

Synthesis and reactivity of 1,8-bis(imino)carbazolide complexes of iron, cobalt and manganese

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The synthesis and characterisation of a new family of monoanionic, tridentate bis(imino)carbazolide ligands (L) and their cobalt, iron and manganese complexes are described. The solid state structure of the five coordinate Fe^{III} complex LFeCl₂ (**9c**) reveals a trigonal bipyramidal geometry with a short Fe–N(carbazolide) bond (1.959(3) Å), indicative of π-donation from the carbazole nitrogen to the metal centre. The cationic derivatives LFeCl(MeCN)⁺ (**11**), LFe(acac)⁺ (**12**) and LCo(MeCN)⁺ (**14**) have been prepared by chloride abstraction from the neutral precursors using AgSbF₆ or Ag(acac). Treatment of LMCl_n (M = Fe, Co) complexes with MeLi affords metal–methyl species, tentatively formulated as LFeMe₂ (**13**), LFeMe (**16a**) and LCoMe (**16b**). All of the Mn, Fe and Co compounds are paramagnetic and generally exhibit magnetic moments consistent with high spin configurations. In certain cases, however, low spin as well as intermediate spin configurations are found, depending on the nature of the co-ligands around the metal centre. The LFeCl₂ **9c** complex exhibits a room temperature magnetic moment of 4.8 μ_B and is a rare example of a trigonal bipyramidal Fe^{III} complex in which a *spin admixture* between a high spin and an intermediate spin state is present. None of the divalent or trivalent bis(imino)carbazolide metal complexes, using a variety of activators, showed activity for ethylene oligomerisation or polymerisation.

Introduction

Compared to the plethora of transition metal amide complexes based on pyrrolide ligands, the number of complexes supported by carbazolides is rather small, though a few examples can be found across the transition metal series.¹ Reports in the patent literature also claim moderate to high ethylene polymerisation activity for simple titanium and zirconium carbazolide complexes of the type (carbazolide)_nM(X)_{4-n} (X = Cl, benzyl, n = 1–4) but little characterisation data are given.² In all cases, unsubstituted carbazole is employed as an anionic, monodentate amide ligand. In our ongoing research on non-metallocene olefin polymerisation catalysts we have recently described the synthesis of bis(imino)carbazolide Co and Fe complexes **1a** and **1b** (Fig. 1).³ The tridentate coordination mode of the carbazolide ligand was confirmed by X-ray analysis of **1a**. It also revealed a distorted tetrahedral coordination mode around the Co centre. Both complexes, when activated with MAO, showed no activity towards the polymerisation of ethylene, which is in stark contrast to the high polymerisation activity of related bis(imino)pyridine complexes of Co and Fe.⁴ In order to probe the influence of steric and electronic factors in bis(imino)carbazolide complexes a range of ligands with a variety of imino substituents have been prepared. In this paper we describe in detail the synthesis of divalent and trivalent late transition metal complexes bearing bis(imino)carbazolide ligands and of their cationic and alkyl derivatives, as well as their evaluation as ethylene polymerisation catalysts.

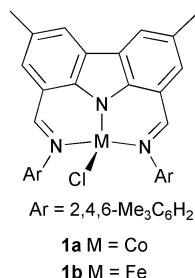


Fig. 1 Bis(imino)carbazolide complexes of Co^{II} and Fe^{II}.

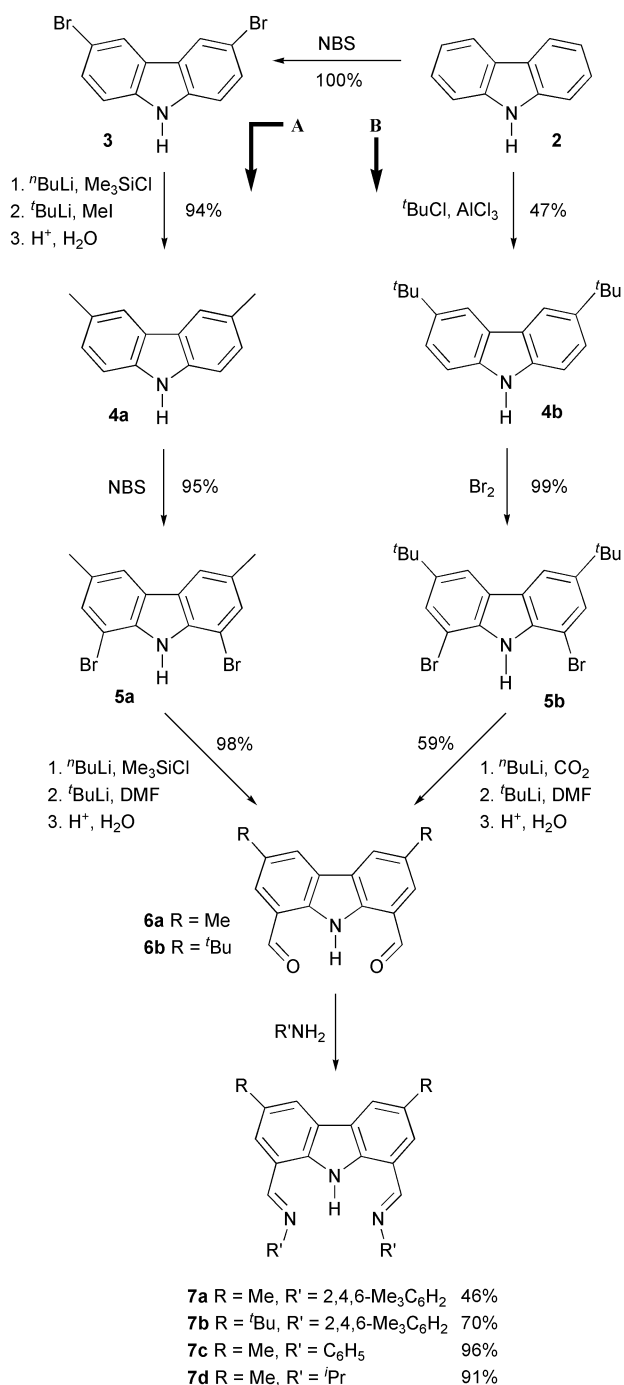
Results and discussion

Complex synthesis

The required carbazole ligand precursor, 1,8-diformylcarbazole, can be prepared in high overall yield from carbazole *via* the previously reported pathway A (Scheme 1), resulting in the formation of the methyl substituted derivative **6a**.³ 'Bu-groups can be introduced into the carbazole moiety through reaction of carbazole with 'BuCl under modified Friedel–Crafts conditions using AlCl₃ catalyst in dichloromethane solution (pathway B). The resulting di-'Bu-carbazole **4b**⁵ can be converted to the dibromo derivative **5b** by bromination with bromine, which is then converted to the 1,8-diformylcarbazole **6b** using CO₂ as the N-protection group during the initial lithiation reaction. Schiff-base condensation of the dialdehydes **6a** and **6b** with different aryl and alkyl amines affords the bis(imino)carbazole ligand precursors **7a–d** which can be isolated as bright yellow crystalline solids (Scheme 1).

In the ¹H NMR spectra of **7a–d** the carbazole N–H proton gives rise to a broad signal between 12.06 and 12.70 ppm, its considerable downfield shift from unsubstituted carbazole being indicative of hydrogen bonding to the imino nitrogens.⁶ This implies an *E*-configuration of the imino C=N double bond; no *E/Z*-isomerism is observed in solution at room temperature. The *E*-isomer also prevails in the solid state as shown by the molecular structure of **7a** (Fig. 2).

The molecule has approximate C_s symmetry about a plane that passes through N(1) and the middle of both the C(7)–C(8) bond and the N(14) ⋯ N(26) vector, and lies orthogonal to the bis(imino)carbazole unit which, excluding the two pendant 2,4,6-trimethylphenyl rings, is planar to within 0.069 Å. Rather than being oriented approximately orthogonal to the plane of the bis(imino)carbazole moiety, the two terminal aryl rings are noticeably inclined [by *ca.* 67° for the C(15)-based ring, and by *ca.* 71° for the C(27)-based ring] in opposite senses such that the C(21) and C(33) methyl groups are brought towards each other whilst the C(23) and C(35) methyl groups are moved further apart [the C(21) ⋯ C(33) and C(23) ⋯ C(35) separations are 3.94 and 7.30 Å respectively]. In contrast to the solution state ¹H NMR studies, in the solid state there is no evidence that the



Scheme 1 Synthesis of the bis(imino)carbazoles **7a–d**.

