

Synthesis and catalytic activity of iron complexes with bidentate NHC ligandst

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A family of well-defined Fe^{II} complexes of the type {BnN(*N*-CH₂(CH₂)_{*n*}-*N'*-*tert*-butyl-imidazole-2-ylidene)₂}-FeCl₂ (Bn = benzyl; *n* = 1 (**1**) or 2 (**2**)), {BnN(*N*-CH₂(CH₂)_{*n*}-*N'*-methylbenzimidazole-2-ylidene)₂}-FeCl₂ (*n* = 1 (**3**) or 2 (**4**)) and {BnN(*N*-CH₂CH₂CH₂-*N'*-methylbenzimidazole-2-ylidene)₂}-FeBr₂ (**5**) has been synthesized. These complexes are rare examples of Fe species supported by bidentate NHC ligands. Complexes **2**, **3**, **4** and **5** were characterized by X-ray crystallography and in all cases a distorted tetrahedral geometry is observed around the Fe center. The magnetic data is consistent with the complexes containing non interacting high spin Fe^{II} centers (*S* = 2) and indicates that a large zero-field splitting (*D*) is present. The new complexes are highly active pre-catalysts for the homo-coupling of Grignard reagents.

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Introduction

In recent years there has been significant interest in the development of Fe complexes as replacements for expensive precious metal catalysts in a wide variety of organic transformations.^{1–5} Not only is Fe significantly cheaper than the precious metals, it is also non-toxic, abundant and environmentally friendly. To date the majority of Fe complexes developed for catalytic applications feature nitrogen or phosphine donors^{1–5} and there is a paucity of systems which use *N*-heterocyclic carbene ligands (NHCs) to stabilize the metal center.⁶ In fact, in general the chemistry of Fe complexes supported by NHC ligands has not been extensively studied compared with the late transition metals.⁶

The first Fe complexes supported by NHC ligands were reported in the 1970s,^{7–9} but it is only in the last fifteen years that a variety of different complexes have been synthesized. Starting from Grubbs' report that free NHC ligands could be

treated with FeX₂ (X = halide) to form complexes of the type (NHC)₂FeX₂,¹⁰ a number of different Fe complexes featuring monodentate NHC ligands have been prepared.¹¹ NHC donors have also been incorporated into multidentate frameworks. For example Fehlhammer,¹² Meyer¹³ and Smith¹⁴ have synthesized a number of Fe complexes with tripodal tridentate NHC ligands, while Danopoulos and co-workers have prepared Fe complexes with tridentate pincer ligands, incorporating two NHC donors.^{15–17}

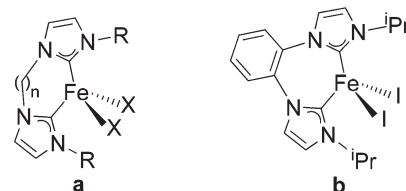
Surprisingly Fe complexes supported by simple bidentate bis(NHC) ligands, which are not part of a multidentate framework, are rare.⁶ In fact, to the best of our knowledge there are only two systems of this type^{18–20} and their catalytic activity has yet to be probed in detail.²⁰ In 2011 the groups of Ingleson¹⁸ and Meyer²⁰ independently prepared Fe^{II} complexes supported with bidentate NHC ligands linked with aliphatic (**a**) or phenylene (**b**) bridges (Fig. 1). In the case of the phenylene linked system it was not possible to separate the Fe dihalide species from homoleptic complexes featuring two

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†Electronic supplementary information (ESI) available: Further information about magnetic measurements and X-ray crystallography. CCDC 907140–907142 and 917785 (these data {BnN-(CH₂CH₂CH₂-*N'*-*tert*-butyl-imidazole-2-ylidene)₂}-FeCl₂ (**2**) (907140), {BnN-(CH₂CH₂-*N'*-methylbenzimidazole-2-ylidene)₂}-FeCl₂ (**3**) (907141), {BnN-(CH₂CH₂CH₂-*N'*-methylbenzimidazole-2-ylidene)₂}-FeCl₂ (**4**) (907142) and {BnN-(CH₂CH₂CH₂-*N'*-methylbenzimidazole-2-ylidene)₂}-FeBr₂ (**5**) (917785)). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt32551b



n = 1, X = Cl, Br or I, R = alkyl or aryl
n = 2, X = Br, R = Me or 2,4,6-Me₃C₆H₂
n = 3, X = Br, R = Me

Fig. 1 Representative examples of Fe^{II} complexes with bidentate NHC ligands which have been prepared in the literature.^{18,20}

bidentate NHC ligands and species of this type were also observed as a by-product for aliphatic linked systems with small alkyl groups as the substituent on the imidazole. Recently, Zlatogorsky and Ingleson demonstrated that in some cases dihalide species with aliphatic linked bidentate NHC ligands could be converted into Fe hydrides in low yield.¹⁹ The only report of catalytic activity using Fe complexes supported by bidentate NHC ligands is from Meyer.²⁰ His group showed that some complexes related to type **a** were pre-catalysts for Kumada type cross-coupling but only moderate activity was observed.

Given that precious metal complexes with bidentate NHC ligands often generate highly active catalysts for a number of different organic transformations,^{21,22} we were interested in expanding the scope of Fe complexes supported by these ligands. Previously, we synthesized Pd, Rh and Ir species supported by bidentate NHC ligands with flexible alkyl linkers containing a central amine.^{23,24} These complexes are active catalysts for the Heck and Suzuki reactions, and transfer hydrogenation. Here, we show that the same ligands can be used to support rare examples of Fe^{II} complexes with bidentate NHC ligands. We demonstrate that these Fe^{II} species are highly active pre-catalysts for the homo-coupling of Grignard reagents.

Results and discussion

Synthesis and characterization

The Fe complexes **1–4** were prepared in high yields through the reaction of Fe{N(SiMe₃)₂}₂ with the appropriate chloride salt of the protonated free ligands in toluene at room temperature (eqn (1)). A related reaction has previously been used to metallate bidentate NHC ligands onto Fe but in contrast to other systems there was no evidence for the formation of complexes with two bidentate carbene ligands or dimeric species.²⁰ In general, the reactions of common Fe^{II} precursors such as FeCl₂, FeBr₂ and FeBr₂(THF)₂ with the free carbene ligands (the free carbene was generated using a literature procedure)²⁴ in both coordinating and non-coordinating solvents failed to yield isolable Fe–NHC complexes. The only exception was the synthesis of the Fe^{II} dibromide **5**, through the reaction of FeBr₂ with the appropriate free carbene (prepared *in situ*) (eqn (2)). It has been observed in the few literature reports of Fe–NHC complexes that the choice of Fe^{II} precursor and solvent and the method of the carbene delivery can lead to very different results¹⁵ and this appears to be the case with our ligand as well. Complexes **1–5** were paramagnetic but unlike other Fe complexes supported by NHC ligands it was only possible to obtain a well defined ¹H NMR spectrum for **5**. We believe that this is due to a combination of the low solubility of **1–4** in all common solvents (even at elevated temperature) and the inherent broadening of paramagnetic NMR spectra. The ¹H NMR spectrum of **5** showed the expected number of peaks with slight shifts of some resonances outside the normal diamagnetic sweep width and significant broadening.

