

# The synthesis, coordination chemistry and ethylene polymerisation activity of ferrocenediyl nitrogen-substituted ligands and their metal complexes

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Available online 11 November 2005

## Abstract

Treatment of aminoferrocene with substituted 2-hydroxybenzaldehydes yields the air- and moisture-stable ligands **1–4**, which were then reacted to form the chromium dichloride complexes **5–7** and the nickel bis-chelate species **8** and **9**. The metal compounds are very air-sensitive but the chromium compounds act as pre-catalysts for the polymerisation of ethylene. Reaction of 1,1'-bis(amino)ferrocene with similarly substituted 2-hydroxybenzaldehydes or simple benzaldehyde gives the ligands **10–12** and **17**, respectively. The X-ray crystal structure of **11** shows the molecule to have non-crystallographic  $C_2$  symmetry and to be linked by C–H... $\pi$  interactions between the anthracene rings. Titanium-containing complexes **13–16** can be formed utilising ligands **10–12** and there is a change in geometry within the complexes dependent on the adjacent co-ligands, whilst ligand **17** can be reacted with PdClMe(COD) to form the chelate complex **18**. Cyclic voltammetric studies have been carried out on **18** and its oxidised analogue **19**, but both complexes are inactive towards ethylene polymerisation.

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**Keywords:** Ferrocene; Catalysis; N-ligands; Transition metals; Ethylene polymerisation

## 1. Introduction

Schiff-base ligands play pivotal roles in homogeneous catalysis. Indeed, salicylaldehyde complexes of group 4 metals [1–5], nickel [6,7] and chromium [8] have all been used as active pre-catalysts for ethylene polymerisation. Similarly group 4 metal complexes based on the family of salen ligands have also been used for ethylene and propylene polymerisation catalysis [9]. These latter ligands have also been successfully utilised in a variety of other catalytic processes, for instance in conjunction with aluminium for

the polymerisation of *rac*-lactide [10,11] and methyl methacrylate polymerisation [11].

In other aspects of catalysis and ligand design, ferrocene ligands have an important role to play: (i) as a backbone or substituent in ligands providing a specific and unique geometry and (ii) via their redox activity and the potential control of the reactivity of a coordinated, catalytically-active metal centre [12,13]. Although substituted ferrocenyl amines are known [14], the formation of N-substituted ferrocenyl and ferrocenediyl species has been limited. In recent years though, efficient routes to ferrocenediyl diamine [15] have been reported and the titanium and zirconium complexes of these and related ligands [16–18] have been highlighted [19] and shown to exhibit moderate ethylene polymerisation activity.

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Thus, as part of our on-going quest to find new sterically-hindered and redox-active ferrocene ligands, this manuscript features the introduction of a ferrocene moiety into a variety of salicylaldehyde, salen and bis(imine) ligands, subsequent coordination to a range of transition metals and an investigation into their potential as catalysts for ethylene polymerisation.

### 1.1. Synthesis of ferrocenyl salicylaldehydes

The ferrocenyl salicylaldehydes **1–4** were conveniently synthesised by the Schiff base condensation of ferrocenylamine with a range of salicylaldehydes (Scheme 1). The reactions were carried out by adding a dichloromethane solution of the substituted salicylaldehyde to a dichloromethane solution of ferrocenylamine and heating the reaction mixture to reflux for 5 h. During this time a colour change of orange to red was observed and after removal of the solvent in vacuo, the resulting red sticky solid was easily recrystallised from ethanol to give the desired products in moderate yields. All analyses were consistent with the named compounds.  $^1\text{H}$  NMR spectra show a characteristic singlet resonance due to the OH proton between 13 and 14 ppm, the high field chemical shift being due to intramolecular H-bonding with the imine nitrogen. A singlet resonance due to the aldimine proton between 8.1 and 8.8 ppm is also observed. All compounds exhibit two pseudo triplets and a singlet resonance in the ferrocenyl region, which is indicative of mono-substitution of one of the cyclopentadienyl rings.

### 1.2. Synthesis of chromium catalysts supported by ferrocenyl salicylaldehydes

Work in our laboratories on chromium catalysts for ethylene polymerisation has shown that a series of substituted salicylaldehyde complexes of chromium can lead to active catalysts [20]. The nature of the phenyl ring substituent(s) and the nitrogen alkyl/aryl group can lead to a difference in the catalytic activity and physical properties of the resulting polymer. Monochelate analogues have also been found to be accessible if the phenoxide *ortho* position contains a bulky substituent such as an anthracenyl group [8]. In order to evaluate the activity of the ferrocenyl salicylaldehydes, in situ polymerisation studies were carried out by the addition of a toluene solution of the ferrocenyl salicylaldehydes with *p*-tolylCrCl<sub>2</sub> · 3THF in a Schlenk vessel to form compounds **5–7**. The reaction proceeds at room temperature and after 3 h the solvent was removed under vacuum to eliminate any THF, which may hinder catalysis. NMR analysis of the chromium compounds **5–7** was problematic due to their paramagnetic nature – only broad unassignable peaks were observed. Elemental analysis suggests that the chromium dichloride complexes are formed, but mass spectrometry indicates the possible formation of a bis chelate-chromium monochloride compound and it is

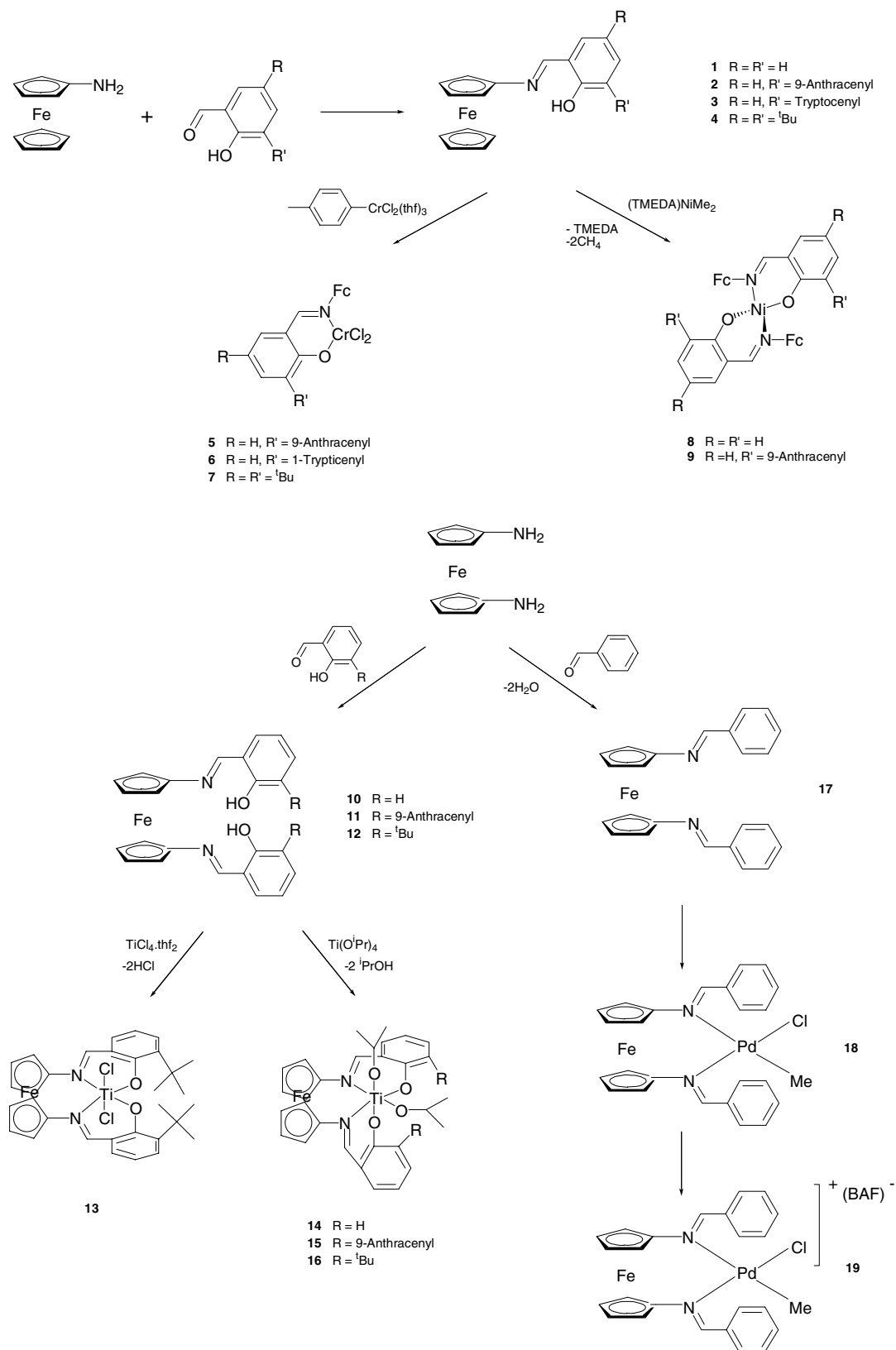
likely that a mixture of products is formed during these reactions.

### 1.3. Polymerisation tests using chromium catalysts **5–7**

In order to test the ethylene polymerisation activity of the chromium species **5–7** the compounds were redissolved in toluene and 100 equiv. of MAO were added to the reaction mixture which was then exposed to 1 bar ethylene pressure for 1 h during which time the precipitation of solid polyethylene was observed. The polymerisation test was terminated by the removal of the ethylene supply and the addition of acidified methanol. The polyethylene was separated from the reaction mixture by filtration and dried in a vacuum oven overnight. The results are summarised in Table 1. The catalysts showed moderate activity, and the anthracenyl-substituted complex (**5**) was found to be comparable with the non-ferrocenyl analogues [8]. Analysis of the polymer formed from **5** showed it to be high molecular weight with a relatively narrow molecular weight distribution ( $M_w$  – 203 000,  $M_n$  – 79 000, PDI 2.6). This is similar to the literature values [8] for this type of system. For compounds **6** and **7**, insoluble polyethylene was obtained indicative of very high molecular weight (>2M Da.).