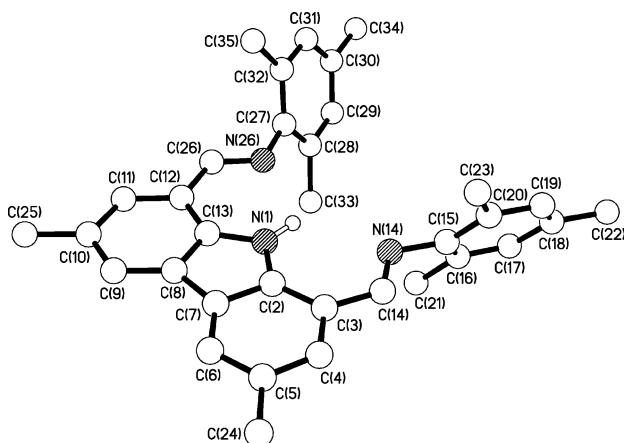
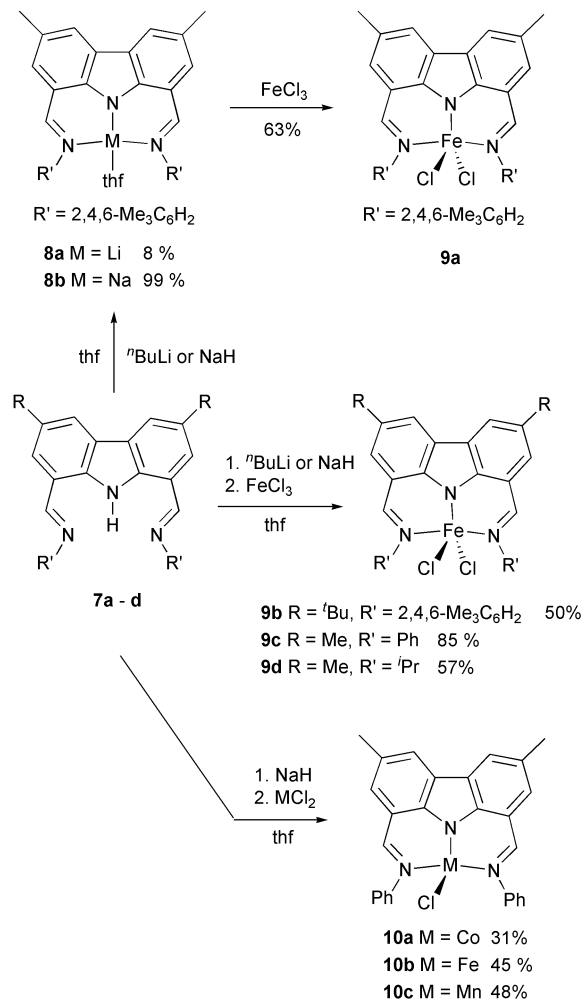


Fig. 2 The molecular structure of **7a**. Selected bond lengths (Å); C(14)–N(14) 1.273(3), C(26)–N(26) 1.270(3).

N(1)–H proton (which was clearly located from a difference electron density map as being bound to N(1) at a conventional N–H distance) is involved in strong hydrogen bonding to the imino nitrogens N(14) and N(26), the H(1) ··· N(14) and H(1) ··· N(26) separations being 2.44 and 2.43 Å respectively. The carbazole ring systems of centrosymmetrically related pairs of molecules π -stack with a mean interplanar separation of 3.52 Å, the centroids of the respective two central five-membered C₄N rings being *ca.* 3.99 Å apart.

Deprotonation of **7a–d** can be achieved in thf solution using ^tBuLi at room temperature or NaH at 65 °C (Scheme 2). The deprotonated ligands were generally used *in situ*, only the mesityl substituted derivatives **8a** and **8b** were isolated and characterised. They are obtained as air and moisture sensitive amorphous solids, the Li salt **8a** showing considerable solubility in pentane, which accounts for its lower isolated yield. In both complexes one thf molecule is coordinated to the metal centre as confirmed by NMR spectroscopy and elemental analyses. Surprisingly, deprotonation of **7b** with NaH to form **8b** does not take place at ambient temperature, even after prolonged reaction times. Forcing conditions with reaction temperatures above 60 °C and reaction times > 8 h are required for complete deprotonation. Steric constraints arising from the bulky aryl-imino substituents might be responsible for hindered access of the NaH base.



Scheme 2 Synthesis of bis(imino)carbazolide complexes **8–10**.

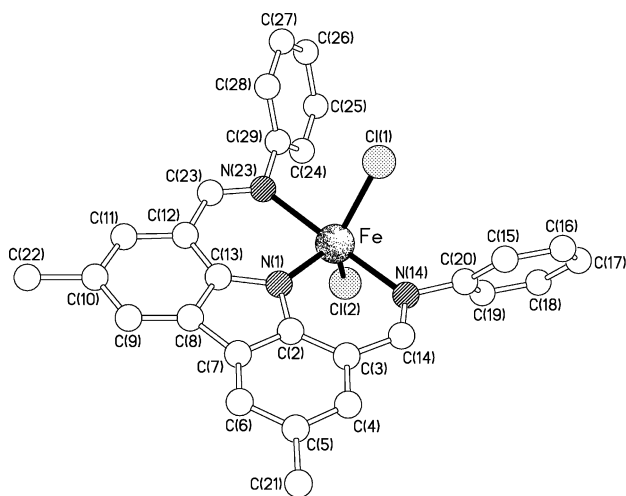
Divalent and trivalent transition metal complexes were formed by analogous procedures to those employed for the synthesis of bis(imino)carbazolide Co^{II} and Fe^{II} complexes described previously,³ *via* salt metathesis reactions with either the isolated or *in situ* generated sodium or lithium salts derived from **7a–d** (Scheme 2). Conveniently, all ligand Na and Li salts

Table 1 Selected bond lengths (Å) and angles (°) for **9c**

Fe–Cl(1)	2.2366(11)	Fe–Cl(2)	2.2318(11)
Fe–N(1)	1.959(3)	Fe–N(14)	2.179(3)
Fe–N(23)	2.223(3)	C(14)–N(14)	1.295(5)
C(23)–N(23)	1.277(5)		
N(1)–Fe–N(14)	89.40(12)	N(1)–Fe–N(23)	88.13(12)
N(14)–Fe–N(23)	174.66(12)	N(1)–Fe–Cl(2)	114.38(9)
N(14)–Fe–Cl(2)	92.95(9)	N(23)–Fe–Cl(2)	92.38(9)
N(1)–Fe–Cl(1)	120.01(9)	N(14)–Fe–Cl(1)	89.66(9)
N(23)–Fe–Cl(1)	87.48(9)	Cl(2)–Fe–Cl(1)	125.57(4)

show a bright green fluorescence in thf solution that disappears upon complexation to transition metals, providing a useful indicator for completion of the reaction. The Fe^{III} complexes **9c** and **9d** as well as complexes **10a–c** are reasonably air stable, whereas complexes **9a** and **9b** bearing bulky mesitylimino substituents decompose in air; they are also less stable in solution under an inert atmosphere. This could be due to unfavourable steric interactions of the chloride ligands with the *ortho*-methyl groups on the mesityl substituents, possibly leading to dissociation of the imino donor group.

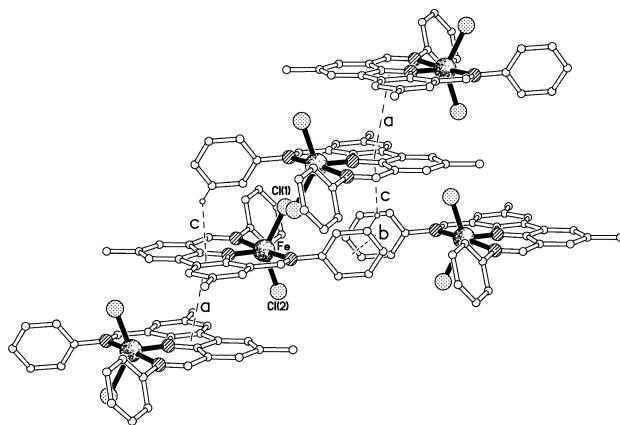
All complexes were characterised by means of ¹H NMR and IR spectroscopies, FAB mass spectrometry, magnetic susceptibility measurements and microanalysis. Crystals of **9c** suitable for X-ray analysis were grown from a concentrated solution in dichloromethane layered with pentane. The molecular structure of **9c**, depicted in Fig. 3, shows the complex to have approximate molecular C_s symmetry about a plane containing the metal centre and the two chloride ligands. The geometry at iron is slightly distorted trigonal bipyramidal with equatorial bond angles in the range 114.38(9)–125.57(4)° and with the axial nitrogen substituents subtending an angle of 174.66(12)° at the metal (Table 1). The bond to the amido nitrogen, [Fe–N(1) 1.959(3) Å] is significantly shorter than the bonds to the imino nitrogens N(14), [2.179(3) Å] and N(23), [2.223(3) Å], suggesting some degree of π-donation from the sp²-hybridized carbazole nitrogen to the metal centre. Similar bond distances are observed in a related trigonal bipyramidal Fe^{III} complex bearing a 1,3-bis(2-pyridylimino)isoindoline ligand, where the Fe–amido distance is 1.963 Å.⁷

**Fig. 3** The molecular structure of **9c**.

Excluding the two phenyl rings the bis(imino)carbazolide moiety is planar to within 0.081 Å (*cf.* 0.069 Å in the structure of the related ligand **7a**) with the iron atom lying 0.130 Å 'below' this plane, in the direction of Cl(2); Cl(1) lies 1.737 Å 'above', and Cl(2) 2.213 Å 'below' the ligand plane. The two phenyl rings are each inclined by *ca.* 67° to the ligand plane (a conformation also seen in **7a**), the *ortho*-hydrogens C(19)–H and C(24)–H being directed towards Cl(2) suggesting a possible pair of C–H ⋯ Cl interactions; the H ⋯ Cl distances are

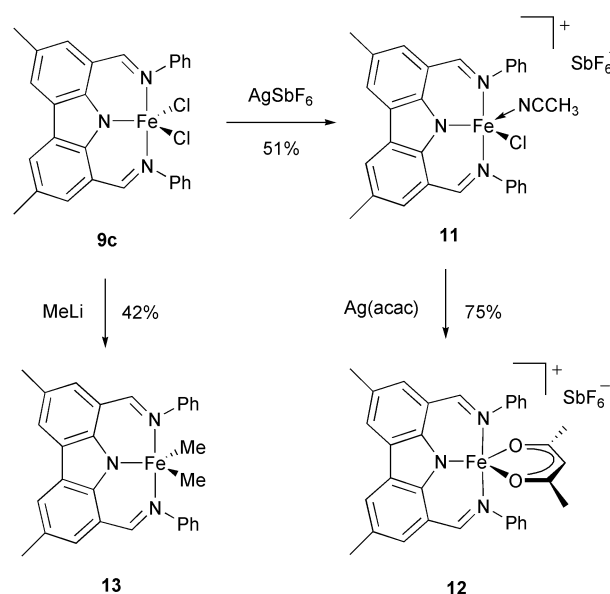
2.72 and 2.69 Å and the associated C–H ⋯ Cl angles are 131 and 134°, respectively.