An Evans' method NMR experiment on **5**, indicated a μ_{eff} of 4.79 μ_{B} , consistent with the presence of a high spin tetrahedral $S = 2$ Fe^{II} center. Compounds **3** and **4** were sufficiently soluble in benzene to determine the magnetic moment using the Evans' method (**1** and **2** were too insoluble) and values of 4.77 and 4.84 μ_{B} , respectively, were obtained. These values also suggest an $S = 2$ ground state. All of the new complexes were characterized by IR spectroscopy and elemental analysis and the structures of **2**, **3**, **4** and **5** were elucidated by X-ray crystallography (Fig. 2–5). Selected structural parameters are given in Table 1.

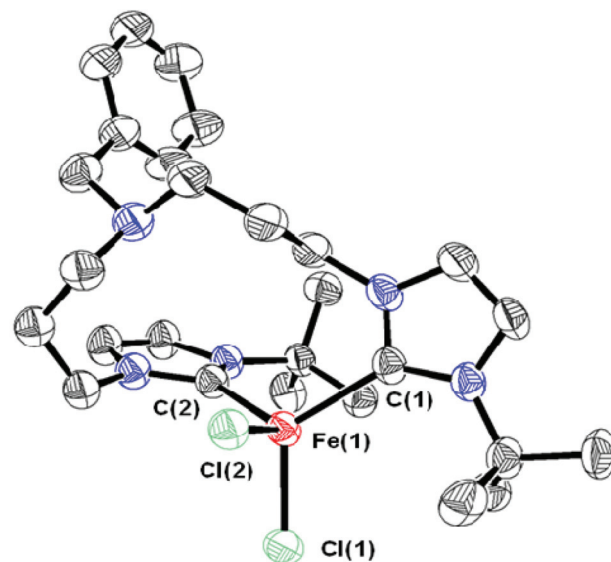
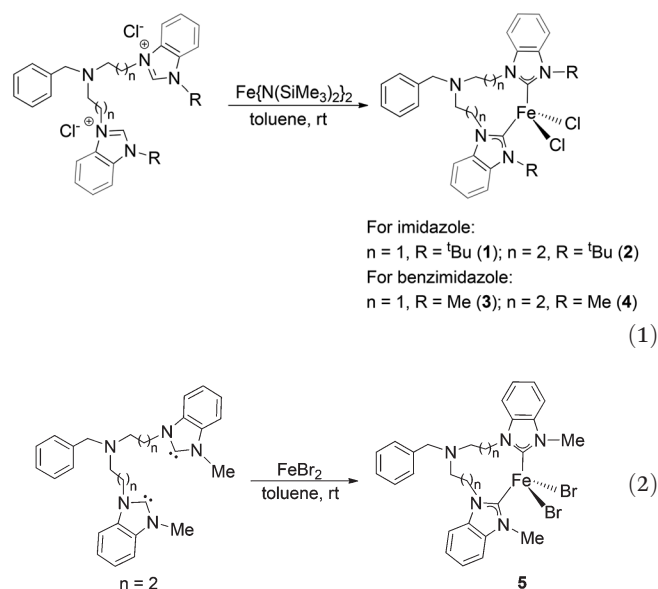


Fig. 2 Thermal ellipsoid plot of **2**. Hydrogen atoms and solvent of crystallization have been removed for clarity. The disorder in the benzyl group has also been omitted. Selected bond lengths (Å) and angles (°): Fe(1)–C(1) 2.161(4), Fe(1)–C(2) 2.165(4), Fe(1)–Cl(1) 2.3147(12), Fe(1)–Cl(2) 2.3523(11), C(1)–Fe(1)–C(2) 113.71(15), C(1)–Fe(1)–Cl(1) 126.20(12), C(1)–Fe(1)–Cl(2) 93.44(11), C(2)–Fe(1)–Cl(1) 102.35(11), C(2)–Fe(1)–Cl(2) 116.57(11), Cl(1)–Fe(1)–Cl(2) 104.91(4).

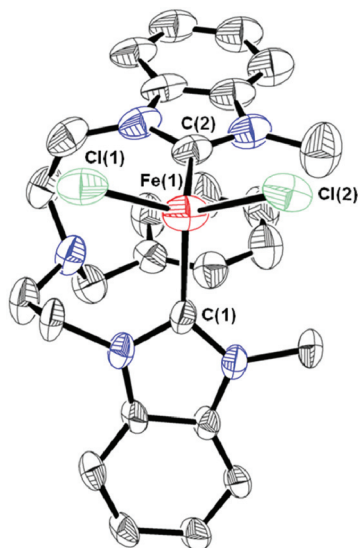


Fig. 3 Thermal ellipsoid plot of **3**. Hydrogen atoms and solvent of crystallization have been removed for clarity. The structure contains two fully disordered molecules, only the major component is shown here. Selected bond lengths (Å) and angles (°): Fe(1)–C(1) 2.113(8), Fe(1)–C(2) 2.110(8), Fe(1)–Cl(1) 2.308(7), Fe(1)–Cl(2) 2.287(7), C(1)–Fe(1)–C(2) 104.1(6), C(1)–Fe(1)–Cl(1) 109.9(5), C(1)–Fe(1)–Cl(2) 106.2(3), C(2)–Fe(1)–Cl(1) 112.6(5), C(2)–Fe(1)–Cl(2) 112.2(4), Cl(1)–Fe(1)–Cl(2) 109.9(5). Distances and angles for minor component are given in the ESI.†

