis-NHCs.⁸ Complex **1** precipitated from the reaction as a deep purple crystalline solid. The

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^{a.} Instituto de Tecnologia Química e Biológica António Xavier, ITQB, Av. da

República, EAN, 2780-157 Oeiras, Portugal. E-mail: broyo@itqb.unl.pt ^{b.} Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

⁺ Electronic Supplementary Information (ESI) available: Details on NMR and MS (ESI-TOF) spectra, and crystal structure determinations. See DOI: 10.1039/x0xx00000x

Journal Name

ARTICLE

analogous phenanthroline complex [Fe(bis-NHC)(phen)I₂] (2) was prepared using [FeCl₂(phen)] by following a similar synthetic procedure. The identity of complexes 1 and 2 was established by elemental analysis and ESI-mass spectroscopy. The ESI mass spectrum of 1 recorded in acetonitrile, displayed a prominent signal at m/z 666.9 assignable to the monocationic iron species [Fe(bis-NHC)(bipy)I]⁺. A lower intensity signal at m/z 270.0 was attributed to the dicationic species [Fe(bis-NHC)(bipy)]²⁺. The ESI-MS spectrum of complex 2 displayed an intense signal at m/z 691.0 due to the cation [Fe(bis-NHC)(phen)I]⁺. Consistent with their paramagnetic nature, the ¹H NMR spectra of 1 and 2 displayed broad signals, so structural information could not be obtained



Scheme 1 Synthesis of iron complexes 1 and 2

Both compounds **1** and **2** were insoluble in non-polar solvents such as hexane and toluene, and also in THF, yet soluble in polar solvents. They were air and moisture stable in the solid state, and were stored for weeks under air without noticeable decomposition.

In order to assess the reactivity of **1** toward oxidation reactions, we explored its catalytic activity in the oxidation of alcohols. First we tested **1** in the oxidation of 1-phenylethanol in the presence *tert*-butyl hydroperoxide (TBHP) as oxidant in a 1:1.5 molar ratio (substrate *vs* oxidant). The reaction was carried out in the absence of solvent at 80 °C, with a catalyst loading of 2 mol%, which afforded a quantitative yield of acetophenone in 4.5 h (Table 1, entry 1). The study of the reaction profile showed conversions already at very early reaction times (5 min, 12% yield), thus indicating that the active species formed rapidly upon addition of TBHP.

Interestingly, the reaction mixture remained active upon 6 consecutive additions of substrate and oxidant, reaching quantitative conversion to the ketone after 4.5 h. An accumulated turnover number (TON) of 1500 was achieved. Using the same conditions, a series of aromatic and aliphatic secondary alcohols were oxidised to the corresponding ketones in excellent yields (Table 1, entries 6-9). Moderate production of hexanaldehyde was obtained in the oxidation of 1-hexanol (61%, Table 1, entry 10), while mixtures of several compounds were obtained when primary benzyl alcohols were used. Catalyst 1 was inactive when the reaction was performed using H_2O_2 as oxidant instead of TBHP (Table 1, entry 11). The phenanthroline iron complex 2 displayed similar catalytic activity compared to 1, indicating that substitution of bipyridine by phenanthroline was irrelevant to the performance of the catalyst.

Table 1 Oxidation of alcohols with TBHP using 1.^a

$$R \xrightarrow{OH} R' \xrightarrow{\text{cat. 1 (2 mol%)}} R \xrightarrow{O} R'$$

Entry	Oxidant/Solvent	Substrate	Time (h)	Yield (%) ^b
1	TBHP/neat	1-phenylethanol	4.5	>99
2	TBHP/THF	1-phenylethanol	8	15
3	TBHP/toluene	1-phenylethanol	8	51
4	TBHP/MeCN	1-phenylethanol	4.5	>99
5	TBHP/water	1-phenylethanol	4.5	>99
6	TBHP/neat	cyclohexanol	8	91
7	TBHP/neat	cyclopentanol	8	96
8	TBHP/neat	1,2,3,4-tetrahydro-1- naphthol	8	95
9	TBHP/neat	1-phenyl-1-propanol	6	90
10	TBHP/neat	1-hexanol	9	61
11	H ₂ O ₂ /neat	1-phenylethanol	24	0

^a Reaction conditions: substrate (0.5 mmol), catalyst 1 (2 mol%), TBHP (0.75 mmol), 80 °C. ^b Yield determined by ¹H NMR using diphenylmethane as an internal standard.

