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Iron complexes bearing iminopyridine and aminopyridine ligands as catalysts for atom transfer radical polymerisation

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A series of iron(II) complexes bearing iminopyridine and aminopyridine ligands with N-alkyl and N-aryl substituents has been synthesised. X-Ray crystal structures of *n*-propyl- and 2,6-diisopropylphenyl-iminopyridine derivatives reveal dinuclear structures with halide bridges; a derivative carrying a cyclododecyl imine substituent and an α-methylpyridine unit is mononuclear. In studies of their atom transfer radical polymerisation behaviour, the mononuclear iminopyridine derivative is found to catalyse the polymerisation of styrene and methyl methacrylate while the dinuclear catalysts polymerise styrene only. The aminopyridine complexes are more efficient ATRP catalysts for styrene polymerisation than their unsaturated iminopyridine relatives.

Introduction

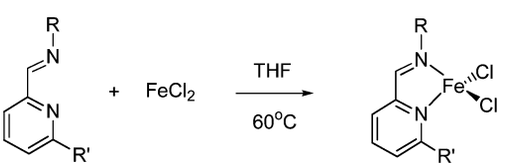
Atom transfer radical polymerisation is an attractive technique for the controlled synthesis of a wide variety of polystyrenic and polyacrylic materials.[1] By their nature, conventional free radical polymerisations are difficult to control due to the extremely reactive nature of radicals which causes irreversible termination reactions. Thus, to produce a controlled radical polymerisation, the concentration of active radical chain ends must be kept low. This can be achieved by establishing a fast and dynamic equilibrium between growing and dormant polymer chains using a metal-mediated halide exchange process. Under these circumstances, a well-controlled, pseudo-living polymerisation, affording good control over molecular weight and molecular weight distributions, can be achieved.

Building on knowledge gained from metal mediated coupling reactions involving organic radicals (the Kharasch reaction),[2] Wang and Matyjaszewski[3] and Sawamoto *et al.*[4] showed that copper- and ruthenium-based catalyst systems, respectively, effect well-controlled polymerisations of styrene and methyl-methacrylate. Since then, catalysts based on a number of other metals have been reported, including systems based on Ru,[5] Rh,[6] Pd,[7] Ni[8] and Fe.[9] Following the initial studies on Cu/bipy systems, a variety of ligands have been investigated for copper, including bi- and tri-dentate amines,[10] aminopyridines,[11] imino-pyridines[12] and tripodal ligands.[13]

Some time ago, we disclosed a new family of four-coordinate iron-based catalysts stabilised by α-diimine ligands,[14] and found that their catalytic behaviour was strongly influenced by the nature of the imine substituents. In the case of alkylimines, well-controlled polymerisations of both styrene and MMA were found. However, for aryl substituents, rapid chain transfer processes are competitive.[15] With a view to obtaining a better understanding of the steric and electronic factors influencing the behaviour of four-coordinate iron ATRP catalysts containing N-donor ligands, we decided to extend our studies to readily accessible imino- and amino-pyridine derivatives. In this paper we report the synthesis of a family of imino- and amino-pyridine complexes, their solution and solid-state structures and their behaviour as ATRP catalysts.

Results and discussion

(i) Synthesis and structural characterisation. The paramagnetic complexes **1**–**6** (Scheme 1) are readily prepared by stirring a solution of anhydrous $FeCl_2$ with a slight excess of the iminopyridine in tetrahydrofuran at 60 °C for 16 h. After cooling, filtration and washing, **1**–**6** can be isolated as microcrystalline, air-stable solids in excellent yields (typically 80–90%). **1**–**6** have been characterised by magnetic moment measurements, infrared spectroscopy, mass spectrometry and elemental analysis.



Scheme 1 Synthesis of complexes **1**–**6** where R′ = H; R = *n*-propyl, **1**; *c*-C_6H_{11}, **2**; *c*-$C_{12}H_{23}$, **3**; R = 2,6 diisopropylphenyl, **4** and R′ = Me; R = *n*-propyl, **5**; *c*-$C_{12}H_{23}$, **6**.

A single crystal X-ray analysis of **5** showed it to be the centrosymmetric dimeric complex illustrated in Fig. 1. The geometry at each iron centre is best described as distorted trigonal bipyramidal, there being within the equatorial plane a noticeable enlargement of the Cl(1)–Fe–Cl(2′) angle [137.54(4)°], and small contractions of the N(7)–Fe–Cl(2′) and

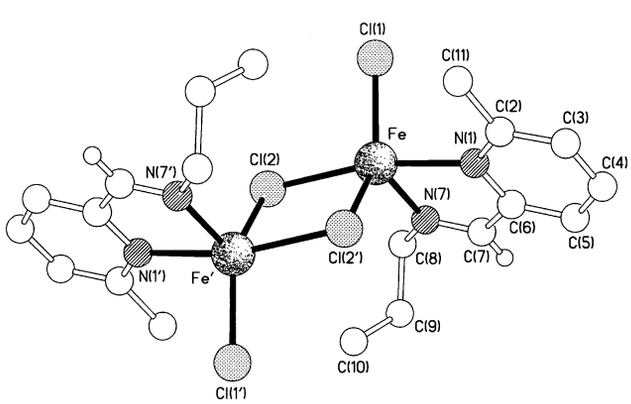


Fig. 1 The molecular structure of **5**. Selected bond lengths (Å) and angles (°): Fe–Cl(1) 2.2890(10), Fe–Cl(2) 2.5246(9), Fe–Cl(2′) 2.4029(10), Fe–N(1) 2.219(3), Fe–N(7) 2.119(3), C(7)–N(7) 1.274(4); Cl(1)–Fe–Cl(2) 96.41(4), Cl(1)–Fe–Cl(2′) 137.65(4), Cl(1)–Fe–N(1) 96.21(7), Cl(1)–Fe–N(7) 112.40(8), Cl(2)–Fe–Cl(2′) 83.79(3), Cl(2)–Fe–N(1) 167.36(7), Cl(2)–Fe–N(7) 97.41(8), Cl(2′)–Fe–N(1) 87.28(7), Cl(2′)–Fe–N(7) 109.53(8), N(1)–Fe–N(7) 77.16(10), Fe–Cl(2)–Fe′ 96.21(3). The transannular Fe ··· Fe separation is 3.669(1) Å.