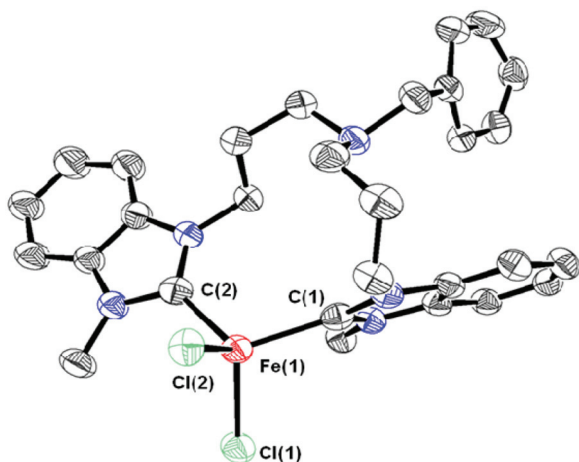


Fig. 4 Thermal ellipsoid plot of **4**. Hydrogen atoms and solvent of crystallization have been removed for clarity. Only one of the two independent molecules is shown. Selected bond lengths (Å) and angles (°): Fe(1)–C(1) 2.090(5), Fe(1)–C(2) 2.125(5), Fe(1)–Cl(1) 2.2746(12), Fe(1)–Cl(2) 2.2787(13), C(1)–Fe(1)–C(2) 108.39(18), C(1)–Fe(1)–Cl(1) 115.40(13), C(1)–Fe(1)–Cl(2) 105.09(13), C(2)–Fe(1)–Cl(1) 106.03(12), C(2)–Fe(1)–Cl(2) 108.35(12), Cl(1)–Fe(1)–Cl(2) 113.36(5).

The solid state structures show that the geometry around Fe is distorted tetrahedral, with only minor differences in the bond lengths and angles around Fe depending on whether there are four carbon or six carbon atoms in the linker. In fact, the change from *tert*-butyl imidazole in **2** to 1-methylbenzimidazole in **4** appears to make a larger difference to the overall structure. In all cases the ligand clearly binds in a bidentate

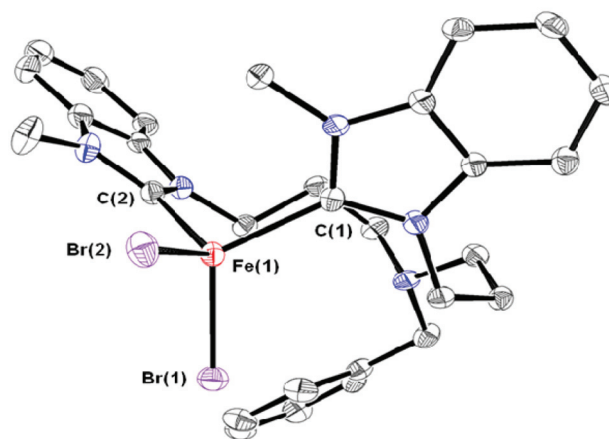


Fig. 5 Thermal ellipsoid plot of **5**. Hydrogen atoms and solvent of crystallization have been removed for clarity. Only one of the two independent molecules is shown. Selected bond lengths (Å) and angles (°): Fe(1)–C(1) 2.115(3), Fe(1)–C(2) 2.109(3), Fe(1)–Br(1) 2.3969(12), Fe(1)–Br(2) 2.4209(6), C(1)–Fe(1)–C(2) 101.90(13), C(1)–Fe(1)–Br(1) 118.58(9), C(1)–Fe(1)–Br(2) 104.96(9), C(2)–Fe(1)–Br(1) 110.93(9), C(2)–Fe(1)–Br(2) 114.63(10), Br(1)–Fe(1)–Br(2) 106.06(2).

Table 1 Structural data for **2–5**

Complex	Fe–NHC (Å)	NHC–Fe–NHC (°)	Yaw angle ^a (°)
2	2.158(6), 2.166(4)	113.71(15)	5.7, 6.2
3^b	2.113(8), 2.110(8)	104.1(6)	2.6, 3.3
	2.112(11), 2.123(11)	103.7(9)	
4^c	2.090(5), 2.125(5)	108.39(18)	3.4, 4.5
	2.102(5), 2.122(5)	100.61(17)	3.1, 5.2
5^c	2.109(3), 2.115(3)	101.90(13)	0.9, 6.3
	2.102(3), 2.117(4)	109.61(13)	3.3, 6.5

^a Yaw angle is the difference between the two M–C–N angles divided by 2. ^b Two fully disordered molecules present. ^c Two independent molecules present in the asymmetric unit.

fashion, as the distance between the central amine of the linker and Fe is greater than 4.5 Å. Similar bidentate binding has been observed when these ligands coordinate to Pd.^{23,25,26} The Fe–NHC bond distances range from a minimum of 2.090(5) Å in **4** to a maximum of 2.166(4) Å in **2**. These distances are consistent with values observed for related Fe–NHC systems with both monodentate and bidentate NHC ligands²⁰ and the longer distances in the *tert*-butyl imidazole species are presumably to minimize steric clash between the *tert*-butyl groups and the chloride ligands. Interestingly the NHC–Fe–NHC bond angles in **2–5** are larger than those observed in most bis(monodentate) and all bidentate systems. The bite angles in **2–5** vary from 100.61(17)° in **4** to 113.71(15)° in **2**, whereas in related Fe systems with a methylene group linking the two NHC donors the angle is approximately 90°.^{18,20} In bis(monodentate) NHC systems the NHC–Fe–NHC angle is around 100°.^{10,27} The large linker length in **2–5** presumably causes the increased bite angle and a similar effect has been observed in late transition metal systems.²² The Yaw angles (a measure of in-plane distortion) are also smaller in **2–5** than in other bidentate systems, indicative of the greater flexibility of the linker. The larger Yaw

angle for the *tert*-butyl complex **2** compared with the 1-methylbenzimidazole complexes **3**, **4** and **5** is consistent with the larger steric bulk of the *tert*-butyl group. The effect of changing from an Fe^{II} dichloride to a Fe^{II} dibromide is negligible as the structures of **4** and **5** are virtually identical. This suggests that in these systems there is relatively little steric crowding around the Fe center as the complex can accommodate the larger bromide ligands without any changes to the Fe–NHC binding. Despite the flexibility of the linker, the solid state conformation of the linker is similar in **2**–**5**. The only major difference is that the nitrogen atom in the amine linker is inverted in **2** compared with **4** and **5**. As a result the orientation of the benzyl group is slightly different.

