# Coordination complexes bearing potentially tetradentate phenoxyamine ligands $\dot{\uparrow}$

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A series of metal complexes containing potentially tetradentate phenoxyamine ligands is described. The ligands are found to bind to main-group metals and first-row transition-metal centres with variable denticity depending upon the requirements of the particular metal centre. Bidentate [Al(III)], tridentate [Mg(II), Ca(II), Zn(II)] and tetradentate [K(I), Cr(III), Fe(II), Co(II)] binding modes have been established unambiguously through single-crystal X-ray structure determinations.

# Introduction

Ligands containing phenoxide donors have enjoyed much success in the stabilization of catalysts for numerous chemical transformations, ranging from oxidation<sup>1</sup> and epoxidation,<sup>2</sup> through to carbon–carbon bond formation<sup>3</sup> and controlled polymerization.<sup>4</sup> The ligand types employed in these processes range from simple bidentate (I) and tridentate (II, III) mono-phenoxide systems through to bi- (IV), tri- (V) and tetra-dentate (VI, VII) bisphenoxide ligands, many of which are derivable *via* straightforward Schiff-base or Mannich condensation procedures.



A potentially important category of phenoxide ligand which, to date, has remained largely unexplored, is the series (VIII) based on tetradentate mono-phenoxide coordination. Matyjaszewski and coworkers recently introduced one ligand from this series, containing diethylamino donors (IX), and described its copper complex,<sup>5</sup> while Kol and co-workers have recently reported zirconium complexes stabilized by a derivative (X) containing methoxy donors.<sup>6</sup>

Herein, we describe the synthesis and characterization of a family of phenoxyamine ligands bearing either additional amine or

ether donors, and their coordination chemistry with metals across the first-row transition series [Cr(III), Fe(II), Co(II), Zn(II)] and for several main-group metal ions [K(I), Mg(II), Ca(II), Al(III)].



# **Results and discussion**

# Ligand synthesis

Ligands 1a-c were synthesised by treatment of 2,4-di-*tert*butylphenol with paraformaldehyde and the relevant secondary amine in refluxing methanol, affording 1a-c as viscous oils in high yield (Scheme 1). NMR data and elemental analyses were consistent with the formation of the targeted phenols.



# Complex synthesis and characterization

**Group I complexes.** Potassium salts of **1a**,**c** were synthesised by slow addition of the phenol to a slurry of potassium hydride at -78 °C (Scheme 2). After 16 h the reaction mixtures were concentrated under reduced pressure to afford waxy solids which could be recrystallised from hot toluene to give **2a** and **2c** as colourless crystals.

The X-ray structure of **2a** showed the complex to be dimeric with approximate  $C_2$  symmetry about an axis perpendicular to the central four-membered K<sub>2</sub>O<sub>2</sub> ring (Fig. 1). This ring has a slightly folded conformation, the two KO<sub>2</sub> planes being inclined

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<sup>†</sup> Electronic supplementary information (ESI) available: Table S1: Crystal data, data collection and refinement parameters for compounds 4c and 5a. Fig. S1–19: Molecular structures of 2a, 3b, 4c (I and II), 5a, 6c (I and II), 7a (I and II), 7b, 8a, 9c, 10c, and overlay diagrams for 6c and 7a. See DOI: 10.1039/b607753f



Fig. 1 The molecular structure of **2a**. The transannular  $K \cdots K$  separation is 3.6417(5) Å.

to each other by *ca*. 7°. The two six-membered N,O chelate rings have boat geometries. For the K(1) ring, {K(1),C(1),C(2),N(8)} is coplanar to within *ca*. 0.02 Å with O(1) and C(7) *ca*. +0.65 and +0.75 Å out of this plane, corresponding to an approximate fold of *ca*. 53° about the O(1)  $\cdots$  C(7) vector, whilst for the counterpart at K(2), {K(2),C(31),C(32),N(38)} is coplanar to within *ca*. 0.06 Å with O(31) and C(37) *ca*. +0.50 and +0.77 Å out of the plane, giving an approximate fold about the O(31)  $\cdots$  C(37) vector of *ca*. 47°. The four N,N' five-membered chelate rings all have the typical twisted geometry. As expected, the bonds to the formally anionic oxygen centres, (ranging between 2.5919(12) and 2.6684(11) Å) are noticeably shorter than those to the neutral nitrogen donors (ranging between 2.8193(13) and 3.0402(15) Å) (Table 1).

Table 1         Selected bond lengths (Å) a	and angles (°) for 2a
---------------------------------------------	-----------------------

K1–O1	2.5919(12)	K1–N8	2.8193(13)
K1–N11	2.9659(15)	K1–N18	2.8798(15)
K1–O31	2.5977(11)	K2–O1	2.6684(11)
K2–O31	2.6092(12)	K2–N38	2.8340(13)
K2–N48	2.9035(16)	K2–N41	3.0402(15)
O1-K1-N8 O1-K1-N18 N8-K1-N11 N8-K1-O31 N11-K1-O31 O1-K2-O31 O1-K2-N41 O31-K2-N48 O31-K2-N48 N38-K2-N48	78.59(4) $114.77(4)$ $63.84(4)$ $155.91(4)$ $139.90(4)$ $90.64(4)$ $151.30(4)$ $76.31(4)$ $116.52(4)$ $65.90(4)$ $97.6(12)$	O1-K1-N11 O1-K1-O31 N8-K1-N18 N11-K1-N18 N18-K1-O31 O1-K2-N38 O1-K2-N48 O31-K2-N41 N38-K2-N41 N41-K2-N48	109.05(4) 92.63(4) 66.24(4) 102.15(4) 98.35(4) 145.40(4) 93.18(4) 101.56(4) 63.29(4) 104.06(5) 98.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2) 99.77(2)