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N(7)–Fe–Cl(1) angles [109.53(8) and 112.40(8)°, respectively]. The axial N(1)–Fe–Cl(2) angle exhibits a small non-linearity [167.36(7)°] and the axial/equatorial N(1)–Fe–N(7) angle is, as expected, substantially contracted [77.16(10)°] as a consequence of the bite of the five-membered chelate ring. The iron coordination distances are unexceptional, exhibiting an expected lengthening of the axial bonds relative to their equatorial counterparts. The chloride bridges are thus asymmetric [Fe–Cl(2) 2.5246(9) Å, Fe–Cl(2′) 2.4029(10) Å]. The five-membered chelate ring is slightly folded about the N(1) ··· N(7) vector such that the iron atom lies 0.204 Å out of the plane of the remaining four atoms which are coplanar to within 0.012 Å. The molecules pack to form end-to-end chains that extend in the crystallographic 011 direction with π–π stacking of symmetry-related pyridyl rings with centroid ··· centroid and mean-interplanar separations of 3.75 and 3.35 Å, respectively. The most closely related structure in the literature is that of bis(μ_2-bromo)dibromo-bis(2,6-bis(isopropyl)phenyl((6-methyl-2-pyridinyl)methylene)amine)-dinickel(II)[16] which has two independent centrosymmetric dimers in the unit cell. In this latter structure the distortion from trigonal bipyramidal geometry at the nickel centre is greater with the pair of equatorial Ni–Br bonds subtending an angle of *ca.* 144°; the chelate geometry is very similar to that observed in **5**.

By contrast, a structure determination of compound **6**, where the *n*-propylimine substituent has been replaced by a cyclododecyl ring, reveals a monomeric complex with a four-coordinate iron atom (Fig. 2). The geometry at the metal is severely distorted tetrahedral, the N(1)–Fe–N(7) ligand bite angle being 77.8(2)° [*cf.* 77.16(10) in **5**]; the remaining angles subtended at the iron centre are in the range 108.6(1)–117.8(1)° and the coordination distances are unexceptional. The five-membered chelate ring is slightly folded with the metal lying 0.15 Å out of the plane of the other four atoms (which are coplanar to within 0.02 Å). Interestingly, the methine hydrogen at the quaternary centre C(9) has exactly the same *syn* relationship with respect to the imino hydrogen on C(7) as was observed in the related bis(cyclohexylimino) species.[14b] The only intermolecular feature of note is a weak C–H ··· Cl interaction between this imino hydrogen and the Cl(2) chlorine centre of a glide-related molecule [H ··· Cl 2.77 Å, C–H ··· Cl 163°] to form pseudo-polymer chains that propagate along the crystallographic *b* direction.

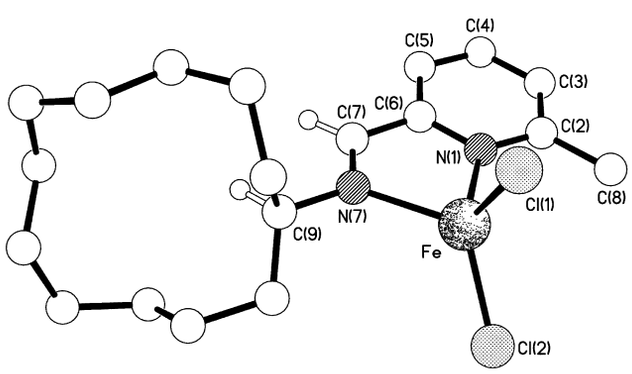


Fig. 2 The molecular structure of **6**. Selected bond lengths (Å) and angles (°): Fe–Cl(1) 2.2233(15), Fe–Cl(2) 2.2307(16), Fe–N(1) 2.145(4), Fe–N(7) 2.111(4), C(7)–N(7) 1.277(6); N(7)–Fe–N(1) 77.82(16), N(7)–Fe–Cl(1) 113.68(12), N(1)–Fe–Cl(1) 108.63(12), N(7)–Fe–Cl(2) 117.84(12), N(1)–Fe–Cl(2) 116.16(12), Cl(1)–Fe–Cl(2) 116.48(6).

Although paramagnetic, **6** affords a reasonably sharp contact-shifted ^{1}H NMR spectrum (Fig. 3). Tentative assignments have been made on the basis of integrated signal intensities and the chemical shifts as an indication of proximity to the paramagnetic iron centre.

Since replacement of the 1° *n*-propyl substituent by the much larger 2° cyclododecyl unit led to a mononuclear complex, we

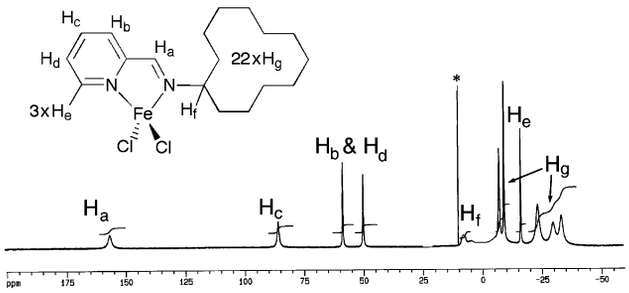


Fig. 3 ^{1}H NMR spectrum of **6** in $CDCl_3$ (* = $CHCl_3$).

envisaged that the bulky 2,6-diisopropylphenyl substituent may also favour a mononuclear structure. An X-ray structure determination of **4**, in which the pyridine α-methyl group is absent, reveals a dimeric species with crystallographic inversion symmetry (Fig. 4). In this complex, the geometry at the two iron centres is probably best described as distorted square pyramidal (*cf.* trigonal bipyramidal in **5**), the four basal atoms [N(1), N(7), Cl(2) and Cl(2′)] being coplanar to within 0.068 Å with the iron atom lying 0.714 Å out of this plane. Consistent with this change in coordination geometry, the Fe coordination distances exhibit distinct differences from their counterparts in **5**. Most noticeable in particular is a reduction in Δ(Fe–Cl) within the bridge from 0.12 Å in **5** to 0.06 Å in **4**. The five-membered chelate ring has a slightly folded geometry with the iron atom lying 0.064 Å out of the plane of the remaining four atoms which are coplanar to within 0.003 Å. The 2,6-diisopropylphenyl ring is inclined almost orthogonally (*ca.* 87°) to the chelate ring plane. The nickel analogue of **4** shows similar structural features.[17] The only intermolecular packing interaction of note is a weak C–H ··· Cl interaction, analogous to that seen in **6**, between the imino hydrogen and the Cl(1) chlorine centre of a glide-related molecule [C ··· Cl 3.60 Å, H ··· Cl 2.76 Å, C–H ··· Cl 149°] to form a pseudo-polymer chain. It would appear that the α-methyl pyridine substituent plays a crucial role in determining whether these iminopyridine complexes are mononuclear or dinuclear in the solid state. Cryoscopic solution molecular weight determinations show that **1**–**5** retain aggregated structures in solution, whereas complex **6** retains its monomeric structure.[18]