The direct current (dc) magnetic susceptibility of complexes **1**–**4** was investigated under an applied dc field of 0.1 T and in the temperature range of 1.9–300 K. The χT vs. T plot for **1** is shown in Fig. 6 (with others given in the ESI[†]). At room temperature (300 K), the χT values are 2.91 (**1**), 2.93 (**2**), 3.04 (**3**) and 3.12 (**4**) cm³ K mol⁻¹, which is in good agreement with the theoretical value of 3.0 cm³ K mol⁻¹ for non-interacting high spin $S = 2$ Fe^{II} ions in a tetrahedral environment. These results

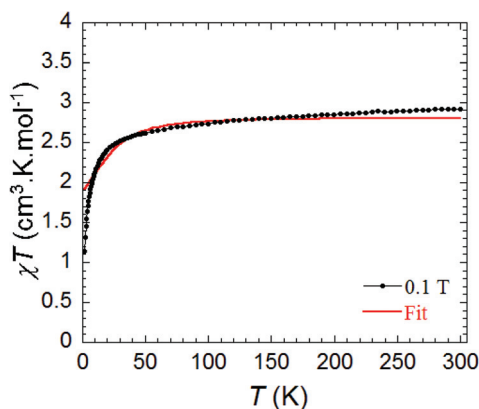


Fig. 6 Temperature dependence of the χT product at 0.1 T for complex **1** (with χ being the molar susceptibility per molecule defined as M/H).

are also consistent with the magnetic moments obtained in solution for compounds **3**–**5**. For compounds **1**–**4**, the χT product was near linear from 300 K down to 50 K, then rapidly decreased below 50 K to reach minimum values of 1.1 (**1**), 1.0 (**2**), 1.5 (**3**), and 2.1 (**4**) cm³ K mol⁻¹ at 1.9 K. The low temperature decrease can be attributed to factors such as weak intermolecular interactions (for example in **2** the closest intermetal distance is approximately 9.46 Å from X-ray crystallography), thermal depopulation and/or magnetic anisotropy arising from mixing of the ground state with low lying excited states. Fitting of the temperature dependence of χT data for **1**–**4** assuming simple zero-field splitting (ZFS) effects reveals $g = 1.93$ (**1**), 1.93 (**2**), 2.05 (**3**), and 2.05 (**4**) and $D = -18.32$ (**1**), -22.2 (**2**), -5.71 (**3**), -5.71 (**4**) K. These large ZFS parameters are consistent with no EPR transitions being observed using an X-band EPR spectrometer.

The field dependence of the magnetization and reduced magnetization of **1** are shown in Fig. 7a and 7b, while the corresponding data for **2**–**4** are given in the ESI.[†] The magnetization of **1**–**4** under 0–7 T applied field displays a rapid increase from 0 T to 2 T followed by a gradual increase without reaching saturation; $M = 1.80$ (**1**), 1.99 (**2**), 2.75 (**3**), and 3.38 (**4**) μ_B at 1.9 K. The non saturation values are lower than the theoretically derived saturation value of 4.89 μ_B . A temperature dependence of the magnetization for complexes **1**–**4** are seen in the M vs. HT^{-1} plots. The curves between 1.9 K and 8 K do not superimpose onto a single master curve, indicative of magnetic anisotropy and/or the presence of low-lying excited states. Overall our magnetic data suggests that the change from *tert*-butyl-imidazole to 1-methylbenzimidazole has a larger effect on the magnetic properties of the complexes than changing the linker length from four carbon atoms to six carbon atoms. This also demonstrates that the magnetic properties of the complexes can be changed by varying the electronics of the ligands.

The Mössbauer spectrum of **4** was measured at 3.0 K. A well defined quadrupole doublet was observed (Fig. 8) with an isomer shift of 0.71 mm s⁻¹ and quadrupole splitting of 3.77 mm s⁻¹, respectively. Although relatively small, the

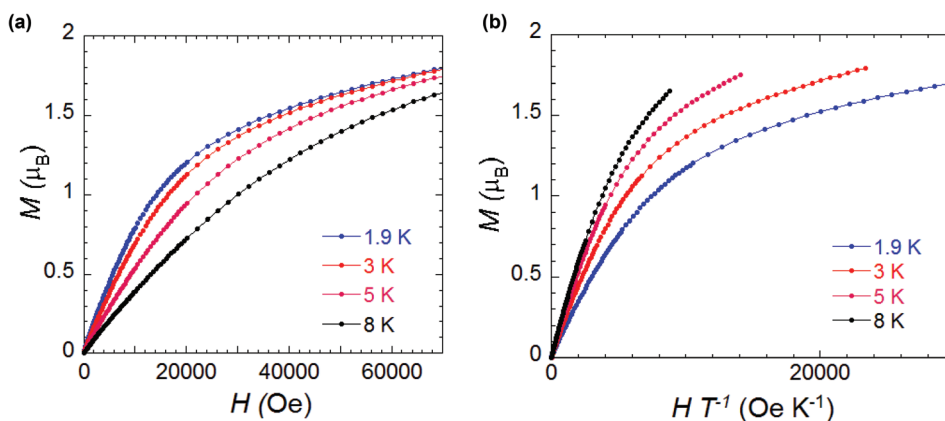


Fig. 7 (a) Field dependence of the magnetization and (b) reduced magnetization for **1** at 1.9, 3, 5, and 8 K.

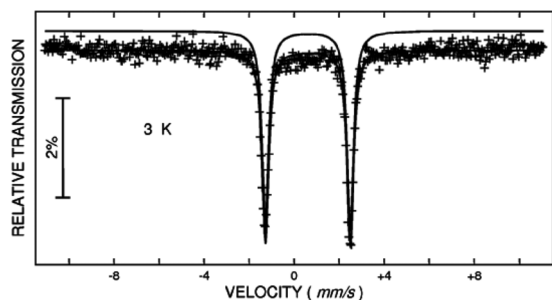


Fig. 8 Mössbauer spectrum of a polycrystalline sample of **4** recorded at 3 K in zero field. The solid line is the result of least-squares fitting of a doublet to the data.

isomer shift values are consistent with other high-spin four-coordinate Fe^{II} ions in a tetrahedral coordination environment^{28,29} and are virtually identical to those reported by Evans and Ingleson for a tetrahedral Fe^{II} complex supported by a bidentate NHC ligand with a methylene bridge.¹⁸ The large quadrupole splitting is due to the high sensitivity of this parameter to small distortions from exact tetrahedral symmetry, which has been demonstrated in previous studies of tetrahedrally coordinated Fe^{II} .³⁰ In the presence of a tetrahedral ligand field environment the free ion 5D state splits into a doublet of E symmetry (containing the d_{z^2} and $d_{x^2-y^2}$ orbitals) and a T_2 triplet (containing the d_{xy} , d_{xz} and d_{yz} orbitals) with the doublet lying lowest in energy. The observation of a large quadrupole splitting confirms that the lower doublet must be split by a distortion of the ion from pure tetrahedral geometry, which is supported by the solid state structure of **4** (*vide supra*).