Centrosymmetrically related pairs of molecules are involved in π–π stacking interactions between their carbazole ring systems, and between their C(20)-containing phenyl rings. These interactions are supplemented further by pairs of short C–H ⋯ π contacts between C(16)–H of one molecule and the pyrrole ring of the next, and *vice versa* (Fig. 4). The π–π stacking interactions have respective centroid ⋯ centroid and mean interplanar separations (Å) of (a) 3.76, 3.47; (b) 4.00, 3.44. The C–H ⋯ π contacts (c) have H ⋯ ring-centroid distances of 2.68 Å and C–H ⋯ π angles of 144°.

**Fig. 4** The intermolecular π–π and C–H ⋯ π interactions present in the crystals of **9c**. The centroid ⋯ centroid and mean interplanar separations (Å) for the π–π stacking interactions are (a) 3.76, 3.47; (b) 4.00, 3.44. The C–H ⋯ π contacts (c) have H ⋯ ring-centroid distances of 2.68 Å and C–H ⋯ π angles of 144°.

Reactivity of bis(imino)carbazolide complexes

In our work on bis(imino)pyridine iron complexes we found that the synthesis of cationic derivatives allowed the use of co-catalysts other than MAO in ethylene polymerisation experiments and influenced the properties of the polymer produced.⁸ Thus the analogous cationic complexes were prepared for bis(imino)carbazolide Fe^{III} complex **9c**. Scheme 3 shows the synthesis of the cationic complexes **11** and **12** *via* sequential abstraction of the chloride ligands with AgSbF₆ and Ag(acac).

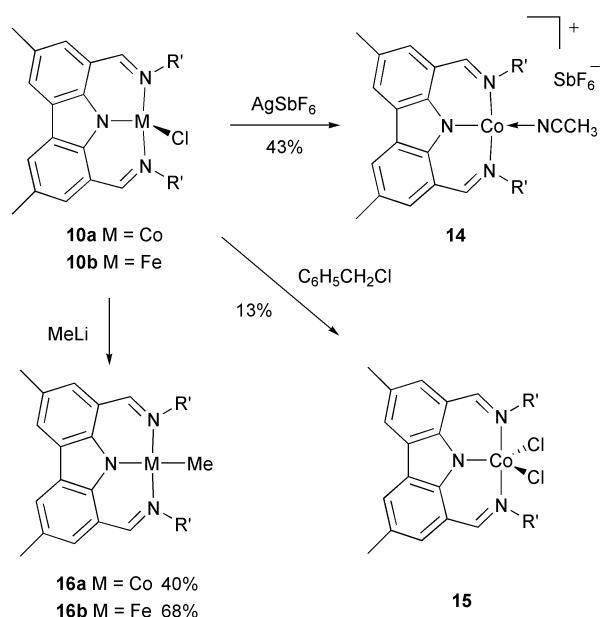
**Scheme 3** Synthesis of bis(imino)carbazolide Fe^{III} derivatives.

Alkylation reactions on **9c**, directed towards the synthesis of a bis(imino)carbazolide Fe^{III} dialkyl complex were also carried out. Addition of two equivalents MeLi to a solution of **9c** in

Et₂O leads to the formation of a dark brown solution from which an air sensitive, microcrystalline solid can be isolated in microanalytical purity. This product is tentatively formulated as the Fe^{III}Me₂ complex **13**. FAB-MS analysis shows signals for the molecular ion of **13** minus one and two methyl groups; no signals corresponding to species containing halide ligands are observed. Several attempts to obtain single crystals for X-ray analysis were unsuccessful.

A survey in the Cambridge Crystallographic Database (version 5.20) shows no structurally characterised Fe^{III} dialkyl complexes, indeed no stable Fe^{III} dialkyl complexes have been isolated.⁹ However, a few Fe^{III} mono-alkyl and aryl complexes have been synthesised and structurally characterised. They are generally stabilised by dianionic tetraaza-annulene,¹⁰ salen¹¹ and porphyrin¹² ligands. Unlike the corresponding high spin halide complexes, their magnetic and spectroscopic properties indicate the presence of a five-coordinate, square pyramidal low spin ($S = 1/2$) metal centre, with the exception of the salen-based Fe^{III} and some perfluorinated aryl Fe^{III} porphyrin¹³ complexes, which are high spin. The magnetic moment for the Fe^{III} dimethyl complex **13** of 1.8 μ_B also suggests the presence of a low spin configuration.

Cationic derivatives can also be prepared from the divalent bis(imino)carbazolide complexes as shown by the synthesis of the Co complex **14** via chloride abstraction with AgSbF₆ (Scheme 4). Oxidation of Co^{II} to Co^{III} can be achieved by reaction of **10a** with excess benzyl chloride over a period of 48 h and the corresponding Co^{III} complex **15** can be isolated in low yield and microanalytical purity. A similar reaction with benzyl halides was observed by Fryzuk and co-workers for the tetrahedral [(PPh₂CH₂SiMe₂)₂N]Co^{III} chloride and bromide complexes and trigonal bipyramidal Co^{III} dihalide complexes were obtained.¹⁴ In this case the reaction proceeds via radical benzyl intermediates, which recombine to form the dibenzyl side product. A similar radical mechanism is believed to be operative in the one electron oxidation of **10a** to **15**. A magnetic moment of 4.9 μ_B is observed for **15**, indicating the presence of a high spin Co^{III} centre.



Scheme 4 Synthesis of bis(imino)carbazolide Fe^{II} and Co^{II} derivatives (R' = 2,4,6-Me₃C₆H₂).

Alkylation reactions of **10a** and **10b** with a view to synthesising mono-alkyl Fe^{II} and Co^{II} complexes were also investigated. Addition of MeLi to a solution of the chloride precursors in Et₂O leads to the formation of a dark brown solution from which air sensitive, microcrystalline solids can be isolated in microanalytical purity. The products **16a** and **16b** are tentatively

formulated as the Fe^{II} and Co^{II} methyl complexes. FAB-MS analysis of both methyl complexes shows signals for the molecular ions and signals for a fragment obtained by the loss of the methyl group. No signals corresponding to species containing halide ligands are observed.

NMR spectroscopy

Paramagnetic contact shifted ¹H NMR spectra were recorded for all Co^{II} and Fe^{II} complexes bearing bis(imino)carbazolide ligands. The Mn^{II} complex **10a** gave only very broad signals, which is generally observed for Mn^{II} complexes.¹⁵ In the case of the Fe^{II} and Co^{II} methyl complexes **16a** and **16b**, highly complicated ¹H NMR spectra were obtained with signals in the chemical shift range -80 to 80 ppm. In many cases not all the expected signals are observed, but the ¹H NMR spectrum can serve as a characteristic fingerprint for the complex.

Infrared spectroscopy

The carbazole based ligand precursors and complexes were studied by IR spectroscopy as thin sample films on NaCl plates or as KBr discs. The uncoordinated bis(imino)carbazoles **7a-d** generally exhibit a weak to medium absorption at ca. 1638 cm⁻¹, which can be assigned to the C=N stretching mode.¹⁶ Upon coordination of a metal centre (complexes **9-16**) only a small shift to lower wavenumber, typically 7-12 cm⁻¹, is observed. This lies in contrast to observations on bis(imino)pyridine Fe and Co complexes where generally a shift by 20-30 cm⁻¹ to lower wavenumbers was observed for the C=N stretching mode compared to the free ligand.⁸ The acac complex **12** also shows two absorption bands at 1557 and 1527 cm⁻¹, indicative of a symmetrical coordination of the acac ligand to the Fe centre.¹⁷ The coordinated MeCN donor in **14** shows a weak absorption at 2285 cm⁻¹ for $\nu(\text{C}\equiv\text{N})$.¹⁸ For the cationic complexes **11**, **12** and **14** the typical absorption band for the Sb-F stretching mode of the SbF₆ counterion is observed at ca. 659 cm⁻¹.¹⁹

Magnetic susceptibility measurements

Complexes **9-16** are paramagnetic, with magnetic moments for complexes **9a** (6.0 μ_B), **10a** (4.5 μ_B), **10b** (5.1 μ_B), **11** (6.3 μ_B) and **15** (4.9 μ_B) indicative of high spin configurations for these d⁵, d⁶ and d⁷ ions.²⁰ By contrast, low spin configurations are found for the Co^{II} complex **14** (2.2 μ_B), as well as for the alkyl derivatives **13** (1.8 μ_B), **16a** (2.9 μ_B) and **16b** (3.0 μ_B). A similar change in spin state upon alkylation is found for Fe^{II} complexes stabilised by bipyridine (bipy) ligands. For example, (bipy)₂FeCl₂ is paramagnetic with a magnetic moment of 5.72 μ_B ,²¹ whereas the alkyl derivative (bipy)₂FeEt₂ possesses a low spin ($S = 0$) ground state and is therefore diamagnetic.²²