Low-temperature <sup>1</sup>H NMR spectra of **2a** and **2c** reveal inequivalent amino and methoxy donors, at 0.61 and 0.71 ppm for the methyl protons of the NEt<sub>2</sub> groups (213 K), and at 2.56 and 3.17 ppm for the methyl protons of the methoxy donors (at 193 K), consistent with the solid-state structure of **2a**. As the samples are warmed to room temperature, these signals coalesce to single resonances (at 0.74 and 2.85 ppm, respectively) indicating an averaging process on the NMR timescale, most likely a result of motion within the dinuclear structure.

**Group II complexes.** An alkyl magnesium complex, **3b**, proved accessible in good yield by deprotonation of ligand **1b** (using *n*-butyllithium) followed by reaction of the lithium salt with 'PrMgCl, (Scheme 3).



The solid-state structure of **3b** revealed the expected distorted tetrahedral coordination geometry at the magnesium centre, with one of the amino side-arms not being bound (Fig. 2). The angles at the metal are in the range 94.23(5)–129.58(6)°, the smallest being associated with the bite of the six-membered N,O chelate ring (Table 2). This ring has a twisted boat geometry, with {Mg,C(1),C(6),N(8)} being coplanar to within *ca.* 0.06 Å with O(1) and C(7) *ca.* +0.33 and +0.68 A, respectively, out of this plane; the fold about the O(1)…C(7) vector is *ca.* 41°. The six-membered N,N' chelate ring has a chair conformation, Mg



Fig. 2 The molecular structure of 3b.

Table 2Selected bond lengths (Å) and angles (°) for 3b

Mg–O1	1.9060(11)	Mg–N8	2.1577(12)
Mg–N12	2.1721(13)	Mg–C30	2.1512(16)
O1-Mg-N8	94.23(5)	O1-Mg-N12	105.19(5)
O1-Mg-C30	129.58(6)	N8-Mg-N12	97.00(5)
N8-Mg-C30	114.91(6)	N12-Mg-C30	110.49(6)

and C(10) lying *ca.* +0.85 and -0.70 Å, respectively, out of the {N(8),C(9),C(11),N(12)} plane which is coplanar to within *ca.* 0.02 Å.

In addition to the magnesium mono-alkyl species, bis-chelate complexes of magnesium and calcium are also accessible. Deprotonation of **1c** with *n*-butyllithium, followed by reaction of the lithium salt with isopropyl magnesium chloride, afforded the homoleptic species **4c**. Similarly the calcium complex **5a** was formed by the reaction of **1a** sequentially with 1 equivalent of  $K[N(SiMe_3)_2]$  and half an equivalent of  $CaI_2$ . **4c** and **5a** can also be synthesised directly by the reaction of **2c** or **2a** with the appropriate metal dihalide precursor.

The quality of the single-crystal X-ray data for 4c and 5a are poor, but nevertheless sufficient to establish the bis(tridentate) ligand coordination within these products. The structure of 5a is shown in Fig. 3 whilst 4c is shown in Fig. S15–S18 in the ESI.†



Fig. 3 The molecular structure of the  $C_i$ -symmetric complex 5a.

Aluminium alkyl species. The aluminium alkyl complex **6c** was formed upon treatment of **1c** with AlMe<sub>3</sub> (Scheme 4). Refluxing the reaction mixture, followed by crystallisation, afforded **6c** in 25% yield.



The X-ray structure of complex **6c** showed the presence of two crystallographically independent molecules (I and II) in the asymmetric unit, though with near identical geometries, the r.m.s. fit of all of the non-hydrogen atoms being *ca*. 0.06 Å (molecule I is shown in Fig. 4, molecule II in Fig. S3 in the ESI,† and an overlay of the two molecules in Fig. S6, ESI†). The coordination geometry is distorted tetrahedral (Table 3), with neither of the methoxy side-

**Table 3** Selected bond lengths (Å) and angles (°) for the two independent complexes (I and II) present in the crystals of 6c

	Mol. I	Mol. II
Al-O1	1.7735(15)	1.7752(16)
Al-C25	1.965(2)	1.961(2)
Al-N8	2.0652(17)	2.0641(17)
Al-C26	1.962(2)	1.961(2)
O1-Al-N8	94.45(7)	94.81(7)
01–A1–C26	104.61(9)	105.76(10)
N8–A1–C26	111.13(9)	110.51(9)
01–A1–C25	106.65(10)	106.94(10)
N8–A1–C25	111.40(9)	111.44(10)
C25–A1–C26	123.96(12)	123.25(12)



Fig. 4 The molecular structure of one (I) of the two independent complexes present in the crystals of **6c**.

arms being bound to the aluminium centre. The most notable departure from an ideal tetrahedral geometry is an opening out of the angle between the two methyl ligands, C(25)–Al–C(26) 123.96(12)° [123.25(12)°], the value in square parentheses referring to molecule II. Associated with this is a close approach of the non-coordinated methoxy oxygen atom O(11) at 2.7259(18) Å [2.7488(18) Å]. The smallest angle at aluminium—94.45(7)° [94.81(7)°]—is the bite of the six-membered N,O chelate ring which has a folded geometry, Al and N(8) lying *ca*. 0.66 Å [0.65 Å] and 1.07 Å [1.06 Å], respectively, out of the {O(1),C(1),C(6),C(7)} plane which is coplanar to within *ca*. 0.03 Å [0.03 Å].

