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Highly active ethylene polymerisation catalysts based on iron: an *ab initio* study

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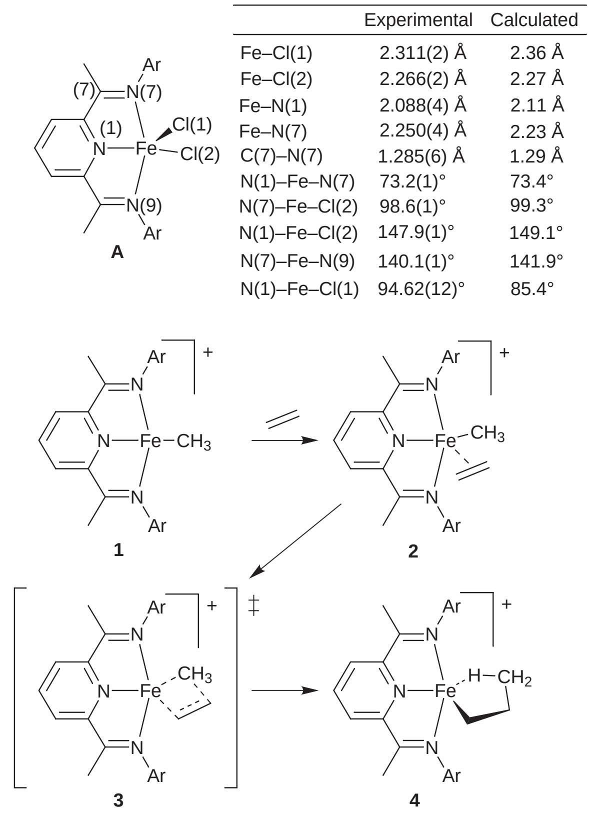
Full *ab initio* calculations are described on an iron-based ethylene polymerisation catalyst bearing a 2,6-bis(imino)-pyridyl ligand.

The development of non-metallocene olefin polymerisation catalysts constitutes a highly active area of academic and industrial research.[1] In particular, late transition metal polymerisation catalysts have become of interest since the discovery by Brookhart and co-workers that Ni^{II} and Pd^{II} complexes containing bulky α-diimine ligands are capable of polymerising ethylene and higher α-olefins to high molar mass polymers.[2] These systems have been the subject of several theoretical investigations.[3–5] In parallel studies, we and Brookhart and co-workers have recently reported highly active ethylene polymerisation catalysts based on iron and cobalt bearing 2,6-bis(imino)pyridyl ligands.[6,7] Here, we present the first theoretical studies on this catalyst system, having assumed the generally accepted Cossee–Arlman polymerisation mechanism.[8] The key features of the reaction pathway are shown in Scheme 1.

Optimisations† were initially performed on the bis(2,6-diisopropylphenylimino)pyridyliron dichloride complex **A** shown in Scheme 1. From the table presented in Scheme 1 it can be seen that the level of agreement between the gas-phase calculated bond parameters and the experimental data[6] is generally good. The results are also in accord with the experimental magnetic moment,[6] since quintet multiplicity (S = 2) was found to correspond to a minimum energy structure within the C_s point group. The optimised structures **1–4**, obtained for the first insertion step, are shown in Fig. 1; a potential energy profile is shown in Fig. 2.

For the methyl cation **1** (Fig. 1), the iron atom lies in the plane defined by the bis(imino)pyridine nitrogens (3N-plane) to within 0.04 Å. The four-coordinate geometry around the iron centre is thus best described as distorted square planar. The



	Experimental	Calculated
Fe–Cl(1)	2.311(2) Å	2.36 Å
Fe–Cl(2)	2.266(2) Å	2.27 Å
Fe–N(1)	2.088(4) Å	2.11 Å
Fe–N(7)	2.250(4) Å	2.23 Å
C(7)–N(7)	1.285(6) Å	1.29 Å
N(1)–Fe–N(7)	73.2(1)°	73.4°
N(7)–Fe–Cl(2)	98.6(1)°	99.3°
N(1)–Fe–Cl(2)	147.9(1)°	149.1°
N(7)–Fe–N(9)	140.1(1)°	141.9°
N(1)–Fe–Cl(1)	94.62(12)°	85.4°