### 1.4. Synthesis and evaluation of nickel catalysts supported by ferrocenyl salicylaldehydes

Grubbs and co-workers [6] have recently shown that a series of salicylaldehyde complexes of Ni with a bulky group *ortho* to the OH group can form highly active ethylene polymerisation catalysts. The bulky groups retard associative displacement reactions in much the same way as for cationic Ni( $\alpha$ -diimine) systems, whilst the formation of inactive bis-ligand complexes is also prevented. Thus, a pronounced dependence of activity on the phenyl substituent (in this case anthracenyl) is observed. The highest activity, of several hundred g mmol<sup>-1</sup> h<sup>-1</sup> bar<sup>-1</sup> is observed with complexes containing a weakly coordinating acetonitrile ligand [6]. In order to investigate whether the ferrocenyl analogues would form active nickel catalysts, reaction of **1** and **2** with (TMEDA)NiMe<sub>2</sub> in the presence of acetonitrile was carried out (Scheme 1). A solution of the salicylaldehyde in acetonitrile was added dropwise to a solution of (TMEDA)NiMe<sub>2</sub> also in acetonitrile at –78 °C and the reaction mixture stirred for 1 h after which it was warmed to room temperature. The resulting red coloured solution was stirred for a further 30 min and the solvent removed in vacuo to give red-orange solids **8** and **9**. In both cases the  $^1\text{H}$  NMR spectra of the product showed broad resonances indicative of a tetrahedral paramagnetic compound plus unreacted (TMEDA)NiMe<sub>2</sub>. The new compounds could be isolated by washing the crude product with cold diethyl ether in order to remove the unreacted starting materials and elemental analysis suggested that in all cases the bis-chelate compound was formed. Floris [21] has previously shown that **1** can react with a range



Scheme 1. The formation of compounds 1–19.

of metal salts (Co(II), Ni(II), Zn(II) and Cu(II)) to give bis-chelate compounds. It was hoped that the bulky substituents would have prevented the formation of the bis-chelate

(which is catalytically inactive), but it is likely that the comparatively small size of the cyclopentadienyl ring as opposed to a substituted phenyl ring means that bis-chelate

Table 1  
Ethylene polymerisation tests with chromium catalysts 5–7

Cat	Cat. conc. ( $\mu\text{mol}$ )	MAO (equiv.)	Time	Temperature ( $^{\circ}\text{C}$ )	Mass polymer (g)	Activity ( $\text{g mmol}^{-1} \text{bar}^{-1} \text{h}^{-1}$ )
5	50	100	20 min <sup>a</sup>	20	2.15	129
5	10	100	1 h	20	0.94	94
5	10	100	1 h	50	0.46	46
6	10	100	1 h	20	0.22	22
7	10	100	1 h	20	0.34	34

<sup>a</sup> Test stopped after 20 min due to difficulty in stirring.

formation is possible. The nickel compounds were tested as ethylene polymerisation catalysts but in all cases were found to be inactive.

### 1.5. Synthesis of ferrocenyl bis-salicylaldimine (Salen type) 'Salfen' ligands

The Schiff base condensation of 1,1'-bis(amino)ferrocene [15,22] with a range of substituted salicylaldehydes proceeds readily in dichloromethane solution to form ligands **10–12** (Scheme 1). The reactions were carried out by adding a dichloromethane solution of the substituted salicylaldehyde to a dichloromethane solution of 1,1'-bis(amino)ferrocene and heating the reaction mixture to reflux for 1 h. During this time a colour change of orange to burgundy was observed. The solvent was removed under vacuum and the resulting burgundy coloured solid was easily recrystallised from dichloromethane:pentane (25:75) solution to give the products in good yields (68–85%). The relationship between this family of ligands and the family of salen ligands can easily be seen and they have recently been coined 'salfen' ligands [15]. In a conventional salen ligand the backbone contains a C2 unit, which has effectively been replaced by a ferrocene unit in a salfen ligand. The distance between the two nitrogen atoms is somewhat larger in a salfen ligand, although it is possible for the ferrocenediyl unit to twist and deform in order to coordinate to a metal centre. All analyses are consistent with the named compounds. The <sup>1</sup>H NMR spectra of the ligands show two pseudo-triplets in the ferrocenyl region, which is consistent with a time-averaged C<sub>2v</sub> symmetry in solution.

A single crystal structure analysis of **11** showed the molecule to have approximate non-crystallographic C<sub>2</sub> symmetry about an axis passing through the iron centre and bisecting the vector linking the centres of the two phenyl rings (Fig. 1). The two cyclopentadienyl rings are inclined by ca. 2° and staggered by ca. 21°. The pattern of bonding in the C(1)–C(12) and C(6)–C(33) chains (Table 2) do not differ significantly from those observed in the structure of *N*-(*o*-hydroxybenzylidene)-ferroceneamine [13]. Here, in **11** the C(12)- and C(33)-containing phenyl rings are rotated by ca. 17° and 15°, respectively, out of the planes of their parent cyclopentadienyl rings (cf. ca. 10° in the literature complex). In both arms of the molecule there is an intramolecular O–H···N hydrogen bond between the phenolic oxy-

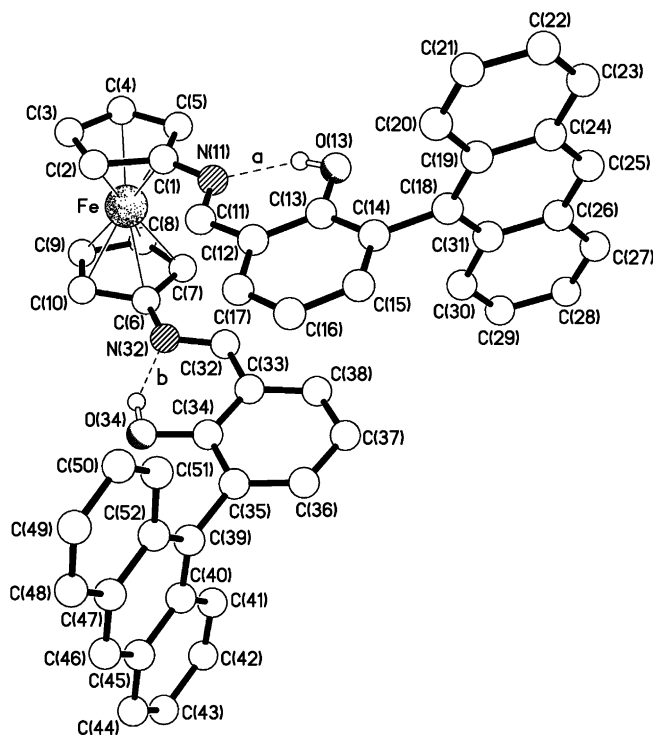


Fig. 1. The molecular structure of **11**. The intramolecular hydrogen bonds have O···N, H···N ( $\text{\AA}$ ), O–H···N ( $^{\circ}$ ): (a) 2.61, 1.83, 145; (b) 2.62, 1.79, 154.

Table 2  
Selected bond lengths ( $\text{\AA}$ ) and angles ( $^{\circ}$ ) for (**11**)

C(1)–N(11)	1.397(4)	C(6)–N(32)	1.402(4)
N(11)–C(11)	1.286(4)	C(11)–C(12)	1.445(4)
N(32)–C(32)	1.287(4)	C(32)–C(33)	1.439(5)
N(11)–C(1)–C(5)	121.7(4)	N(11)–C(1)–C(2)	129.9(4)
N(32)–C(6)–C(10)	122.5(3)	N(32)–C(6)–C(7)	130.0(3)
C(11)–N(11)–C(1)	121.4(3)	N(11)–C(11)–C(12)	122.2(3)
C(17)–C(12)–C(11)	119.5(3)	C(13)–C(12)–C(11)	121.6(3)
C(32)–N(32)–C(6)	120.3(3)	N(32)–C(32)–C(33)	122.5(3)
C(38)–C(33)–C(32)	119.7(3)	C(34)–C(33)–C(32)	122.0(3)

gen atom and the amino nitrogen. The anthracene and phenyl rings are oriented approximately orthogonally to each other, the torsional twists about the C(14)–C(18) and C(35)–C(39) bonds being ca. 78° and 89°, respectively. The two phenyl rings are  $\pi$ -stacked with a mean interplanar separation of ca. 3.65  $\text{\AA}$  and a centroid···centroid distance

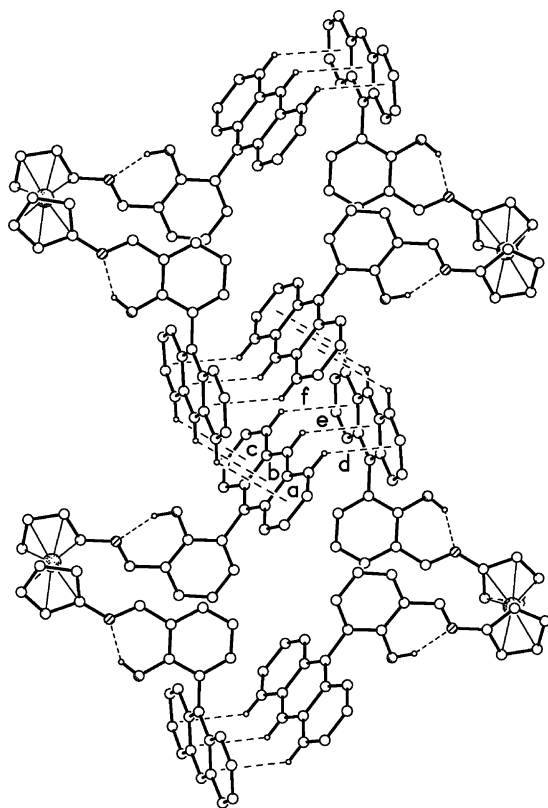


Fig. 2. Part of one of the C–H··· $\pi$  linked chains of molecules in the structure of **11**. The H···ring-centroid distances (Å) are: (a) 3.10; (b) 3.18; (c) 3.16; (d) 2.78; (e) 2.80; (f) 2.76.

of 4.00 Å; the rings are inclined by ca. 8°. Centrosymmetrically related pairs of molecules are linked by C–H··· $\pi$  interactions between the anthracene rings to form chains that extend in the crystallographic 110 direction (Fig. 2).