Organometallic zinc complexes 7a-c were formed by the reaction of diethyl zinc with ligands 1a-c (Scheme 5). The ethyl zinc products were crystallised from heptane in reasonable



Table 4Selected bond lengths (Å) and angles (°) for the two independentcomplexes (I and II) present in the crystals of 7a

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	Mol. I	Mol. II	
Zn–O1 Zn–N11 Zn–N8 Zn–C21	1.952(2) 2.139(3) 2.139(2) 1.067(4)	1.948(2) 2.133(3) 2.155(2)	
2n-C31 O1-Zn-N8 O1-Zn-C31 N8-Zn-C31 O1-Zn-N11 N8-Zn-N11 N11-Zn-C31	1.967(4) 93.67(9) 127.12(18) 121.97(17) 100.98(9) 85.26(11) 118.2(2)	1.987(3) 93.52(9) 127.46(18) 121.64(14) 100.68(9) 85.57(12) 118.24(18)	

yields (>60%). The formation of the desired products was confirmed by NMR spectroscopy, elemental analysis and mass spectrometry.

As was observed for 6c, the structure of 7a also has two crystallographically independent molecules (I and II) in the asymmetric unit, and excluding the atoms of the non-coordinated side-arm (vide infra) the two molecules have an r.m.s. fit of ca. 0.07 Å (molecule I is shown in Fig. 5, molecule II in Fig. S7, and the overlay of the two molecules in Fig. S10, ESI<sup>†</sup>). The geometry at the zinc centre is distorted tetrahedral (Table 4) with one of the amino side-arms non-bound; this second side-arm is disordered in both independent molecules. The angles at the metal are in the range 85.26(11)-127.12(18)° [85.57(12)-127.46(18)° in molecule II], the most acute being associated with the bite of the five-membered N,N' chelate ring. This ring has a twisted conformation with C(9) and C(10) lying ca. +0.33 Å [+0.32 Å] and -0.32 Å [-0.33 Å] respectively out of the ZnN<sub>2</sub> plane. The six-membered N,O chelate ring has a boat conformation, O(1) and N(7) lying ca. +0.76 Å [+0.76 Å] and +0.60 Å [+0.60 Å] out of the  $\{Zn, C(1), C(6), N(8)\}$  plane which is coplanar to within *ca*. 0.09 Å [0.09 Å]; the associated fold about the O(1)  $\cdots$  C(7) vector is *ca*. 58° [58°].



Fig. 5 The molecular structure of one (I) of the two independent complexes present in the crystals of 7a.

Table 5Selected bond lengths (Å) and angles (°) for 7b

Zn–O1	1.9456(12)	Zn–N8	2.1599(14)
Zn–N12	2.1560(15)	Zn–C29	1.9930(19)
O1–Zn–N8	93.85(5)	O1–Zn–N12	102.82(5)
O1–Zn–C29	130.97(7)	N8–Zn–N12	97.43(6)
N8–Zn–C29	114.27(7)	N12–Zn–C29	111.65(7)

X-Ray analysis of crystals of 7b revealed a structure (Fig. 6) similar to that seen for each independent molecule of 7a (vide supra). The phenoxyamine ligand is again tridentate, one of the amine side-arms being non-coordinating. The coordination geometry is distorted tetrahedral (Table 5) with angles in the range 93.85(5)–130.97(7)°. In contrast to 7a, here the smallest angle is associated with the bite of the six-membered N,O chelate ring, the extra methylene in the six-membered N,N' chelate ring allowing this latter chelate to adopt a less strained coordination geometry [bite angle of  $97.43(6)^{\circ}$ ] than was possible for the five-membered N,N' chelate ring in 7a [bite angles of 85.26(11) and 85.57(12)° for the two independent molecules]. The N,O chelate ring again has a boat conformation, O(1) and C(7) lying ca. +0.50 and +0.68 Å out of the  $\{Zn, C(1), C(6), N(8)\}$  plane which is coplanar to within *ca*. 0.03 Å; the associated fold about the O(1)  $\cdots$  C(7) vector is *ca*. 48°. The N,N' chelate ring adopts a chair conformation, Zn and C(10)lying ca. +0.78 and -0.71 Å out of the {N(8),C(9),C(11),N(12)} plane which is coplanar to within ca. 0.02 Å.



Fig. 6 The molecular structure of 7b.

Room-temperature solution <sup>1</sup>H NMR data for **7c** revealed that the bound and pendant OMe groups exchange rapidly on the NMR timescale: a single methyl resonance is observed for the methoxy donor at 2.85 ppm along with a single set of multiplets (of a  $H_{ABXY}$  system) for the methylene protons of the donor arms. A similar effect is observed for the amino donors **7a** or **7b**, which gave a single resonance for the amino donor substituents. The spectra remained largely unchanged, with only slight broadening, to 213 K.