The magnetic moments for complexes **9b** (4.1 μ_B), **9c** (4.8 μ_B), **9d** (5.5 μ_B) and **12** (4.2 μ_B) are inconsistent with either high spin or low spin configurations. There are a number of possible explanations for this unusual magnetic behaviour. In the case of **9c**, the molecular structure reveals a monomeric formulation which rules out any close contact of two Fe centres that could result in Fe-Fe exchange interactions. Its magnetic moment is, therefore, likely to result from an intermediate $S = 3/2$ spin state that contains some high spin $S = 5/2$ character. A possible explanation is that the room temperature magnetic moment reflects a thermal equilibrium between different spin state transitions. There are numerous examples for such spin-crossover phenomena for high spin ($S = 5/2$) to low spin ($S = 1/2$) transitions in Fe^{III} complexes, but these are less common for transitions involving the intermediate spin state $S = 3/2$.²³ An example is trigonal bipyramidal FeCl₃(PMe₃)₂, which displays a room temperature magnetic moment of 5.2 μ_B , falling to 4.2 at 233 K, thus indicating a transition from a high spin $S = 5/2$ to an intermediate $S = 3/2$ state.²⁴ Typical for a thermal equilibrium

of two spin systems are a large temperature dependence of the magnetic moment and a sigmoidal-type curve of the moment *versus* temperature. Alternatively, instead of observing a spin equilibrium, a quantum mechanical mixing of the two states can occur to create a new, discrete *spin-admixed* ground state, that has elements of both $S = 5/2$ and $S = 3/2$ states.^{25,26} Such admixed states have been studied intensively for square pyramidal and octahedral porphyrin-²⁷ and phthalocyanin-based²⁸ Fe^{III} complexes, giving rise to room temperature magnetic moments that lie between the intermediate and high spin extremes of 3.9 and 5.9 μ_B , the extent of spin-state mixing depending on the ligand set. The temperature dependence of the magnetic moment of such a spin-admixed system follows essentially the Curie law. In practice, however, a slight reduction of the magnetic moment over a wide temperature range for spin-admixed complexes is observed. Fryzuk and co-workers recently reported an example of a trigonal bipyramidal Fe^{III} complex, [(PPh₂CH₂SiMe₂)₂N]FeBr₂, exhibiting such behaviour.²⁵ Variable temperature SQUID magnetometer measurements revealed a slow and smooth lowering of the magnetic moment from 4.70 μ_B at 300 K to 4.45 μ_B at 20 K, ruling out a spin-crossover situation and indicating the likely presence of spin-admixture in this complex. Very similar behaviour is observed for **9c** (Fig. 5). The magnetic moment decreases from 4.62 μ_B at 295 K to 4.35 μ_B at 30 K and no sharp spin crossover transition is observed. At 5 K the observed moment is 3.51 μ_B , which is very close to the value obtained for the spin-admixed [(PPh₂CH₂SiMe₂)₂N]FeBr₂ complex (3.49 μ_B at 2K).²⁵ The solid state magnetic moment at room temperature of 4.62 μ_B for **9c** is also in good agreement with the solution value of 4.8 μ_B obtained by Evans' NMR method. From these data it can be concluded that complex **9c** is a rare example of a trigonal bipyramidal Fe^{III} system, in which spin-admixture between $S = 5/2$ and $S = 3/2$ states has occurred, giving rise to an intermediate magnetic moment at room temperature.

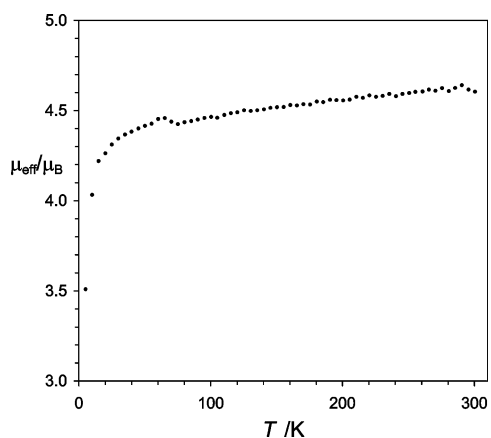


Fig. 5 Plot of magnetic moment (μ_{eff}) *versus* temperature for **9c**. Diamagnetic corrections were neglected.

EPR spectroscopy

Further evidence for an intermediate $S = 3/2$ ground state in **9c** was obtained from EPR spectroscopy on powdered samples. For a high spin Fe^{III} complex with five unpaired electrons in a ligand field with high symmetry a very strong EPR absorption without hyperfine splitting, and with a g value close to 2.00, is expected.²⁹ At lower symmetries, zero field splitting increases and, in the case of axial symmetry, two absorptions with g values close to 2 and 6 are observed.³⁰

From the EPR spectrum of **9c** (Fig. 6), two weak and very broad absorptions with g values of 4.7 and 2.0 are observed at room temperature, excluding the presence of a high spin $S = 5/2$ ground state. These g values are typical for a $S = 3/2$ ground state,²⁶ and similar EPR spectra have been reported for a spin-admixed Fe^{III} porphyrin complex²⁷ and for

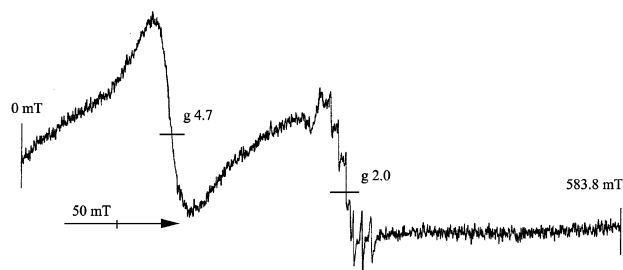


Fig. 6 The powder EPR spectrum of **9c** at rt, microwave frequency 9.57 GHz, microwave power 21 mW, field sweep 0–583.8 mT.

[2,6-bis{(dimethylamino)methyl}phenyl]FeCl₂.³¹ Interestingly, [(PPh₂CH₂SiMe₂)₂N]FeBr₂ is EPR silent despite its magnetic properties also indicating a $S = 3/2$ ground state.²⁵

Olefin polymerisation

Ethylene polymerisation tests were carried out with complexes **9–12**, **14** and **15** in a Radley's GreenHouseTM parallel synthesis reactor and the following co-catalysts: (a) 640 eq MAO (rt and 80 °C in toluene solution), (b) 400 eq Me₂AlCl (rt in hexane solution) and (c) 10 eq Me₃Al (rt in toluene solution). In all cases no ethylene polymerisation activity was observed. This was confirmed by carrying out separate polymerisation tests under typical Schlenk-line conditions at 1 bar ethylene pressure and 100 eq. MAO co-catalyst with the Fe^{III} complexes **9a–d**. Addition of MAO to the Fe^{III} complexes **9a–d** results in an immediate colour change from green to yellow, indicating the formation of a new species, which is inactive. In a separate experiment, the yellow solution obtained from complex **9d** was hydrolysed by the addition of dilute aqueous HCl. From the resulting yellow toluene solution the free ligand **7d** was isolated as the only organic material. This excludes attack of the MAO co-catalyst on the ligand framework as a cause for the formation of a catalytically inactive species. In all Schlenk-line tests the reaction mixture at the end of the polymerisation run was also analysed by GC-MS. No oligomeric reaction products were detected. The ethylene polymerisation activity of the Fe^{III} dialkyl derivative **13** was tested under Schlenk-line conditions with a variety of co-catalysts such as MAO, as well as borane-based Lewis and Brønsted acids such as B(C₆F₅)₃, [CPh₃]-[B(C₆F₅)₄] and [H(OEt)₂][B{3,5-(CF₃)₂C₆H₃}₄]. However, no oligomeric or polymeric products were obtained.

The absence of any ethylene polymerisation activity is most likely a consequence of steric crowding around the metal centre. By comparison with the bis(imino)pyridine ligand system,⁴ the two additional carbon atoms in the backbone of the carbazolidine ligand allow an extended reach of the imine donors to the front side of the complex, closing down the space available to coordinate olefin. It is known from extensive studies on the bis(imino)pyridine systems that the active site is already rather hindered, one consequence of which is an exceptional selectivity towards ethylene over higher α -olefins.³² It would appear that changing the imino-substituents from mesityl to phenyl in the carbazolidine system is insufficient to make the metal site accessible. However, an alternative influence on ethylene polymerisation activity that cannot be ruled out is the presence of the highly nucleophilic charged central donor atom in the carbazolidine ligand.

Conclusion

A family of bis(imino)carbazoles has been synthesised and complexed as monoanionic, tridentate ligands to cobalt, iron and manganese. All of the products are paramagnetic, with some showing unusual magnetic behaviour. Cationic derivatives and metal–methyl species have also been synthesised. Ethylene

polymerisation tests using high throughput screening methodology, supported by conventional Schlenk-line tests, afford no oligomeric or polymeric products. The absence of reactivity of the bis(imino)carbazolide complexes towards ethylene is believed to be a consequence of steric congestion, though an electronic influence arising from the highly nucleophilic central donor group cannot be ruled out.

Experimental

General considerations

All manipulations of air and/or moisture sensitive compounds were performed using standard Schlenk and cannula techniques. Air sensitive compounds were transferred in a nitrogen filled glove-box and, unless stated otherwise, stored at room temperature. Crystal data were collected on Siemens P4/PC diffractometers. NMR spectra were recorded on Bruker AC-250 MHz or DRX-400 MHz spectrometers. Infrared spectra were obtained using thin sample films between NaCl plates or as KBr discs on a Perkin Elmer 1760X FT-IR spectrometer. Mass spectra were recorded on either a VG Autospec or a VG Platform II spectrometer. Elemental analyses were performed by the microanalytical services of the Chemistry Departments of Imperial College and the University of North London. Magnetic susceptibilities were determined by Evans' NMR method⁸ in CD₂Cl₂/cyclohexane (95 : 5 v/v) solution or on a SQUID magnetometer (MPMS7, Quantum Design) over the temperature range 5–300 K using an applied field of 10 mT. EPR spectra were recorded on a Bruker 200D spectrometer operating at X-band frequency (*ca.* 9.5 Ghz) with 100 kHz modulation at Queen Mary and Westfield College, University of London.