Encouraged by these results, we explored the reactivity of **1** under oxidative conditions in different solvents. When the reaction was carried out in THF or toluene, low yields were obtained, probably due to the insolubility of the catalyst (Table 1, entries 2 and 3). In contrast, quantitative conversion of 1-phenylethanol to acetophenone was observed when polar solvents (acetonitrile or water) were used (Table 1, entries 4 and 5). We also performed the stoichiometric reaction of **1** with TBHP in the presence of one equivalent of 1-phenylethanol in acetonitrile. The reaction mixture was heated at 80 °C for 30 min, and the resulting acetonitrile solution was filtered and subjected to ESI-MS analysis, showing a significant signal at m/z 270 (z = 2), due to [Fe(bis-NHC)(bipy)]²⁺. This experiment strongly suggests that the NHC ligand remains bound to the iron center under the oxidative conditions used for the catalytic reactions.⁹

The stability of 1 in acetonitrile was explored by ESI-MS spectroscopy. In a typical experiment 1 was dissolved in acetonitrile, and then solution was stirred for 2 or 4 hours before the ESI-MS spectra were taken. The mass spectra displayed the same pattern as those recorded with freshly prepared solutions, showing the diagnostic signal at 666.9 assigned to the iron cation [Fe(bis-NHC)(bipy)I]⁺. This result is strongly indicating that 1 is stable in acetonitrile solutions for at least a few hours. After 16 h in MeCN, the colour of the solution changed from the initial deep purple to purplish red. The ¹H NMR spectrum (in CD₃CN) became well-resolved and suggested the formation of a diamagnetic product mixture. The observed resonances were attributed to [Fe(bis-NHC)(bipy)₂]I₂ (**3**) and $[Fe(bipy)_3]^{2+}$, along with small quantities of bis-imidazolium salt (in a proportion of 46.5 %, 40.8 %, and 12.4 %, respectively). The identity of complex 3 was confirmed by single crystal X-ray diffraction (vide infra). The complex $[Fe(bipy)_3]^{2+}$ and the bis-imidazolium salt were identified by comparing their spectra with the ones taken from pure samples. As a diagnostic of the presence of the NHC ligand

Journal Name

bound to the metal, the ¹³C NMR spectrum of **3** shows a signal at 189 ppm, which is a clear indication of the presence of a carbene carbon. Similar evolution of **1** was observed in water and methanol. The NMR spectra of **1** in D₂O and MeOD recorded after 16 h displayed the same NMR pattern as in the acetonitrile solution.

The molecular structure of **3** is displayed in Figure **1**. The cation displays a slightly distorted octahedral geometry defined by the carbon atoms of the bis-NHC ligand (C1 and C12) and the nitrogen atoms of the two bipy ligands (N5, N6, N7 and N8). The equatorial plane is defined by N5, N6, N8 and C12 while the axial positions are occupied by C1 and N7. The angles between the mutually *trans* ligands range between 171.8(1)° and 175.1(2)°. The Fe1-C1 (1.976(4) Å) and Fe1-C12 bond lengths (1.965(4) Å) are within the range observed for other dicationic bis-NHC iron complexes (1.818 Å < Fe-C_{NHC} < 2.007 Å).¹⁰ The Fe-N_{bipy} distances are also in agreement with commonly reported values.¹¹



Figure 1 ORTEP-3 diagram of the cation of 3, using 30% probability level ellipsoids. Hydrogen atoms and counter-anions (two iodides) are omitted for clarity. Selected distances (Å): Fe1-C1 1.976(4), Fe1-C12 1.965(4), Fe1-N8 1.967(3), Fe1-N5 1.983(3), Fe1-N7 1.987(3), Fe1-N6 2.007(3). Selected angles (°): N8-Fe1-N5 171.8(1), C1-Fe1-N7 175.1(2), C12-Fe1-N6 173.1(2).

In light of these results, we decided to explore the catalytic activity of acetonitrile solutions of **1** after being incubated for 16 h. Then, TBHP and 1-phenylethanol were added and heated at 80 °C for 4.5 h. Under these conditions, 40% yield of acetophenone was obtained. We also evaluated the catalytic activity of a series of iron salts for comparative purposes. As shown in Table 2, FeCl₂, FeCl₃, FeCl₂(bipy), and [Fe(bipy)₃]Cl₂ catalysed the reaction to a much lower extend (<45 %) than **1**. These results strongly support that complex **1** is a pre-catalyst in the catalytic oxidation reaction, thus indicating a beneficial role of the NHC in the coordination sphere of the metal.