**Chromium complex.** We next explored the coordination of these ligands to transition metals in order to gain further insight

into the possible coordination geometries adopted by these multidonor ligands.

The chromium(III) complex **8a** was formed by the addition of the potassium salt **2a** to  $CrCl_3(THF)_3$ , creating a green–black solution (Scheme 6). Crystals suitable for X-ray diffraction studies were obtained from a layered toluene–pentane solution.



The structure of **8a** shows the ligand to be tetradentate, with the two amino side-arms coordinating in a mutually *trans* disposition at the chromium centre (Fig 7). The coordination geometry is distorted octahedral with *cis* angles in the range 82.11(11)–98.96(7)°, the two most acute angles [82.11(11) and 82.66(11)] being the bites of the N(8)/N(18) and N(8)/N(11) five-membered N,N' chelate rings, respectively (Table 6). Both of these rings adopt envelope conformations; for the N(8)/N(11) ring, C(9) lies *ca.* 0.67 Å out of the {Cr,N(8),C(10),N(11)} plane which is coplanar to better than 0.01 Å, whilst for the N(8)/N(15) ring C(16) lies



Fig. 7 The molecular structure of 8a.

Table 6 Sel	ected bond	lengths (	A) and	angles (	°)	for	8a
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Cr–Cl1	2.3615(11)	Cr–Cl2	2.3337(10)
Cr–O1	1.915(2)	Cr–N8	2.107(3)
Cr–N11	2.259(3)	Cr–N18	2.283(3)
Cl1-Cr-Cl2 Cl1-Cr-N8 Cl1-Cr-N18 Cl2-Cr-N8 Cl2-Cr-N18 O1-Cr-N11 N8-Cr-N11 N11-Cr-N18	91.79(4) 92.56(8) 87.47(8) 175.44(9) 96.74(7) 89.78(10) 82.66(11) 163.29(10)	C11-Cr-O1 C11-Cr-N11 C12-Cr-O1 C12-Cr-N11 O1-Cr-N8 O1-Cr-N18 N8-Cr-N18	175.56(8) 86.37(8) 86.62(7) 98.96(7) 89.13(10) 96.83(10) 82.11(11)

*ca.* 0.68 Å out of the {Cr,N(8),C(17),N(18)} plane which is coplanar to within *ca.* 0.03 Å. The six-membered N,O chelate ring has a twisted boat conformation, O(1) and C(7) lying *ca.* +0.42 and +0.41 Å out of the {Cr,C(1),C(6),N(8)} plane which is coplanar to within *ca.* 0.10 Å; the associated fold about the O(1)...C(7) vector is *ca.* 35°.

**Iron complex.** The iron(II) complex **9c** was synthesised by the transmetallation reaction between potassium salt **2c** and  $\text{FeCl}_2(\text{THF})_{1.5}$  (Scheme 7). The crude complex was recrystallised from hot toluene to afford colourless needles.



The solid-state structure determination for **9c** revealed a  $C_i$ symmetric dimer with a central, flat, Fe<sub>2</sub>Cl<sub>2</sub> ring (Fig. 8). The coordination geometry is distorted octahedral [*cis* angles in the range 75.62(4)–105.80(3)°], the aminophenolate ligand binding in a tetradentate fashion (Table 7). The two most acute angles at the iron centre are the bites of the five-membered N,O chelate rings, both of which have envelope conformations. For the N(8)/O(11) ring, C(9) lies *ca.* 0.65 Å out of the {Fe,N(8),C(10),O(11)} plane which is coplanar to within *ca.* 0.02 Å. The N(8)/O(15) ring is a bit more distorted, C(14) lying *ca.* 0.64 Å out of the



Fig. 8 The molecular structure of the centrosymmetric complex 9c. The transannular Fe  $\cdots$  Fe separation is 3.5866(4) Å.

Table 7Selected bond lengths (Å) and angles (°) for 9c

Fe-Cl	2.4192(4)	Fe–O1	1.9449(10)
Fe-N8	2.2027(12)	Fe–O11	2.2815(11)
Fe-O15	2.2905(12)	Fe–ClA	2.5453(4)
Cl-Fe-O1	105.80(3)	Cl-Fe-N8	163.93(3)
Cl-Fe-O11	89.50(3)	Cl-Fe-O15	95.58(3)
Cl-Fe-ClA	87.520(14)	O1-Fe-N8	88.47(4)
O1-Fe-O11	164.29(4)	O1-Fe-O15	94.35(5)
O1-Fe-ClA	98.92(4)	N8-Fe-O11	75.90(4)
N8-Fe-O15	75.62(4)	N8-Fe-ClA	97.70(3)
O11-Fe-O15	80.36(4)	O11-Fe-ClA	85.02(3)
O15-Fe-ClA	165.01(3)	Fe-Cl-FeA	92.480(14)

{Fe,N(8),C(13),O(15)} plane which is coplanar to within *ca.* 0.09 Å. The six membered N,O chelate ring has a bite angle of 88.47(4)° and adopts a folded geometry similar to that seen in the structure of **7**, Fe and N(8) lying *ca.* 0.61 and 1.09 Å, respectively out of the {O(1),C(1),C(6),C(7)} plane which is coplanar to better than 0.01 Å.