#### 1.6. Reaction of 10–12 with titanium precursors

The reaction of the Salfen type ligands with titanium precursors  $\text{TiCl}_4 \cdot (\text{THF})_2$  and  $\text{Ti}(\text{O}^i\text{Pr})_4$  was investigated (Scheme 1). Reactions were carried out by addition of a toluene solution of the ligand to a toluene solution of the titanium precursor and stirring at 40 °C for 3 h. The solvent was removed in vacuo and the product washed with cold pentane to give the products. The dichloride product **13** could be successfully recrystallised from dichloromethane:pentane (25:75) solution and isolated as brown needles in 66% yield. The diisopropyl products **14–16** were isolated as red powders in moderate yields (45–77%). The size of Ti(IV) means that the Salfen ligand can coordinate to the titanium as a tetradentate  $[N, O^-, N', O'^-]$  ligand. Octahedral salen metal complexes have been shown to display a range of coordination modes (Fig. 3) and, depending on the metal precursor, the salfen ligands can also show different coordination geometries. In the case of the dichloride product **13** the ferrocenyl region of the  $^1\text{H}$  NMR spectrum shows two pseudo triplet resonances, whereas the NMR spectra of the diisopropyl complexes **14–16** is much more

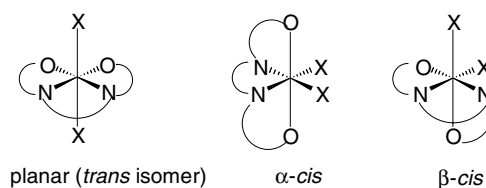


Fig. 3. Possible coordination geometries of salen ligands.

complicated and shows eight individual ferrocenyl resonances. Arnold [15] has shown that **12** can coordinate to  $\text{Ti}(\text{Bn})_4$  and  $\text{Zr}(\text{Bn})_4$  in a planar fashion and the  $^1\text{H}$  NMR spectra of the ferrocene region is reported to have two pseudo triplet references, suggesting that the salfen- $\text{TiCl}_2$  complex **13** has a similar geometry. In contrast, the  $^1\text{H}$  NMR spectrum of the salfen $\text{Ti}(\text{O}^i\text{Pr})_2$  complexes are, however, much more complicated. The  $^1\text{H}$  NMR spectrum of **16** shows two sets of resonances for the imino protons (at 8.26 and 8.51 ppm), the aryl protons and the *tert*-butyl protons. The ferrocenyl region shows eight multiplets – indicating that each of the ferrocenyl protons is inequivalent. Furthermore, two distinct septets are visible for the  $\text{CH}(\text{CH}_3)_2$  isopropyl protons and four doublets are noted for isopropyl  $\text{CH}_3$  groups. This indicates that one of the ligand O atoms is *trans* to an isopropyl unit and the other is *cis* to an isopropyl unit. The reason for the change in geometry is probably due to the larger size of the isopropyl groups compared to a chloride or benzyl group.

Isolation of X-ray quality crystals for all the titanium species was difficult and only the structures of oxo-bridged dimers could be obtained. Two are detailed here: **A** is the oxo-bridged titanium dichloride complex of ligand **10**, whilst **B** is the oxo-bridged dimer of **14**. The X-ray analysis of **A** revealed an oxo-bridged dimer structure, as illustrated in Fig. 4. The geometries at the two titanium centres are

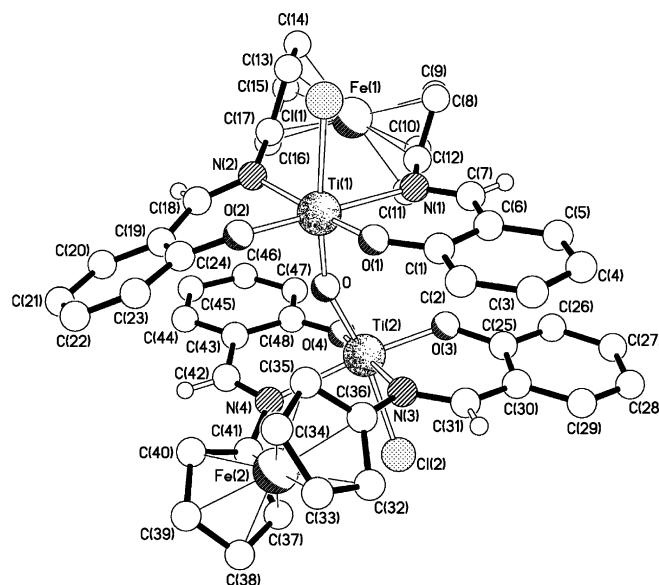


Fig. 4. The molecular structure of **A**.

distorted octahedral with *cis* angles at the metal centres ranging between 82.4(1)° and 99.8(1)° at Ti(1), and 82.1(1)° and 100.8(1)° at Ti(2); the Cl(1)–Ti(1)–O and Cl(2)–Ti(2)–O angles are 166.2(1)° and 168.2(1)°, respectively. The gross structure is very similar to that observed in the related oxo-bridged complex dichloro-( $\mu_2$ -oxo)-bis(*N,N'*-disalicylidene-(*R,R*)-1,2-cyclohexane-diamine-*O,O',N,N'*-di-titanium(IV)) [23]. The Ti–O(oxo) distances [1.838(3) and 1.824(3) Å] and the Ti–O(salicylidene) bond lengths [range 1.846(3)–1.878(3) Å] (Table 3) do not differ significantly from those in the above literature structure, though the folding at the oxo atom in **A** is greater at 155.8(2)° cf. 168°. The Ti–N distances in **A** [range 2.250(4)–2.279(4) Å] are all ca. 0.1 Å longer than those in the above structure reflecting the change from a cyclohexyl to a ferrocenyl bridge between the nitrogen centres. The N(1),O(1) chelate ring is nearly planar with Ti(1) lying only 0.06 Å out of the plane of the remaining atoms, which are coplanar to within 0.02 Å. By contrast, the other three *N,O* chelate rings are all folded significantly out of plane about their N···O vectors with fold angles of 27°, 23°, and 26° for the N(2),O(2), N(3),O(3), and N(4),O(4) containing rings, respectively; the deviations of their associated titanium centres are 0.69, 0.61 and 0.68 Å respectively. The bending at the oxo bridge results in the N(3)=C(31) double bond overlaying the C(1)–C(6) phenyl ring in a  $\pi$ - $\pi$  stacking arrangement, the distance of the centre of the bond to the ring plane being only 3.25 Å. Both ferrocenyl units have staggered geometries, with stagger angles of 21° and 28° for Fe(1) and Fe(2), respectively; the cyclopentadienyl rings are inclined by ca. 1° [Fe(1)] and ca. 4° [Fe(2)]. The structure contains an MeCN molecule of solvation and there are no noteworthy intermolecular packing interactions.

Table 3  
Selected bond lengths (Å) and angles (°) for **A**

Ti(1)–O	1.838(3)	Ti(1)–O(1)	1.846(3)
Ti(1)–O(2)	1.878(3)	Ti(1)–N(1)	2.279(4)
Ti(1)–N(2)	2.250(4)	Ti(1)–Cl(1)	2.393(2)
Ti(2)–O	1.824(3)	Ti(2)–O(3)	1.861(3)
Ti(2)–O(4)	1.873(3)	Ti(2)–N(3)	2.268(4)
Ti(2)–N(4)	2.252(4)	Ti(2)–Cl(2)	2.4176(14)
O–Ti(1)–O(1)	97.5(2)	O–Ti(1)–O(2)	96.83(14)
O(1)–Ti(1)–O(2)	94.44(14)	O–Ti(1)–N(2)	88.23(14)
O(1)–Ti(1)–N(2)	173.8(2)	O(2)–Ti(1)–N(2)	82.38(13)
O–Ti(1)–N(1)	84.86(13)	O(1)–Ti(1)–N(1)	83.21(14)
O(2)–Ti(1)–N(1)	177.29(14)	N(2)–Ti(1)–N(1)	99.82(13)
O–Ti(1)–Cl(1)	166.16(11)	O(1)–Ti(1)–Cl(1)	88.44(12)
O(2)–Ti(1)–Cl(1)	95.15(11)	N(2)–Ti(1)–Cl(1)	86.51(10)
N(1)–Ti(1)–Cl(1)	83.45(11)	O–Ti(2)–O(3)	100.77(14)
O–Ti(2)–O(4)	94.9(2)	O(3)–Ti(2)–O(4)	95.13(14)
O–Ti(2)–N(4)	85.66(13)	O(3)–Ti(2)–N(4)	173.57(14)
O(4)–Ti(2)–N(4)	84.2(2)	O–Ti(2)–N(3)	91.01(14)
O(3)–Ti(2)–N(3)	82.09(13)	O(4)–Ti(2)–N(3)	173.8(2)
N(4)–Ti(2)–N(3)	97.93(13)	O–Ti(2)–Cl(2)	168.16(10)
O(3)–Ti(2)–Cl(2)	89.31(11)	O(4)–Ti(2)–Cl(2)	90.29(12)
N(4)–Ti(2)–Cl(2)	84.30(10)	N(3)–Ti(2)–Cl(2)	84.18(10)
Ti(2)–O–Ti(1)	155.8(2)		

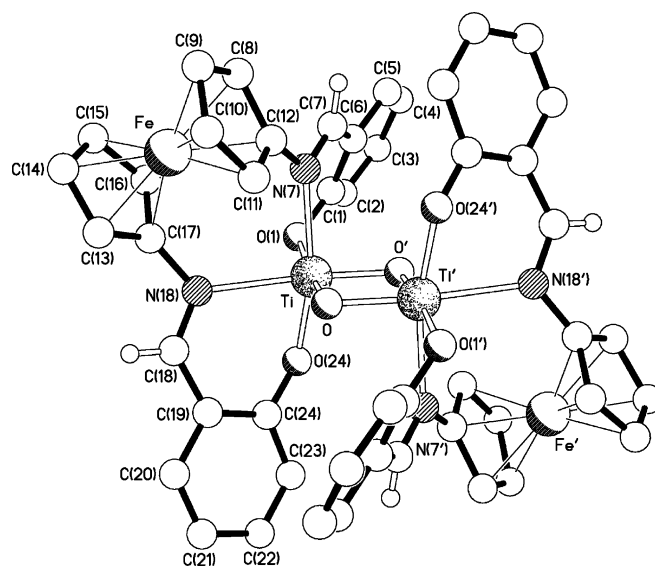


Fig. 5. The molecular structure of **B**.

