Synthesis, structures and catalytic properties of iron(III) complexes with asymmetric *N*-capped tripodal NO_3 ligands and a pentadentate N_2O_3 ligand†

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A new family of *N*-capped tripodal NO_3 proligands *N*,*N*-bis(2-hydroxy-3,5-di-*tert*-butylbenzyl)-*N*-(2′-hydroxy-5′-R-phenyl)amine [$H_3(L^n)$] [when R= Me, $n = 1$; R= ^{t}Bu, $n = 2$; R = Cl, $n = 3$] with different substituents in one of the aryl rings and *N*,*N*-bis(2-hydroxy-3-*tert*-butylbenzyl)-*N*-(2′-hydroxy-5′-methylphenyl)amine [$H_3(L^4)$] were synthesised. The preparation of a new pentadentate proligand *N*-methyl-*N*,*N*′,*N*′-tris(2-hydroxy-3,5-di-*tert*-butylbenzyl)ethane-1,2-diamine [$H_3(L^5)$] with an N_2O_3 donor set is also reported. Reaction of the proligands [$H_3(L^n)$] ($n = 1$–4) with iron(III) chloride in the presence of base (triethylamine) and 1-methylimidazole (1-Meim) as co-ligand led to the formation of iron complexes of the type [Fe(L^n)(1-Meim)] ($n = 1$–4) (**1**–**4**) respectively, while treatment of the trilithium salt of [$H_3(L^5)$] with iron(III) chloride afforded [Fe(L^5)] (**5**). All complexes were structurally characterised by X-ray crystallography. In complexes **1**–**4**, the ligands form five- and six-membered chelate rings with the iron centres which have distorted trigonal bipyramidal geometry with an N_2O_3 coordination environment. Complex **5** adopts a similar distorted trigonal bipyramidal geometry also with N_2O_3 coordination around the iron centre. The catalytic activity of these iron complexes towards epoxidation of styrene was examined.

Introduction

The chemistry of *N*-capped tripodal NO_3 ligands (Fig. 1) has received considerable attention over recent years.[1–21] The symmetric amine triphenolate type ligands (type I) bearing three identical benzyl side arms have demonstrated rich coordination chemistry with a wide variety of main group and transition metals.[3–18] Their complexes show a range of catalytic properties in reactions such as aza-Diels–Alder,[7] lactide polymerisation[12] and sulfoxidation.[14] All these have taken advantage of the tetradentate nature of the ligands to stabilise well-defined monomeric complexes under catalytic conditions. Substituents on the phenolate rings have been shown to alter not only the binding mode,[16,17] but also the stability[17] and catalytic activities of the metal complexes[18] by modifying the electronic and steric properties of the metal centres. Amine triphenolate-type ligands with one or two aromatic side arms replaced by the aliphatic methoxy side-arm donors ($CH_2CH_2OCH_3$) (type II)[19,20] or alkanol groups (CH_2CH_2OH) (type III)[21] have also been investigated for their binding modes and catalytic behaviour over a range of metal complexes. Recently, an amine triphenolate ligand with a stereogenic centre incorporated into one of the methylene carbons (type IV) has been synthesised with a view to potential applications in chiral recognition and asymmetric catalysis by the resulting enantiopure titanium complex.[11] However, to our knowledge, examples of metal complexes supported by amine triphenolate-type ligands containing two different arm lengths, have not been reported.

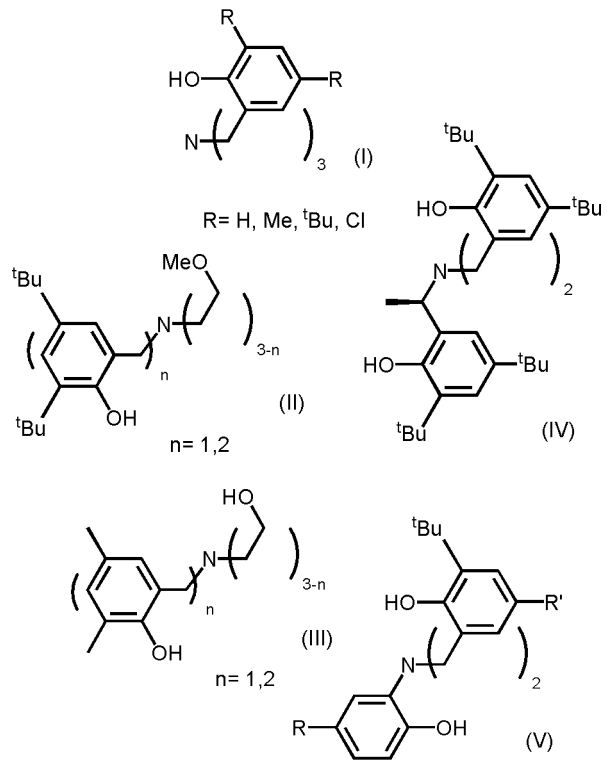

Fig. 1 Structures of *N*-capped tripodal ligands.

Iron complexes have been shown to display catalytic activities for a range of organic transformations.[22] However, their role in

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the epoxidation of olefins has received relatively less attention compared with other transition metal complexes.[23] Much of the previous effort has been directed to mechanistic studies of porphyrin-based catalysts[24] and only a handful of examples of non-heme iron-based epoxidation catalysts are known.[25–28] Recently, Beller and co-workers reported a series of iron complexes supported by *N*-donor bi- and tridentate ligands which have demonstrated excellent activity for epoxidation of olefins with hydrogen peroxide as oxidant.[29]

We report herein a new series of iron(III) complexes supported by the asymmetric *N*-capped tripodal NO_3 ligands with {5,6,6} chelate ring-sizes and substituents with different steric and electronic properties on the aryl rings (type V). We discuss their synthesis, structures and catalytic properties for the epoxidation of styrene in the presence of *tert*-butylhydroperoxide as oxidant. The structure and catalytic activity of a related iron(III) complex supported by a new pentadentate ligand offering an N_2O_3 coordination were also examined.