The dimeric nature of **9c** appears to be retained in solution, with an Evans' method magnetic moment determination affording a  $\mu_{\rm eff}$  value of 8.7 $\mu_{\rm B}$ , attributable to the presence of magnetically isolated high-spin Fe(II) centres.

**Cobalt complex.** The high-spin cobalt(II) complex **10c** ( $\mu_{eff} = 3.7 \,\mu_B$ ) was formed by the metathesis reaction of cobalt dichloride and the potassium salt **2c** (Scheme 8). Crystals of **10c** were isolated as blue needles from hot toluene.



The single-crystal X-ray structure revealed a five-coordinate distorted trigonal bipyramidal coordination geometry (Fig. 9, Table 8). The two most acute angles at the metal centre are the bites of the N(8)/O(11) and N(8)/O(15) five-membered N,O chelate rings, respectively, both of which have twisted geometries. The sixmembered N,O chelate ring [which has a bite angle of 90.62(4)°] adopts a boat conformation with O(1) and C(7) lying *ca.* +0.29 and +0.67 Å out of the {Co,C(1),C(6),N(8)} plane which is coplanar to within *ca.* 0.07 Å; the corresponding fold about the O(1) ··· C(7) vector is *ca.* 39°.

Table 8	Selected bond	lengths (Å)	and angles (°	) for <b>10c</b>
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Co–Cl Co–N8 Co–O15	2.2932(4) 2.1773(10) 2.0934(10)	Co-O1 Co-O11	1.9040(9) 2.1256(10)
Cl-Co-O1 Cl-Co-O11 O1-Co-N8 O1-Co-O15 N8-Co-O15	101.78(3) 93.60(3) 90.62(4) 108.98(4) 78.98(4)	Cl-Co-N8 Cl-Co-O15 O1-Co-O11 N8-Co-O11 O11-Co-O15	167.53(3) 97.96(3) 124.44(4) 78.05(4) 121.31(4)



Fig. 9 The molecular structure of 10c.

#### Discussion

The solid-state structure determinations reveal useful insight into the coordination flexibility of this ligand family. For example, for the group of complexes 2a (K), 7a (Zn) and 8a (Cr) containing the same diethylamino donors, the potassium and chromium derivatives show tetradentate coordination while the zinc derivative has one of the diethylamino groups non-bound, the latter clearly being a consequence of the lower coordination number/electron count requirements of the zinc centre. However, in the two cases where the ligand is tetradentate, the potassium derivative possesses a much smaller angle between the Et<sub>2</sub>N nitrogen donor atoms (104.06(5) vs. 163.29(10)° for chromium). The pseudo-trans displacement of the amino donors in this chromium complex contrasts the cis arrangement of the MeO donors in the iron complex, while the angle between the methoxy donors in the cobalt derivative **10c** is intermediate  $(121.31(4)^{\circ})$  and compliant with a trigonal bipyramidal coordination geometry at the cobalt centre.

Solution NMR studies, *e.g.* on **7a–c**, indicate that bound and non-bound donor arms readily exchange, which may have important implications for catalytic applications of these complexes.

# Conclusion

A series of metal complexes stabilised by a family of monoanionic phenoxyamine ligands has been synthesised and characterised. The denticity of the ligands is found to vary from bidentate (Al) to tridentate (Mg, Zn, Ca) to tetradentate (K, Cr, Fe, Co) depending on the coordination requirement of the metals. The ligand is also found to accommodate a range of metal coordination geometries, a consequence of the flexibility of the donor arms. Such characteristics have considerable merit for their use in catalysis. Current work is focused on exploring the potential of these complexes as catalysts for small-molecule and macromolecule synthesis.

# Experimental

#### General

All solvents were distilled over standard drying agents under nitrogen and deoxygenated before use. 4,6-di-*tert*-butyl-2-bis(2-methoxyethyl)aminomethylphenol 1c,<sup>6</sup> CrCl<sub>3</sub>·THF<sub>3</sub>,<sup>7</sup> and FeCl<sub>2</sub>·THF<sub>1.5</sub>,<sup>8</sup> were synthesised using literature procedures. Potassium hydride was bought as a dispersion over oil, which was washed with heptane three times prior to use. All other chemicals were bought from Aldrich Chemical Co. and used as received.

NMR spectra were recorded on Bruker AC-250 MHz, AV-400 MHz or AM-500 MHz spectrometers. NMR chemical shifts are quoted in ppm relative to the residual solvent resonances. Magnetic susceptibilities were determined using the Evans' NMR method using 0.001–0.002 g ml<sup>-1</sup> complex dissolved in 10% CH<sub>2</sub>Cl<sub>2</sub>–90% CDCl<sub>3</sub>.<sup>9</sup> Microanalysis were performed at the London Metropolitan University. Mass spectra were recorded on either a VG Autospec or a VG Platform II spectrometer.