Table 2 Oxidation of 1-phenylethanol using Fe species^a



Entry	Catalysts	Yield (%) ^b
1	Fe(bis-NHC)(bipy)I ₂ (1)	>99
2	Fe(bipy)Cl ₂	33
3	[Fe(bipy) ₃]Cl ₂	42
4	FeCl ₂	30
5	FeCl ₃	22
6	[bis-NHC]I ₂	0

^a Reaction conditions: alcohol (0.5 mmol), catalyst (2 mol%), TBHP (0.75 mmol), MeCN (0.4 mL), 80 °C, 4.5 h.^b Yield determined by ¹H NMR using diphenylmethane as a internal standard.

Finally, we have performed spin trap experiments, which showed that radicals such as ^tBuO[•] or ^tBuO[•] could be involved in the oxidation reaction catalysed by **1**. When the catalytic oxidation of 1-phenylethanol with TBHP in acetonitrile was performed in the presence of an oxygen-radical trap, such as Ph_2NH , the yield of acetophenone was reduced to 5%, indicating that the oxidation reaction proceeds via a radical mechanism involving oxygen-centered radicals. In contrast, the presence of CBrCl₃, a carbon-radical trap did not affect the catalytic reaction.

Conclusions

In summary, we prepared two iron(II) bis-NHC complexes bearing bipypidyl and phenanthroline ligands in good yields. These complexes were used in the oxidation of alcohols with TBHP. The reaction can be performed in the absence of solvent, and the active species can be reused over 6 cycles without measurable loss of activity. The catalytic reaction can also be performed in polar solvents such as acetonitrile and water, affording quantitative yield of the corresponding ketones. Compound **1** is stable in acetonitrile solution for at least 4 h, although after 16 h evolves to a mixture of [Fe(bis-NHC)(bipy)₂]l₂, (**3**), [Fe(bipy)₃]²⁺ and bis-imidazolium salt. The molecular structure of **3** has been determined by X-ray diffraction studies.

Our work constitutes the first example of an iron(II)-NHC complex catalysing the oxidation of alcohols with TBHP. We believe that our research may inspire future research in the field of metal-abundant-based catalysts.

Experimental details

General methods

All manipulations were carried out under nitrogen atmosphere using standard Schlenk techniques, and solvents were purified from appropriate drying agents. Deuterated solvents were degassed and stored over molecular sieves. FeCl₂(bipy),¹²

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Journal Name

ARTICLE

FeCl₂(phen),¹³ and 1,1'-methylene-3,3'-di-benzylimidazolium diiodide¹⁴ were synthesised according to the method described in the literature. All other reagents were purchased from commercial suppliers and used without further purification. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance III 500 MHz. Assigment of resonances was made from HMQC and HMBC experiments. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument; nitrogen was employed as drying and nebulising gas. Elemental analyses were performed in our ITQB laboratory services.

X-ray crystallography

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Crystals suitable for single-crystal X-ray analysis were obtained for complex **3** by slow diffusion of Et₂O in acetonitrile solutions of 1. The data were collected using graphite monochromated Mo-K_{α} radiation (λ = 0.71073 Å) on a Bruker AXS-KAPPA APEX II diffractometer equipped with an Oxford Cryosystem openflow nitrogen cryostat. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT on all observed reflections. Absorption corrections were applied using SADABS.¹⁵ The structures were solved and refined using direct methods with program SIR2004¹⁶ using WINGX-Version 2014.1¹⁷ SHELXL¹⁸ system of programs. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were inserted in idealised positions and allowed to refine riding on the parent carbon atom. The molecular diagrams were drawn with ORTEP-3 for Windows¹⁹ included in the software package. For crystallographic experimental data and structure refinement parameters see Table S2. CCDC 1455061 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

General procedure for the synthesis of complexes 1 and 2

Two equivalents of $[LiN(SiMe_3)_2]$ were added to a suspension of [FeCl₂L] (L = bipy, phen) (1 equiv.) in toluene at 0 °C, and the mixture was stirred overnight at room temperature. The toluene solution was evaporated and all the volatiles were removed under vacuum to yield a green residue, which was redissolved in THF (10 mL). Solid 1,1'-methylene-3,3'-dibenzylimidazolium diiodide (1 equiv.) was added at once to the THF solution, and the reaction mixture was stirred for 16 h at room temperature. A deep purple crystalline solid insoluble in THF was isolated by filtration, washed several times with THF and Et₂O to yield the pure product.