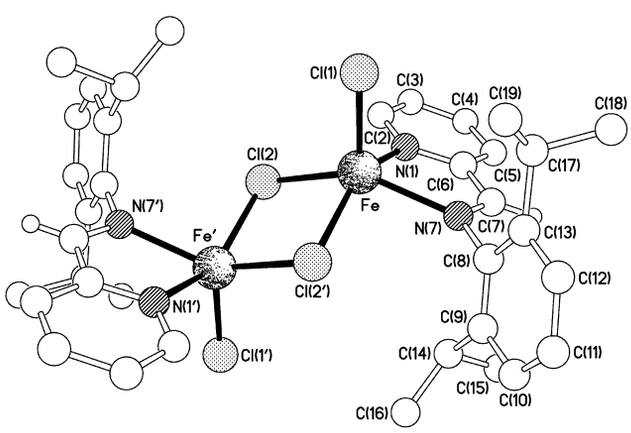


Fig. 4 The molecular structure of **4**. Selected bond lengths (Å) and angles (°): Fe–N(1) 2.150(3), Fe–N(7) 2.227(2), Fe–Cl(1) 2.2649(11), Fe–Cl(2) 2.4693(10), Fe–Cl(2′) 2.4056(11), C(7)–N(7) 1.272(4); N(1)–Fe–N(7) 75.11(10), N(1)–Fe–Cl(1) 101.34(8), N(7)–Fe–Cl(1) 108.38(7), N(1)–Fe–Cl(2′) 146.47(7), N(7)–Fe–Cl(2′) 90.53(7), Cl(1)–Fe–Cl(2′) 111.98(5), N(1)–Fe–Cl(2) 88.27(7), N(7)–Fe–Cl(2) 140.90(7), Cl(1)–Fe–Cl(2) 109.49(4), Cl(2)–Fe–Cl(2′) 84.22(4), Fe–Cl(2)–Fe′ 95.78(3). The transannular Fe ··· Fe separation is 3.617(1) Å.

(ii) Styrene polymerisation. The use of **1**–**6** in the bulk polymerisation of styrene initiated by 1-phenylethyl chloride (1-PECl) has been monitored at 120 °C under an inert

Table 1 Styrene polymerisation data for complexes **1**–**6**[a]

Catalyst	k_{obs}/h^{-1}	$M_{n,th}$	M_n	M_w/M_n
1	0.06	19000	18400	1.34
2	0.05	17200	18000	1.41
3	0.05	17400	19000	1.32
4	–[b]	19400	5000	1.79
5	0.06	19200	18600	1.39
6	0.17	21000	23300	1.34

[a] Polymerisation performed over 24 h. [b] Non-linear kinetics.

atmosphere. The experimentally determined rate constants are given in Table 1 along with molecular weights and molecular weight distributions at *ca.* 100% conversion. Semilogarithmic plots of ln([M]$_o$/[M]) *vs.* time were found to be linear in the cases of **1**, **2**, **3**, **5** and **6**, indicating that the radical concentration is constant throughout the polymerisation runs. Typical plots for catalysts **3** and **6** are shown in Fig. 5.

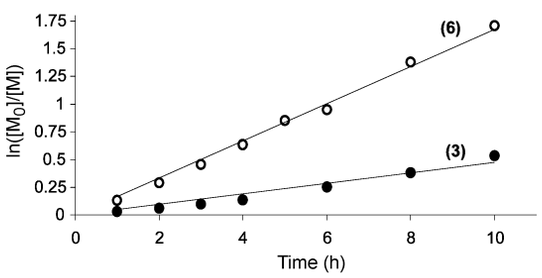


Fig. 5 Plot of ln([M]$_0$/[M]) *vs.* time for **3** (●) and **6** (○). ([catalyst]$_0$ = 5.0×10^{-4} M, [PECl]$_0$ = 5.0×10^{-4} M, [St]$_0$ = 0.1 M).

The molecular weights (M_n) of the resultant polystyrene samples increase linearly with time and are in good agreement with calculated molecular weights. Polydispersities (M_w/M_n) are slightly higher (typically *ca.* 1.4) than for previously reported iron(II) diimine complexes.[14b] ^{1}H NMR spectroscopic analysis of the resultant polystyrene samples show the presence of the halide capping group (ClC*H*(Ph)CH$_2$–, δ 4.5 ppm) which is also supported by halide microanalysis.[19]

Complex **6** affords a significantly faster polymerisation rate than the dimeric complex, **3** [k_{obs}(**3**) = 0.05 h^{-1}, k_{obs}(**6**) = 0.17 h^{-1}], possibly a consequence of the need to cleave the halide bridges prior to halogen atom transfer. Molecular weights (M_n) increase linearly with conversion and with monomer to initiator ratio; a plot of M_n *vs.* monomer:initiator ratio for catalyst **6** is shown in Fig. 6.

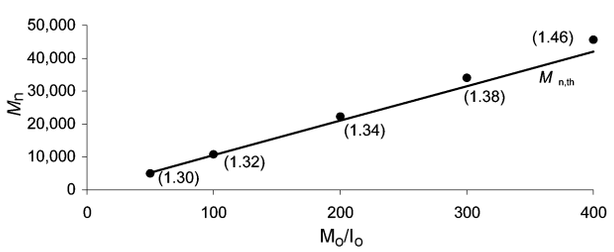


Fig. 6 Plot of molecular weight *vs.* M_0/I_0 for **6** with M_w/M_n in parentheses ([**6**]$_0$ = 1.0×10^{-3} M, [PECl]$_0$ = 1.0×10^{-3} M, [St]$_0$ = 0.05, 0.1, 0.2, 0.3 and 0.4 M).

For comparative purposes, styrene polymerisations were also investigated using **6** and an aryl sulfonyl halide initiator (phenoxy disulfonyl chloride, PDSC). These proceeded in a similarly well-controlled manner (M_w/M_n = 1.33) with a polymerisation rate close to that reported using 1-PECl as initiator (k_{obs}(PDSC) = 0.19 h^{-1} *vs.* k_{obs}(1-PECl) = 0.17 h^{-1}). The other alkyl complexes also gave comparable polymerisation results when either 1-PECl or PDSC were used as initiators. Changing the initiator to a bromo derivative, 1-PEBr, slows the polymerisation markedly (*cf.* for **6**: k_{obs}(1-PEBr) = 0.04 h^{-1} *vs.* k_{obs}(1-PECl) = 0.17 h^{-1}).

Table 2 MMA polymerisation results for **6**[a]

	TosCl	EBrB	MBPA
M_n	23600	25200	24500
$M_{n,th}$	20000	20000	20000
M_w/M_n	1.49	1.62	1.64

[a] MMA polymerisations (200 equiv.) at 80 °C in 10% v/v toluene, for 32 h.

Overall, styrene polymerisations using the iminopyridine complexes **1**, **2**, **3** and **5** are quite well controlled, though *ca.* five times slower than their diimine analogues (*cf.* **2**, k_{obs} = 0.05 h^{-1}; iron(II)diimines, k_{obs} *ca.* 0.25 h^{-1}).[14b] For the mononuclear derivative **6**, polymerisations are considerably faster than for **1**, **2**, **3** and **5** but still slower than for its α-diimine analogues. Thus, whereas pyridylimine ligands on copper do not slow down the rate of polymerisation,[20] on iron significantly slower rates are found.