# 4,6-Di-*tert*-butyl-2-bis(2-(diethylamino)ethyl)aminomethylphenol, 1a

Paraformaldehyde (1.40 g, 46.4 mmol) and N,N,N',N'tetraethyldiethylenetriamine (12.0 cm<sup>3</sup>, 46.4 mmol) were refluxed in methanol (100 cm<sup>3</sup>) for 90 min. A solution of 2,4-di-*tert*butylphenol (9.58 g, 46.4 mmol) in methanol (50 cm<sup>3</sup>) was then added and the mixture refluxed for a further 24 h. Removal of the volatile components under reduced pressure afforded **1a** as a golden–brown oil, which was used without further purification (17.4 g, 86% yield).

<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  10.55 (1H, br s, Ar–O*H*), 7.17 (1H, d, J = 2.3 Hz, Ar*H*), 6.81 (1H, d, J = 2.3 Hz, Ar*H*), 3.72 (2H, s, ArCH<sub>2</sub>N), 2.60 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>NEt<sub>2</sub>), 2.57 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>N), 2.47 (8H, q, J = 7.1 Hz, NCH<sub>2</sub>CH<sub>3</sub>), 1.40 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.26 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 0.96 (12H, t, J = 7.1 Hz, NCH<sub>2</sub>CH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.0, 139.9, 135.3, 123.5, 122.5, 121.7, 58.4, 51.9, 50.3, 47.0, 34.6, 31.5, 29.4, 11.4 (Found: C, 74.65, H, 11.84, N, 9.86. C<sub>27</sub>H<sub>51</sub>N<sub>3</sub>O requires: C, 74.77, H, 11.85, N, 9.69%).

# 4,6-Di-*tert*-butyl-2-bis(3-(dimethylamino)propyl)aminomethylphenol, 1b

Ligand **1b** was prepared in an analogous manner to **1a** using paraformaldehyde (1.6 g, 53.4 mmol), bis[3-(dimethylamino)propyl]amine (11.9 cm<sup>3</sup>, 53.4 mmol) and 2,4-di*tert*-butylphenol (11.0 g, 53.4 mmol), affording **1b** as a light brown oil, which was used without further purification (19.5 g, 90% yield).

<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  10.97 (1H, br s, Ar–OH), 7.18 (1H, d, J = 2.3 Hz, ArH), 6.81 (1H, d, J = 2.2 Hz, ArH), 3.72 (2H, s, ArCH<sub>2</sub>N), 2.55 (4H, t, J = 7.5 Hz, N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>), 2.18 (12H, s, N(CH<sub>3</sub>)<sub>2</sub>), 2.13 (4H, J = 7.5 Hz, N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>), 1.70 (4H, qnt, J = 7.4 Hz, N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>), 1.41 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.27 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.1, 140.1, 135.2, 123.2, 122.4, 121.2, 59.0, 57.5, 51.3, 45.3, 34.6, 33.9, 31.6, 29.4, 24.4 (Found: C, 74.10; H, 11.70, N, 10.27. C<sub>25</sub>H<sub>47</sub>N<sub>3</sub>O requires C, 74.02; H, 11.68, N, 10.36%).

#### Potassium 4,6-di-*tert*-butyl-2-bis(2-diethylamino)ethyl)aminomethylphenoxide, 2a

To a stirring slurry of potassium hydride (0.18 g, 2.3 mmol) in toluene (30 cm<sup>3</sup>) at -78 °C was added a solution of **1a** (1 g, 2.3 mmol) in toluene (50 cm<sup>3</sup>). The mixture was stirred for 16 h at room temperature after which the clear solution was filtered and concentrated under reduced pressure to give a waxy solid. This was recrystallised from hot toluene to afford **2a** as colourless crystals (0.73 g, 67%).

<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.27 (d, J = 2.8 Hz, 1H, ArH), 7.15 (d, 1H, J = 2.8 Hz, ArH), 2.42 (br s, N(CH<sub>2</sub>CH<sub>2</sub>N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>), 1.62 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.46 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.74 (t, J = 7.0 Hz, 12H, N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  167.5, 135.8, 129.1, 129.0, 123.6, 123.0, 61.3, 51.4, 45.6, 35.4, 34.0, 33.6, 30.5, 9.9. MS data (FAB –ve, *m/z*): 432 [M – K]<sup>-</sup>. (Found: C, 68.80, H, 10.57, N, 8.86. C<sub>27</sub>H<sub>50</sub>KN<sub>3</sub>O requires C, 68.73, H, 10.68, N, 8.91%).

#### Potassium 4,6-di-*tert*-butyl-2-bis(2methoxyethyl)aminomethylphenoxide, 2c

Complex **2c** was prepared in an analogous manner to **2a** using **1c** (1 g, 2.8 mmol) and potassium hydride (0.23 g, 5.7 mmol). Recrystallisation from hot toluene gave **2c** as a white solid (0.61 g, 57%).

<sup>1</sup>H NMR (400 MHz,  $C_6D_6$ ):  $\delta$  7.52 (d, J = 2.8 Hz, 1H, Ar*H*), 7.14 (d, J = 2.8, 1H, Ar*H*), 3.67 (br s, 2H, Ar*CH*<sub>2</sub>N), 3.07 (br s, 4H, NCH<sub>2</sub>C*H*<sub>2</sub>O), 2.85 (s, 6H, OC*H*<sub>3</sub>), 2.44 (br s, 4H, NC*H*<sub>2</sub>C*H*<sub>2</sub>O), 1.68 (s, 9H, C(*CH*<sub>3</sub>)<sub>3</sub>), 1.52 (s, 9H, C(*CH*<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz,  $C_6D_6$ ):  $\delta$  167.8, 135.9, 129.3, 129.0, 123.7, 123.2, 70.5, 61.4, 58.0, 54.3, 35.4, 34.0, 32.6, 30.2. MS data (FAB –ve, *m/z*): 390 (45%, [M]<sup>-</sup>), 351 (100%, [M – K]<sup>-</sup>) (Found: C, 64.89, H, 9.42, N, 3.49.  $C_{21}H_{36}$ KNO<sub>3</sub> requires C, 64.74, H, 9.31, N, 3.60%).