Table 4  
Selected bond lengths (Å) and angles (°) for **B**

Ti–O	1.912(3)	Ti–O'	1.792(3)
Ti–O(1)	1.948(3)	Ti–N(7)	2.247(3)
Ti–N(18)	2.365(4)	Ti–O(24)	1.910(3)
O'–Ti–O(24)	101.07(13)	O'–Ti–O	83.26(13)
O(24)–Ti–O	97.39(13)	O'–Ti–O(1)	96.07(13)
O(24)–Ti–O(1)	92.26(13)	O–Ti–O(1)	170.28(13)
O'–Ti–N(7)	90.85(13)	O(24)–Ti–N(7)	166.72(14)
O–Ti–N(7)	89.74(12)	O(1)–Ti–N(7)	80.57(13)
O'–Ti–N(18)	167.75(13)	O(24)–Ti–N(18)	79.66(13)
O–Ti–N(18)	84.52(12)	O(1)–Ti–N(18)	96.12(13)
N(7)–Ti–N(18)	89.94(13)	Ti'–O–Ti	96.74(13)

A single crystal structure of **B** showed the complex to be dimeric and centrosymmetric with the tetradentate ligands adopting an axial/equatorial coordination (Fig. 5) in contrast to the all-equatorial geometry observed in **A**. The geometry at titanium is distorted octahedral with *cis* angles in the range 79.7(1)–101.1(1)° and *trans* angles of between 166.7(1)° and 170.3(1)° (Table 4). The gross structure is very similar to that of the cyclohexyl containing analogue, bis( $\mu_2$ -oxo)-(N,N'-(cyclohexane-1,2-diyl)-bis(salicylaldiminato))-titanium(IV) [24]. The Ti–O(salicylidene) bond lengths [1.910(3) Å (*trans* to N) and 1.948(3) Å (*trans* to oxo)] are very similar to those observed in the related literature structure, whereas those to nitrogen [2.247(3) Å to N(7) and 2.365(4) Å to N(18)] are ca. 0.1 Å longer. The two Ti–O(oxo) bonds in **B** [1.792(3) and 1.912(3) Å] are markedly asymmetric, though these distances are the same as those observed in the N–CH<sub>2</sub>–CH<sub>2</sub>–N linked analogue bis( $\mu_2$ -oxo)-(N,N'-disalicylidene-1,2-diaminoethane)-titanium(IV) [25]. The two *N,O* chelate rings have more steeply folded geometries than those observed in **A** with fold angles about their N···O vectors of 40° [N(7),O(1)] and 31° [N(18),O(24)] and associated out-of-plane displacements

of the titanium atom of 1.03 and 0.84 Å, respectively. The ferrocenyl unit has a staggered geometry (29°) with its cyclopentadienyl rings being inclined by ca. 9°. The crystals contain a CHCl<sub>3</sub> molecule of solvation which is disordered, and the only intermolecular packing interaction of note is a  $\pi$ – $\pi$  stacking of the C(1)–C(6) rings of centrosymmetrically related pairs of molecules. The centroid···centroid and mean interplanar separations are 4.10 and 3.40 Å, respectively.

### 1.7. Synthesis of *N,N'*-bis(benzylimido)ferrocenediamine (**17**) and some palladium complexes (**18** and **19**)

The Schiff-base condensation of 1,1'-bis(amino)ferrocene with benzaldehyde proceeds readily in toluene solution at room temperature. Freshly distilled benzaldehyde was added to a toluene solution of 1,1'-bis(amino)ferrocene and the reaction mixture stirred for 3 h during which time the initial yellow colour became deep red. The toluene and excess benzaldehyde were removed in vacuo to yield a burgundy solid, which was washed with pentane to give the red coloured, air-stable bis(imine) in 75% yield (Scheme 1) [18]. Although compound **17** has a bis-imino type functionality, attempts at forming coordination compounds with metal precursors (dme)NiBr<sub>2</sub> and FeCl<sub>2</sub> failed; it was thought that the twist energy of the imine arms and their relative rigidity precluded coordination. However, it was anticipated that a larger metal such as palladium might form complexes, and indeed this has now been achieved. Reaction of **17** with Pd(COD)MeCl [26] in DCM at 40 °C for 72 h, and removal of the solvent gave an orange terracotta-coloured solid **18**, that was crystallised at –30 °C from pentane/dichloromethane (Scheme 1). Spectroscopic analysis of the compound in both <sup>1</sup>H and <sup>13</sup>C NMR revealed that the two halves of the ligands were now no longer equivalent, owing to the different influences exerted by the methyl and chloride groups on the palladium centre, hence two imine peaks are observed and the ferrocene gives eight separate peaks in the <sup>13</sup>C-spectrum. Orange needle-like crystals of **18** suitable for X-ray diffraction studies were obtained from a 2-layer solution of dichloromethane/hexane. The structure of **18** (Fig. 6) is very similar to that of its dichloro analogue (1,1'-bis(benzylideneamino)ferrocene-*N,N'*-dichloro-palladium(II) [27], the principal difference being in the inclination of the phenyl rings to their associated cyclopentadienyl rings. In **18** the C(2)–C(6) ring is inclined by ca. 74° to C(13)–C(18) whereas the C(7)–C(11) ring is inclined by only ca. 7° to C(20)–C(25). In the former case the inclination is made up of torsional twists of ca. 48° and 25° in the same sense about the C(2)–N(12) and C(12)–C(13) bonds, respectively, whereas in the later the torsional twists about C(7)–N(19) and C(19)–C(20), each ca. 29°, are in opposite senses. In the literature structure, which contains two independent molecules, the cyclopentadienyl and their associated phenyl rings are inclined by angles ranging between only 10° and 18°. The geometry at palladium is distorted square planar

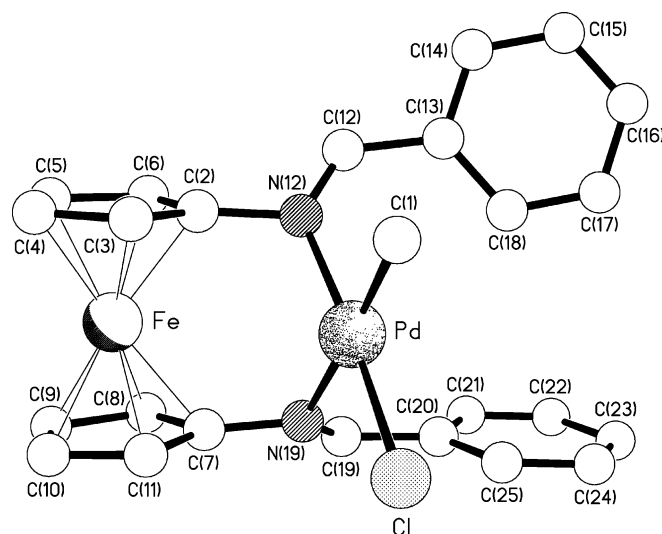


Fig. 6. The molecular structure of **18**. The Fe···Pd separation is 3.60 Å.

with *cis* angles in the range 88.2(5)–92.8(5)° with *trans* angles of 172.8(3) and 177.1(5)° (Table 5). The Pd–N(12) and Pd–Cl distances do not differ significantly from those observed for the dichloro analogue. The Pd–N(19) bond length is significantly longer, reflecting the difference of N *trans* to Me cf. N *trans* to Cl. The ferrocenyl unit has a slightly staggered geometry (ca. 6°) the rings being inclined by ca. 5°. The only packing interaction of note is a weak  $\pi$ – $\pi$  stacking of the C(13)–C(18) ring of one molecule with the C(20)–C(25) ring of a symmetry related neighbour, and vice versa; the mean interplanar separation is 3.66 Å.

With a view to potential application as an ethylene polymerisation catalyst **18** was reacted with sodium tetrakis(3,5-bis-trifluoromethyl-phenyl)borate (BAF) [28] to form the new compound  $\{[1,1'$ -bis(benzylimino)ferrocene}Pd<sup>+</sup>Me(MeCN)[BAF<sup>–</sup>]**19**. As in the preparation of **18**, reactants for **19** were heated together in dichloromethane at 40 °C, this time overnight. Removal of the solvent gave a brown/orange/yellow lustrous solid in 59% yield. As before the two halves of the compound are still inequivalent due to one imine being *trans* to a methyl group whilst the other is *trans* to a loosely coordinated acetonitrile molecule. Multiple splittings are therefore again seen in both the <sup>1</sup>H and <sup>13</sup>C NMR, particularly in the aryl region, where full assignment was made by comparison with literature values [28] for BAF<sup>–</sup>. Further evidence for the existence of **18** and **19** came from mass spectra and elemental analysis. Attempts are currently underway to

Table 5  
Selected bond lengths (Å) and angles (°) for **18**

Pd–Cl	2.298(4)	Pd–C(1)	2.046(10)
Pd–N(12)	2.030(13)	Pd–N(19)	2.200(10)
N(12)–Pd–C(1)	88.5(6)	N(12)–Pd–N(19)	90.2(4)
C(1)–Pd–N(19)	177.1(5)	N(12)–Pd–Cl	172.8(3)
C(1)–Pd–Cl	88.2(5)	N(19)–Pd–Cl	92.8(3)

obtain crystals of **19** that are suitable for X-ray diffraction studies in order to see whether any change in the structure occurs as a result of the presence of the Pd<sup>+</sup> species such as a palladium-iron bond, analogous to those found for [FcS<sub>2</sub>]Pd/Pt and [FcP<sub>2</sub>]Pd-type species [29].

In order to test the potential ethylene polymerisation activity of **19**, the palladium compound was dissolved in DCM and exposed to 1 bar ethylene pressure for 1 h during which time the orange solution turned green, and there was no visible evidence of any solid polyethylene being formed. Upon quenching the reaction with HCl the solution turned lilac and upon standing became a pale yellow colour. An aliquot was removed for GPC analysis which revealed that no oligomers had been formed either, meaning that compound **19** unfortunately showed no activity as an ethylene polymerisation catalyst.