In the case of **4**, the semilogarithmic plot of ln([M]$_o$/[M]) *vs.* time was non-linear: M_n did not increase linearly over time and did not agree with theoretical molecular weights. ($M_{n,th}$ = 16800, M_n = 4700 and M_w/M_n = 1.79). Such behaviour is reminiscent of α-diimine derivatives bearing aryl substituents and has been shown to be attributable to competitive chain transfer processes.[15]

The trichloride analogue of **6**, complex **7**, was synthesised by an analogous procedure to that shown in Scheme 1, except iron trichloride was employed. The product was washed with diethyl ether to afford **7** as a microcrystalline, paramagnetic solid in 84% yield. Both solid-state and solution studies indicate that this complex exists as a mononuclear species.[21] **7** was tested for the reverse ATRP of styrene (200 equiv., bulk) initiated by azobisisobutyronitrile (AIBN) at 110 °C. The semilogarithmic plot of ln([M]$_o$/[M]) *vs.* time is linear with a k_{obs} of 0.19 h^{-1} indicating a constant radical concentration throughout the polymerisation. The molecular weight (M_n) increases linearly with time and agrees with calculated molecular weights (Fig. 7). The polydispersities (M_w/M_n) are slightly higher than those obtained using **6**, a common feature of reverse ATRP polymerisations.[22]

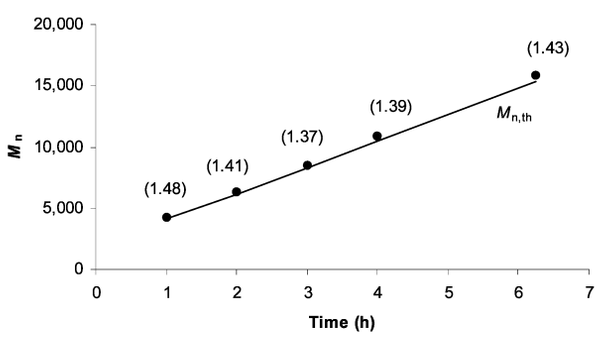


Fig. 7 Plot of molecular weight with M_w/M_n in parentheses *vs.* time for **7** ([**7**]$_0$ = 5.0×10^{-4} M, [AIBN]$_0$ = 3.125×10^{-4} M, [St]$_0$ = 0.1 M).

(iii) Methyl methacrylate (MMA) polymerisation. Complexes **1**–**6** were tested as catalysts for the ATRP of MMA under various conditions using a range of different initiators. However, all of these complexes, with the exception of mononuclear **6**, were found to be ineffective catalysts for MMA. For **6**, promising polymerisation results were obtained using sulfonylhalide (tosyl chloride), α-bromoester (ethyl 2-bromoisobutyrate) or phenylacetate (methyl-α-bromophenylacetate) initiators. The results are summarised in Table 2 which shows fairly good agreement between M_n(obs) and $M_{n,th}$ though molecular weight distributions are quite broad. The tacticity of

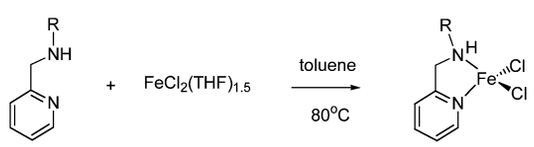
Table 3 Redox potentials ($E_{1/2}$) and peak separation (ΔE_p) for **1**–**9**

	$E_{1/2}$/mV	ΔE_p/mV
1	1200	190
2	1100	180
3	1100	190
4	840	240
5	1100	190
6	1100	100
7	−10	140
8	1100	130
9	890	230

Ferrocene/ferrocenium couple $E_{1/2}$ = 450 mV and ΔE_p = 110 mV.

the resultant PMMA was found to be consistent with the syndio-rich atactic form (mm : rm : rr *ca.* 3 : 33 : 64) which is typical of PMMA synthesised using conventional radical polymerisation methods.[23]

(iv) Aminopyridine complexes. It has been shown that saturated nitrogen donor ligands can improve the control and efficiency in copper ATRP systems due to their increased reducing power.[24] Thus, the study was extended to include saturated aminopyridine analogues. These complexes were synthesised using analogous procedures to those described for their iminopyridine counterparts (Scheme 2). Solution molecular weight determinations on the cyclohexyl and 2,6-diisopropylphenyl derivatives **8** and **9** are consistent with aggregated structures[25] possibly related to their iminopyridine analogues. Attempts to grow crystals of these complexes were unsuccessful.



Scheme 2 Synthesis of complexes **8** and **9** where R = *c*-C_6H_{11}, **8** and R = 2,6 diisopropylphenyl, **9**.

Styrene polymerisations using **8** and **9** were performed under similar conditions to their iminopyridine analogues. **8** behaved similarly to its unsaturated counterpart, **2**, although the polymerisation was significantly faster (*cf.* k_{obs}(**8**) = 0.16 h^{-1}; k_{obs}(**2**) = 0.08 h^{-1}) and some loss of control was observed. (*cf.* **8**; M_w/M_n = 1.52; **2**; M_w/M_n = 1.41) Polymerisations using **9**, as for the unsaturated aryl derivative **4**, were found to be uncontrolled and non-living in character ($M_{n,th}$ = 16400, M_n = 5000 and M_w/M_n = 1.72).

(v) Cyclic voltammetry. In order to obtain a better understanding of the differing behaviour of these complexes as ATRP catalysts, the redox potentials ($E_{1/2}$) and reversibility (ΔE_p) of **1**–**9** (Table 3) were probed using cyclic voltammetry (CV). Although CV measurements are not performed under conditions that mimic precisely the conditions of the ATRP experiments, they can provide an indication of the efficiency of ATRP catalysis and, in certain cases, the propensity for chain transfer. A typical trace, for complex **6**, is shown in Fig. 8. The main feature, at *ca.* 1.1 V, is attributed to the reversible Fe(II)/Fe(III) couple relevant to ATRP catalysis; a second weaker feature at *ca.* −1.0 V is assigned to an irreversible Fe(I)/Fe(II) couple.