#### Isopropyl magnesium 4,6-di-*tert*-butyl-2-bis(3-(dimethylamino)propyl)aminomethylphenoxide, 3b

At -78 °C, a 2.5 M hexanes solution of <sup>*n*</sup>BuLi (1.64 cm<sup>3</sup>, 4.1 mmol) was added to a solution of **1b** (1.63 g, 4.0 mmol) in toluene (20 cm<sup>3</sup>). The mixture was allowed to warm to room temperature and, after 1 h, a 2 M <sup>*i*</sup>PrMgCl solution in THF (2.05 cm<sup>3</sup>, 4.10 mmol) was added. After stirring for a further 2 h, the solution was filtered, the solid washed with pentane and the combined filtrates concentrated under reduced pressure. A small amount of pentane was added to the solid and then removed *in vacuo* at -78 °C, affording **3b** as a white solid (1.36 g, 71% yield). Crystals suitable for X-ray analysis were grown from *n*-heptane.

<sup>1</sup>H NMR (250 MHz,  $C_6D_6$ ):  $\delta$  7.63 (d, 1H, J = 2.7 Hz, ArH), 6.94 (d, 1H, J = 2.6 Hz, ArH), 3.52 (br s, 2H, ArCH<sub>2</sub>N), 2.35 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.13 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.98 (s, 12H, N(CH<sub>3</sub>)<sub>2</sub>), 1.85 (6H, d, J = 8.7 Hz, Mg–CH(CH<sub>3</sub>)<sub>2</sub>), 1.84 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.38 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 1.52 (9H, s, ArC(CH<sub>3</sub>)<sub>3</sub>), 0.25 (1H, sept, J = 8.0, Mg–CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz,  $C_6D_6$ ):  $\delta$  163.5, 137.4, 134.1, 126.0, 124.1, 121.5, 68.6, 58.7, 53.5, 45.4, 35.7, 32.4, 31.8, 30.2, 26.5, 25.2, 8.8 (Found: C, 71.14, H, 11.30, N, 9.02.  $C_{28}H_{33}MgN_3O$  requires C, 71.24, H, 11.32, N, 8.90%).

# Synthesis of magnesium bis(4,6-di-*tert*-butyl-2-bis(2-methoxyethyl)aminomethylphenoxide), 4c

**2c** (1.17 g, 3 mmol) and MgCl<sub>2</sub> (0.15 g, 1.6 mmol) were stirred in THF (40 cm<sup>3</sup>) at room temperature for 16 h. The reaction mixture was then filtered and concentrated *in vacuo* to afford a waxy white solid which was recrystallised from hot toluene to give **4c** (0.34 g, 29%).

<sup>1</sup>H NMR (250 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.60 (d, J = 2.5, 1H, Ar*H*), 6.98 (d, J = 2.5, 1H, Ar*H*), 3.00 (br s, ArCH<sub>2</sub>N(CH<sub>2</sub>CH<sub>2</sub>-), 2.86 (s, 6H, OCH<sub>3</sub>), 1.74 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.50 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  164.7, 136.3, 133.1, 125.7, 123.6, 122.4, 70.6, 69.1, 62.1, 58.7, 35.5, 34.1, 32.5, 30.4 (Found C, 69.70, H, 9.84, N, 3.93. C<sub>42</sub>H<sub>72</sub>MgN<sub>2</sub>O<sub>6</sub> requires C, 69.55, H, 10.01, N, 3.86%).

#### Calcium bis(4,6-di-*tert*-butyl-2-bis(2diethylamino)ethyl)aminomethylphenoxide), 5a

**2a** (1.00 g, 2 mmol) and CaI<sub>2</sub> (0.31 g, 1 mmol) were stirred in THF (40 cm<sup>3</sup>) at room temperature for 16 h. The reaction mixture was then filtered and concentrated *in vacuo* to afford a waxy white solid which was recrystallised from hot toluene to afford **5a** (0.27 g, 30%).

<sup>1</sup>H NMR (500 MHz,  $C_6D_6$ ):  $\delta$  7.61 (d, J = 2.8 Hz, 1H, Ar*H*), 7.21 (d, 1H, J = 2.8 Hz, Ar*H*), 4.01 (br s, ArCH<sub>2</sub>N), 2.53 (br s, 12H, N(CH<sub>2</sub>CH<sub>2</sub>N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 1.81 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.46 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.82 (s, 12H, N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  165.4, 136.0, 132.5, 126.9, 124.1, 122.9, 61.1, 52.2, 47.2, 46.6, 35.7, 34.1, 32.4, 30.4, 12.0 (Found C, 71.57, H, 11.08, N, 9.37. C<sub>54</sub>H<sub>100</sub>CaN<sub>6</sub>O<sub>2</sub> requires C, 71.63, H, 11.13, N, 9.28%).