Experimental

General procedures

All reactions were carried out using standard Schlenk line techniques under an atmosphere of dinitrogen; workups were performed in air. Tetrahydrofuran (THF), diethyl ether (Et_2O) and toluene were distilled from sodium benzophenone. Methanol (MeOH) and triethylamine (Et_3N) were distilled from magnesium methoxide and sodium respectively. Anhydrous *tert*-butylhydroperoxide[30] (TBHP) was obtained according to the literature procedures. 3,5-di-*tert*-butyl-2-hydroxybenzylbromide[31] was prepared according to the literature procedures with minor modification. Silica gel (70–230 mesh) for flash-column chromatography was purchased from Fluka. All other reagents were purchased from Aldrich and used as received. All ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Varian Mercury VX300 spectrometer (^{1}H, 300 MHz and ^{13}C, 75.4 MHz) using $CDCl_3$ as solvent. Chemical shifts were relative to internal $SiMe_4$ ($\delta = 0$). Atmospheric-pressure chemical-ionization (APCI) mass spectra were recorded on a Hewlett-Packard 1050 Series Mass Spectrometer. Elemental analyses were performed by the microanalysis laboratory of the Inorganic Chemistry Laboratory, University of Oxford, UK. Gas-chromatography (GC) analyses were performed on an Unicam Pro-GC equipped with a flame ionization detector (FID). The column had internal diameter 4 mm and was packed with 3% Carbowax 20M on Supercoport 100/120 mesh support.

Preparations

3-*tert*-Butyl-2-hydroxybenzyl alcohol. To a solution of 3-*tert*-butyl-2-hydroxybenzaldehyde (4.34 g, 24.4 mmol) in MeOH (50 cm^3) was added $NaBH_4$ (1.84 g, 48.8 mmol) slowly. During addition, the mixture turned from pale yellow to colourless and stirring was continued for 1 h at room temperature. The volatiles were then removed using a rotary evaporator and the residue was mixed with water (50 cm^3). The pH of this mixture was neutralised with glacial acetic acid before being extracted with CH_2Cl_2 (3 × 150 cm^3). The combined extracts were dried over anhydrous $MgSO_4$, concentrated to give a pale-yellow liquid. Yield: 4.22 g (96%). ^{1}H NMR: δ 7.74 (s, 1H, ArOH), 7.26 (dd, $J = 1.2$, 7.8 Hz, 1H, ArH), 6.90 (d, $J = 6.9$ Hz, 1H, ArH), 6.80 (t, $J = 7.5$ Hz, 1H, ArH), 4.86 (s, 2H, $ArCH_2$), 1.44 (s, 9H, ^{t}Bu).

3-*tert*-Butyl-2-hydroxybenzylbromide. To a solution of 3-*tert*-butyl-2-hydroxybenzyl alcohol (4.22 g, 23.4 mmol) in $CHCl_3$ (50 cm^3) was added PBr_3 (1.10 cm^3, 11.7 mmol). White fumes appeared immediately during addition and stirring was continued for 1 h at room temperature. Then cold water (30 cm^3) was added with vigorous stirring for 2 min. The organic layer was separated and the aqueous residue was extracted with $CHCl_3$ (2 × 50 cm^3). The combined extracts were dried over anhydrous $MgSO_4$, concentrated and dried *in vacuo* to give a pale-yellow liquid, which was used without further purification. Yield: 5.57 g (98%).

General procedure for the preparation of (H_3L^n) (n = 1–4). To a solution of 2-hydroxy-5-R-aniline (R = Me, ^{t}Bu, Cl) in THF (20 cm^3) was added a solution of 3,5-di-*tert*-butyl-2-hydroxybenzylbromide or 3-*tert*-butyl-2-hydroxybenzylbromide (2 equiv.) in THF (20 cm^3) followed by triethylamine (2 equiv.) at room temperature. After heating under reflux overnight, the mixture was cooled, and the resulting white solid was filtered and discarded. The brown filtrate was concentrated with a rotary evaporator and the residue was chromatographed on a silica gel column. The second band was collected and concentrated to give a pale-yellow solid.

***N*,*N*-Bis(2-hydroxy-3,5-di-*tert*-butylbenzyl)-*N*-(2′-hydroxy-5′-methylphenyl)amine (H_3L^1).** According to the general procedure, 2-hydroxy-5-methylaniline (0.98 g, 8.0 mmol) was treated with 3,5-di-*tert*-butyl-2-hydroxybenzylbromide (4.78 g, 16.0 mmol) and triethylamine (2.23 cm^3, 16.0 mmol) to give H_3L^1. The crude product was purified by flash-column chromatography using CH_2Cl_2 as eluant. Yield: 3.67 g (82%). Mp: 169–171 °C. ^{1}H NMR: δ 7.16 (d, $J = 2.4$ Hz, 2H, ArH), 7.01 (s, 1H, ArH), 6.96 (m, 2H, ArH), 6.73 (m, 2H, ArH), 4.11 (s, 4H, $ArCH_2$), 2.21 (s, 3H, $ArCH_3$), 1.39 (s, 18H, ^{t}Bu), 1.27 (s, 18H, ^{t}Bu). ^{13}C{^{1}H} NMR: δ 152.0, 148.5, 141.4, 135.4, 135.0, 129.7, 125.9, 125.8, 123.3, 122.7, 121.6, 115.6, 56.3, 34.7, 34.2, 31.7, 29.8, 20.9. MS (APCI): m/z 560 (20%) [M + H]$^+$. Anal. calc. for $C_{37}H_{53}NO_3$: C, 79.4; H, 9.5; N, 2.5%. Found: C, 79.1; H, 9.3; N, 2.1%.