All of the divalent alkylimine complexes **1**, **2**, **3**, **6**, **7** and **9** possess surprisingly high $E_{1/2}$ values (typically *ca.* 1000 mV) compared to their α-diimine relatives where $E_{1/2}$ values lie in the range −20 to −130 mV.[14b] This is unexpected given the lower π-acceptor capacity of iminopyridine ligands[26] and may indicate more complex solution behaviour than revealed by

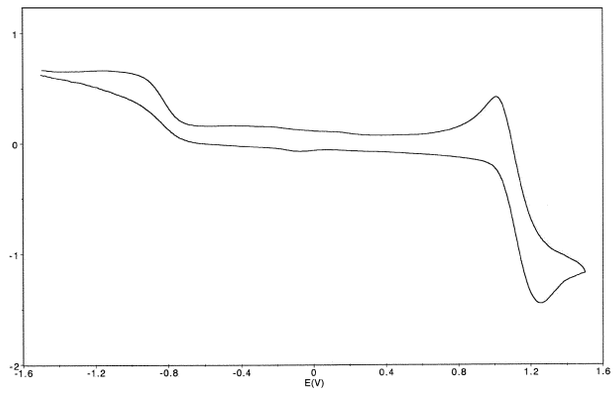


Fig. 8 Cyclic voltammetry trace for **6**: start potential: −1500 mV, end potential: −1500 mV, sweep rate: 250 mV s^{-1}.

other characterisation techniques. For example, it is possible that one arm of the bidentate donor could dissociate in solution and, under those circumstances, a direct comparison of α-diimines and iminopyridines may not be valid. Alternatively, acetonitrile, the solvent in which the CV measurements are conducted, may bind to the iron centres substantially altering the coordination geometry. We were surprised that complexes with such high $E_{1/2}$ values could function so efficiently as ATRP catalysts, possibly indicating that their catalytic behaviour is driven by exceptionally high halogenophilicities.

As for their α-dimine analogues, ΔE_p values seem to provide a useful indicator of catalytic performance. For the dinuclear alkylimino complexes **1**, **2**, **3** and **5**, ΔE_p is *ca.* 180–190 mV while for the arylimino derivative **4** this value is raised to 240 mV. The higher ΔE_p for the latter, as for its related diimine relatives, appears to correlate with chain transfer behaviour.[14b,15] It is only for the mononuclear complex **6** that ΔE_p, at 100 mV, is low and comparable to its α-diimine analogues, and where the best control is found. For the pyridylamino complexes **8** and **9**, high $E_{1/2}$ values are again observed, and a similar difference in ΔE_p values are seen for the alkyl *vs.* aryl derivatives (130 mV for **8** *vs.* 230 mV for **9**). Consistently, the alkyl derivative, **8**, affords reasonably well-behaved ATRP, while the aryl catalyst, **9**, gives rise to chain transfer.

Conclusion

A series of iron(II) complexes containing iminopyridine and aminopyridine ligands has been synthesised and evaluated in atom transfer radical polymerisation. These ligands, even for relatively bulky N-substituents, are generally found to stabilise binuclear species in solution and the solid state and, as a consequence, are found to be relatively slow ATRP catalysts. It proved possible to isolate a mononuclear derivative by employing a bulky imine substituent along with an α-methyl substituent on the pyridyl ring, and here relatively fast and well controlled polymerisations of styrene and MMA are observed. Expectedly, the trichloride analogue of **6** (complex **7**) was found to be an effective reverse ATRP catalyst. A notable feature of these systems, which is also found in their α-diimine relatives, is the differing ATRP behaviour of catalysts bearing alkyl *vs.* aryl substituents. The former, with their relatively low ΔE_p values, facilitate well-controlled ATRP, while the latter, with higher ΔE_p values, favour chain transfer. Overall, these iminopyridine complexes appear to be better suited to the ATRP of styrene rather than MMA.

Experimental

General considerations

All manipulations were carried out under a nitrogen atmosphere using Schlenk vacuum-line techniques and glove boxes.

All starting materials and initiators were purchased from Aldrich Chemical Co and used as supplied without further purification unless otherwise stated. All reaction solvents were dried by prolonged reflux over appropriate drying agents and were degassed immediately prior to use. Styrene (>98%) was purified by vacuum distillation and then stored in an inert atmosphere over molecular sieves at −15 °C. MMA was stirred over CaH_2 for 24 h and then freshly distilled before use. 1-Phenylethylchloride, 1-PECl was prepared according to a literature preparation and purified by column chromatography.[27] AIBN was recrystallised twice from diethyl ether and stored at −30 °C. $FeCl_2(THF)_{1.5}$ was synthesised as described in the literature.[28] The ligands used to synthesise **1** and **4** were prepared as described in the literature.[12b,29]

Characterisation

NMR spectra were recorded on a Bruker AC 250 MHz instrument. Chemical shifts are reported as δ (in ppm) and referenced to residual proton impurity present in the NMR solvent. Magnetic moments were determined using the Evans NMR method in dichloromethane spiked with cyclohexane.[30] Mass spectra were recorded on a Micromass GC 8000 Autospec mass spectrometer. IR spectra were recorded on a Perkin-Elmer 1710 FTIR instrument using NaCl plates. Microanalyses (C, H and N) were carried out by Dr S. Boyer at London Metropolitan University, London. Halide microanalyses was performed by Dr G. A. Maxwell at University College London. GPC chromatograms were recorded on a Knauer differential refractometer connected to a Gynotek HPLC pump (model 300) and two 10 μm columns (PSS) at a flow rate of 1.00 cm^3 min^{-1} using $CHCl_3$ as the eluent. The columns were calibrated against polystyrene standards with molecular weights ranging from 1560 to 128000 and polymethylmethacrylate standards ranging from 2400 to 174000. Analysis was performed using Version 3.0 of the Conventional Calibration module of the Viscotek SEC^3 software package. Cyclic voltammetry (CV) was performed using a MacLab potentiostat operated by EChem 1.3.2. software. The working electrode and reference electrode were purchased from Bioanalytical (ref: MF-2013 and RE-5B) Solution molecular weights were determined by melting point depression of bromoform[31] by means of a TC Ltd platinum resistance thermometer mounted coaxially in a vacuum jacketed cell containing a solution of approximately 0.02 M concentration and cooled in an ice-bath. The thermometer was connected to an Autotherm II instrument interfaced to an PC-486 running the Mettler Toledo Balance Link software programme (Version 3.01). Cooling curves were collected over 45 minutes and temperature was sampled every 30 s.

Preparations

Dichloro(*N*-propylimino-2-pyridyl)iron(II), 1. To a stirred suspension of $FeCl_2$ (2.54 g, 0.02 mol) in tetrahydrofuran (20 ml) at 60 °C was added dropwise a solution of *N*-propylimino-2-pyridine[12b] (3.11 g, 0.021 mol) in tetrahydrofuran (15 ml). This suspension was stirred overnight at 60 °C and then allowed to cool and filtered. The residue was washed with tetrahydrofuran (3 × 10 ml). The purple microcrystalline solid, **1**, was dried overnight in *vacuo*. Yield 4.67 g, 85%. Found: C, 39.5; H, 4.4; N, 10.1; Cl, 25.2. $C_9H_{12}N_2FeCl_2$ requires C, 39.3; H, 4.4; N. 10.2; Cl, 25.8%; λ_{max}/cm^{-1} (C=N) 1671s; MS (+FAB) (*m*/*z*): $[2(LFeCl_2) - Cl]^+$ = 513, $[2LFeCl_2]^+$ = 387, $[2LFe]^+$ = 352, $[LFeCl]^+$ = 239. μ_{eff} = 3.24 μ_B.