Catalysis

The homo-coupling of Grignard reagents is considered to be an easy and efficient method for accessing a variety of di- or poly-aromatic and conjugated olefinic species.³¹ Since the initial report by Kharasch and Field in 1941 that FeCl_3 could catalyze homo-coupling reactions,³² it has been demonstrated that a number of different Fe complexes can catalyze this reaction.^{33–36} Furthermore, recently several groups studying iron catalyzed Kumada reactions have observed the homo-coupling of the Grignard reagent as a side reaction.^{37–41} In general, either 1,2-dichloroethane, an aryl halide or O_2 are used as the oxidants for Fe catalyzed homo-coupling reactions, although there are two reports describing the reaction in the absence of an oxidant.^{42,43} Complexes **1–5** were all active pre-catalysts for the homo-coupling of *p*-tolylmagnesium bromide in a THF–diethyl ether mixture, with high yields of 4,4'-dimethyl-1,1'-biphenyl observed (Table 2, entries 7–11). In all cases, the yields were better than those obtained using standard Fe^{II} precursors such as FeCl_2 , FeBr_2 or $\text{FeBr}_2(\text{THF})_2$ (entries 2–4), while no activity was observed when there is no Fe source present (entry 1). A preformed complex does not need to be utilized and premixing the free carbene,²⁴ $\text{BnN}(\text{CH}_2\text{CH}_2\text{CH}_2\text{-}N\text{-tert-butyl-imidazole-2-ylidene})_2$ with FeCl_2 , followed by addition of a Grignard reagent, also resulted in

Table 2 Catalyst screen for homo-coupling of *p*-tolylmagnesium bromide^a

Entry	Catalyst	Oxidant/additive	Yield ^b (%)
1	No catalyst	None	<2
2	FeCl_2	None	83
3	FeBr_2	None	80
4	$\text{FeBr}_2(\text{THF})_2$	None	85
5	FeCl_3	None	79
6	$(\text{IMes})_2\text{FeCl}_2^c$	None	63
7	1	None	99
8	2	None	98
9	3	None	99
10	4	None	99
11	5	None	99
12	FeCl_2 + free carbene ^d	None	87
13	FeCl_3 + free carbene ^d	None	84
14	1 ^e	None	65
15	2 ^e	None	56
16	3 ^e	None	60
17	4 ^e	None	67
18	4 ^f	CHCl_3	99
19	4 ^f	1,2-Dichloroethane	53
20	4 ^g	O_2	41
21	4 ^f	4-Chlorobenzene	82
22	4 ^f	4-Bromobenzene	89
23	4 ^h (<i>in situ</i> Grignard)	None	33
24	4	Drop of Hg	92

^aThe conditions for the reaction were *p*-tolylmagnesium bromide (0.36 mL of a 0.5 M solution in diethyl ether, 0.18 mmol), catalyst (0.0036 mmol, 2 mol%) in 0.9 mL THF at room temperature. After 30 minutes the reaction was quenched by addition of wet 0.2 mL CHCl_3 . ^bThe yield of the reaction is the average from two runs determined by ^1H NMR spectroscopy after 30 minutes using 1,3,5-trimethoxybenzene as an internal standard. ^cIMes = 1,3-bis-(2,4,6-trimethylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene. The compound $(\text{IMes})_2\text{FeCl}_2$ was prepared according to a literature procedure.¹¹ⁱ ^dThe free carbene ligand $\text{BnN}(\text{CH}_2\text{CH}_2\text{CH}_2\text{-}N\text{-tert-butyl-imidazole-2-ylidene})_2$ prepared as described in ref. 24 was utilized. In these reactions the Fe salt was stirred with the free carbene for 30 minutes and the Grignard reagent was introduced. ^e1 mol% of catalyst (0.0018 mmol) was used. ^f0.18 mmol of the additives were used. ^gExcess 1 atm O_2 was used. ^hThe Grignard reagent was generated *in situ*. The conditions for the reaction were 1-bromo-4-methylbenzene (30.8 mg, 0.18 mmol), Mg turnings (8.7 mg, 0.36 mmol), catalyst (0.0036 mmol, 2 mol%) in 0.9 mL THF at room temperature. The catalyst was added after the reaction mixture had been filtered to remove excess Mg turnings.

homo-coupling with only slightly reduced yield (entry 12). Performing a similar reaction with $\text{BnN}(\text{CH}_2\text{CH}_2\text{CH}_2\text{-}N\text{-tert-butyl-imidazole-2-ylidene})_2$ and FeCl_3 also gave a high yield of the homo-coupling product (entry 13), demonstrating that either an Fe^{II} or Fe^{III} species could be used as the pre-catalyst. However, the yield for the mixture containing FeCl_3 and the free carbene was only slightly higher than that obtained by simply using FeCl_3 (entry 5). The yield for homo-coupling using our bidentate systems was also higher than that obtained using $(\text{IMes})_2\text{FeCl}_2$ ¹¹ⁱ (IMes = 1,3-bis-(2,4,6-trimethylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene) (entry 6), which contains two monodentate NHC ligands. Overall, these results strongly suggest that our bidentate ligand is assisting in catalysis although the effect is relatively small.

Complexes 1–4 all gave similar activity after 30 minutes at a loading of 2 mol%, but at lower loading (1 mol%) there were slight differences in performance (entries 14–17). At this stage the exact reasons why certain ligands give slightly better activity are unclear and there is no obvious trend based on electronics or sterics. In our experiments, we believe that the CHCl_3 used to quench the reactions is the oxidant. This is supported by a high yield of the homo-coupling product being obtained in an experiment in which CHCl_3 was added to the reaction mixture and not used as the quenching reagent (entry 18). In contrast, a greatly reduced yield was observed when the reaction was performed without an oxidant and then worked up without the addition of CHCl_3 . Interestingly, the addition of other oxidants resulted in inhibition of the reaction (entries 19–22). Both O_2 and 1,2-dichloroethane lower the yield by between 40–50%, while a smaller decrease was seen when either 4-chlorobenzene or 4-bromobenzene were added. It should be noted that no cross-coupling products from a Kumada type reaction are observed when 4-chlorobenzene or 4-bromobenzene were added. This means that our systems are selective for homo-couplings in the presence of an aryl chloride, whereas the catalysts used by Bedford and Nakamura for the Kumada coupling,^{37–39} give high selectivity for cross-coupling and only small amounts of the homo-coupling product. It is not understood what causes this change in selectivity.