***N*,*N*-Bis(2-hydroxy-3,5-di-*tert*-butylbenzyl)-*N*-(2′-hydroxy-5′-*tert*-butylphenyl)amine (H_3L^2).** According to the general procedure, 2-hydroxy-5-*tert*-butylaniline (1.32 g, 8.0 mmol) was treated with 3,5-di-*tert*-butyl-2-hydroxybenzylbromide (4.78 g, 16.0 mmol) and triethylamine (2.23 cm^3, 16.0 mmol) to give H_3L^2. The crude product was purified by flash-column chromatography using $CHCl_3$–hexane (1 : 2) as eluant. Yield: 1.97 g (41%). Mp: 182–184 °C. ^{1}H NMR: δ 6.76–7.29 (m, 7H, ArH), 4.17 (s, 4H, $ArCH_2$), 1.41 (s, 18H, ^{t}Bu), 1.29 (s, 18H, ^{t}Bu), 1.27 (s, 9H, ^{t}Bu). ^{13}C{^{1}H} NMR: δ 152.4, 148.7, 143.5, 141.7, 135.7, 134.9, 125.8, 123.8, 122.4, 122.0, 119.4, 115.5, 56.7, 35.0, 34.7, 34.5, 32.0, 31.9, 30.2. MS (APCI): m/z 602 (100%) [M + H]$^+$. Anal. calc. for $C_{40}H_{59}NO_3$: C, 79.8; H, 9.9; N, 2.3%. Found: C, 79.9; H, 9.5; N, 2.5%.

***N*,*N*-Bis(2-hydroxy-3,5-di-*tert*-butylbenzyl)-*N*-(2′-hydroxyl-5′-chlorophenyl)amine (H_3L^3).** According to the general procedure, 2-hydroxy-5-chloroaniline (1.15 g, 8.0 mmol) was treated with 3,5-di-*tert*-butyl-2-hydroxybenzylbromide (4.78 g, 16.0 mmol) and

triethylamine (2.23 cm^3, 16.0 mmol) to give H_3L^3. The crude product was purified by flash-column chromatography using CH_2Cl_2 as eluant. Yield: 2.64 g (57%). Mp: 153–155 °C. ^1H NMR: δ 6.75–7.31 (m, 7H, ArH), 4.08 (s, 4H, $ArCH_2$), 1.39 (s, 18H, ^{t}Bu), 1.28 (s, 18H, ^{t}Bu). $^{13}C\{^1H\}$ NMR: δ 153.6, 148.1, 144.4, 142.8, 135.9, 134.6, 127.8, 124.1, 122.2, 122.1, 119.7, 114.1, 56.7, 34.3, 34.0, 32.3, 30.8. MS (APCI): m/z 580 (100%) $[M + H]^+$. Anal. calc. for $C_{36}H_{50}ClNO_3$: C, 74.5; H, 8.7; N, 2.4; Cl, 6.1%. Found: C, 74.8; H, 8.8; N, 2.4; Cl, 5.6%.

***N*,*N*-Bis(2-hydroxy-3-*tert*-butylbenzyl)-*N*-(2′-hydroxy-5′-methylphenyl)amine (H_3L^4).** According to the general procedure, 2-hydroxy-5-methylaniline (0.50 g, 4.1 mmol) was treated with 3-*tert*-butyl-2-hydroxybenzylbromide (1.99 g, 8.2 mmol) and triethylamine (1.14 cm^3, 8.2 mmol) to give H_3L^4. The crude product was purified by flash-column chromatography using CH_2Cl_2 as eluant. Yield: 1.43 g (78%). Mp: 164–166 °C. ^1H NMR: δ 7.16 (dd, $J = 1.8$, 7.7 Hz, 2H, ArH), 7.03 (d, $J = 1.8$ Hz, 1H, ArH), 6.96 (dd, $J = 1.5$, 7.2 Hz, 2H, ArH), 6.77–6.69 (m, 4H, ArH), 4.12 (s, 4H, $ArCH_2$), 2.23 (s, 3H, $ArCH_3$), 1.38 (s, 18H, ^{t}Bu). $^{13}C\{^1H\}$ NMR: δ 154.6, 148.3, 136.4, 135.0, 130.1, 128.9, 126.5, 126.2, 122.7, 122.3, 119.2, 115.7, 56.1, 34.5, 29.7, 20.9. MS (APCI): m/z 448 (25%) $[M + H]^+$. Anal. calc. for $C_{29}H_{37}NO_3$: C, 77.8; H, 8.3; N, 3.1%. Found: C, 77.5; H, 8.1; N, 3.2%.

***N*-Methyl-*N*,*N*′,*N*′-tris(2-hydroxy-3,5-di-*tert*-butylbenzyl)-ethane-1,2-diamine (H_3L^5).** To a solution of *N*-methylethylenediamine (0.54 ml, 6.2 mmol) in THF (50 cm^3) was added a solution of 3,5-di-*tert*-butyl-2-hydroxybenzylbromide (5.56 g, 18.6 mmol) in THF (50 cm^3) followed by triethylamine (2.59 cm^3, 18.6 mmol). After stirring at room temperature for three days, the resulting white solid was filtered and discarded. The brown filtrate was concentrated with a rotary evaporator and the residue was chromatographed on a silica gel column using $CHCl_3$–hexane (1 : 1) as eluant. The second band was collected and concentrated to give a pale yellowish–brown solid. Yield: 1.81 g (40%). Mp: 66–68 °C. ^1H NMR: δ 6.89–7.31 (m, 6H, ArH), 3.76 (m, 4H, $ArCH_2$), 3.71 (m, 2H, $ArCH_2$), 2.86 (m, 2H, NCH_2CH_2N), 2.76 (m, 2H, NCH_2CH_2N), 2.24–2.25 (s, 3H, NCH_3), 1.53 (s, 9H, ^{t}Bu), 1.51 (s, 9H, ^{t}Bu), 1.48 (s, 9H, ^{t}Bu), 1.47 (s, 9H, ^{t}Bu), 1.39 (s, 9H, ^{t}Bu), 1.38 (s, 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR: δ 153.6, 152.6, 152.1, 141.8, 141.4, 140.5, 135.8, 135.7, 125.0, 124.5, 123.8, 123.6, 123.4, 123.0, 121.4, 121.0 (two overlapping signals), 71.4, 62.5, 57.3, 53.5, 50.8, 41.3, 35.0, 34.9 (one overlapping signal), 34.3, 34.2 (one overlapping signal), 31.7 (one overlapping signal), 30.1, 29.8, 29.7, 29.6. MS (APCI): m/z 729 (100%) $[M + H]^+$. Anal. calc. for $C_{48}H_{76}N_2O_3$: C, 79.1; H, 10.5; N, 3.8%. Found: C, 78.8; H, 10.3; N, 3.3%.