Solvents and reagents

Solvents were dried by standard procedures. Ethylene was purchased from BOC Gases and used without further purification. Dimethylformamide (DMF) was dried over calcium hydride and vacuum-transferred prior to use. Benzyl chloride and methyl iodide (MeI) were dried over 4 Å molecular sieves and vacuum-transferred into an ampoule sealed with a Young's tap, degassed by repeated freeze–pump–thaw cycles and stored in a refrigerator. B(C₆F₅)₃³³ and [H(OEt)₂][B{3,5-(CF₃)₂-C₆H₃]₄]³⁴ were prepared according to published procedures. 2,6-Diisopropylaniline was purchased from Aldrich Chemicals and distilled over zinc powder prior to use. All other reagents are commercially available and were used without further purification.

3,6-Di-*tert*-butyl-9H-carbazole (4b)

AlCl₃ (8.8 g, 66 mmol) and carbazole **2** (10.0 g, 60 mmol) were suspended in dichloromethane (100 cm³). Over a period of 90 min, 2-chloro-2-methylpropane (13 cm³, 120 mmol) was added by syringe pump at 0 °C. After the addition was complete, the dark brown solution was stirred at room temperature for 16 h. The solution was then diluted with dichloromethane (400 cm³) and washed with 1 M aqueous HCl solution (2 × 100 cm³) and 3 M aqueous NaCl solution (1 × 100 cm³). After drying over MgSO₄, the solution was isolated by filtration, and the solvent then removed on a rotary evaporator. The product was purified by crystallisation from hot hexane to afford an off-white, amorphous solid. Yield: 7.8 g (47%). *R*_F (SiO₂, hexane/EtOAc 2 : 1) 0.55. ¹H NMR (250 MHz, CDCl₃, rt): δ (ppm) 1.44 (s, 18H, C(CH₃)₃), 7.31 (d, 2H, ³*J*(HH) = 8.4 Hz, Ar-*H*), 7.45 (dd, 2H, ³*J*(HH) = 8.4 Hz, ⁴*J*(HH) = 1.7 Hz, Ar-*H*) 7.82 (br, 1H, NH), 8.07 (d, 2H, ⁴*J*(HH) = 1.7 Hz, Ar-*H*). EI mass spectrum (*m/z*): 279 (M⁺), 264 ([M - CH₃]⁺). The spectroscopic data are consistent with previously published values for **4b**.⁵

1,8-Dibromo-3,6-di-*tert*-butyl-9H-carbazole (5b)

4b (152 mg, 0.54 mmol) was dissolved in glacial acetic acid (15 cm³). At room temperature and with exclusion of light, bromine (62 μl, 1.20 mmol) was added dropwise *via* syringe. After stirring for 60 min, the volatile components were removed on a rotary evaporator. The residue was dissolved in EtOAc (100 cm³) and washed with 1 M aqueous NaOH (3 × 30 cm³) and 1M NaHCO₃ (1 × 50 cm³) solutions. The organic phase was then dried over MgSO₄, filtered, and the solvent was removed on a rotary evaporator to afford a yellow solid. Yield: 445 mg (99%). Mp 171–172 °C. *R*_F (SiO₂, hexane/EtOAc 5 : 1) 0.63. ¹H NMR (250 MHz, CDCl₃, rt): δ (ppm) 1.42 (s, 18H, C(CH₃)₃), 7.62 (s, 2H, Ar-*H*), 7.95 (s, 2H, Ar-*H*), 8.11 (br, 1H, NH). ¹³C{¹H} NMR (100 MHz, CDCl₃, rt): δ (ppm) 31.9 (C(CH₃)₃), 34.9 (C(CH₃)₃), 104.0, 115.9, 124.8, 126.6, 136.3, 144.7 (all Ar-*C*). EI mass spectrum (*m/z*): 437 (M⁺), 422 ([M - CH₃]⁺). Anal. calcd. for C₂₀H₂₃Br₂N: C, 54.94; H, 5.30; N, 3.20; found: C, 54.76; H, 5.41; N, 3.09%.

1,8-Diformyl-3,6-di-*tert*-butyl-9H-carbazole (6b)

ⁿBuLi (1.1 cm³, 2.5 M in hexane, 2.8 mmol) was added to a solution of **5b** (1.13 g) in degassed thf (60 cm³) at 0 °C. After stirring at this temperature for 1 h, the reaction mixture was allowed to warm to rt while CO₂ gas (dried by passing through a CaCl₂ filled wash bottle) was bubbled through the solution for 15 min. The solvent was then removed *in vacuo* and the residue was redissolved in degassed thf (60 cm³). At -78 °C, ⁿBuLi (7.5 cm³, 1.5 M in pentane, 11.3 mmol) was added slowly and the reaction mixture was stirred at 0 °C for 3 h. At -78 °C, anhydrous DMF (1.0 cm³, 12.9 mmol) was added and the reaction mixture was allowed to warm to room temperature overnight. The mixture was hydrolysed at 0 °C by addition of 1 M aqueous HCl (10 cm³) and then diluted with EtOAc (100 cm³). The organic phase was washed with 1 M aqueous NaOH (2 × 50 cm³) and 1M NaHCO₃ (2 × 50 cm³) solutions, dried over MgSO₄, filtered, and the solvent removed on a rotary evaporator. The crude product was purified by recrystallisation from hot hexane to afford a yellow solid. Yield: 0.50 g (59%). Mp 190–191 °C. *R*_F (SiO₂, hexane/EtOAc 5 : 1) 0.32. ¹H NMR (250 MHz, CDCl₃, rt): δ (ppm) 1.49 (s, 18H, C(CH₃)₃), 7.93 (s, 2H, Ar-*H*), 8.38 (s, 2H, Ar-*H*), 10.22 (s, 2H, O=CH), 11.44 (br, 1H, NH). ¹³C{¹H} NMR (100 MHz, CD₃CN, rt): δ (ppm) 32.2 (C(CH₃)₃), 35.6 (C(CH₃)₃), 120.9, 124.3, 125.2, 130.8, 137.6, 144.5 (all Ar-*C*), 194.9 (O=CH). IR (KBr): 3430 (s, ν(N-H)), 1682 (s, ν(C=O)) cm⁻¹. EI mass spectrum (*m/z*): 335 (M⁺), 320 ([M - CH₃]⁺). Anal. calcd. for C₂₂H₂₅NO₂: C, 78.77; H, 7.51; N, 4.18; found: C, 78.89; H, 7.61; N, 3.97%.

1,8-Bis(2,4,6-trimethylphenylimino)-3,6-dimethyl-9H-carbazole (7a)³

6a (470 mg, 1.87 mmol) and 2,4,6-trimethylaniline (530 μl, 3.77 mmol) were dissolved in chloroform (100 cm³). After addition of 5 drops of glacial acetic acid and 4 Å molecular sieves, the reaction mixture was refluxed for 3 days and then filtered while hot. The volatile components were removed on a rotary evaporator to afford a yellow solid which was then recrystallised from hot ethanol/hexane. Yield: 640 mg (70%). Crystals suitable for X-ray analysis were grown by slow cooling of a hot, concentrated solution in hexane to ambient temperature. Mp 226–227 °C. ¹H NMR (250 MHz, CDCl₃, rt): δ (ppm) 2.09 (s, 12H, *o*-CH₃), 2.25 (s, 6H, *p*-CH₃), 2.58 (s, 6H, CH₃), 6.82 (s, 4H, Ph-*H*_m), 7.39 (s, 2H, Ar-*H*), 8.03 (s, 2H, Ar-*H*), 8.41 (s, 2H, N=CH), 12.27 (br, 1H, NH). ¹³C{¹H} NMR (100 MHz, CDCl₃, rt): δ (ppm) 18.3 (*o*-CH₃), 20.7 (*p*-CH₃), 21.3 (CH₃), 119.2, 123.4, 123.4, 127.6, 128.2, 128.7, 130.8, 132.8, 136.5, 149.1 (all Ar-*C*), 163.5 (N=CH). IR (thin film): 3385 (m, ν(N-H)), 1638 (m, ν(C=N)) cm⁻¹. EI mass spectrum (*m/z*): 485 (M⁺), 470

([M - CH₃]⁺). Anal. calcd. for C₃₄H₃₅N₃: C, 84.08; H, 7.26; N, 8.65; found: C, 84.16; H, 7.17; N, 8.77%.