***N*-Cyclohexylimino-2-pyridine.** *N*-Cyclohexylimino-2-pyridine[29] was prepared by a modification of a literature method.[12b] To a stirred solution of 2-pyridinecarbaldehyde (10.71 g, 0.1 mol) in 30 ml diethyl ether at 0 °C was added cyclohexylamine (13.86 g, 0.14 mol) dropwise. The solution was stirred at room temperature for 15 min prior to the addition of a large excess of $MgSO_4$ (5 g). The suspension was stirred for 2 h and then filtered. The $MgSO_4$ was thoroughly washed with diethyl ether and then the filtrate was reduced in volume to yield a pale yellow oil. This was purified by vacuum distillation at 130 °C and 5 mmHg to produce a yellow oil. Yield 17.32 g, 92%. Found: C, 76.7; H, 8.6; N, 15.0. $C_{12}H_{16}N_2$ requires C, 76.6; H, 8.6; N. 14.9%; IR/cm^{-1}: 1648s, ν(C=N); δ_H ($CDCl_3$) 8.41 (1H, s, CH), 8.20 (1H, s, N=CH), 7.77 (1H, d, *J*(HH) 4 Hz, CH), 7.47 (1H, t, *J*(HH) 8 Hz, CH), 7.04 (1H, m, CH), 3.07 (1H, q, *J*(HH) 4 Hz, CH), 1.59 (4H, m, $2CH_2$), 1.42 (6H, m, $3CH_2$); δ_C ($CDCl_3$) 159.3 (1C, s, N=CH), 154.8 (1C, s, C), 149.1 (1C, s, CH), 136.3 (1C, s, CH), 124.2 (1C, s, CH), 121.1 (1C, s, CH), 69.4 (1C, s, CH), 34.0 (4C, s, $4CH_2$), 25.4 (4C, s, $4CH_2$), 24.5 (1C, s, CH_2); MS (+CI) (*m*/*z*): 189 $[M + H]^+$

Dichloro(*N*-cyclohexylimino-2-pyridyl)iron(II), 2. The same procedure was employed as for **1**. After drying a purple microcrystalline solid, **2**, was isolated. Yield 5.42 g, 86%. Found: C, 45.7; H, 5.1; N, 8.9; Cl, 23.4. $C_{12}H_{16}N_2FeCl_2$ requires C, 45.8; H, 5.1; N. 8.9; Cl, 22.5%; IR/cm^{-1}: 1594m, ν(C=N); MS (+FAB) (*m*/*z*): $[2LFeCl]^+$ = 467, $[LFeCl_2]^+$ = 314. μ_{eff} = 3.19 μ_B.

***N*-Cyclododecylimino-2-pyridine.** *N*-Cyclododecylimino-2-pyridine was prepared as described for *N*-cyclohexylimino-2-pyridine. On reduction of the filtrate a pale yellow solid resulted. This was purified by recrystallisation from ethanol to produce a pale yellow solid. Yield 24.78 g, 91%. Found: C, 79.6; H, 10.4; N, 10.1. $C_{18}H_{28}N_2$ requires C, 79.4; H, 10.4; N. 10.3%; IR/cm^{-1}: 1646s, ν(C=N); δ_H ($CDCl_3$) 8.62 (1H, d, *J*(HH) 5 Hz, CH), 8.37 (1C, s, N=CH), 7.70 (1H, t, *J*(HH) 6 Hz, CH), 7.28 (1H, m, CH), 3.47 (1H, s, CH), 1.84 (4H, m, $2CH_2$), 1.39 (18H, m, $9CH_2$); δ_C ($CDCl_3$) 159.9 (1C, s, N=CH), 154.9 (1C, s, C), 149.3 (1C, s, CH), 136.5 (1C, s, CH), 124.5 (1C, s, CH), 121.3 (1C, s, CH), 66.8 (1C, s, CH), 31.2 (2C, s, $2CH_2$), 24.3 (1C, s, CH_3), 23.6 (8C, m, CH_2), 21.6 (1C, s, CH_2); MS (+CI) (*m*/*z*): 273 $[M + H]^+$

Dichloro(*N*-cyclododecylimino-2-pyridyl)iron(II), 3. The same complexation procedure was employed as for **1**. After drying **3** was isolated as a pale pink microcrystalline solid. Yield 7.10 g, 89%. Found: C, 39.5; H, 4.4; N, 10.1; Cl, 17.8. $C_{18}H_{28}N_2FeCl_2$ requires C, 39.3; H, 4.4; N. 10.2; Cl, 17.8%; IR/cm^{-1}: 1594m, ν(C=N); MS (+FAB) (*m*/*z*): $[2LFeCl]^+$ = 635, $[LFeCl]^+$ = 363. μ_{eff} = 3.25 μ_B.

Dichloro(*N*-2,6-diisopropylphenylimino-2-pyridyl)iron(II), 4. The same procedure was employed as for **1**. After drying a purple microcrystalline solid **4** was isolated. Yield 6.45 g, 82%. Found: C, 55.0; H, 5.6; N, 7.1; Cl 16.3. $C_{18}H_{22}N_2FeCl_2$ requires C, 55.0; H, 5.6; N. 7.1; Cl 18.0%; IR/cm^{-1}: 1560m, ν(C=N); MS (+FAB) (*m*/*z*): $[2LFeCl]^+$ = 623, $[LFeCl]^+$ = 357. μ_{eff} = 3.50 μ_B.

2-(*N*-Propylimino)-6-methylpyridine. To a stirred solution of 6-methyl-2-pyridinecarbaldehyde (4.5 g, 0.037 mol) in 30 ml diethyl ether was added *n*-propylamine (2.25 g, 0.038 mol) dropwise. The solution was stirred at room temperature for 10 min prior to the addition of a large excess of $MgSO_4$ (10 g). The suspension was stirred for 2 h and then filtered. The $MgSO_4$ was thoroughly washed with diethyl ether and then the filtrate was reduced in volume to yield a pale yellow oil. This was purified by vacuum distillation at 110 °C and 5 mmHg to produce a yellow oil. Yield 5.52 g, 92%. Found: C, 74.6; H, 8.7; N, 17.6. $C_{10}H_{14}N_2$ requires C, 74.0; H, 8.7; N. 17.3%; IR/cm^{-1}: 1650s, ν(C=N); δ_H ($CDCl_3$) 8.15 (1H, s, N=CH), 7.39 (1H, t, *J*(HH) 8 Hz, CH), 7.59 (1H, d, *J*(HH) 8 Hz, CH), 6.93 (1H, d, *J*(HH) 8 Hz, CH), 3.40 (2H, t, *J*(HH) 7 Hz, CH_2), 2.37 (3H, s, CH_3), 1.54 (2H, st, *J*(HH) 7 Hz, CH_2), 0.75 (3H, t, *J*(HH) 7 Hz, CH_3) δ_C ($CDCl_3$) 161.8 (1C, s, N=CH), 157.8 (1C, s, C), 153.9 (1C, s, $C(CH_3)$), 136.4 (1C, s, CH), 124.0 (1C, s, CH), 118.0 (1C, s,