### 1.8. Redox chemistry

Although complex **19** showed no activity for ethylene polymerisation, it was considered possible that the oxidised ferrocenium species may exhibit activity. Investigations into the electrochemistry of **19** and its precursors **17** and **18** were therefore performed in order to determine what common chemical oxidants were appropriate to generate the ferrocenium-active complex. The experiments were performed on 0.001 M dichloromethane solutions of compounds **17–19**, with supporting electrolyte 0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub>, using Ag/AgCl as the reference electrode, along with platinum working and auxiliary electrodes, and a scan rate of 100 mV s<sup>-1</sup>. The results of the electrochemical investigations are shown in Table 6 and Fig. 7. In each case a quasi-reversible ( $\Delta E_p < 0.1$  V), one-electron transfer for the Fe(II)–Fe(III) redox couple is observed. Upon incorporation of the palladium centre in **18** there is a large shift in the standard redox potential to a more positive voltage as compared to **17**. This shift allows observation of a small imine to amine reduction peak at approximately 0.45 V that was previously masked in **17** by the iron redox couple. A similar phenomenon has been observed in other Fc-imine ligands where the imine–amine reduction peak occurs at 0.16–0.19 V [22]. There is another anodic shift for the positively charged palladium centre in **19**, which means that the iron redox couple occurs very close to the limits of the solvent window. Extending the scans to more positive potentials (1.4 V) gave some indication of another reduction peak (~1.1 V) that overlapped with the Fe(III)–Fe(II) peak that may speculatively be attributed to a Pd(II)–Pd(I) reduction, although the degra-

Table 6  
Cyclic voltammetry studies on Fc, FcPF<sub>6</sub>, and compounds **17–19**

Compound	$E_p^A$ (V)	$E_p^C$ (V)	$E_{1/2}$ (V)	$\Delta E_p$ (V)
Fc	0.489	0.403	0.441	0.096
FcPF <sub>6</sub>	0.460	0.368	0.414	0.092
<b>17</b>	0.516	0.425	0.471	0.091
<b>18</b>	0.778	0.692	0.735	0.086
<b>19</b>	0.858	0.768	0.813	0.090

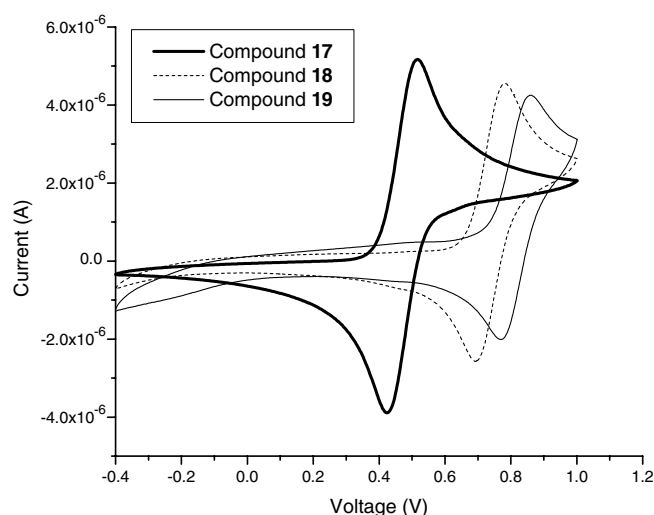


Fig. 7. Cyclic voltammogram of **17–19**.

ation of the solvent at these high potentials cannot be ruled out entirely.

Complexation to the palladium centre shifts the oxidation potential to higher values, in other words the Fe(II)–Fe(III) is harder to access due to the electron withdrawing capacity of the palladium fragment. This means that FcPF<sub>6</sub> may not be used to chemically oxidise compound **19** as it has a lower redox potential than **19**. Indeed such a large anodic shift in the case of **19** may indicate some sort of an interaction between the iron and the palladium centres, that results in binding of ethylene to the palladium centre, with a resultant positive charge on the iron. This may explain the lack of ethylene polymerisation activity, and the observed green-colour, as Fc<sup>+</sup> species are typically blue/green colour in solution.

## 2. Experimental

**General.** All preparations were carried out under an atmosphere of nitrogen using standard Schlenk techniques or an inert atmosphere (nitrogen) glove box, unless otherwise stated. All solvents were distilled over standard drying agents under nitrogen directly before use and deoxygenated. Silica gel (Kieselgel grade 60) was used for chromatographic separations. All NMR spectra were recorded using a Delta upgrade on a JEOL EX270 MHz spectrometer. Chemical shifts are reported in  $\delta$  (ppm) using residual proton impurities in CDCl<sub>3</sub> (<sup>1</sup>H  $\delta$  7.25 ppm, <sup>13</sup>C  $\delta$  77.0 ppm) as the reference solvent. Mass spectra were recorded using positive FAB methods for organometallic compounds, and EI for organic compounds, on a micromass Autospec spectrometer (primary ion beam 35 keV Cs<sup>+</sup> and 3-nitrobenzyl alcohol matrix) by Mr J. Barton, Imperial College. Microanalyses were carried out by Mr S Boyer of the London Metropolitan University.

Polyethylene analysis was performed at BP Chemicals Limited by J. Boyle (NMR) and G. Audley (GPC). GPC



traces were recorded using PL gel 2 × mixed bed – D, 30 cm, 5 micron columns, trichlorobenzene eluent and a flow rate of 1.0 ml/min at 150 °C using a refractive index detector.

### 2.1. Starting materials

Starting materials were prepared according to adapted literature procedures (referenced where appropriate), and were characterised by <sup>1</sup>H NMR and <sup>13</sup>C NMR and mass spectrometry where appropriate. All other chemicals were purchased from Aldrich Chemical Company and used without further purification unless stated. Research grade ethylene (BOC) was used for all ethylene polymerisation experiments. Methyl aluminoxane (MAO) was obtained as a 1.6 M solution in toluene. Ferrocenylamine [30], 3-anthracenyl-2-hydroxybenzaldehyde, and 3-triptyceny-2-hydroxybenzaldehyde [8] were formed via modified literature procedures. (TMEDA)NiMe<sub>2</sub> was synthesised in our laboratories by Dr. D.J. Jones. All other starting materials were obtained from commercial sources. 1,1'-Bis(amino)ferrocene was formed using a modified procedure of Nesmeyanov [31].

### 2.2. Synthesis of *N*-(2-hydroxybenzylidene)ferroceneamine (1)

The experimental method of Floris [21] was used with minor modifications as necessary to produce a red coloured product (55%).

### 2.3. Synthesis of *N*-(2-hydroxy,3-anthracenylbenzylidene)ferroceneamine (2)

To a solution of ferrocenylamine (0.65 g, 3.2 mmol) in dichloromethane (20 ml) was added a solution of 3-anthracenyl-2-hydroxybenzaldehyde (0.96 g, 3.2 mmol) also in dichloromethane (30 ml). The mixture was heated to reflux for 5 h and the volatiles removed in vacuo to yield a red coloured solid. The product was recrystallised from ethanol to yield crystalline **2** (1.3 g, 84%). Anal. Calc. for C<sub>31</sub>H<sub>23</sub>FeNO: C, 77.33; H, 4.78; N, 2.91. Found: C, 77.49; H 4.89; N, 2.84%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 4.15 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.26 (t, 2H, C<sub>5</sub>H<sub>4</sub>), 4.54 (t, 2H, C<sub>5</sub>H<sub>4</sub>), 7.17 (m, 2H, C<sub>14</sub>H<sub>9</sub>), 7.47 (m, 2H, C<sub>14</sub>H<sub>9</sub>), 7.75 (d, 2H, C<sub>14</sub>H<sub>9</sub>), 8.07 (d, 2H, C<sub>14</sub>H<sub>9</sub>), 8.55 (s, 1H, *ipso*-C<sub>14</sub>H<sub>9</sub>) 8.78 (s, 1H, CH=N), 13.72 (s, 1H, OH); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 62.4 (C<sub>5</sub>H<sub>5</sub>-Cp), 67.6 (C<sub>5</sub>H<sub>4</sub>-Cp), 69.6 (C<sub>5</sub>H<sub>4</sub>-Cp), 101.9 (*ipso*-C C<sub>5</sub>H<sub>4</sub>-Cp), 118.9 (Ar-H), 119.9, 125.1, 125.5, 126.6, 126.9, 128.6, 130.4, 131.0, 131.5, 135.3, 159.1 (Ar-H), 159.9 (CH=N). FAB+ve; *m/z*: 481 [M]<sup>+</sup>.

### 2.4. Synthesis of *N*-(2-hydroxy,3-triptycenybenzylidene)ferroceneamine (3)

An analogous procedure to that employed for **2** was utilised using aminoferrocene (0.1 g, 0.50 mmol) and 3-triptyceny-2-hydroxybenzaldehyde (0.18 g, 0.48 mmol) to

yield crystalline **3** (0.21 g, 76%). Anal. Calc. for C<sub>37</sub>H<sub>27</sub>FeNO: C, 79.71; H, 4.85; N, 2.51. Found: C, 79.48; H, 4.31; N, 2.43%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 4.14 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.26 (tr, 2H, C<sub>5</sub>H<sub>4</sub>), 4.54 (tr, 2H, C<sub>5</sub>H<sub>4</sub>), 5.41 (s, 1H, bridgehead CH C<sub>20</sub>H<sub>13</sub>) 6.96 (m, 8H, Ar-H), 7.16 (m, 1H, Ar-H), 7.22 (m, 11H, Ar-H), 7.41 (m, 4H, Ar-H), 7.53 (m, 1H, Ar-H), 8.55 (m, 1H, Ar-H) 8.77 (s, 1H, CH=N), 14.18 (s, 1H, OH); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 55.30 (bridgehead-C C<sub>20</sub>H<sub>13</sub>), 58.5 (bridgehead-C C<sub>20</sub>H<sub>13</sub>), 62.4 (C<sub>5</sub>H<sub>5</sub>-Cp), 67.7 (C<sub>5</sub>H<sub>4</sub>-Cp), 69.9 (C<sub>5</sub>H<sub>4</sub>-Cp), 101.9 (*ipso*-C C<sub>5</sub>H<sub>4</sub>-Cp), 118.25, 120.54, 123.50, 124.37, 124.53, 124.89, 125.01, 128.24, 128.92, 131.11, 134.44, 145.55, 146.21, 159.72 (Ar-C), 161.06 (CH=N). FAB+ve; *m/z*: 557 [M]<sup>+</sup>.