1,8-Bis(2,4,6-trimethylphenylimino)-3,6-di-*tert*-butyl-9H-carbazole (7b)

6b (457 mg, 1.36 mmol) and 2,4,6-trimethylaniline (400 μl, 2.85 mmol) were dissolved in ethanol (30 cm³) and 5 drops of glacial acetic acid were added. After refluxing for 16 h, all volatiles were removed on a rotary evaporator. The crude product was purified by crystallisation from hot hexane to afford a dark yellow solid. Yield: 360 mg (46%). Mp 230–231 °C. ¹H NMR (250 MHz, CDCl₃, rt): δ (ppm) 1.46 (s, 18H, C(CH₃)₃), 2.10 (s, 12H, *o*-CH₃), 2.25 (s, 6H, *p*-CH₃), 6.82 (s, 4H, Ph-*H_m*), 7.60 (s, 2H, Ar-*H*), 8.28 (s, 2H, Ar-*H*), 8.45 (s, 2H, N=CH), 12.26 (br, 1H, NH). ¹³C{¹H} NMR (100 MHz, CDCl₃, rt): δ (ppm) 18.4 (*o*-CH₃), 20.8 (*p*-CH₃), 32.0 (C(CH₃)₃), 34.7 (C(CH₃)₃), 119.0, 119.6, 123.4, 127.4, 127.6, 128.7, 132.7, 136.6, 142.1, 149.1 (all Ar-*C*), 163.7 (N=CH). IR (thin film): 3387 (m, ν(N-H)), 1639 (m, ν(C=N)) cm⁻¹. EI mass spectrum (*m/z*): 569 (M⁺). Anal. calcd. for C₄₀H₄₇N₃: C, 84.46; H, 8.15; N, 7.39; found: C, 84.61; H, 8.26; N, 6.98%.

1,8-Diphenylimino-3,6-dimethyl-9H-carbazole (7c)

6a³ (1.02 g, 4.1 mmol) and aniline (820 μl, 9.0 mmol) were dissolved in toluene (100 cm³). After addition of 4 Å molecular sieves, the reaction mixture was refluxed for 16 h and then filtered hot. The volatile components were removed on a rotary evaporator to afford a yellow solid. The crude product was purified by crystallisation from hot MeCN. Yield: 1.58 g (96%). Mp 192–194 °C. ¹H NMR (250 MHz, CDCl₃, rt): δ (ppm) 2.59 (s, 6H, CH₃), 7.26 (m, 2H, Ph-*H*), 7.38 (m, 8H, Ph-*H*), 7.48 (s, 2H, Ar-*H*), 8.00 (s, 2H, Ar-*H*), 8.78 (s, 2H, N=CH), 12.70 (br, 1H, NH). ¹³C{¹H} NMR (63 MHz, DMSO-*d*₆, rt): δ (ppm) 21.0 (CH₃), 118.9, 121.4, 122.8, 124.1, 126.8, 128.3, 129.2, 131.4, 135.8, 150.9 (all Ar-*C*), 161.1 (N=CH). IR (thin film): 3372 (w, ν(N-H)), 1635 (w, ν(C=N)) cm⁻¹. UV/VIS (CH₂Cl₂): λ_{max} [nm] (ε_{max} [dm³ mol⁻¹ cm⁻¹]) = 396 (15000), 321 (22000), 241 (33000). EI mass spectrum (*m/z*): 401 (M⁺), 324 ([M - Ph]⁺). Anal. calcd. for C₂₈H₂₃N₃: C, 83.76; H, 5.77; N, 10.47; found: C, 83.69; H, 5.84; N, 10.54%.

1,8-Diisopropylimino-3,6-dimethyl-9H-carbazole (7d)

6a³ (1.0 g, 4.0 mmol) and isopropylamine (3.2 cm³, 37.5 mmol) were dissolved in dichloromethane (100 cm³). After addition of 4 Å molecular sieves and 5 drops of glacial acetic acid, the reaction mixture was refluxed for 16 h. The solution was then filtered hot and the solvent was removed on a rotary evaporator to afford a yellow solid. Yield: 1.21 g (91%). Mp 114–116 °C. ¹H NMR (250 MHz, CDCl₃, rt): δ (ppm) 1.44 (d, 12H, ³J(HH) = 6.5 Hz, ¹Pr-CH₃), 2.59 (s, 6H, CH₃), 3.61 (sept, 2H, ³J(HH) = 6.5 Hz, ¹Pr-CH), 7.28 (s, 2H, Ar-*H*), 7.90 (s, 2H, Ar-*H*), 8.53 (s, 2H, N=CH), 12.06 (br, 1H, NH). ¹³C{¹H} NMR (63 MHz, CDCl₃, rt): δ (ppm) 21.3 (CH₃), 24.9 (¹Pr-CH), 62.6 (¹Pr-CH₃), 119.2, 122.2, 123.2, 127.6, 129.6, 136.6 (all Ar-*C*), 158.8 (N=CH). IR (thin film): 3372 (m, ν(N-H)), 1643 (m, ν(C=N)) cm⁻¹. EI mass spectrum (*m/z*): 333 (M⁺), 290 ([M - ¹Pr]⁺). Anal. calcd. for C₂₂H₂₇N₃: C, 79.24; H, 8.16; N, 12.60; found: C, 79.14; H, 8.12; N, 12.62%.

(1,8-Bis(2,4,6-trimethylphenylimino)-3,6-dimethylcarbazolide)-Li(thf) (8a)

Thf (25 cm³) was added to **7a** (0.35 g, 0.72 mmol) and the mixture cooled to 0°C. ⁿBuLi (0.43 cm³, 2.5 M in hexane, 0.73 mmol) was then added at 0°C, and the reaction mixture was brought to rt and stirred for 1 h. The solvent was removed *in vacuo* and the resulting yellow solid was suspended in pentane (10 cm³) and stored at -78 °C for 5 h. The supernatant solution was isolated by filtration and the residue was dried *in vacuo* to

afford the product as a yellow microcrystalline solid in an isolated yield of 8%. ¹H NMR (250 MHz, C₆D₆, rt): δ (ppm) 1.21 (m, 4H, OCH₂CH₂), 2.05 (s, 12H, *o*-CH₃), 2.08 (s, 6H, *p*-CH₃), 2.60 (s, 6H, CH₃), 3.27 (m, 4H, OCH₂CH₂), 6.68 (s, 4H, Ph-*H_m*), 7.32 (s, 2H, Ar-*H*), 8.26 (br, 4H, Ar-*H* and N=CH). ¹³C{¹H} NMR (63 MHz, CDCl₃, rt): δ (ppm) 18.6 (*o*-CH₃), 20.7 (*p*-CH₃), 21.4 (CH₃), 25.5 (OCH₂CH₂), 67.9 (OCH₂CH₂), 119.0, 123.4, 124.1, 125.7, 128.4, 129.3, 131.9, 133.8, 148.5, 149.7 (all Ar-*C*), 169.4 (N=CH). IR (thin film): 1628 (w, ν(C=N)) cm⁻¹. Anal. calcd. for C₃₈H₄₂LiN₃O: C, 80.97; H, 7.51; N, 7.45; found: C, 81.07; H, 7.41; N, 7.48%.

(1,8-Bis(2,4,6-trimethylphenylimino)-3,6-dimethylcarbazolide)-Na(thf) (8b)

A solution of **7a** (2.30 g, 4.7 mmol) in thf (80 cm³) was added to a suspension of NaH (1.11 g, 46.2 mmol) in thf (20 cm³) at room temperature. After stirring at 65 °C for 16 h, the resulting deep orange solution was isolated by filtration and the solvent was removed *in vacuo*. The oily red residue was co-evaporated with pentane (2 × 20 cm³) to afford the product as a dark orange solid. Yield: 2.45 g (99%). ¹H NMR (250 MHz, CD₂Cl₂, rt): δ (ppm) 1.62 (m, 4H, OCH₂CH₂), 2.14 (s, 12H, *o*-CH₃), 2.25 (s, 6H, *p*-CH₃), 2.58 (s, 6H, CH₃), 3.40 (m, 4H, OCH₂CH₂), 6.90 (s, 4H, Ph-*H_m*), 7.31 (s, 2H, Ar-*H*), 8.11 (s, 2H, Ar-*H*), 8.33 (s, 2H, N=CH). ¹³C{¹H} NMR (63 MHz, CD₂Cl₂, rt): δ (ppm) 18.6 (*o*-CH₃), 20.8 (*p*-CH₃), 21.2 (CH₃), 25.7 (OCH₂CH₂), 68.0 (OCH₂CH₂), 120.5, 123.1, 124.7, 127.0, 129.0, 129.2, 133.4, 134.1, 149.8, 150.6 (all Ar-*C*), 170.0 (N=CH). IR (thin film): 1627 (m, ν(C=N)) cm⁻¹. Anal. calcd. for C₃₈H₄₂NaN₃O: C, 78.73; H, 7.30; N, 7.25; found: C, 78.86; H, 7.37; N, 7.09%.

(1,8-Bis(2,4,6-trimethylphenylimino)-3,6-dimethylcarbazolide)-FeCl₂ (9a)

A solution of **8b** (200 mg, 0.34 mmol) in thf (40 cm³) was added to a solution of FeCl₃ (63 mg, 0.39 mmol) in thf (20 cm³) at room temperature and stirred for 2 h. The solvent was then removed under reduced pressure and the residue was extracted with dichloromethane. The resulting green solution was concentrated to 5 cm³ and the product was precipitated by the addition of pentane (50 cm³). The solid was isolated by filtration and dried *in vacuo* to give the product as an olive green, microcrystalline solid. Yield: 131 mg (63%). ¹H NMR (250 MHz, CD₂Cl₂, rt, all peaks appear as broad singlets): δ (ppm) 28.1 (12H), 73.5 (2H), 96.51 (4H). IR (KBr): 1631 (w, ν(C=N)) cm⁻¹. FAB mass spectrum (*m/z*): 575 ([M - Cl]⁺), 540 ([M - 2Cl]⁺). Anal. calcd. for C₃₄H₃₄Cl₂FeN₃·CH₂Cl₂: C, 60.37; H, 5.21; N, 6.03; found: C, 60.60; H, 4.90; N, 5.86%. μ_{eff} (Evans' NMR method) = 6.0 μ_B.