Preparation and characterisation of [Fe(bis-NHC)(bipy)I₂] (1). Following the general procedure, $[LiN(SiMe_3)_2]$ (150 mg, 0.90 mmol), [FeCl₂(bipy)] (127 mg, 0.45 mmol) and 1,1⁻methylene-3,3'-di-benzylimidazolium diiodide (475 mg, 0.81 mmol) afforded 1 (520 mg, 0.65 mmol, 80%) as deep purple solid. Data for 1: Anal. Calc for C₃₁H₂₈N₆Fel₂ (794.25): C, 46.88; H, 3.55; N, 10.58. Found: C, 47.10; H, 3.86; N, 10.27. MS (ESI-TOF) in acetonitrile: $m/z [M]^{+}$ calcd for $[C_{31}H_{28}N_6Fel]^{+}$, 667, found: 666.9; $[C_{31}H_{28}N_6Fe]^{2+}$, 270 found: 270; $[C_{42}H_{40}N_8Fel]^+$.

Preparation and characterisation of [Fe(bis-NHC)(phen)I₂] (2). Following the general procedure, [LiN(SiMe₃)₂] (119 mg, 0.71 mmol), [FeCl₂(phen)] (109 mg, 0.36 mmol), and 1,1'-

Characterisation of [Fe(bis-NHC)(bipy)2]I2 (3). Crystals of complex 3 was obtained by slow diffusion of Et₂O into a MeCN solution of **1**. ¹H NMR (298 K, 400MHz, CD₃CN): δ = 8.26 (d, 2H, ${}^{3}J_{HH}$ = 8.1 Hz, H_{bipy}), 8.08 (d, 2H, ${}^{3}J_{HH}$ = 8.0 Hz, H_{bipy}), 7.97 (t, 2H, ³J_{HH} = 7.8 Hz, H_{bipy}), 7.48-7.43 (m, 4H, H_{Ar}), 7.43-7.38 (m, 4H, $H_{\rm Ar}),~7.20\text{-}7.15$ (m, 2H, $H_{\rm Ar}),~7.13\text{-}7.07$ (m, 4H, $H_{\rm Ar}),~7.07\text{-}7.02$ (m, 4H, H_{Ar}), 6.71 (t, 2H, ${}^{3}J_{HH}$ = 6.5 Hz, Ph), 6.31 (s ap., 2H, H_{imid}), 6.29 (s ap., 2H, H_{imid}), 6.27 (s, 2H, NCH₂N), 4.50 (d, 2H, $^{2}J_{HH} = 16.9 \text{ Hz}, \text{ NCH}_{2}\text{Ph}), 4.22 (d, 2H, <math>^{2}J_{HH} = 16.9 \text{ Hz}, \text{ NCH}_{2}\text{Ph}).$ ¹³C NMR (298 K, 400MHz, CD₃CN): δ = 189.8 (Fe-CNHC), 161.0, 158.8, 158.3, 155.3 (C_{ipso}), 152.0, 138.3, 137.6 (CH, Ar), 137.5 (C_{ipso}), 129.2 128.1, 127.1, 126.8, 126.4 (CH, Ar), 125.9 (C_{imid}), 124.6, 124.0 (CH, Ar), 63.2 (NCH₂N), 53.0 (CH₂Ph).

Typical procedure for the oxidation of alcohols

An open air flask was charged with catalyst, and alcohol (0.5 mmol). Then, TBHP (5.0-6.0 M in decane, 0.75 mmol) was added. The progress of the reactions were monitored by taking aliquots of the reaction mixtures and subjecting them to ¹H NMR in chloroform- d_3 , indicating the presence of the corresponding ketones and unreacted alcohols. The yield was determined by ¹H NMR using diphenylmethane as internal standard. The corresponding ketones were extracted in dichloromethane, and identified by comparison of their NMR spectral data to the literature.²⁰

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