Performing the catalysis when the Grignard reagent was generated *in situ* (entry 23), from Mg turnings and 1-bromo-4-methylbenzene, resulted in a lower yield of the homo-coupling product. In this reaction the excess Mg turnings were removed by filtration prior to the addition of the Fe catalyst, so there was no possibility of a reaction between 4 and Mg, although an independent control experiment confirmed that 4 does not react with Mg. Although the reaction mixtures appear homogeneous, the possibility of heterogeneous iron particles forming and catalyzing the reaction cannot be discounted. A control reaction performed with a drop of Hg added to the reaction mixture (entry 24) resulted in a very small decrease in yield, suggesting that the reaction is homogeneous.⁴⁴ However, the Hg test is not always definitive and it has not been conclusively established that the homo-coupling observed in this work is homogeneous. Furthermore, it was not possible to isolate a well defined Fe complex from the reaction mixture after quenching with CHCl_3 .

The substrate scope for homo-coupling was explored using compound 4 as the pre-catalyst (Table 3). The reaction is tolerant to substitution in the *ortho*, *meta* and *para* position of the aromatic ring (entries 2–5). There is a slight decrease in yield when the electron donating methoxy group is present in the *para* position (entry 4), while no reaction is observed with the electron withdrawing CF_3 group in the *para* position (entry 6). Successful coupling of sp^3 hybridized carbon atoms in benzylic systems was achieved (entries 8 and 9) but no reaction was observed using a sp hybridized alkynyl substrate (entry 10). Interestingly the reaction can also be performed using a Mg chloride salt (entry 11) with a relatively small

Table 3 Fe catalyzed homo-coupling of Grignard reagents^a

X = Cl or Br

Entry	Substrates	Yield ^b (%)
1	Phenylmagnesium bromide	82
2	<i>o</i> -Methoxyphenylmagnesium bromide	63
3	<i>m</i> -Tolylmagnesium bromide	86
4	<i>p</i> -Methoxyphenylmagnesium bromide	65
5	<i>p</i> -Tolylmagnesium bromide	84
6	<i>p</i> -Trifluoromethylphenylmagnesium bromide	0
7	1-Naphthylmagnesium bromide	45
8	Benzylmagnesium bromide	68
9	<i>p</i> -Methylbenzylmagnesium bromide	77
10	(Phenylethynyl)magnesium bromide	0
11	Phenylmagnesium chloride	51

^a The conditions for the reaction were substrate (0.54 mmol), catalyst (6 mg, 0.0108 mmol, 2 mol%) in 3 mL THF at room temperature. After 30 minutes the reaction was quenched by addition of wet 0.2 mL CHCl_3 . ^b Isolated yield.

decrease in yield compared with the corresponding Mg bromide salt (entry 1). This is the first time that chloride salts have been utilized for Fe catalyzed homo-coupling.

Conclusions

We have synthesized and characterized a number of distorted tetrahedral $S = 2$ Fe^{II} complexes supported by a bidentate NHC ligand containing an amine linker. These complexes are some of the most active Fe pre-catalysts for the homo-coupling of Grignard reagents and in one case can even couple a Mg chloride salt. In future work we will look to further explore the reactivity of these unusual Fe complexes with small molecules and understand the mechanism by which homo-coupling occurs.

Experimental details

General methods

Experiments were performed under a dinitrogen atmosphere in an M-Braun dry box or using standard Schlenk techniques. (Under standard glovebox conditions purging was not performed between uses of pentane, hexane, diethyl ether, benzene and toluene; thus when any of these solvents were used, traces of all these solvents were in the atmosphere and could be found intermixed in the solvent bottles.) Moisture- and air-sensitive liquids were transferred by stainless steel cannula on a Schlenk line or in a dry box. The solvents for air- and moisture-sensitive reactions were dried by passage through a column of activated alumina followed by storage under dinitrogen. All commercial chemicals were used as received except where noted. Phenylmagnesium bromide and *p*-tolylmagnesium bromide were purchased from Aldrich. 1-Naphthylmagnesium bromide, 2-methoxyphenylmagnesium

Table 4 Crystal and refinement data for complexes 2, 3, 4 and 5

	2	3	4	5
Empirical formula	C _{37.85} H _{53.01} Cl ₂ FeN ₅	C ₂₉ H ₃₃ Cl ₂ FeN ₅ O _{0.50}	C ₃₂ H ₃₆ Cl ₂ FeN ₅	C ₆₅ H ₇₄ Br ₄ Fe ₂ N ₁₀
Formula weight	679.56	586.35	617.41	1426.68
Temperature (K)	93(2)	93(2)	93(2)	150(2)
<i>a</i> (Å)	9.5506(2)	12.9406(3)	9.3137(2)	9.434(4)
<i>b</i> (Å)	14.1282(3)	9.3355(2)	29.3333(5)	30.1020(7)
<i>c</i> (Å)	14.2614(10)	22.9686(16)	22.4626(16)	23.0220(16)
α (°)	85.624(6)	90.00	90.00	90.00
β (°)	87.635(6)	91.132(6)	98.700(7)	101.188(15)
γ (°)	86.017(6)	90.00	90.00	90.00
Volume (Å ³)	1912.84(15)	2774.2(2)	6066.2(5)	6414(3)
<i>Z</i>	2	4	8	4
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>d</i> _{calc} (mg m ⁻³)	1.224	1.404	1.352	1.478
θ range (°)	3.11 to 65.82	3.85 to 65.09	6.51 to 55.99	2.99 to 26.37
μ (mm ⁻¹)	4.665	6.362	5.835	2.992
Abs. correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
GO ^F	1.075	1.144	1.079	1.071
<i>R</i> ₁ , ^a <i>wR</i> ₂ ^b	0.0832, 0.2388	0.0832, 0.1768	0.0627, 0.1627	0.0429, 0.0904
[<i>I</i> > 2 σ (<i>I</i>)]				

$$^a R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|. \quad ^b wR_2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}.$$