(1,8-Bis(2,4,6-trimethylphenylimino)-3,6-di-*tert*-butylcarbazolide)FeCl₂ (9b)

To a solution of **7b** (150 mg, 0.25 mmol) in thf (20 cm³) was added ⁿBuLi (100 μl, 2.5 M in hexane, 0.25 mmol) at -78 °C. The resulting deep orange solution was allowed to warm to ambient temperature over a period of 1 h. A solution of FeCl₃ (45 mg, 0.28 mmol) in thf (20 cm³) was then added dropwise over a period of 45 min. After stirring for 5 h at rt the solvent was removed under reduced pressure and the residue was extracted with toluene. The solution was then pumped to dryness and the crude product recrystallised from hot toluene/hexane. Yield: 90 mg (50%). IR (thin film): 1631 (m, ν(C=N)) cm⁻¹. FAB mass spectrum (*m/z*): 659 ([M - Cl]⁺), 624 ([M - 2Cl]⁺). Anal. calcd. for C₄₀H₄₆Cl₂FeN₃: C, 69.07; H, 6.67; N, 6.04; found: C, 69.11; H, 6.57; N, 6.19%. μ_{eff} (Evans' NMR method) = 4.1 μ_B.

(1,8-Diphenylimino-3,6-dimethylcarbazolide)FeCl₂ (9c)

Sodium hydride (940 mg, 39.0 mmol) and **7c** (1.63 g) were placed in a Schlenk flask, thf (40 cm³) added and the reaction

mixture stirred at 65 °C for 16 h. After cooling to rt the resulting deep orange solution was isolated by filtration and added to a solution of FeCl₃ (659 mg, 4.1 mmol) in thf (20 cm³). The reaction mixture was stirred at rt for 16 h. The solvent was then removed under reduced pressure and the residue was extracted with dichloromethane. The resultant solution was concentrated to 10 cm³ and the product was precipitated by addition of pentane (60 cm³). The residue was isolated by filtration, washed with diethyl ether (2 × 30 cm³) and dried *in vacuo* to give the product as a brown, microcrystalline solid. Yield: 1.83 g (85%). Crystals suitable for X-ray analysis were grown from a concentrated dichloromethane solution layered with pentane. ¹H NMR (250 MHz, CD₂Cl₂, rt, all peaks appear as broad singlets): δ (ppm) -19.0 (2H), 29.7 (10H), 31.2 (2H), 91.1 (2H), 105.4 (6H). IR (KBr): 1628 (w, ν(C=N)) cm⁻¹. UV/VIS (CH₂Cl₂): λ_{max} [nm] (ε_{max} [dm³ mol⁻¹ cm⁻¹]) = 621 (1700), 378 (13300), 300 (22500), 234 (50000). FAB mass spectrum (*m/z*): 527 (M⁺), 491 ([M - Cl]⁺), 456 ([M - 2Cl]⁺). Anal. calcd. for C₂₈H₂₂Cl₂FeN₃: C, 63.78; H, 4.21; N, 7.97; found: C, 63.82; H, 4.17; N, 7.88%. μ_{eff} (Evans' NMR method) = 4.8 μ_B.

(1,8-Diisopropylimino-3,6-dimethylcarbazolide)FeCl₂ (9d)

An analogous procedure to that employed for **9c**, but using ligand precursor **7d**, gave **9d** as a green, microcrystalline solid in 57% yield. ¹H NMR (250 MHz, CD₂Cl₂, rt, all peaks appear as broad singlets): δ (ppm) 27.6 (2H), 31.9 (12H), 83.6 (4H), 101.2 (6H). IR (thin film): 1633 (w, ν(C=N)) cm⁻¹. FAB mass spectrum (*m/z*): 458 (M⁺), 423 ([M - Cl]⁺), 388 ([M - 2Cl]⁺). Anal. calcd. for C₂₂H₂₆Cl₂FeN₃: C, 57.54; H, 5.71; N, 9.15; found: C, 57.53; H, 5.72; N, 8.97%. μ_{eff} (Evans' NMR method) = 5.5 μ_B.

(1,8-Diphenylimino-3,6-dimethylcarbazolide)CoCl (10a)

An analogous procedure to that employed for **9c**, but using ligand precursor **7c** and CoCl₂, gave **10a** as a red, microcrystalline solid in 31% yield. ¹H NMR (250 MHz, CD₂Cl₂, rt, all peaks appear as broad singlets): δ (ppm) -28.7 (4H), -8.58 (2H), 10.7 (4H), 20.8 (2H), 42.3 (6H), 47.0 (2H). IR (KBr): 1632 (w, ν(C=N)) cm⁻¹. UV/VIS (CH₂Cl₂): λ_{max} [nm] (ε_{max} [dm³ mol⁻¹ cm⁻¹]) = 438 (10500), 329 (20000), 289 (21000), 236 (40500). FAB mass spectrum (*m/z*): 494 (M⁺), 459 ([M - Cl]⁺). Anal. calcd. for C₂₈H₂₂ClCoN₃: C, 67.96; H, 4.48; N, 8.49; found: C, 67.76; H, 4.32; N, 8.71%. μ_{eff} (Evans' NMR method) = 4.5 μ_B.

(1,8-Diphenylimino-3,6-dimethylcarbazolide)FeCl (10b)

An analogous procedure to that employed for **9c**, but using ligand precursor **7c** and FeCl₂, gave **10b** as a green, microcrystalline solid in 45% yield. ¹H NMR (250 MHz, CD₂Cl₂, rt, all peaks appear as broad singlets): δ (ppm) -6.5 (2H), 16.5 (10H), 25.4 (2H), 28.9 (6H), 51.6 (2H). IR (KBr): 1628 (w, ν(C=N)) cm⁻¹. UV/VIS (CH₂Cl₂): λ_{max} [nm] (ε_{max} [dm³ mol⁻¹ cm⁻¹]) = 646 (630), 570 (1000), 423 (10500), 362 (10000), 299 (12500), 231 (40000). FAB mass spectrum (*m/z*): 456 ([M - Cl]⁺). Anal. calcd. for C₂₈H₂₂ClFeN₃: C, 68.38; H, 4.51; N, 8.54; found: C, 68.42; H, 4.58; N, 8.54%. μ_{eff} (Evans' NMR method) = 5.1 μ_B.

(1,8-Diphenylimino-3,6-dimethylcarbazolide)MnCl (10c)

An analogous procedure to that employed for **9c**, but using ligand precursor **7c** and MnCl₂, gave **10c** as an orange, microcrystalline solid in 48% yield. IR (KBr): 1629 (w, ν(C=N)) cm⁻¹. UV/VIS (CH₂Cl₂): λ_{max} [nm] (ε_{max} [dm³ mol⁻¹ cm⁻¹]) = 455 (12500), 353 (13500), 302 (15000), 239 (48000). FAB mass spectrum (*m/z*): 455 ([M - Cl]⁺). Anal. calcd. for C₂₈H₂₂ClMnN₃: C, 68.51; H, 4.52; N, 8.56; found: C, 68.69; H, 4.42; N, 8.69%. μ_{eff} (Evans' NMR method) = 4.6 μ_B.

(1,8-Diphenylimino-3,6-dimethylcarbazolide)FeCl(MeCN)-SbF₆ (11)

Silver hexafluoroantimonate (124 mg, 0.36 mmol) and **9c** (190 mg, 0.36 mmol) were dissolved in MeCN (30 cm³). After stirring at rt for 16 h, the solvent was removed under reduced pressure and the residue was extracted with dichloromethane. After evaporation of the solvent, the residue was washed with diethyl ether (2 × 30 cm³) and dried *in vacuo* to give the product as a dark brown, microcrystalline solid. Yield: 140 mg (51%). ¹H NMR (250 MHz, CD₂Cl₂, rt, all peaks appear as broad singlets): δ (ppm) -7.2 (2H), 19.9 (10H), 21.3 (2H), 55.0 (2H), 93.1 (6H). IR (thin film): 1626 (w, ν(C=N)), 658 (s, ν(SbF₆)) cm⁻¹. UV/VIS (CH₂Cl₂): λ_{max} [nm] (ε_{max} [dm³ mol⁻¹ cm⁻¹]) = 411 (12000), 345 (16000), 299 (20000), 240 (46000). FAB mass spectrum (*m/z*): 491 ([M - SbF₆]⁺-MeCN), 456 ([M - SbF₆]⁺-MeCN-Cl). Anal. calcd. for C₃₀H₂₅ClF₆FeN₄Sb: C, 46.88; H, 3.28; N, 7.29; found: C, 47.00; H, 3.15; N, 7.15%. μ_{eff} (Evans' NMR method) = 6.3 μ_B.

(1,8-Diphenylimino-3,6-dimethylcarbazolide)Fe(acac)SbF₆ (12)

Silver hexafluoroantimonate (127 mg, 0.37 mmol) and **9c** (195 mg, 0.37 mmol) were dissolved in MeCN (40 cm³) and stirred at rt for 6 h. The reaction mixture was then added to a suspension of silver acetylacetonate (76 mg, 0.37 mmol) in MeCN (10 cm³). After stirring at rt for 16 h the solution was isolated by filtration and the solvent was removed under reduced pressure. The residue was then washed with 4 × 30 cm³ diethyl ether, and dried *in vacuo* to give the product as a dark green, microcrystalline solid. Yield: 220 mg (75%). IR (thin film): 1628 (w, ν(C=N)), 1557 (m, ν(C=C) + ν(C=O)), 1527 (m, ν(C=C) + ν(C=O)), 658 (s, ν(SbF₆)) cm⁻¹. UV/VIS (CH₂Cl₂): λ_{max} [nm] (ε_{max} [dm³ mol⁻¹ cm⁻¹]) = 670 (1900), 394 (12000), 328 (16000), 281 (24500), 232 (48000). FAB mass spectrum (*m/z*): 555 ([M - SbF₆]⁺), 456 ([M - SbF₆]⁺-acac). Anal. calcd. for C₃₀H₂₅ClF₆FeN₄Sb: C, 50.10; H, 3.69; N, 5.31; found: C, 50.21; H, 3.70; N, 5.26%. μ_{eff} (Evans' NMR method) = 4.2 μ_B.