CH), 63.1 (1C, s, CH_2), 24.1 (1C, s, $C(CH_3)$), 23.7 (1C, s, CH_2), 11.67 (1C, s, CH_3); MS (+CI) (*m*/*z*): 163 $[M + H]^+$

Dichloro[2-(*N*-propylimino)-6-methylpyridyl]iron(II), 5. A similar procedure was employed as for **1**. After drying a **5** was isolated as a red microcrystalline solid. Yield 4.97 g, 86%. Found: C, 41.4; H, 4.8; N, 9.7; Cl 25.9. $C_{10}H_{14}N_2FeCl_2$ requires C, 41.6; H, 4.9; N, 9.7; Cl 24.5%; IR/cm^{-1}: 1591m, *ν*(C=N); MS (+FAB) (*m*/*z*): $[2LFeCl]^+$ = 415, $[LFeCl_2]^+$ = 288, $[LFeCl]^+$ = 253. μ_{eff} = 3.39 μ_B.

2-(*N*-Cyclododecylimino)-6-methylpyridine. 2-(*N*-Cyclododecylimino)-6-methylpyridine was prepared as described for 2-(*N*-propylimino)-6-methylpyridine. On reduction of the filtrate a yellow solid resulted. This was purified by recrystallisation from diethyl ether to produce a pale yellow solid. Yield 10.17 g, 96%. Found: C, 79.6; H, 10.5; N, 9.8. $C_{19}H_{30}N_2$ requires C, 79.7; H, 10.6; N. 9.8%; IR/cm^{-1}: 1646m, *ν*(C=N); δ_H ($CDCl_3$) 8.34 (1H, s, N=CH), 7.79 (1H, d, *J*(HH) 8 Hz, CH), 7.57 (1H, t, *J*(HH) 8 Hz, CH), 7.12 (1H, d, *J*(HH) 8 Hz, CH) 3.45 (1H, m, CH), 2.55 (3H, s, CH_3), 1.82 (4H, m, $2CH_2$), 1.36 (18H, br m, *c*-$C_{11}H_{22}$); δ_C ($CDCl_3$) 160.3 (1C, s, N=CH), 157.9 (1C, s, C), 154.3 (1C, s, $C(CH_3)$), 136.7 (1C, s, CH), 124.1 (1C, s, CH), 118.1 (1C, s, CH), 66.7 (1C, s, CH), 31.2 (2C, s, $2CH_2$), 24.3 (1C, s, CH_3), 23.4 (8C, m, CH_2), 21.6 (1C, s, CH_2); MS (+CI) (*m*/*z*): 287 $[M + H]^+$

[2-(*N*-Cyclododecylimino)-6-methylpyridyl]dichloroiron(II), 6. A similar procedure was employed as for **1**. After drying **6** was obtained as a bright pink microcrystalline solid. Yield 7.11 g, 86%. Found: C, 55.2; H, 7.3; N, 6.7; Cl 17.2. for $C_{19}H_{30}N_2FeCl_2$ requires C, 55.2; H, 7.3; N. 6.8; Cl 17.2%; IR/cm^{-1}: 1595m, *ν*(C=N); MS (−CI) (*m*/*z*): $[LFeCl_2]^-$ = 412, $[LFeCl]^-$ = 377. μ_{eff} = 5.07 μ_B.

Trichloro(*N*-cyclododecylimino-2-pyridyl)iron(III), 7. To a stirred suspension of $FeCl_3$ (2.54 g. 0.02 mol) in tetrahydrofuran (20 ml) was added dropwise a solution of *N*-cyclohexylimino-2-pyridine (6.02 g, 0.021 mol) in tetrahydofuran (15 ml). This suspension was heated to 60 °C, stirred overnight and then filtered. The residue was washed with diethyl ether (3 × 10 ml). Complex **7** was isolated as a orange–yellow microcrystalline solid and was dried overnight in *vacuo*. Yield 7.53 g, 84%. Found: C, 49.9; H, 6.6; N, 6.3; Cl 23.9. for $C_{19}H_{30}N_2FeCl_3$ requires C, 50.8; H, 6.7; N. 6.3; Cl 23.7%; IR/cm^{-1}: 1596w, *ν*(C=N); MS (−CI) (*m*/*z*): $[LFeCl_2]^-$ = 412. μ_{eff} = 4.69 μ_B.

***N*-Cyclohexylamino-2-pyridine.** *N*-Cyclohexylamino-2-pyridine was prepared by reduction of *N*-cyclohexylamino-2-pyridine. To a stirred solution of *N*-cyclohexylamino-2-pyridine (8.0 g, 0.04 mol) in methanol (30 ml) was added excess $NaBH_4$ (6.47 g, 0.17 mol). The reaction was stirred overnight, and then water was added to remove any excess $NaBH_4$. The product was extracted into dichloromethane and washed with water and dried over Na_2SO_4. The solvent was removed to afford a white solid. Yield 6.77 g, 89%. Found: C, 75.1; H, 9.3; N, 14.1. $C_{12}H_{18}N_2$ requires C, 75.7; H, 9.5; N. 14.7%; IR/cm^{-1} 3302w *ν*(NH); δ_H ($CDCl_3$) 8.34 (1H, d, *J*(HH) 4 Hz, CH), 7.42 (1H, t, *J*(HH) 5 Hz, CH), 7.11 (1H, d, *J*(HH) 4 Hz, CH), 6.93 (1H, t, *J*(HH) 5 Hz, CH), 3.74 (2H, s, CH_2), 2.44 (1H, br s, NH), 2.30 (1H, q, *J*(HH) 5 Hz, CH), 1.54 (4H, m, $2CH_2$), 1.37 (6H, m, $3CH_2$); δ_C ($CDCl_3$) 159.9 (1C, s, C), 149.0 (1C, s, CH), 136.3 (1C, s, CH), 122.2 (1C, s, CH), 121.7 (1C, s, CH), 56.4 (1C, s, CH_2), 52.1 (1C, s, CH_2), 33.3 (4C, s, $4CH_2$), 26.0 (4C, s, $4CH_2$), 24.8 (1C, s, CH_2); MS (+CI) (*m*/*z*): 381 $[2M + H]^+$, 191 $[M + H]^+$