### 2.5. Synthesis of *N*-(2-hydroxy, 3,5-di-*tert*-butylbenzylidene)ferroceneamine (4)

To a solution of aminoferrocene (1 g, 5 mmol) in toluene (20 ml) was added a solution of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (1.16 g, 5 mmol) also in toluene. The mixture was heated to 80 °C for 3 h and the volatiles removed in vacuo to yield a resulting red coloured solid. The product **4** was recrystallised from ethanol (1.2 g, 57%). Anal. Calc. for C<sub>25</sub>H<sub>31</sub>FeNO: C, 71.94; H, 7.43; N, 3.36. Found: C, 71.89; H 7.58; N, 3.26%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.33 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.46 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 4.18 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.26 (t, 2H, C<sub>5</sub>H<sub>4</sub>), 4.59 (t, 2H, C<sub>5</sub>H<sub>4</sub>), 7.14 (d, 1H, C<sub>6</sub>H<sub>2</sub>), 7.42 (d, 1H, C<sub>6</sub>H<sub>2</sub>), 8.64 (s, 1H, CH=N), 13.76 (s, 1H, OH); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 29.6 (CH<sub>3</sub>), 31.6 (CH<sub>3</sub>), 34.2 (C(CH<sub>3</sub>)<sub>3</sub>), 35.1 (C(CH<sub>3</sub>)<sub>3</sub>), 62.4 (C<sub>5</sub>H<sub>5</sub>-Cp), 67.4 (C<sub>5</sub>H<sub>4</sub>-Cp), 69.8 (C<sub>5</sub>H<sub>4</sub>-Cp), 102.6 (*ipso*-C C<sub>5</sub>H<sub>4</sub>-Cp) 118.8 (C<sub>6</sub>H<sub>2</sub>), 125.8 (C<sub>6</sub>H<sub>2</sub>), 127.0 (C<sub>6</sub>H<sub>2</sub>), 136.9 (C<sub>6</sub>H<sub>2</sub>), 140.4 (C<sub>6</sub>H<sub>2</sub>), 157.9 (C<sub>6</sub>H<sub>2</sub>), 161.4 (CH=N). FAB+ve; *m/z*: 417 [M]<sup>+</sup>.

### 2.6. Synthesis of *N*-(2-hydroxy,3-anthracenylbenzylidene)ferroceneamine chromium dichloride (5)

To a solution of *p*-tolylCrCl<sub>2</sub> · 3THF (0.18 g, 0.42 mmol) in toluene (50 ml) was added a solution of **2** (0.2 g, 0.42 mmol) also in toluene (50 ml). The resulting solution was stirred over a period of 3 h during which time the colour had changed from red to brown. The volatiles were removed in vacuo and the resulting red-brown solid washed with pentane. The solid was dried under vacuum (0.21 g, 83%). Anal. Calc. for C<sub>31</sub>H<sub>22</sub>Cl<sub>2</sub>CrFeNO: C, 61.70; H, 3.65; N, 2.32. Found: C, 61.83; H 3.75; N, 2.19%. FAB+ve; *m/z*: 1047 [(**2**)<sub>2</sub>CrCl]<sup>+</sup>, 1012 [(**2**)<sub>2</sub>Cr]<sup>+</sup>, 603 [(**2**)CrCl<sub>2</sub>]<sup>+</sup>.

### 2.7. In situ polymerisation using *N*-(2-hydroxy,3-anthracenylbenzylidene)ferroceneamine chromium dichloride (5)

In a Schlenk vessel **2** (0.0048 g, 0.01 mmol) was dissolved in toluene (25 ml) and added to *p*-tolylCrCl<sub>2</sub> · 3THF (0.0043 g, 0.010 mmol) also in toluene (25 ml). The reaction mixture was stirred for 2 h and the volatiles removed in

vacuo. The product was redissolved in toluene (100 ml) and 100 equiv. of MAO (1.6 M in toluene) added. The Schlenk vessel was exposed to 1 bar ethylene for 1 h. The polymerisation test was terminated by removal of the ethylene supply and addition of acidified methanol. The polymer was filtered and dried in a vacuum oven overnight.

2.8. *In situ* polymerisation using *N*-(2-hydroxy-3-triptylphenylbenzylidene)ferroceneamine chromium dichloride (**6**) and *N*-(2-hydroxy-3,5-di-*tert*-butylbenzylidene)ferroceneamine chromium dichloride (**7**)

An analogous procedure to that employed for **5** was followed, using **3** (0.0055 g, 0.01 mmol) and *p*-tolyl-CrCl<sub>2</sub> · 3THF (0.0043 g, 0.010 mmol) to form **6**, and reacting **4** (0.0042 g, 0.01 mmol) and *p*-tolylCrCl<sub>2</sub> · 3THF (0.0043 g, 0.010 mmol) to form **7**.

2.9. Synthesis of bis-*N*-(2-hydroxybenzylidene)-ferroceneamine nickel(II) (**8**)

To a solution of (TMEDA)NiMe<sub>2</sub> (0.1 g, 0.5 mmol) in acetonitrile (20 ml) was added a solution of **1** (0.15 g, 0.5 mmol) also in acetonitrile (20 ml). The resulting orange coloured solution was stirred for 2 h during which time a red precipitate formed. The product was filtered and washed with two portions of cold pentane (−30 °C). The resulting orange solid was dried under vacuum to give **8** (0.07 g, 21%). Characterising data were found to be in agreement with the literature values [21].

2.10. Synthesis of bis-*N*-(2-hydroxy-3-anthracenyl-benzylidene)ferroceneamine nickel(II) (**9**)

An analogous procedure to that employed for **8** was utilised using (TMEDA)NiMe<sub>2</sub> (0.1 g, 0.5 mmol) and **2** (0.24 g, 0.5 mmol). Anal. Calc. for C<sub>62</sub>H<sub>44</sub>Fe<sub>2</sub>N<sub>2</sub>NiO<sub>2</sub>: C, 73.01; H, 4.32; N, 2.75. Found: C, 73.49; H 4.89; N, 2.70%. FAB+ve; *m/z*: 1019 [M]<sup>+</sup>.

2.11. Synthesis of *N,N'* bis-(2-hydroxybenzaldimine)ferroceneamine (**10**)

To a solution of 1,1'-bis(amino)ferrocene (0.21 g, 1 mmol) in dichloromethane (50 ml) was added salicylaldehyde (0.61 g, 5 mmol). The solution was refluxed for 1 h and the volatiles removed in vacuo. The resulting oily solid was recrystallised from ethanol to yield the burgundy coloured **10** (0.36 g, 85%). Anal. Calc. for C<sub>24</sub>H<sub>20</sub>FeN<sub>2</sub>O<sub>2</sub>: C, 67.92; H, 4.72; N, 6.60. Found: C, 68.10; H, 4.40; N, 6.40%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 4.32 (t, 4H, C<sub>5</sub>H<sub>4</sub>), 4.59 (t, 4H, C<sub>5</sub>H<sub>4</sub>), 6.72 (m, 4H, C<sub>6</sub>H<sub>4</sub>), 7.01 (m, 2H, C<sub>6</sub>H<sub>4</sub>), 7.17 (m, 2H, C<sub>6</sub>H<sub>4</sub>), 8.37 (s, 2H, N=CH), 13.05 (s, 2H, OH); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 64.08 (C<sub>5</sub>H<sub>4</sub>), 69.09 (C<sub>5</sub>H<sub>4</sub>), 102.42 (*ipso*-C C<sub>5</sub>H<sub>4</sub>), 116.84, 118.85, 119.51, 131.10, 131.86, 160.42 (C<sub>6</sub>H<sub>4</sub>), 161.19 (C=N). FAB+ve; *m/z*: 424 [M]<sup>+</sup>.

2.12. Synthesis of *N,N'* bis-(2-hydroxy-3-anthracenylbenzaldimine)ferroceneamine (**11**)

An analogous procedure to that employed for **10** was utilised using 1,1'-bis(amino)ferrocene (0.21 g, 1 mmol) and 3-anthracenyl-2-hydroxybenzaldehyde (0.58 g, 2 mmol) to yield crystalline **11** (0.65 g, 85%). Anal. Calc. for C<sub>52</sub>H<sub>36</sub>FeN<sub>2</sub>O<sub>2</sub>: C, 80.41; H, 4.64; N, 3.61. Found: C, 80.50; H, 4.82; N, 3.42%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 4.24 (t, 4H, C<sub>5</sub>H<sub>4</sub>, *J* 1.9 Hz), 4.43 (tr, 4H, C<sub>5</sub>H<sub>4</sub>, *J* 2.0 Hz), 6.94 (m, 2H, Ar-H), 7.17 (m, 2H, Ar-H), 7.38 (m, 8H, Ar-H), 7.70 (m, 4H, Ar-H), 8.10 (d, 4H, Ar-H), 8.56 (s, 2H Ar-H), 8.60 (s, 2H, C=N), 13.65 (s, 2H, OH); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 64.60 (C<sub>5</sub>H<sub>4</sub>), 69.40 (C<sub>5</sub>H<sub>4</sub>), 102.32 (*ipso*-C C<sub>5</sub>H<sub>4</sub>), 118.89, 125.13, 125.52, 126.58, 126.96, 128.62, 130.41, 131.27, 131.58, 135.42, 152.55, 159.09, 160.49, 162.11 (Ar-C), 166.07 (C=N). FAB+ve; *m/z*: 776 [M]<sup>+</sup>. Crystal data for **11**: C<sub>52</sub>H<sub>36</sub>N<sub>2</sub>O<sub>2</sub> · Fe · 2CH<sub>2</sub>Cl<sub>2</sub>, *M* = 946.53, triclinic, *P*<sub>1</sub> (no. 2), *a* = 11.1166(8), *b* = 13.5027(8), *c* = 17.1512(9) Å, α = 95.435(4), β = 106.702(5), γ = 111.536(4)°, *V* = 2235.0(2) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.406 g cm<sup>−3</sup>, μ(Cu-Kα) = 5.261 mm<sup>−1</sup>, *T* = 193 K, orange/red platy prisms; 6608 independent measured reflections, *F*<sup>2</sup> refinement, *R*<sub>1</sub> = 0.051, *wR*<sub>2</sub> = 0.118, 5059 independent observed absorption-corrected reflections [*|F<sub>o</sub>|* > 4σ(*|F<sub>o</sub>|*)], 2θ<sub>max</sub> = 120°, 631 parameters. CCDC 271797.