(1,8-Diphenylimino-3,6-dimethylcarbazolide)FeMe₂ (13)

To a solution of **9c** (205 mg, 0.39 mmol) in thf (30 cm³) was added dropwise methyl lithium (490 μl, 1.6 M in Et₂O, 0.78 mmol) at -78 °C. Upon completion of the addition, the reaction mixture was allowed to warm to ambient temperature and was stirred for a further 1 h. The solvent was then removed under reduced pressure and the residue was extracted with toluene. The resulting toluene solution was pumped to dryness and the residue washed with pentane (10 cm³). After drying *in vacuo* the product was obtained as a dark brown solid. Yield: 80 mg (42%). IR (thin film) 1632 (w, ν(C=N)) cm⁻¹. FAB mass spectrum (*m/z*): 472 ([M - Me]⁺), 456 ([M - 2Me]⁺). Anal. calcd. for C₃₀H₂₈FeN₃: C, 74.08; H, 5.80; N, 8.64; found: C, 73.96; H, 5.73; N, 8.72%. μ_{eff} (Evans' NMR method) = 1.8 μ_B.

(1,8-Bis(2,4,6-trimethylphenylimino)-3,6-dimethylcarbazolide)-Co(MeCN)SbF₆ (14)

Silver hexafluoroantimonate (107 mg, 0.31 mmol) and **10a** (180 mg, 0.31 mmol) were dissolved in MeCN (30 cm³). After stirring at rt for 16 h the solvent was removed under reduced pressure and the residue extracted with dichloromethane. The resultant solution was then concentrated to 5 cm³ and the product precipitated by the addition of pentane (50 cm³). The solid was isolated by filtration and dried *in vacuo* to give the product as a dark red, microcrystalline solid. Yield: 120 mg (43%). ¹H NMR (250 MHz, CD₂Cl₂, rt, all peaks appear as broad singlets): δ (ppm) -6.2 (12H), -2.6 (2H), 3.0 (12H), 7.9 (4H), 9.9 (2H). IR (KBr): 1631 (m, ν(C=N)), 660 (s, ν(Sb-F)) cm⁻¹. FAB mass spectrum (*m/z*): 543 ([M - SbF₆]⁺-MeCN). Anal. calcd. for C₃₆H₃₇CoF₆N₄Sb: C, 52.71; H, 4.55;

N, 6.83; found: C, 52.49; H, 4.40; N, 6.73%. μ_{eff} (Evans' NMR method) = 2.2 μ_{B} .

(1,8-Bis(2,4,6-trimethylphenylimino)-3,6-dimethylcarbazolide)-CoCl₂ (15)

Benzyl chloride (360 μl , 3.2 mmol) was added dropwise to a solution of **10a** (185 mg, 0.32 mmol) in toluene (20 cm³). After stirring at rt for 48 h the solution was isolated by filtration and concentrated to 10 cm³. This solution was then layered with pentane (30 cm³) and stored at -20 °C, upon which the product crystallised as dark red crystals. Yield: 25 mg (13%). ¹H NMR (250 MHz, CD₂Cl₂, rt, all peaks appear as broad singlets): δ (ppm) -16.1 (12H), 10.9 (4H), 18.5 (6H), 21.8 (2H), 42.3 (6H), 49.4 (2H). IR (thin film): 1626 (m, $\nu(\text{C}=\text{N})$) cm⁻¹. FAB mass spectrum (m/z): 578 ([M - Cl]⁺), 543 ([M - 2Cl]⁺). Anal. calcd. for C₃₄H₃₄Cl₂CoN₃: C, 66.46; H, 5.58; N, 6.84; found: C, 66.60; H, 5.38; N, 6.85%. μ_{eff} (Evans' NMR method) = 4.9 μ_{B} .

(1,8-Bis(2,4,6-trimethylphenylimino)-3,6-dimethylcarbazolide)-CoMe (16a)

To a solution of **10a** (211 mg, 0.36 mmol) in thf (30 cm³) was added dropwise methyl lithium (230 μl , 1.6 M in Et₂O, 0.36 mmol) at -78 °C. Upon completion of the addition, the reaction mixture was allowed to warm to ambient temperature and was stirred for a further hour. The solvent was then removed under reduced pressure and the residue was extracted with toluene. The resulting toluene solution was concentrated to 5 cm³ and layered with pentane (30 cm³). After storage at -20 °C the product crystallised as brown crystals. Yield: 80 mg (40%). ¹H NMR (250 MHz, CD₂Cl₂, rt, all peaks appear as broad singlets): δ (ppm) -13.7 (12H), 17.5 (6H), 40.3 (6H). IR (thin film): 1630 (w, $\nu(\text{C}=\text{N})$) cm⁻¹. FAB mass spectrum (m/z): 557 (M⁺), 543 ([M - CH₃]⁺). Anal. calcd. for C₃₅H₃₇CoN₃: C, 75.25; H, 6.68; N, 7.52; found: C, 75.06; H, 6.79; N, 7.64%. μ_{eff} (Evans' NMR method) = 2.9 μ_{B} .

(1,8-Bis(2,4,6-trimethylphenylimino)-3,6-dimethylcarbazolide)-FeMe (16b)

Employing an analogous procedure to that described above, but using **10b**, gave **16b** as a red-brown, microcrystalline solid in 68% yield. IR (thin film): 1633 (m, $\nu(\text{C}=\text{N})$) cm⁻¹. FAB mass spectrum (m/z): 556 (M⁺), 540 ([M - CH₃]⁺). Anal. calcd. for C₃₅H₃₇FeN₃: C, 75.67; H, 6.71; N, 7.56; found: C, 75.53; H, 6.81; N, 7.52%. μ_{eff} (Evans' NMR method) = 3.0 μ_{B} .

High-throughput polymerisation screening at atmospheric ethylene pressure

In a nitrogen atmosphere glove box, 5 μmol of pre-catalyst was weighed into an 8 cm³ sample vial and 2 cm³ of the co-catalyst solution was added (MAO, 10 wt% in toluene, Me₂AlCl, 1.0 M in hexane or Me₃Al, 0.025 M in toluene). After weighing the filled sample vials they were placed into a rack holding 24 such vials in a Radleys Greenhouse™ reactor. The reactor was closed and purged with ethylene outside the glove box. A mercury bubbler was used to maintain one atmosphere pressure of ethylene throughout the 30 min run time. When the polymerisation reaction was carried out at 80 °C, the Greenhouse reactor was heated to the desired temperature over a period of 10 min prior to the addition of ethylene. Replacing the ethylene atmosphere in the reactor by nitrogen using several pump-refill cycles terminated the runs. The reactor was then transferred back into the glove box and the sample vials were re-weighed to determine the polymer yield.

Schlenk-line 1 bar ethylene tests

The pre-catalyst was dissolved in toluene (120 cm³) and a solution of the co-catalyst was added. The Schlenk tube was purged

with ethylene, and the contents were magnetically stirred and maintained under ethylene (1 bar) throughout the polymerisation run. Releasing the ethylene pressure and adding aqueous HCl and methanol terminated the runs.

X-ray crystallography

Crystal data for 7a

C₃₄H₃₅N₃, $M = 485.7$, triclinic, $P\bar{1}$ (no. 2), $a = 8.538(1)$, $b = 11.096(1)$, $c = 15.042(1)$ Å, $\alpha = 86.82(1)$, $\beta = 75.43(1)$, $\gamma = 81.57(1)^\circ$, $V = 1364.1(1)$ Å³, $Z = 2$, $D_c = 1.182$ g cm⁻³, $\mu(\text{Cu-K}\alpha) = 0.53$ mm⁻¹, $T = 293$ K, pale yellow prisms; 4056 independent measured reflections, F^2 refinement, $R_1 = 0.055$, $wR_2 = 0.144$, 3197 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$], $2\theta_{\text{max}} = 120^\circ$], 339 parameters.

Crystal data for 9c

C₂₈H₂₂N₃Cl₂Fe, $M = 527.2$, triclinic, $P\bar{1}$ (no. 2), $a = 9.477(1)$, $b = 11.460(1)$, $c = 11.741(1)$ Å, $\alpha = 94.90(1)$, $\beta = 101.51(1)$, $\gamma = 97.38(1)^\circ$, $V = 1231.1(1)$ Å³, $Z = 2$, $D_c = 1.422$ g cm⁻³, $\mu(\text{Cu-K}\alpha) = 7.07$ mm⁻¹, $T = 293$ K, deep red prisms; 3649 independent measured reflections, F^2 refinement, $R_1 = 0.045$, $wR_2 = 0.103$, 2962 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$], $2\theta_{\text{max}} = 120^\circ$], 284 parameters.

CCDC reference numbers 204103–204104.

See <http://www.rsc.org/suppdata/dt/b3/b301902k/> for crystallographic data in CIF or other electronic format.

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