General procedure for the preparation of [Fe(L^n)(1-Meim)] (n = 1–4) (1–4). To a mixture of H_3L^n (n = 1–4) and $FeCl_3$ (1 equiv.) in MeOH (20 cm^3) was added with triethylamine (3 equiv.) and 1-methylimidazole (1-Meim) (6 equiv.). After heating under reflux overnight, the mixture was cooled and left at room temperature for slow evaporation. The brown crystalline solids grown in the dark solution were collected, washed with cold Et_2O and hexane, and dried *in vacuo*.

[Fe(L^1)(1-Meim)] (1). According to the general procedure, $FeCl_3$ (0.16 g, 1.0 mmol) was treated with H_3L^1 (0.56 g, 1.0 mmol), triethylamine (0.42 cm^3, 3.0 mmol) and 1-methylimidazole (1-Meim) (0.48 cm^3, 6.0 mmol) to give [Fe(L^1)(1-Meim)] (0.49 g, 70%). Anal. calc. for $C_{41}H_{56}FeN_3O_3$: C, 70.9; H, 8.1; N, 6.1%. Found: C, 71.0; H, 8.3; N, 6.3%.

[Fe(L^2)(1-Meim)] (2). According to the general procedure, $FeCl_3$ (0.16 g, 1.0 mmol) was treated with H_3L^2 (0.60 g, 1.0 mmol), triethylamine (0.42 cm^3, 3.0 mmol) and 1-methylimidazole (0.48 cm^3, 6.0 mmol) to give [Fe(L^2)(1-Meim)] (0.38 g, 51%). Anal. calc. for $C_{44}H_{62}FeN_3O_3$: C, 71.7; H, 8.5; N, 5.7%. Found: C, 71.4; H, 8.6; N, 5.9%.

[Fe(L^3)(1-Meim)] (3). According to the general procedure, $FeCl_3$ (0.16 g, 1.0 mmol) was treated with H_3L^3 (0.58 g, 1.0 mmol), triethylamine (0.42 cm^3, 3.0 mmol) and 1-methylimidazole (0.48 cm^3, 6.0 mmol) to give [Fe(L^3)(1-Meim)] (0.43 g, 60%). Anal. calc. for $C_{40}H_{53}ClFeN_3O_3 \cdot 0.36(CH_3OH)$: C, 66.7; H, 7.6; N, 5.8; Cl, 4.9%. Found: C, 66.9; H, 7.6; N, 5.8; Cl, 4.9%. The result of elemental analysis suggests the presence of 0.36 equiv. of methanol molecule incorporated per unit cell in the crystal structure.

[Fe(L^4)(1-Meim)] (4). According to the general procedure, $FeCl_3$ (0.19 g, 1.2 mmol) was treated with H_3L^4 (0.54 g, 1.2 mmol), triethylamine (0.50 cm^3, 3.6 mmol) and 1-methylimidazole (0.57 cm^3, 7.2 mmol) to give [Fe(L^4)(1-Meim)] (0.44 g, 63%). Anal. calc. for $C_{33}H_{40}FeN_3O_3$: C, 68.0; H, 6.9; N, 7.2%. Found: C, 68.2; H, 7.1; N, 7.0%.

[Fe(L^5)] (5). To a mixture of $FeCl_3$ (0.16 g, 1.0 mmol) and H_3L^5 (0.73 g, 1.0 mmol) in MeOH (20 cm^3) was added with MeOLi (0.11 g, 3.0 mmol). The mixture was heated under reflux overnight. The volatiles were removed using a rotary evaporator and the residue was chromatographed on a silica gel column using CH_2Cl_2 as eluant. The second band was collected and concentrated to give a brown solid. Yield: (0.35 g, 45%). Anal. calc. for $C_{48}H_{73}FeN_2O_3$: C, 73.7; H, 9.4; N, 3.6%. Found: C, 73.7; H, 9.1; N, 3.7%.

General procedure for catalytic activity study of the complexes towards oxidation of styrene under anaerobic condition. A mixture of metal complex (**1**, **2**, **3** and **5**) (5 mmol%), *tert*-butylhydroperoxide (TBHP) (2.5 mmol) and styrene (1 mmol) in toluene (10 cm^3) was heated under reflux for 24 h (Scheme 3). The reaction mixture was filtered through a short-bed of celite. The catalytic product (styrene oxide) was identified by comparing the retention time with the authentic sample and the percentage conversion of the product was determined by gas chromatography.

X-Ray crystallographic analysis†

Crystal data and data processing parameters for the five iron(III) structures are given in Tables 1 and 2. X-Ray quality crystals of **1**, **3**, **4** and **5**† were grown by slow evaporation of MeOH solution of the metal complexes at room temperature. X-Ray quality crystals of **2**† were obtained by slow diffusion of Et_2O into the MeOH solution of the metal complex at room temperature. Crystals were mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150 K in a stream of cold nitrogen using an Oxford Cryosystems CRYOSTREAM unit, except **2** which was cooled to 250K. All diffraction data were collected on an Enraf-Nonius KappaCCD diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å). The θ range for all data collection was $5.0 \leq \theta \leq 27.5°$. Intensity data were processed using the DENZO-SMN package.[32] All these structures were solved using the direct-methods program SIR92,[33] which located all