bromide and 4-methoxyphenylmagnesium bromide were purchased from Acros. The other Grignard reagents were prepared in dry diethyl ether from the corresponding commercially available organic bromide by the standard method.⁴⁵ Anhydrous iron(II) chloride and iron(III) chloride were purchased from Alfa Aesar. Anhydrous iron(II) bromide was purchased from Acros. NMR spectra were recorded on Bruker AMX-400, -500 spectrometers at ambient probe temperatures. Robertson Microlit Laboratories, Inc. performed the elemental analyses (inert atmosphere). IR spectra were measured using a diamond smart orbit ATR on a Nicolet 6700 FT-IR instrument. The Mössbauer spectrum was acquired using a conventional spectrometer in constant-acceleration mode equipped with a ⁵⁷Co source (3.7 GBq) in a rhodium matrix. Isomer shifts are given relative to α -Fe at room temperature. The Mössbauer spectral absorbers contained 45 mg cm⁻² of finely powdered compound 4. The sample was inserted inside an Oxford Instruments Mössbauer-Spectromag 4000 Cryostat. Mössbauer spectra were evaluated using the NORMOS package program. Literature procedures were used to prepare the following compounds: 1,3-bis(2,6-diisopropylphenyl)-imidazolium chloride (IMesHCl),⁴⁶ Fe{N(SiMe₃)₂}₂,⁴⁷ [BnN(CH₂CH₂-*N-tert*-butyl-imidazolium)₂]₂·2[Cl],²³ [BnN(CH₂CH₂CH₂-*N-tert*-butyl-imidazolium)₂]₂·2[Cl],²⁴ {BnN(CH₂CH₂-*N*-methylbenzimidazolium)₂}₂·2[Cl],²³ {BnN(CH₂CH₂CH₂-*N*-methylbenzimidazolium)₂}₂·2[Cl],²⁴ FeBr₂(THF)₂⁴⁸ and (IMes)₂FeCl₂.¹¹ⁱ

Magnetic measurements

A magnetic analysis was performed on crushed polycrystalline samples of 1–4, wrapped in a polyethylene membrane sealed in a glove box to prevent any sample degradation. The direct current (dc) magnetic susceptibility measurements were obtained using a Quantum Design SQUID magnetometer

MPMS-XL7 operating between 1.9 and 300 K for dc-applied fields ranging from -7 to 7 T. The magnetization data was collected at 100 K to check for ferromagnetic impurities which were found to be absent in (1–4). Diamagnetic corrections were applied for the sample holder and the core diamagnetism from the sample (estimated with Pascal constants). Further data for compounds 2–4 is provided in the ESI.†

X-ray crystallography

Low-temperature diffraction data (ω -scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu K α (λ = 1.54178 Å) or on a Rigaku R-Axis RAPID diffractometer coupled to a R-Axis RAPID imaging plate detector with Mo K α radiation (λ = 0.71073 Å). All structures were solved by direct methods using SHELXS⁴⁹ and refined against *F*² on all data by full-matrix least squares with SHELXL-97⁵⁰ using established refinement techniques.⁵¹ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl groups). All disorders were refined with the help of similarity restraints on the 1,2- and 1,3-distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. Details of the crystal and refinement data for complexes 2, 3, 4 and 5 are given in Table 4 and the ESI.†

Synthesis and characterization of new compounds

{BnN(CH₂CH₂-*N-tert*-butyl-imidazole-2-ylidene)₂}FeCl₂ (1). Fe-{N(SiMe₃)₂}₂ (141 mg, 0.38 mmol) was added to a suspension of [BnN(CH₂CH₂-*N-tert*-butyl-imidazolium)₂]₂·2[Cl] (180 mg,

0.38 mmol) in 20 mL toluene. The mixture was stirred at room temperature for 50 hours, after which stirring was stopped, and the precipitate was allowed to settle for several hours. The solution was carefully decanted from the precipitate, which was washed with toluene and pentane and dried under vacuum to give **1** as a white powder. Yield: 191 mg (96%).

IR (diamond tip, cm^{-1}): 3459 (m), 3385 (br), 3264 (w), 3123 (m), 3092 (s), 3048 (s), 2978 (m), 2887 (w), 2829 (m), 2802 (m), 2355 (w, br), 1637 (w), 1565 (s), 1555 (s), 1448 (m), 1411 (w), 1374 (s), 1313 (w), 1294 (w), 1257 (w), 1236 (m), 1204 (s), 1151 (s), 1129 (s), 1116 (w), 1060 (w), 1053 (m), 1029 (w), 1002 (w), 984 (m), 938 (w), 925 (w). Anal. calcd (found) for $\text{C}_{25}\text{H}_{37}\text{Cl}_2\text{N}_5\text{Fe}$: C, 56.19 (55.36); H, 6.98 (6.66); N, 13.11 (12.19).

{BnN(CH₂CH₂CH₂-*N*-tert-butyl-imidazole-2-ylidene)₂}FeCl₂ (2). $\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}_2$ (69 mg, 0.18 mmol) was added to a suspension of $[\text{BnN}(\text{CH}_2\text{CH}_2\text{CH}_2\text{-N-tert-butyl-imidazolium})_2]\cdot 2[\text{Cl}]$ (93 mg, 0.18 mmol) in 12 mL toluene. The mixture was stirred at room temperature for 50 hours, after which stirring was stopped, and the precipitate was allowed to settle for several hours. The solution was carefully decanted from the precipitate, which was washed with toluene and pentane and dried under vacuum to give **2** as a white powder. Single crystals for X-ray analysis were grown from a benzene/pentane solution at room temperature. Yield: 91 mg (88%).

IR (diamond tip, cm^{-1}): 3350 (br), 3133 (w), 3118 (m), 3081 (m), 3058 (w), 3025 (w), 2980 (s), 2932 (m), 2870 (w), 2825 (w), 2812 (m), 2735 (w), 2110 (w, br), 1581 (w), 1564 (w), 1544 (m), 1492 (w), 1461 (m), 1452 (m), 1438 (w), 1405 (w), 1379 (m), 1370 (m), 1353 (w), 1339 (w), 1313 (w), 1285 (w), 1261 (w), 1223 (s), 1202 (s), 1160 (w), 1130 (s), 1087 (w), 1075 (m), 1035 (w), 996 (w), 915 (w). Anal. calcd (found) for $\text{C}_{27}\text{H}_{41}\text{Cl}_2\text{N}_5\text{Fe}$: C, 57.65 (56.73); H, 7.35 (7.25); N, 12.45 (12.03).

{BnN(CH₂CH₂-*N*-methylbenzimidazole-2-ylidene)₂}FeCl₂ (3). $\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}_2$ (440 mg, 1.17 mmol) was added to a suspension of $\{\text{BnN}(\text{CH}_2\text{CH}_2\text{-N-methylbenzimidazolium})_2\}\cdot 2[\text{Cl}]$ (580 mg, 1.17 mmol) in 30 mL toluene. The mixture was stirred at room temperature for 50 hours, after which stirring was stopped, and the precipitate was allowed to settle for several hours. The solution was carefully decanted from the product, which was washed with toluene and pentane and dried under vacuum to give **3** as an off-white powder. Single crystals for X-ray analysis were grown from a THF/pentane solution at room temperature. Yield: 555 mg (86%).