2.13. Synthesis of *N,N'* bis-(2-hydroxy-3-*tert*-butylbenzaldimine)ferroceneamine (**12**)

An analogous procedure to that employed for **10** was utilised using 1,1'-bis(amino)ferrocene (0.21 g, 1 mmol) and 3-*tert*-butyl-2-hydroxybenzaldehyde (0.46 g, 2 mmol) to yield crystalline **12** (0.44 g, 68%). Anal. Calc. for C<sub>32</sub>H<sub>36</sub>FeN<sub>2</sub>O<sub>2</sub>: C, 71.64; H, 6.72; N, 5.22. Found: C, 71.11; H, 6.72; N, 5.01%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.46 (s, 18H, CH<sub>3</sub>), 4.31 (t, 4H, C<sub>5</sub>H<sub>4</sub>), 4.56 (t, 4H, C<sub>5</sub>H<sub>4</sub>), 6.69 (m, 2H, C<sub>6</sub>H<sub>3</sub>), 6.92 (m, 2H, C<sub>6</sub>H<sub>3</sub>), 7.30 (m, 2H, C<sub>6</sub>H<sub>3</sub>), 8.46 (s, 2H, CH=N), 13.80 (s, 2H, OH); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 28.76 (C(CH<sub>3</sub>)<sub>3</sub>), 34.14 (C(CH<sub>3</sub>)<sub>3</sub>), 63.69 (C<sub>5</sub>H<sub>4</sub>), 68.39 (C<sub>5</sub>H<sub>4</sub>), 102.16 (*ipso*-C C<sub>5</sub>H<sub>4</sub>), 117.57, 118.73, 128.74, 129.06, 136.45, 159.28 (C<sub>6</sub>H<sub>3</sub>), 160.97 (CH=N). FAB+ve; *m/z*: 536 [M]<sup>+</sup>.

2.14. Synthesis of *N,N'* bis-(2-hydroxy-3-*tert*-butylbenzaldimine)ferroceneamine TiCl<sub>2</sub> (**13**)

A solution of **12** (0.49 g, 1 mmol) in toluene (30 ml) was added dropwise to a solution of TiCl<sub>4</sub>THF<sub>2</sub> (0.33 g 1 mmol) also in toluene (30 ml). The resulting brown coloured solution was stirred for 18 h and the solvent removed under vacuum. The crude product was recrystallised from dichloromethane:pentane (25:75) to give analytically pure **13** (0.43 g, 66%). Anal. Calc. for C<sub>32</sub>H<sub>34</sub>Cl<sub>2</sub>FeN<sub>2</sub>O<sub>2</sub>Ti: C, 58.81; H, 5.21; N, 4.29. Found: C, 58.87; H, 5.01; N, 3.86%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 1.59 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 4.31

(t, 4H, C<sub>5</sub>H<sub>4</sub>), 4.96 (t, 4H, C<sub>5</sub>H<sub>4</sub>), 7.12 (m, 2H, C<sub>6</sub>H<sub>3</sub>), 7.46 (m, 2H, C<sub>6</sub>H<sub>3</sub>), 7.66 (m, 2H, C<sub>6</sub>H<sub>3</sub>), 8.52 (s, 2H, CH=N); <sup>13</sup>C NMR (CDCl<sub>3</sub>); δ 30.59 (C(CH<sub>3</sub>)<sub>3</sub>), 35.69 (C(CH<sub>3</sub>)<sub>3</sub>), 66.81 (C<sub>5</sub>H<sub>4</sub>), 69.54 (C<sub>5</sub>H<sub>4</sub>), 110.64 (*ipso*-C C<sub>5</sub>H<sub>4</sub>), 122.93, 127.62, 133.28, 133.41, 137.71, 163.66 (C<sub>6</sub>H<sub>4</sub>), 168.68 (CH=N). FAB+ve; *m/z*: 653 [M<sup>+</sup>].

#### 2.15. Synthesis of *N,N'* bis-(2-hydroxybenzalimine)-ferroceneamine Ti(<sup>*i*</sup>OPr)<sub>2</sub> (**14**)

A solution of **10** (0.42 g, 1 mmol) in toluene (30 ml) was added dropwise to a solution of Ti(<sup>*i*</sup>OPr)<sub>4</sub> (0.28 g, 1 mmol) also in toluene (30 ml). The resulting red coloured solution was stirred for 18 h and the solvent removed under vacuum. The crude product was recrystallised from dichloromethane:pentane (25:75) to give analytically pure **14** (0.42 g, 71%). Anal. Calc. for C<sub>30</sub>H<sub>32</sub>FeN<sub>2</sub>O<sub>4</sub>Ti: C, 61.22; H, 5.44; N, 4.76. Found: C, 61.06; H, 5.50; N, 4.71%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.92 (m, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.51 (m, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.62 (m, H, C<sub>5</sub>H<sub>4</sub>), 3.79 (m, H, C<sub>5</sub>H<sub>4</sub>), 3.85 (m, H, C<sub>5</sub>H<sub>4</sub>), 3.92 (m, H, C<sub>5</sub>H<sub>4</sub>), 3.96 (m, H, C<sub>5</sub>H<sub>4</sub>), 4.12 (m, H, C<sub>5</sub>H<sub>4</sub>), 4.65 (m, H, C<sub>5</sub>H<sub>4</sub>), 4.80 (sept, H, CH(CH<sub>3</sub>)<sub>2</sub>), 5.18 (sept, H, CH(CH<sub>3</sub>)<sub>2</sub>), 5.79 (m, H, C<sub>5</sub>H<sub>4</sub>), 6.98 (m, 4H, C<sub>6</sub>H<sub>4</sub>), 8.04 (s, H, CH=N), 8.12 (s, H, CH=N). FAB+ve; *m/z*: 588 [M<sup>+</sup> - <sup>*i*</sup>Pr].

#### 2.16. Synthesis of *N,N'* bis-(2-hydroxy-3-anthracenylbenzalimine)ferroceneamine Ti(<sup>*i*</sup>OPr)<sub>2</sub> (**15**)

An analogous procedure to that utilised for **14** was employed using **11** (0.77 g, 1 mmol) and Ti(<sup>*i*</sup>OPr)<sub>4</sub> (0.28 g, 1 mmol) to yield **15** (0.72 g, 77%). Anal. Calc. for C<sub>58</sub>H<sub>48</sub>FeN<sub>2</sub>O<sub>4</sub>Ti: C, 73.96; H, 5.10; N, 2.98. Found: C, 73.94; H, 5.08; N, 2.88%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ -0.65 (d, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), -0.02 (d, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.68 (d, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.44 (sept, H, CH(CH<sub>3</sub>)<sub>2</sub>), 4.05 (m, H, C<sub>5</sub>H<sub>4</sub>), 4.12 (m, H, C<sub>5</sub>H<sub>4</sub>), 4.18 (m, H, C<sub>5</sub>H<sub>4</sub>), 4.23 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 4.26 (sept, H, CH(CH<sub>3</sub>)<sub>2</sub>), 4.41 (m, H, C<sub>5</sub>H<sub>4</sub>), 4.19 (m, H, C<sub>5</sub>H<sub>4</sub>), 5.68 (m, H, C<sub>5</sub>H<sub>4</sub>), 6.18 (m, 2H, Ar-H), 6.38 (m, 1H, Ar-H), 6.69 (m, H, Ar-H), 6.79 (m, 2H, Ar-H), 7.34 (overlapping m, 6H, Ar-H), 7.58 (m, H, Ar-H), 7.60 (m, H, Ar-H), 7.75 (m, H, Ar-H), 7.81 (m, H, Ar-H), 7.86 (m, H, Ar-H), 7.90 (m, H, Ar-H), 7.98 (m, H, Ar-H), 8.01 (m, H, Ar-H), 8.09 (m, 2H, Ar-H) 8.35 (s, H, CH=N), 8.46 (s, H, CH=N), 8.72 (m, 2H, Ar-H). FAB+ve; *m/z*: 897 [M<sup>+</sup> - <sup>*i*</sup>Pr].

#### 2.17. Synthesis of *N,N'* bis-(2-hydroxy-3-tertbutylbenzalimine)ferroceneamine Ti(<sup>*i*</sup>OPr)<sub>2</sub> (**16**)

An analogous procedure to that utilised for **14** was employed using **12** (0.056 g, 0.1 mmol) and Ti(<sup>*i*</sup>OPr)<sub>4</sub> (0.028 g, 0.1 mmol) to yield **16** (0.032 g, 46%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 0.82 (m, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.02 (d, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.15 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.23 (d, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.47 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 3.77 (m, H, C<sub>5</sub>H<sub>4</sub>), 4.03 (m, H, C<sub>5</sub>H<sub>4</sub>), 4.14 (m, H, C<sub>5</sub>H<sub>4</sub>), 4.23 (m, H,

C<sub>5</sub>H<sub>4</sub>), 4.32 (m, H, C<sub>5</sub>H<sub>4</sub>), 4.52 (sept, H, CH(CH<sub>3</sub>)<sub>2</sub>), 4.54 (m, H, C<sub>5</sub>H<sub>4</sub>), 4.97 (sept, H, CH(CH<sub>3</sub>)<sub>2</sub>), 5.77 (m, H, C<sub>5</sub>H<sub>4</sub>), 6.56 (t, H, C<sub>6</sub>H<sub>3</sub>), 6.79 (t, H, C<sub>6</sub>H<sub>3</sub>) 7.30 (m, 4H, C<sub>6</sub>H<sub>3</sub>), 8.26 (s, H, CH=N), 8.51 (s, H, CH=N); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>); δ 24.92, 25.10, 26.33, 26.41 (CH(CH<sub>3</sub>)<sub>2</sub>), 29.44, 29.98 (C(CH<sub>3</sub>)<sub>3</sub>), 34.57, 35.10 (C(CH<sub>3</sub>)<sub>3</sub>), 62.88 (C<sub>5</sub>H<sub>4</sub>), 64.38 (CH(CH<sub>3</sub>)<sub>2</sub>), 64.63, 66.57, 67.71, 68.24, 68.73 (C<sub>5</sub>H<sub>4</sub>), 69.07 (CH(CH<sub>3</sub>)<sub>2</sub>), 70.19, 10.47 (C<sub>5</sub>H<sub>4</sub>), 79.69, 107.95 (*ipso*-C C<sub>5</sub>H<sub>4</sub>), 111.88, 115.54, 116.95, 123.81, 124.26, 130.68, 131.30, 131.54, 132.74, 138.00, 139.72, 164.62 (C<sub>6</sub>H<sub>3</sub>). FAB+ve; *m/z*: 657 [M<sup>+</sup> - <sup>*i*</sup>Pr].

