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Four-coordinate iron complexes bearing α-diimine ligands: efficient catalysts for Atom Transfer Radical Polymerisation (ATRP)

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Four-coordinate iron(II) complexes bearing α-diimine ligands with alkyl substituents are shown to be efficient catalysts for the well-controlled atom transfer radical polymerisation of styrene; catalysts containing aryldiimine ligands support competitive β-hydrogen chain transfer processes.

One of the most significant advances in controlled polymerisation over the past few years has been the development of transition metal based catalysts for atom transfer radical polymerisation (ATRP).[1] Following the key observation by Wang and Matyjaszewski[2] that copper(I) complexes bearing bipyridine ligands afford highly efficient ATRP catalysts, a number of different metal ligand combinations have been investigated, including systems based on Ru,[3] Rh,[4] Pd,[5] Ni[6] and Fe.[7]

We have been studying the use of unsaturated nitrogen ligands for iron-based ethylene polymerisation catalysts,[8] and became interested in iron-mediated ATRP. Iron is particularly attractive for this purpose due to its low cost and low toxicity. Göbelt and Matyjaszewski have reported the use of five-coordinate bis(imino)pyridine iron complexes for the polymerisation of methylmethacrylate (MMA), though styrene is not polymerised by this system.[7e] We considered that the activity of the system may be raised by moving to a 4⇔5 coordination manifold. Here we report a family of four-coordinate iron ATRP catalysts based on the readily accessible and derivatisable α-diimine ligand frame, and the observation that alkylimino substituents favour well-controlled ATRP of styrene while arylimino substituents give rise to competitive β-hydrogen chain transfer processes.

The series of $FeCl_2[N,N]$ complexes (where $[N,N]$ = $[RN{=}CH{-}CH{=}NR]$ and R = *tert*-butyl, cyclohexyl, mesityl or 2,6-diisopropylphenyl) was readily prepared according to Scheme 1. Stirring a solution of $FeCl_2$ and $[N,N]$ in diethyl ether at room temperature followed by extraction into dichloromethane gave **1–4** as microcrystalline, air stable solids in excellent yields. Crystals of **2** suitable for an X-ray structure determination were grown from hot benzene and the structure is shown in Fig. 1.† The molecule has crystallographic C_2 symmetry about an axis passing through the metal centre and the middle of the C(1)–C(1′) bond. The geometry at iron is distorted tetrahedral with inter-bond angles in the range 78.0(2)–120.1(1)°, the acute angle being associated with the bite of the *N,N′*-chelate ligand. There is a small torsional twist of *ca.* 3° from orthogonal about the C_2 axis of the $FeCl_2$ plane with respect to that of FeN_2. The C(2)–H bond is rotated with respect to its C(2′)–H counterpart, about the molecular C(2)···C(2′) axis, by 45°. The bonding within the essentially planar (to within 0.005 Å) five-membered chelate ring exhibits a very distinct pattern of bond ordering with the C=N linkages being very short at 1.239(6) Å and the C–C bond long [1.495(9) Å] showing there to be no noticeable bond delocalisation. The bond lengths observed here, including those to the metal centre, do not differ significantly from those in the related diiodo(*N,N′*-diisopropyl-1,4-diaza-1,3-butadiene)iron(II) complex.[9] This pattern contrasts with the substantially delocalised bonding present in the formally iron(0) species (η^6-toluene)(*N,N′*-bis(cyclohexyl)ethylenediimine)iron(0).[10] There are no intermolecular packing interactions of note.

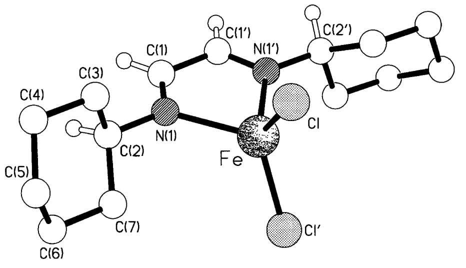
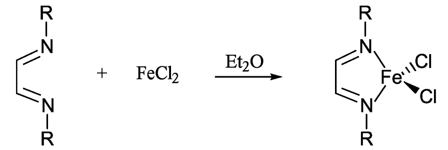


Fig. 1 The molecular structure of **2**. Selected bond lengths (Å) and angles (°); Fe–Cl 2.231(2), Fe–N(1) 2.125(4), C(1)–N(1) 1.239(6), C(1)–C(1′) 1.495(9); Cl–Fe–N(1) 111.13(11), Cl–Fe–N(1′) 114.57(10), Cl–Fe–Cl′ 120.08(10), N(1)–Fe–N(1′) 78.0(2).



Scheme 1 Synthesis of complexes **1–4** where R = ${}^tBu$, **1**; C_6H_{11}, **2**; Mes, **3** and 2,6-dipp, **4**.