Table 1 Crystallographic data† for complexes **1**, **2** and **3**

Compound	**1**	**2**	**3**
Empirical formula	$C_{41}H_{56}FeN_3O_3$	$C_{44}H_{62}FeN_3O_3 \cdot 1.5[(C_2H_5)_2O]$	$C_{40}H_{53}ClFeN_3O_3 \cdot 0.36(CH_3OH)$
Formula weight	694.76	848.03	726.63
Temperature/K	150	250	150
Colour	Brown prism	Brown plate	Dark-brown block
Crystal size/mm^3	0.08 × 0.20 × 0.20	0.04 × 0.20 × 0.24	0.18 × 0.18 × 0.22
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a/Å	10.1469(1)	14.3625(2)	11.2778(2)
b/Å	32.0173(3)	13.6632(2)	13.6398(3)
c/Å	12.6860(1)	26.7778(4)	14.0391(3)
α/°	90	90	94.0494(11)
β/°	103.5726(4)	100.8828(5)	94.7940(11)
γ/°	90	90	112.5924(11)
V/Å^3	4006.28(6)	5160.31(13)	1974.47(7)
Z	4	4	2
D_{calcd}/Mg m^{-3}	1.152	1.091	1.222
μ/mm^{-1}	0.415	0.335	0.490
$F_{(000)}$	1492	1840	774
Transmission coefficients (min, max)	0.95, 0.97	0.94, 0.99	0.92, 0.92
Number of data measured	33 694	39 433	27 291
Number of unique data (R_{int})	9281 (0.039)	12 027 (0.060)	8924 (0.041)
Number of observed data ($I > 3\sigma(I)$)	5947	6508	6725
Number of parameters, p	470	505	442
R	0.0437	0.0656	0.0461
wR	0.0505	0.0657	0.0655
S (GOF)	1.0592	1.1413	1.0417
Largest difference peak and hole/e Å^{-3}	+0.36 and −0.36	+0.66 and −0.43	+1.16 and −1.05

Table 2 Crystallographic data† for complexes **4** and **5**

Compound	**4**	**5**
Empirical formula	$C_{33}H_{40}FeN_3O_3$	$C_{48}H_{73}FeN_2O_3$
Formula weight	582.55	781.97
Temperature/K	150	150
Colour	Black block	Brown fragment
Crystal size/mm^3	0.10 × 0.20 × 0.28	0.08 × 0.20 × 0.20
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a/Å	13.3141(2)	15.4928(3)
b/Å	10.7638(1)	19.4211(4)
c/Å	22.3380(3)	16.9802(4)
α/°	90	90
β/°	102.1568(6)	115.7166(7)
γ/°	90	90
V/Å^3	3129.48(7)	4603.07(17)
Z	4	4
D_{calcd}/Mg m^{-3}	1.236	1.128
μ/mm^{-1}	0.518	0.367
$F_{(000)}$	1236	1700
Transmission coefficients (min, max)	0.90, 0.95	0.93, 0.97
Number of data measured	41 442	40 111
Number of unique data (R_{int})	7470 (0.057)	10 776 (0.053)
Number of observed data ($I > 3\sigma(I)$)	4882	7387
Number of parameters, p	361	487
R	0.0380	0.0390
wR	0.0490	0.0453
S (GOF)	1.0218	1.0376
Largest difference peak and hole/e Å^{-3}	+0.35 and −0.41	+0.46 and −0.43

non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite.[34] In **1**, one of the *tert*-butyl groups was disordered over two orientations and the occupancies of these were refined, subject to constraint of the total occupancy to unity. Geometric similarity restraints were applied to the two positions. One of the *tert*-butyl groups in **2** was refined isotropically. The methyl carbon atoms of a *tert*-butyl group in **2** were disordered over two orientations. One of these was disordered over two orientations not related by crystallographic symmetry whereas the second was disordered

over two orientations related by a crystallographic centre of inversion. Coordinates, isotropic thermal parameters and, where appropriate, site occupancies of disordered non-hydrogen atoms were refined, with chemically equivalent atoms constrained to have common thermal parameters. Geometric restraints were applied to bond lengths and angles within the disordered fragments. In **3**, a solvated methanol molecule is disordered over a crystallographic centre of inversion. The thermal parameters of the solvent carbon and oxygen atoms refined to unreasonably large values, which was taken to indicate that the solvent site was only partially occupied. Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. Hydrogen atoms were positioned geometrically after each cycle of refinement. 4-Term {for complex **1**} and 3-Term {for complexes **2–5**} Chebychev polynomial weighting schemes were applied.