*Crystal data for A*: C<sub>50</sub>H<sub>39</sub>N<sub>5</sub>O<sub>5</sub>Cl<sub>2</sub>Fe<sub>2</sub>Ti<sub>2</sub>, *M* = 1068.26, monoclinic, *P*<sub>2</sub><sub>1</sub>/*c* (no. 14), *a* = 14.889(3), *b* = 13.2811(13), *c* = 23.064(2) Å, β = 97.575(12)°, *V* = 4520.8(10) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.570 g cm<sup>-3</sup>, μ(Mo-Kα) = 1.143 mm<sup>-1</sup>, *T* = 203 K, dark brown blocks; 7960 independent measured reflections, *F*<sup>2</sup> refinement, *R*<sub>1</sub> = 0.050, *wR*<sub>2</sub> = 0.099, 5461 independent observed absorption-corrected reflections [*I*<sub>o</sub>] > 4σ(*I*<sub>o</sub>)], 2θ<sub>max</sub> = 50°, 595 parameters. CCDC 271798. *Crystal data for B*: C<sub>48</sub>H<sub>36</sub>N<sub>4</sub>O<sub>6</sub>Fe<sub>2</sub>Ti<sub>2</sub> · 2CH<sub>2</sub>Cl<sub>2</sub>, *M* = 1142.16, monoclinic, *P*<sub>2</sub><sub>1</sub>/*n* (no. 14), *a* = 10.7063(9), *b* = 13.5040(7), *c* = 16.3743(7) Å, β = 95.637(5)°, *V* = 2355.9(3) Å<sup>3</sup>, *Z* = 2 [*C*<sub>i</sub> symmetry], *D*<sub>c</sub> = 1.610 g cm<sup>-3</sup>, μ(Cu-Kα) = 10.170 mm<sup>-1</sup>, *T* = 293 K, ruby red rhombs; 3497 independent measured reflections, *F*<sup>2</sup> refinement, *R*<sub>1</sub> = 0.050, *wR*<sub>2</sub> = 0.120, 2715 independent observed absorption-corrected reflections [*I*<sub>o</sub>] > 4σ(*I*<sub>o</sub>)], 2θ<sub>max</sub> = 120°, 344 parameters. CCDC 271799.

#### 2.18. Synthesis of *N,N'*-bis(benzalimine)ferroceneamine (**17**)

Benzaldehyde (5 ml) was added to a toluene (50 ml) solution of 1,1-bis(amino)ferrocene (0.25 g, 1.16 mmol). The solution was stirred for 3 h during which the initial yellow colour became deep burgundy. The toluene and excess benzaldehyde were removed *in vacuo* to yield a burgundy solid **17**, which was washed with pentane (20 ml). (0.34 g, 75%). Anal. Calc. for C<sub>24</sub>H<sub>20</sub>FeN<sub>2</sub>: C, 73.47; H, 5.10; N, 7.14. Found: C, 73.50; H, 5.10; N, 7.10%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 4.29 (4H, t, C<sub>5</sub>H<sub>4</sub>), 4.61 (4H, t, C<sub>5</sub>H<sub>4</sub>), 7.57 (6H, m, C<sub>6</sub>H<sub>5</sub>), 7.63 (4H, m, C<sub>6</sub>H<sub>5</sub>), 8.47 (2H, s, NC=H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 64.42 (C<sub>5</sub>H<sub>4</sub>), 68.65 (C<sub>5</sub>H<sub>4</sub>), 105.55 (*ipso*-C C<sub>5</sub>H<sub>4</sub>), 127.97, 128.55, 130.31, 136.57 (C<sub>6</sub>H<sub>5</sub>), 158.31 (C=N). FAB+ve; *m/z*: 392 [M<sup>+</sup>].

#### 2.19. Synthesis of [1,1'-bis(benzylimino)ferrocene] palladium methyl chloride (**18**)

Compound **17** (0.35 g, 0.9 mmol) and Pd(COD)MeCl [26] (0.24 g, 0.9 mmol) were dissolved in dry dichloromethane and stirred at 40 °C for 72 h. The solvent was removed *in vacuo* to leave a bright orange/red solid that was washed with cold pentane to remove excess COD. The solid was then redissolved in dichloromethane/pentane, hot filtered and cooled to -30 °C to obtain the purified product **18** (0.23 g, 46%). Anal. Calc. for

$C_{25}H_{23}ClFeN_2Pd$ : C 54.68, H 4.22, N 5.10. Found: C 54.49, H 4.18, N 4.98%.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  0.81 (s, 3H, PdMe), 4.23 (br s, 2H,  $C_5H_4$ ), 4.46 (br s, 2H,  $C_5H_4$ ), 4.53 (br s, 2H,  $C_5H_4$ ), 5.82 (br s, 1H,  $C_5H_4$ ), 6.18 (br s, 1H,  $C_5H_4$ ), 7.19 (m, 2H, Ar–H), 7.45 (m, 4H, Ar–H), 8.25 (s, 1H,  $HC=N$ ), 8.33 (s, 1H,  $HC=N$ ), 8.58 (m, 2H, Ar–H), 8.68 (m, 2H, Ar–H);  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  7.54 (PdMe), 59.42, 60.68, 67.43, 70.23, 71.63, 72.72 ( $C_5H_4$ ), 110.45, 110.92 (*ipso*- $C_5H_4$ ), 128.45, 128.71 (*para*-C, Ar), 130.21, 130.51 (*meta*-C, Ar), 131.36, 131.85 (*ortho*-C, Ar), 132.64, 134.34 (*ipso*-C, Ar), 164.76, 164.94 ( $C=N$ ). FAB +ve;  $m/z$ : 548 ( $M^+$ ), 533 ( $M - Me^+$ ), 513 ( $M - Cl^+$ ), 497 ( $M - MeCl^+$ ), 392 ( $M - PdMeCl^+$ ). *Crystal data for 18*:  $C_{25}H_{23}N_2ClFePd$ ,  $M = 549.15$ , orthorhombic,  $Pbca$  (no. 61),  $a = 16.138(4)$ ,  $b = 11.550(3)$ ,  $c = 23.677(7)$  Å,  $V = 4413(2)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_c = 1.653$  g cm<sup>-3</sup>,  $\mu(Cu-K\alpha) = 13.060$  mm<sup>-1</sup>,  $T = 293$  K, orange needles; 3270 independent measured reflections,  $F^2$  refinement,  $R_1 = 0.066$ ,  $wR_2 = 0.118$ , 1520 independent observed absorption-corrected reflections [ $|F_o| > 4\sigma(|F_o|)$ ,  $2\theta_{max} = 120^\circ$ ], 249 parameters. CCDC 271800.

## 2.20. Synthesis of [ $\{1,1'$ -bis(benzylimino)ferrocene $\}Pd^+Me\}[BAF^-](MeCN)$ (**19**)

$[Fc(NBenz)_2]PdMeCl$  **18** (0.15 g, 0.27 mmol) and NaBAF [28] (0.242 g, 0.27 mmol) were weighed out into a Schlenk tube in the glovebox, then dissolved in DCM (30 ml) and dry degassed MeCN (2 ml) added. The dark purple solution was heated overnight at 40 °C, then the solvent removed and the solid washed with pentane to give the product, a brown/orange/yellow lustrous solid **19** (0.23 g, 59%). Anal. Calc. for  $C_{59}H_{38}BF_2FeN_3Pd$ : C 49.97, H 2.70, N 2.96. Found: C 49.86, H 2.74, N 2.81%.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  0.91 (s, 3H, PdMe), 2.26 (s, 3H, MeCN), 4.28 (m, 2H,  $C_5H_4$ ), 4.46 (m, 2H,  $C_5H_4$ ), 4.60 (m, 2H,  $C_5H_4$ ), 5.44 (m, 1H,  $C_5H_4$ ), 5.48 (m, 1H,  $C_5H_4$ ), 7.27 (m, 2H, Ar–H), 7.44 (m, 4H, Ar–H), 7.50 (br m, 4H, *para*-H BAF), 7.70 (br m, 8H, *ortho*-H BAF) 8.08 (m, 2H, Ar–H), 8.22 (s, 1H,  $HC=N$ ), 8.32 (m, 2H, Ar–H), 8.41 (s, 1H,  $HC=N$ );  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  -4.40 (PdMe), 3.02 (MeCN), 60.81, 61.94, 68.65, 68.70, 69.98, 70.38, 70.92 ( $C_5H_4$ ), 109.64, 109.80 (*ipso*- $C_5H_4$ ), 117.49 (*para*-C BAF), 121.32, 123.49, 125.66, 127.82 ( $CF_3$  BAF), 128.56, 128.82, 129.07, 129.75, (*meta*-C BAF), 128.96, 129.27 (*para*-C, Ar), 130.14, 130.44 (*meta*-C, Ar), 132.92, 133.27 (*ortho*-C, Ar), 134.02 (*ipso*-C, Ar), 134.81 (*ipso*-C, Ar, and *ortho*-C BAF), 161.13, 161.53, 161.92, 162.32 (*ipso*-C BAF), 167.14, 167.76 ( $C=N$ ). FAB +ve  $m/z$ : 513 ( $M^+$ ), 497 ( $M - Me^+$ ), 392 ( $M - PdMe^+$ ).

## 2.21. Cyclic voltammetry

In all cases measurements were performed using an Autolab PGSTAT12 potentiometer with Gpes software; with 0.1 M tetrabutylammonium-hexafluorophosphate as

the electrolyte in dichloromethane. The sample solution was approximately 1 mM concentration in this electrolyte. The working electrode was platinum – circular and 1 mm in diameter, the reference was an Ag/AgCl electrode and the counter electrode was a platinum wire. The cyclic voltammograms were measured at rates of 100 mV s<sup>-1</sup> and the potentials calculated using ferrocene as a comparison.

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