The homogenous ATRP of styrene (200 equiv., bulk) initiated with 1-phenylethyl chloride (1-PECl) and the alkyl substituted diimine complexes, **1** and **2**, was monitored at 120 °C under inert atmosphere.‡ The semilogarithmic plot of $\ln([M]_o/[M]_t)$ *vs.* time (Fig. 2) is linear in both cases with a pseudo-first order rate constant (k_{obs}) of 0.27 h^{-1} for **1** and 0.25 h^{-1} for **2** indicating that the radical concentration is constant throughout the polymerisation run. The molecular weight (M_n) increases linearly with time and agrees with calculated molecular weights, thus demonstrating good control. Polydispersities (M_w/M_n) are quite low (typically *ca.* 1.3) and decrease with monomer conversion (Fig. 3). ^1H NMR spectra

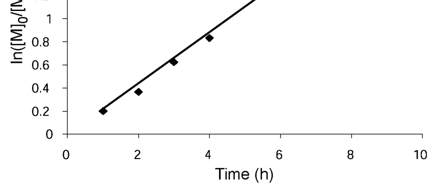


Fig. 2 First order kinetic plot of $\ln([M]_o/[M]_t)$ *versus* time for complex **2** ($[\mathbf{2}]_0$ = 5.0 × 10^{-4} mol, $[PECl]_0$ = 5.0 × 10^{-4} mol, $[St]_0$ = 0.1 mol).

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on the resultant polystyrene samples show the presence of the halide capping group (ClCH(Ph)CH$_2$, δ 4.5) which is also supported by halide microanalysis.§ Accordingly, the above results clearly indicate that polymerisations with complexes **1** and **2** exhibit characteristics of a well-controlled atom transfer radical polymerisation.

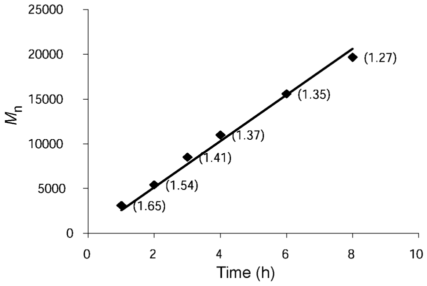

Fig. 3 Plot of molecular weight and PDIs (in parentheses) *versus* time for complex **2**.

The polymerisation of styrene using the aryl substituted diimine complexes **3** and **4** was monitored under similar conditions (120 °C, 200 equiv., bulk, 1-PECl initiator). In these cases the semilogarithmic plot of $\ln([M]_o/[M]_t)$ *vs.* time was non-linear: M_n did not increase linearly over time and did not agree with theoretical molecular weights. Monomer conversion, however, did increase in a semi-linear manner with time thus suggesting that a different polymerisation mechanism may be operating. Halide microanalyses on the resultant polymers showed no halide content and end group analyses (by NMR) showed vinyl end groups (δ 6.05–6.65). This is consistent with a β-hydrogen chain transfer process, most likely proceeding *via* an OSET mechanism[11] due to the enhanced oxidising power of the iron complexes bearing diimine ligands with aryl substituents.

In order to gain further insight into the differing catalyst behaviour, the redox potentials and reversibility of this series of iron complexes were analysed by cyclic voltammetry (CV).[12] The alkyl complexes **1** and **2** were found to have an accessible and reversible one-electron redox couple, ΔE_p(complex) 120 and 130 mV, respectively, which compare with a value of 130 mV for ferrocene. However the aryl complexes **3** and **4** were found to possess an irreversible redox couple [ΔE_p(complex) 210 and 270, respectively, Table 1] which accounts for their poor behaviour in atom transfer catalysis.

Table 1 Redox potentials ($E_{1/2}$) and peak separation (ΔE_p) for complexes **1–4**

Complex	$E_{1/2}$/mV	ΔE_p/mV
1	−40	120
2	−130	130
3	−80	210
4	−20	270

The complexes described here represent a small fraction of readily accessible α-diimine iron catalysts. Fine tuning of the complex sterics, electronics and solubility characteristics, as well as judicious choice of a compatible radical initiator would be expected to yield even more active and well-controlled polymerisation systems. Further studies are examining these features and their effect on the polymerisation of styrene and other monomers.

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Notes and references

† *Crystal data* for **2**: $C_{14}H_{24}N_2Cl_2Fe$, M = 347.1, monoclinic, $I2/a$ (no. 15), a = 13.028(3), b = 6.768(2), c = 20.069(5) Å, β = 101.50(1)°, V = 1734.0(8) Å^3, Z = 4 (C_2 symmetry), D_c = 1.330 g cm^{-3}, μ(Cu-Kα) = 9.71 mm^{-1}, T = 293 K, pink/magenta dichroic platy needles; 1186 independent measured reflections, F^2 refinement, R_1 = 0.052, wR_2 = 0.138, 981 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 120°$], 87 parameters. CCDC 186199. See http://www.rsc.org/suppdata/cc/b2/b204510a/ for crystallographic data in CIF or other electronic format.

‡ Polymerisations were performed under dinitrogen, 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 and catalyst in a 200:1:1 ratio. The ampoules were transferred to a preheated oil bath, at 120 °C. 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 ^{1}H NMR spectrum of the crude product (in CDCl$_3$). The polymer was purified by precipitating from a rapidly stirred acidified (5%) methanol solution. GPC chromatograms were recorded on a Knauer differential refractometer connected to a Gynotek HPLC pump (model 300) and two 10 m 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 128 000. Analysis was performed using Version 3.0 of the Conventional Calibration module of the Viscotek SEC^3 software package.

§ Microanalysis for polystyrene produced using **2**, M_n = 2,400; %Cl, found (calc.): 1.38 (1.47).

CV analyses were performed in MeCN, under dinitrogen, using a Pt counter and working electrode and a Ag/AgCl reference electrode with [^{n}Bu$_4$N][PF$_6$] as an electrolyte. Benchmarked redox couple with ferrocene(II)/(III) couple at $E_{1/2}$ = −150 mV and ΔE_p = 130 mV.

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