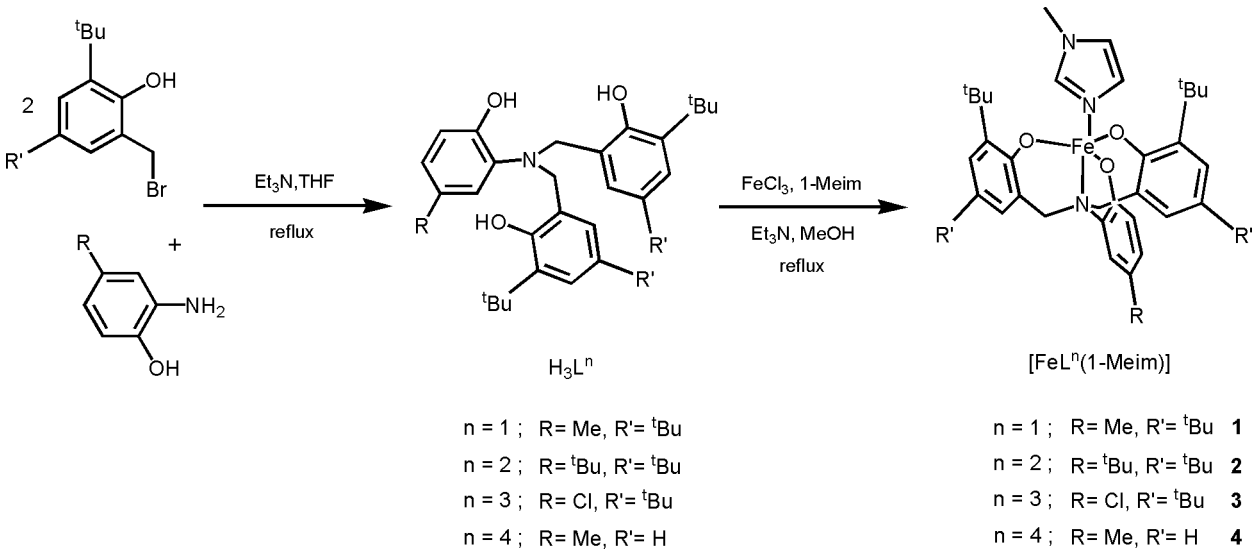
Results and discussion

Synthesis of ligands

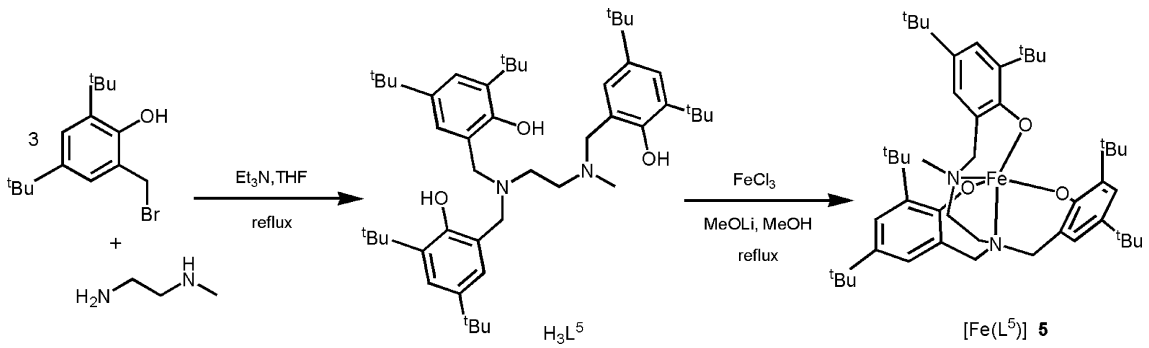
The synthesis of a series of previously unknown *N*-capped tripodal NO_3-type proligands H_3L^n (n = 1–4) is shown in Scheme 1. The sole differences in H_3L^n (n = 1–3) are the substituents on one of the aryl rings. The coupling between 3,5-di-*tert*-butyl-2-hydroxybenzylbromide with differently substituted 2-hydroxy-5-R-aniline [R = Me, n = 1; R = ^{t}Bu, n = 2; R = Cl, n = 3] in the presence of base (triethylamine) afforded the proligands in 41–82% yield. Reaction of the same bromide with commercially available *N*-methylethylenediamine under similar conditions gave the new N_2O_3 pentadentate proligand H_3L^5 in 40% yield (Scheme 2). The proligand H_3L^4 was synthesised by a similar procedure using 3-*tert*-butyl-2-hydroxybenzylbromide and 2-hydroxy-5-methylaniline as reagents in 78% yield (Scheme 1).

Synthesis of iron(III) complexes

Reaction of the tripodal proligands H_3L^n (n = 1–4) with iron(III) chloride in the presence of three equivalents of triethylamine and six equivalents of 1-methylimidazole (1-Meim) in MeOH afforded the corresponding complexes **1–4** in 51–70% (Scheme 1). Treatment of the trilithium salt of H_3L^5 with iron(III) chloride in MeOH afforded the five coordinate complex **5** in 45% yield (Scheme 2). All these iron complexes possessed good solubility in common organic solvents such as methanol, chloroform and toluene, except **4** which was sparingly soluble in toluene. Crystals of all iron complexes suitable for X-ray crystallography were obtained by slow evaporation of a methanolic solution of the complexes, except for **2**, for which crystals were grown by slow



Scheme 1 Synthesis of tripodal ligands H_3L^n (n = 1–4) and iron(III) complexes **1–4**.



Scheme 2 Synthesis of pentadentate ligand H_3L^5 and iron(III) complex **5**.

diffusion of diethyl ether into the methanolic solution of the complex. Elemental analysis data of these complexes were in good agreement with the structural formula determined from X-ray crystallography,† except **2** where the solvated diethyl ether molecules were not observed.

Structural studies

The molecular structures of **1–4** are shown in Fig. 2–5 respectively. Selected bond distances and angles for these complexes are summarised in Tables 3 and 4. The crystallographic data are in Tables 1 and 2.† Complex **1** crystallises in the monoclinic space group $P2_1/n$. Complexes **2** and **4** crystallise in the monoclinic space group $P2_1/c$, while **3** crystallises in the triclinic space group $P\bar{1}$. For **1**, the iron centre is surrounded by three equatorial phenolate oxygen atoms (O(1)–O(3)) and two axial nitrogen atoms (bridgehead N(1) and imidazole N(2)) in a distorted trigonal bipyramid geometry, with the N(1)–Fe–N(2) angle of 166.55(7)°. The iron atom is out of the plane (*ca.* 0.11 Å) of the three oxygen donors towards the imidazole nitrogen. The bond distances and angles are comparable to those in a related structure [Fe{N(CH_2-*o*-$C_6H_4O)_3$}(1-Meim)] reported by Koch *et al.*[3] Not surprisingly, the five-membered chelate ring displays different geometric features with respect to those in the six-membered systems: (i) the angle O(1)–Fe–N(1) [80.11(6)°] is considerably smaller than that for O(2)–Fe–N(1) and O(3)–Fe–N(1) [90.51(6)° and 90.11(6)° respectively], and (ii) the Fe–O(1) bond distance [1.9226(17) Å] is longer than Fe–O(2) and Fe–O(3) bonds [1.8823(15) and 1.8602(15) Å respectively]. It is also observed that the imidazole nitrogen bends towards the five-membered chelate ring, indicated by the smaller angle of N(2)–Fe–O(1) compared with N(2)–Fe–O(2) and N(2)–Fe–O(3). Such a conformation is likely to minimise the steric hindrance between the axial ligand and the *tert*-butyl groups in the *ortho* positions on the other two aryl rings.

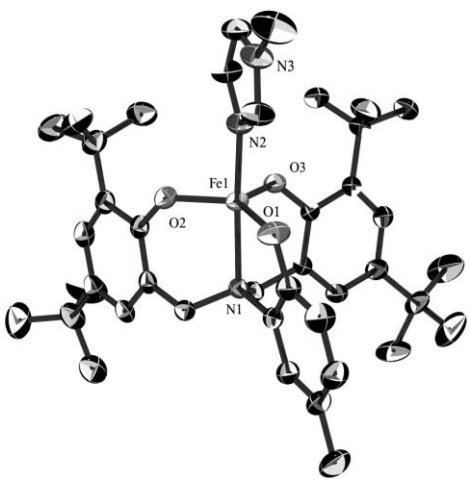


Fig. 2 ORTEP representation (40% probability ellipsoids) of the molecular structure and atom labeling scheme for [Fe(L^1)(1-Meim)] **1**. Hydrogen atoms are omitted for clarity.