Dichloro(*N*-cyclohexylamino-2-pyridyl)iron(II), 8. To a stirred suspension of $FeCl_2(THF)_{1.5}$ (2.35 g. 0.01 mol) in toluene (20 ml) at 80 °C was added dropwise a solution of *N*-cyclohexylamino-2-pyridine (2.10 g, 0.011 mol) in toluene (15 ml). This suspension was stirred overnight at 80 °C and then allowed to cool and then filtered. The residue was washed with toluene (3 × 10 ml). The pale yellow microcrystalline solid **8** was dried overnight in *vacuo*. Yield 2.35 g, 74%. Found: C, 45.9; H, 5.6; N, 8.6; Cl 24.3. for $C_{12}H_{18}N_2FeCl_2$ requires C, 45.5; H, 5.7; N. 8.8; Cl 22.4%; IR/cm^{-1} 2941w *ν*(NH); MS (+FAB) (m/z): **7**: $[2LFeCl_2]^+$ = 507, $[LFeCl_2]^+$ = 316, $[LFeCl]^+$ = 281. μ_{eff} = 3.01 μ_B.

***N*-2,6-Diisopropylphenylamino-2-pyridine.** *N*-2,6-Diisopropylphenylamino-2-pyridine was prepared as described for *N*-cyclohexylamino-2-pyridine. On reduction of the filtrate a white solid resulted. Yield 9.77 g, 91%. Found: C, 80.5; H, 9.1; N, 10.3. $C_{18}H_{24}N_2$ requires C, 80.5; H, 9.0; N. 10.4%; IR/cm^{-1} 3358w *ν*(NH); δ_H ($CDCl_3$) 8.64 (1H, d, *J*(HH) 6 Hz, CH), 7.66 (1H, d of t, *J*(HH) 6 and 2 Hz, CH), 7.32 (1C, d, *J*(HH) 7 Hz, CH), 7.21 (1C, d of t, *J*(HH) 6 and 2 Hz, CH), 7.12 (3H, m, 3CH), 4.21 (2H, s, CH_2), 4.09 (1H, br s, NH), 3.39 (2H, sp, *J*(HH) 7 Hz, 2CH), 1.26 (12H, d, *J*(HH) 7 Hz, $4CH_3$); δ_C ($CDCl_3$) 159.0 (1C, s, C), 149.4 (1C, s, CH), 143.1 (1C, s, C), 142.7 (1C, s, C), 136.5 (1C, s, CH), 123.9 (2H, s, 2CH), 123.6 (1H, s, CH), 122.2 (1C, s, CH), 122.0 (1C, s, CH), 56.8 (1C, s, CH_2), 27.7 (2C, s, CH), 24.3 (4C, s, $4CH_3$); MS (+CI) (*m*/*z*): 268 $[M + H]^+$

Dichloro(*N*-2,6-diisopropylphenylamino-2-pyridyl)iron(II), 9. The same complexation procedure was employed as for **8**. After drying an off-white microcrystalline solid **9** was isolated. Yield 2.85 g, 72%. Found: C, 54.6; H, 6.2; N, 7.0; Cl 17.9. for $C_{18}H_{24}N_2FeCl_2$ requires C, 54.7; H, 6.1; N. 7.1; Cl 17.9%; MS (+FAB) (*m*/*z*): $[2LFeCl]^+$ = 627, $[LFeCl_2]^+$ = 394. μ_{eff} = 3.19 μ_B.

Polymerisation procedure

Normal ATRP reactions were performed under nitrogen, in a 15 cm^3 glass ampoule fitted with a Teflon stopcock. The ampoule was equipped with a magnetic stirrer bar and the following were placed in it in the order, monomer, initiator solvent and catalyst. The ampoules were transferred to a preheated oil bath, at 120 °C (St) and 80 °C (MMA). After magnetic stirring for the allotted period of time an aliquot (0.1 ml) was removed and quenched by addition of THF (1 ml). Conversion was determined by integration of monomer *vs.* polymer backbone resonances in the ^1H NMR spectrum of the crude product (in $CDCl_3$). The polymer was purified by precipitating from a rapidly stirred acidified (5%) methanol solution. For reverse ATRP experiments all conditions were identical with the exception that the polymerisation temperature was 110 °C.

Cyclic voltammetry

CV analyses were performed in acetonitrile (10 cm^3), under a nitrogen atmosphere, using a platinum (0.05 mm wire) counter and working electrode and a Ag/AgCl reference electrode with $[^nBu_4N][PF_6]$ (0.1 M) as a supporting electrolyte. The ferrocene(II)/(III) couple ($E_{1/2}$ = 450 mV and ΔE_p = 110 mV) was used as a benchmarked redox couple. In all cases, the reversibility was confirmed by altering the scan rate. This resulted in no changes to the aniodic or cathodic peak positions.

Crystallography

Crystal data for 4. $C_{36}H_{44}N_4Cl_4Fe_2$, *M* = 786.3, monoclinic, $P2_1/n$ (no. 14), *a* = 9.805(2), *b* = 14.496(2), *c* = 14.204(2) Å, β = 107.35(2)°, *V* = 1927.0(6) $Å^3$, *Z* = 2 (C_i symmetry), D_c = 1.355 g cm^{-3}, μ(Mo-Kα) = 1.06 mm^{-1}, *T* = 203 K, red–brown blocks; 3157 independent measured reflections, F^2 refinement, R_1 = 0.041, wR_2 = 0.093, 2448 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 50°$], 208 parameters.

Crystal data for 5. $C_{20}H_{28}N_4Cl_4Fe_2$, M = 578.0, triclinic, $P\bar{1}$ (no. 2), a = 7.943(1), b = 8.337(1), c = 10.505(1) Å, α = 107.01(1), β = 108.41(1), γ = 97.02(1)°, V = 613.3(1) Å^3, Z = 1 (C_i symmetry), D_c = 1.565 g cm^{-3}, μ(Mo-Kα) = 1.63 mm^{-1}, T = 293 K, orange–red blocks; 2116 independent measured reflections, F^2 refinement, R_1 = 0.035, wR_2 = 0.071, 1653 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 50°$], 145 parameters.

Crystal data for 6. $C_{19}H_{30}N_2Cl_2Fe$, M = 413.2, orthorhombic, *Pbca* (no. 61), a = 8.177(1), b = 13.524(2), c = 37.608(6) Å, V = 4159(1) Å^3, Z = 8, D_c = 1.320 g cm^{-3}, μ(Mo-Kα) = 0.99 mm^{-1}, T = 203 K, orange platy blocks; 3401 independent measured reflections, F^2 refinement, R_1 = 0.052, wR_2 = 0.093, 1886 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 50°$], 218 parameters.

CCDC reference numbers 206397–206399.

See http://www.rsc.org/suppdata/dt/b3/b303094f/ for crystallographic data in CIF or other electronic format.

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