Ar = 2,6-diisopropylphenyl

Scheme 1

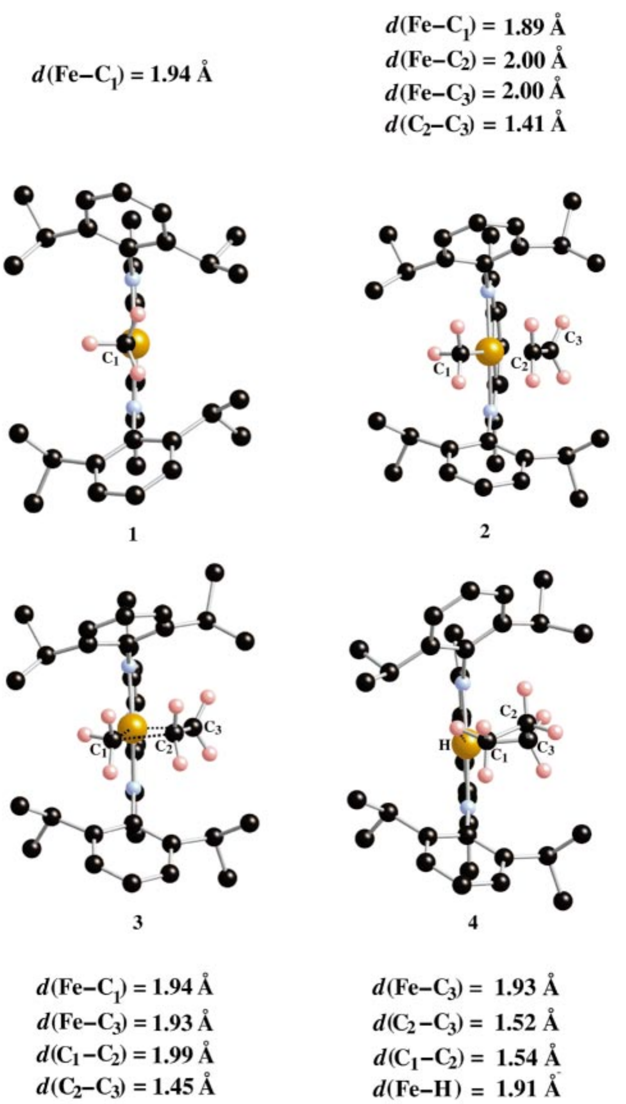


Fig. 1 The optimised structures of the reactant **1**, the ethylene π-complex **2**, the transition state **3**, and the γ-agostic product **4**. Selected atoms have been labelled. The pyridyl nitrogen is obscured by the iron atom.

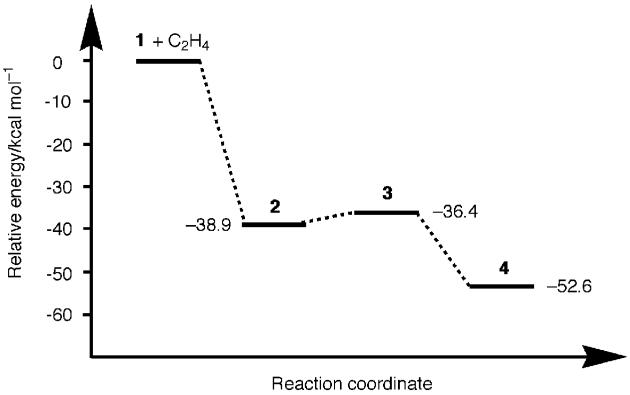


Fig. 2 Potential energy profile of ethylene insertion into the Fe–CH_3 bond of **1**.

distortion arises largely within the square plane due to the constrained nature of the ligand system, the N(imino)–Fe–N(imino) bond angle being 160.8°. Additionally, the methyl group (C_1) is bent out of the square plane by 6.4°. Compared to the dichloride (**A**), the Fe–N(imino) and Fe–N(pyridyl) distances have shortened considerably, presumably a consequence of the lower coordination number and the positively charged iron centre. The former now average 2.00 Å while the latter is 1.93 Å, the Fe–N(imino) distances vary by less than 0.01 Å in structures **1**–**4**; the Fe–C_1 distance is 1.94 Å. The 2,6-diisopropylphenyl rings have tilted relative to those in the dichloride by 9.1° and are now inclined at 70.3° to the 3N-plane.