The structural features of **2–4** show strong resemblances to those in **1**, with similar bond distances and angles as in the parent compound. The steric and electronic demands of the substituents (Me, ^{t}Bu and Cl) on the aryl ring appear to have no significant effect on the overall structure in these complexes. The crystals of **2** incorporate approximately 1.5 Et_2O per molecule of the complex while that in **3** contains 0.36 MeOH of solvation.

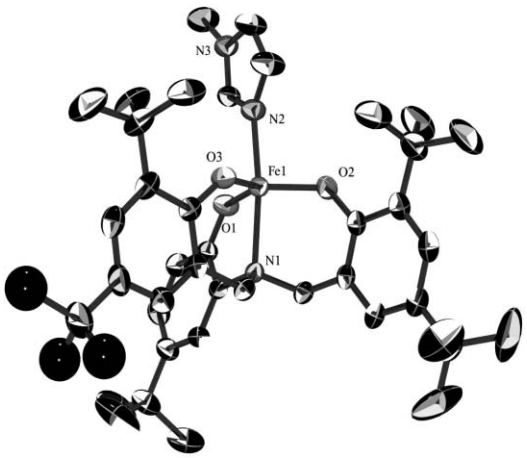


Fig. 3 ORTEP representation (40% probability ellipsoids) of the molecular structure and atom labeling scheme for [Fe(L^2)(1-Meim)] **2**. Hydrogen atoms are omitted for clarity.

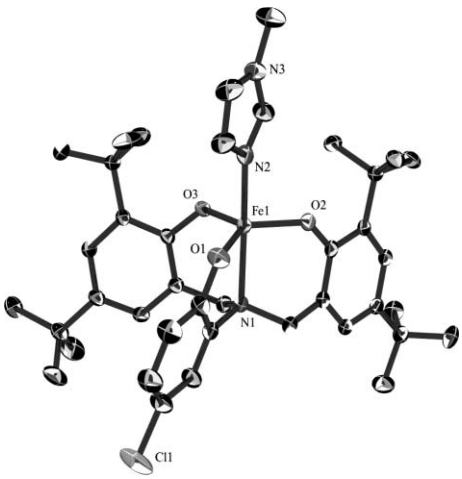


Fig. 4 ORTEP representation (40% probability ellipsoids) of the molecular structure and atom labeling scheme for [Fe(L^3)(1-Meim)] **3**. Hydrogen atoms are omitted for clarity.

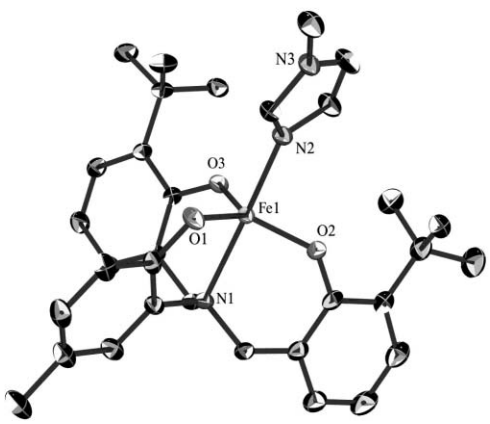


Fig. 5 ORTEP representation (40% probability ellipsoids) of the molecular structure and atom labeling scheme for [Fe(L^4)(1-Meim)] **4**. Hydrogen atoms are omitted for clarity.

Table 3 Selected bond distances (Å) and angles (°) for complexes **1**, **2** and **3**

[Fe(L^1)(1-Meim)] **1**		[Fe(L^2)(1-Meim)] **2**		[Fe(L^3)(1-Meim)] **3**	
Fe(1)–O(1)	1.9226(17)	Fe(1)–O(1)	1.918(2)	Fe(1)–O(1)	1.9362(16)
Fe(1)–O(2)	1.8823(15)	Fe(1)–O(2)	1.866(2)	Fe(1)–O(2)	1.8848(14)
Fe(1)–O(3)	1.8602(15)	Fe(1)–O(3)	1.864(2)	Fe(1)–O(3)	1.8740(14)
Fe(1)–N(1)	2.2160(16)	Fe(1)–N(1)	2.212(3)	Fe(1)–N(1)	2.2137(17)
Fe(1)–N(2)	2.0938(18)	Fe(1)–N(2)	2.099(3)	Fe(1)–N(2)	2.1000(18)
O(1)–Fe(1)–O(2)	129.00(8)	O(1)–Fe(1)–O(2)	124.26(11)	O(1)–Fe(1)–O(2)	125.69(7)
O(1)–Fe(1)–O(3)	118.61(8)	O(1)–Fe(1)–O(3)	121.00(11)	O(1)–Fe(1)–O(3)	119.20(7)
O(2)–Fe(1)–O(3)	111.35(7)	O(2)–Fe(1)–O(3)	113.74(11)	O(2)–Fe(1)–O(3)	113.74(7)
O(1)–Fe(1)–N(1)	80.11(6)	O(1)–Fe(1)–N(1)	80.18(9)	O(1)–Fe(1)–N(1)	79.66(6)
O(2)–Fe(1)–N(1)	90.51(6)	O(2)–Fe(1)–N(1)	91.4(1)	O(2)–Fe(1)–N(1)	90.12(6)
O(3)–Fe(1)–N(1)	90.11(6)	O(3)–Fe(1)–N(1)	89.1(1)	O(3)–Fe(1)–N(1)	89.17(6)
O(1)–Fe(1)–N(2)	86.92(7)	O(1)–Fe(1)–N(2)	87.3(1)	O(1)–Fe(1)–N(2)	88.30(7)
O(2)–Fe(1)–N(2)	94.92(7)	O(2)–Fe(1)–N(2)	96.58(11)	O(2)–Fe(1)–N(2)	94.50(7)
O(3)–Fe(1)–N(2)	99.31(7)	O(3)–Fe(1)–N(2)	96.52(11)	O(3)–Fe(1)–N(2)	99.45(7)
N(1)–Fe(1)–N(2)	166.55(7)	N(1)–Fe(1)–N(2)	167.5(1)	N(1)–Fe(1)–N(2)	167.58(7)