IR (diamond tip, cm^{-1}): 3378 (br), 3144 (w), 3080 (m), 3057 (m), 3026 (m), 2098 (w), 2951 (m), 2913 (w), 2894 (w), 2845 (w), 2812 (m), 2799 (w), 2766 (w), 2120 (w), 1570 (s), 1488 (m), 1462 (s), 1447 (s), 1429 (m), 1413 (w), 1393 (w), 1380 (m), 1364 (w), 1352 (m), 1298 (w), 1280 (m), 1262 (m), 1208 (s), 1175 (w), 1134 (s), 1095 (m), 1070 (m), 1047 (m), 1021 (s), 1008 (m), 956 (m), 929 (m), 911 (m), 862 (w), 841 (m), 816 (w). Magnetic susceptibility (C_6D_6): 4.77 μ_{B} . Anal. calcd (found) for $\text{C}_{27}\text{H}_{29}\text{Cl}_2\text{N}_5\text{Fe}\cdot\text{THF}$: C, 59.92 (60.56); H, 5.84 (5.54); N, 11.27 (11.54). The molecule was recrystallized from THF for purification.

{BnN(CH₂CH₂CH₂-*N*-methylbenzimidazole-2-ylidene)₂}FeCl₂ (4). $\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}_2$ (94 mg, 0.25 mmol) was added to a suspension of $\{\text{BnN}(\text{CH}_2\text{CH}_2\text{CH}_2\text{-N-methylbenzimidazolium})_2\}\cdot 2[\text{Cl}]$ (131 mg, 0.25 mmol) in 12 mL toluene. The mixture was stirred at room temperature for 16 hours, after which stirring was stopped, and the precipitate was allowed to settle for several hours. The solution was carefully decanted from the precipitate, which was washed with toluene and pentane and dried under vacuum to give **4** as a pale yellow powder. Single crystals for X-ray analysis were grown from a benzene/pentane solution at room temperature. Yield: 136 mg (93%).

IR (diamond tip, cm^{-1}): 3371 (br), 3060 (w), 3021 (w), 2948 (s), 2883 (w), 2843 (m), 2807 (m), 2116 (m), 1608 (w), 1568 (s), 1485 (s), 1460 (s), 1454 (s), 1438 (s), 1393 (s), 1381 (s), 1368 (s), 1349 (s), 1313 (w), 1293 (w), 1277 (w), 1265 (w), 1254 (w), 1233 (w), 1210 (s), 1188 (m), 1170 (w), 1140 (m), 1126 (w), 1094 (w), 1061 (s), 1038 (m), 1026 (m), 1013 (m), 1004 (w), 967 (w), 935 (w), 910 (w), 897 (w), 881 (w), 860 (w), 832 (w), 817 (w). Magnetic susceptibility (C_6D_6): 4.84 μ_{B} . Anal. calcd (found) for $\text{C}_{29}\text{H}_{33}\text{Cl}_2\text{N}_5\text{Fe}\cdot\text{THF}$: C, 60.93 (60.61); H, 6.37 (6.24); N, 10.77 (10.55). The molecule was recrystallized from THF for purification.

{BnN(CH₂CH₂CH₂-*N*-methylbenzimidazole-2-ylidene)₂}FeBr₂ (5). KO^tBu (68 mg, 0.6 mmol) was added to a suspension of $\{\text{BnN}(\text{CH}_2\text{CH}_2\text{CH}_2\text{-N-methylbenzimidazolium})_2\}\cdot 2[\text{Cl}]$ (105 mg, 0.2 mmol) in 10 mL THF. The mixture was stirred for three hours. The volatiles were removed under vacuum. The resulting residue was extracted using toluene (2 × 6 mL) and filtered through celite. To this toluene solution, FeBr_2 (39 mg, 0.18 mmol) was added. The suspension was stirred for 21 hours. The mixture was filtrated through celite and the filtrate collected. The volume of the filtrate was reduced to approximately 1 mL and 5 mL pentane was added. The solution was carefully decanted from the precipitate, which was washed with pentane and dried under vacuum to give **5** as a yellow powder. Single crystals for X-ray analysis were grown from a toluene/pentane solution at room temperature. Yield: 65 mg (52%).

¹H NMR (400 MHz, C_6D_6): 10.50 (3H), 9.47 (2H), 8.83 (2H), 7.79 (2H), 6.04 (1H), 5.67 (2H), 3.37 (6H), 2.76 (4H), 2.12 (4H), 1.84 (4H), 0.96 (2H). IR (diamond tip, cm^{-1}): 3461 (br), 3058 (m), 3025 (m), 2940 (s), 2813 (s), 2723 (w), 2661 (w), 2323 (s), 2117 (s), 1992 (m), 1700 (s), 1619 (m), 1602 (m), 1569 (m), 1498 (s), 1481 (s), 1452 (s), 1432 (w), 1388 (w), 1363 (s), 1346 (w), 1292 (w), 1245 (m), 1207 (w), 1186 (m), 1176 (w), 1137 (m), 1126 (m), 1089 (w), 1072 (m), 1043 (w), 1025 (w), 1014 (s), 971 (br), 912 (w), 883 (w), 844 (m). Magnetic susceptibility (C_6D_6): 4.84 μ_{B} . Anal. calcd (found) for $\text{C}_{29}\text{H}_{33}\text{Br}_2\text{N}_5\text{Fe}$: C, 52.20 (53.28); H, 4.98 (5.23); N, 10.50 (10.27).

General procedure for homo-coupling reactions in Table 2

To a solution of iron catalyst (0.0036 mmol) in 0.9 mL THF and additive (0.18 mmol, if necessary), *p*-tolylmagnesium bromide (0.36 mL, 0.18 mmol, 0.5 M in diethyl ether) was added at room temperature. After 30 minutes the reaction was quenched by

addition of wet 0.2 mL CHCl₃. The volatiles were removed under vacuum and internal standard trimethoxybenzene (11.7 mg, 0.07 mmol) was added. A ¹H NMR spectrum of the mixture was recorded in CDCl₃ to calculate the yield.

General procedure for homo-coupling reactions in Table 3

The substrate (0.54 mmol) in THF or diethyl ether was added to a stirred solution of catalyst **4** (6 mg, 0.0108 mmol) in 3 mL THF. The mixture was stirred at room temperature for 30 minutes and then 1 mL wet CHCl₃ was added. The solution was filtered through silica gel and the resulting mixture was evaporated to dryness. The products were then separated by column chromatography on silica gel (250–400 mesh) with either pentane or pentane–diethyl ether (50 : 1) as the eluent. The homo-coupling products were identified by comparison of the ¹H NMR spectra with those previously reported in the literature and the isolated yields were recorded.

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