In the structure of the ethylene π-complex **2** (Fig. 1), the methyl group has tilted further away from the 3N-plane to an inclination of 24.1° to accommodate the incoming ethylene. The geometry around the iron centre is now distorted trigonal bipyramidal with the N(pyridyl) atom, the methyl group and the complexed ethylene in the equatorial positions. The angle C_1–Fe-(midpoint of C_2–C_3) is 96.9°. The Fe–C_1 bond distance of 1.89 Å in the complex is shorter than in **1**; no rotation of the methyl group is observed. The iron atom lies at a distance of 2.00 Å to both olefinic carbons which are 1.41 Å apart. Additionally, the hydrogens of the ethylene are orientated away from the metal, consistent with partial re-hybridization of the carbon centres. The Fe–N(pyridyl) bond length shrinks slightly to 1.90 Å. In order to assist the approach of the olefin the 2,6-diisopropylphenyl rings have tilted through 18.6° away from the approach path of the incoming olefin. This tilting may protect the sterically less-hindered side of the metal centre from further coordination whilst insertion occurs. The binding energy of the ethylene is 38.9 kcal mol^{-1}.

In the transition state **3** (Fig. 1) the four centres involved, C_1–Fe–C_3–C_2, are nearly coplanar, the olefinic carbon C_2 lying only 0.08 Å above the C_1–Fe–C_3 plane. The methyl group is pulled back and is now inclined at 18.9° to the 3N-plane. Simultaneously the C_3 atom has moved from an equatorial to an apical site thus returning the geometry around the metal centre towards distorted square pyramidal with the basal site becoming vacant as the C_1–Fe bond is broken. The Fe–C_3 bond length shortens to 1.93 Å whilst the Fe–C_1 bond has elongated to 1.94 Å and the C_2–C_3 bond length has increased to 1.45 Å. The activation energy is 2.5 kcal mol^{-1}. This is a very low barrier indicating a facile insertion process.

For the insertion product **4** (Fig. 1), the carbon of the methyl group C_1 and the olefinic carbon C_2 have twisted below and above the plane containing the pyridyl nitrogen and the Fe–C_3 bond, respectively. This puckering of the propyl chain leads to a further tilting of the 2,6-diisopropylphenyl rings by 8.4° away from the propyl chain. A weak γ-agostic interaction has been formed in which the C_1–H bond length is stretched to 1.12 Å. The Fe–H distance is 1.91 Å and the Fe–N(pyridyl) distance is further shrunk to 1.82 Å. The structure is now distorted square pyramidal with the fourth basal site occupied by the agostic hydrogen of the propyl chain and C_3 occupying the apical site. The product **4** is lower in energy than **2** by 13.7 kcal mol^{-1}. Preliminary investigations have shown that the insertion of the second ethylene molecule is accompanied by a rearrangement of the propyl chain from the apical position to the in-plane site (*cf.* structure **1**).

In summary, full *ab initio* calculations have been performed on the bis(imino)pyridyliron ethylene polymerisation catalyst system, and key structures operating for the first monomer insertion within a cationic alkyl mechanism have been identified. The energetics associated with complexation and insertion are comparable with values calculated for the Ni^{II} α-diimine catalyst system, the barrier to insertion however is significantly lower.[3–5] Further studies are in progress on the propagation and termination steps for this new system.

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Notes and references

† All *ab initio* calculations were carried out using the GAUSSIAN98 package (ref. 9). Geometry optimisations on the parent dichloride (**A**) were performed using the B3LYP, BP86 and B3P86 functionals. The B3P86 (ref. 10, 11) functional was found to give the best agreement with experiment (Scheme 1) and was thus employed to calculate the structures of the catalytic cycle. For the carbon and hydrogen atoms of the alkyl chain and the chlorine and nitrogen atoms, the 6-31G** (ref. 12) basis set was employed. For the iron atom the Ahlrichs (ref. 13) pVDZ basis set was used. The STO-3G (ref. 14) basis set was placed on all other atoms. The dichloride was calculated with C_s symmetry and quintet multiplicity ($S = 2$). The mirror plane contains the iron atom, the pyridyl nitrogen atom and both chlorine atoms. All structures **1**–**4** of the catalytic cycle were calculated without symmetry constraints; attempts to impose C_s symmetry led to higher energy structures. For the purpose of this study, the cationic Fe^{II} species have been assigned singlet ($S = 0$) multiplicities. Electronic wavefunction stability calculations reveal that **2**, **3** and **4** are all singlets. Frequency calculations were performed on all optimised structures to confirm the existence of true minimum energy structures for **1**, **2** and **4**. The first order saddle point of **3** was confirmed by the presence of a single imaginary frequency in the Hessian.

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