Table 4 Selected bond distances (Å) and angles (°) for complexes **4** and **5**

[Fe(L^4)(1-Meim)] **4**		[Fe(L^5)] **5**	
Fe(1)–O(1)	1.9202(13)	Fe(1)–O(1)	1.8712(12)
Fe(1)–O(2)	1.8612(13)	Fe(1)–O(2)	1.8728(12)
Fe(1)–O(3)	1.8686(13)	Fe(1)–O(3)	1.8895(12)
Fe(1)–N(1)	2.2005(15)	Fe(1)–N(1)	2.2407(14)
Fe(1)–N(2)	2.0957(16)	Fe(1)–N(2)	2.2185(14)
O(1)–Fe(1)—O(2)	130.67(6)	O(1)–Fe(1)–O(2)	114.36(6)
O(1)–Fe(1)—O(3)	117.15(6)	O(1)–Fe(1)–O(3)	91.90(5)
O(2)–Fe(1)—O(3)	111.37(6)	O(2)–Fe(1)–O(3)	106.81(5)
O(1)–Fe(1)—N(1)	80.68(6)	O(1)–Fe(1)–N(1)	87.33(5)
O(2)–Fe(1)—N(1)	90.77(6)	O(2)–Fe(1)–N(1)	91.89(5)
O(3)–Fe(1)—N(1)	90.47(6)	O(3)–Fe(1)–N(1)	159.71(5)
O(1)–Fe(1)—N(2)	87.90(6)	O(1)–Fe(1)–N(2)	137.45(5)
O(2)–Fe(1)–N(2)	92.53(6)	O(2)–Fe(1)–N(2)	106.17(5)
O(3)–Fe(1)–N(2)	99.69(6)	O(3)–Fe(1)–N(2)	88.32(5)
N(1)–Fe(1)–N(2)	167.32(6)	N(1)–Fe(1)–N(2)	78.74(5)

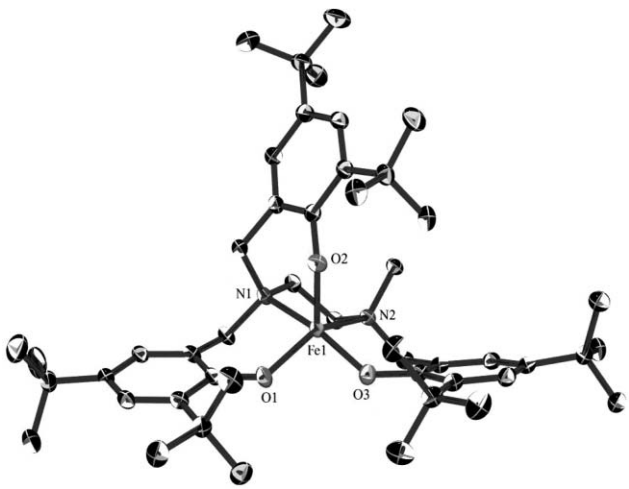
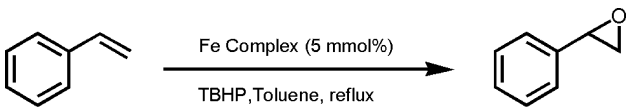


Fig. 6 ORTEP representation (40% probability ellipsoids) of the molecular structure and atom labeling scheme for [Fe(L^5)] **5**. Hydrogen atoms are omitted for clarity.

The molecular structure of **5** is shown in Fig. 6. Selected bond distances and angles for the complex are given in Table 4 and crystallographic data in Table 2. Complex **5** crystallises in the monoclinic space group of $P2_1/n$. The iron resides in a distorted trigonal bipyramidal geometry with the unmethylated nitrogen N(1) and one of the phenolate oxygens O(3) occupying the two axial positions, giving an O(3)–Fe(1)–N(1) angle of 159.71(5)°. The methylated nitrogen N(2) along with the other two phenolate atoms O(1) and O(2) define the equatorial plane. The iron atom is 0.158 Å out of the equatorial plane towards the axial oxygen O(3). The two nitrogen atoms form a five-membered chelate ring with the iron(III) centre whereas all three phenolate arms form six-membered chelate rings. The Fe–N and Fe–O bond distances are within the range of those reported for other iron(III) complexes containing related ligands.[35] In general, the structural details of **5** show resemblance to a recently reported five-coordinate iron(III) complex supported by a similar pentadentate ligand.[36]

Catalysis studies

The catalytic properties of **1**, **2**, **3** and **5** for the epoxidation of styrene were briefly examined (Scheme 3). In a typical experiment, 5 mmol% of the complex, 1 mmol of styrene and 2.5 mmol TBHP were dissolved in toluene and heated under reflux for 24 h under nitrogen.[30,37] The percentage conversion of the substrate was determined by gas chromatography. All these iron complexes were found to be catalytically active for the oxidation of styrene to styrene oxide with a similar percentage conversion (45–55%). Despite their modest conversions compared with the recently reported iron catalysts where quantitative conversions of aromatic alkenes to corresponding epoxides were observed,[29] the results here suggest a new type of catalytically active iron complex for epoxidation. Formation of additional products was also observed, which may be attributable to the instability of the styrene in the reaction medium. No transformation from styrene to styrene oxide was observed in the absence of the iron complexes under similar conditions. The electronic and steric properties



Scheme 3

of the substituent in the ligands only showed a little effect on the percentage conversion in the epoxidation. Owing to limited solubility in toluene, the catalytic activity of **4** was not examined. The fact that the five-coordinate complex **5** bearing no co-ligand (1-methylimidazole) showed similar catalytic activity as **1**–**3** suggests that the catalytic process may involve a six- or even higher-coordinate metastable intermediate. Other examples of amine triphenolate metal complexes with catalytic activity towards styrene epoxidation have been reported in the literature but their conversion rates are comparatively slow (2–3 turnovers per day).[17]

Conclusions

In summary, a series of iron(III) complexes with asymmetric *N*-capped tripodal NO_3 ligands and a pentadentate N_2O_3 ligand were synthesised and structurally characterised by X-ray crystallography.† These iron complexes showed catalytic activity towards epoxidation of styrene and despite their modest conversions, they represent new types of iron-based epoxidation catalysts. The substituents with different steric and electronic properties on the five-membered chelate ring were shown to have little impact on the overall molecular structure and the catalytic activity of the complexes.

Acknowledgements

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