#### Dimethyl aluminium 4,6-di-*tert*-butyl-2-bis(2-methoxyethyl)aminomethylphenoxide, 6c

A 2 M trimethyl aluminium solution in toluene (11 cm<sup>3</sup>, 22 mmol) was added to a solution of **1c** (7.21 g, 21 mmol) in toluene (100 cm<sup>3</sup>). The reaction was then stirred at reflux temperature for 16 h. The resultant orange solution was concentrated under reduced pressure to afford a waxy oil which was left to stand to form crystals of **6c** (2.12 g, 25%).

<sup>1</sup>H NMR (500 MHz,  $C_6D_6$ ):  $\delta$  7.59 (d, J = 2.5 Hz, 1H, Ar*H*), 6.79 (d, J = 2.5 Hz, 1H, Ar*H*), 3.49 (s, 1H, Ar*CH*<sub>2</sub>N), 3.23– 3.18 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>O), 3.03–2.98 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>O), 2.83 (s, 6H, OC*H*<sub>3</sub>), 2.79–2.64 (m, 4H, NC*H*<sub>2</sub>CH<sub>2</sub>O), 1.73 (s, 9H, C(C*H*<sub>3</sub>)<sub>3</sub>), 1.41 (s, 9H, C(C*H*<sub>3</sub>)<sub>3</sub>), -0.36 (s, 6H, Al(C*H*<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  157.5, 138.2, 137.8, 125.1, 124.7, 120.0, 67.1, 59.3, 58.4, 50.4, 35.4, 34.2, 32.1, 30.3, 30.0, -9.4. MS data (CI, *m*/*z*): 408 [M]<sup>+</sup> (Found C, 67.68, H, 10.20, N, 3.28. C<sub>25</sub>H<sub>42</sub>AlNO<sub>3</sub> requires C, 67.78, H, 10.39, N, 3.44%).

# Ethyl zinc 4,6-di-*tert*-butyl-2-bis(2-diethylamino)ethyl)aminomethylphenoxide, 7a

**1a** (2.07 g, 4.8 mmol) in toluene (40 cm<sup>3</sup>) was added to a solution of diethyl zinc (0.62 g, 5.0 mmol) in toluene (20 cm<sup>3</sup>) at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 16 h. The resultant colourless solution was concentrated under reduced pressure to yield a waxy off-white solid, which was

<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.60 (d, J = 2.7 Hz, 1H, Ar*H*), 7.00 (d, J = 2.6 Hz, 1H, Ar*H*), 3.34 (s, 1H, Ar*CH*<sub>2</sub>N), 2.63–2.56 (m, 2H, NC*H*<sub>2</sub>CH<sub>3</sub>), 2.46–2.30 (m, 12H, NC*H*<sub>2</sub>C*H*<sub>2</sub>N), 2.23–2.17 (m, 2H, (C*H*<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 1.86 (s, 9H, C(C*H*<sub>3</sub>)<sub>3</sub>), 1.58 (t, J = 8.1 Hz, 3H, ZnCH<sub>2</sub>C*H*<sub>3</sub>), 1.48 (s, 9H, C(C*H*<sub>3</sub>)<sub>3</sub>), 0.82 (t, J = 7.1 Hz, 12H, N(CH<sub>2</sub>C*H*<sub>3</sub>)<sub>2</sub>), 0.37 (q, J = 8.1 Hz, 2H, ZnCH<sub>2</sub>C*H*<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  165.4, 138.2, 134.8, 125.3, 124.2, 122.8, 58.3, 53.7, 49.8, 46.3, 35.9, 32.2, 30.2, 22.7, 14.3, 13.7, 10.4, –1.4. MS data (CI, *m*/*z*): 526 [M + H]<sup>+</sup> (Found C, 66.18, H, 10.72, N, 7.97. C<sub>29</sub>H<sub>55</sub>N<sub>3</sub>OZn requires C, 66.07, H, 10.52, N, 7.97%).

#### Ethyl zinc 4,6-di-*tert*-butyl-2-bis(2-dimethylamino)propyl)aminomethylphenoxide, 7b

Complex 7b was formed in an analogous manner to 7a using 1b (3.00 g, 6.5 mmol) and diethyl zinc (0.84 g, 6.8 mmol). Recrystallisation from hot heptane afforded 7b as colourless crystals (1.99 g, 62%).

<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.60 (d, J = 2.7 Hz, 1H, Ar*H*), 6.61 (d, J = 2.7 Hz, 1H, Ar*H*), 3.72 (s, 1H, ArCH<sub>2</sub>N), 2.45–2.30 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.00 (s, 12H, N(CH<sub>3</sub>)<sub>2</sub>), 1.97–1.79 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.85 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>) 1.63 (t, J = 8.1 Hz, 3H, ZnCH<sub>2</sub>CH<sub>3</sub>), 1.50 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.38–1.18 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 0.37 (q, J = 8.1 Hz, 2H, ZnCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  164.6, 137.9, 133.9, 125.6, 123.9, 121.0, 59.6, 55.0, 46.2, 35.9, 34.2, 32.5, 30.3, 22.7, 21.3, 14.3, –2.8. MS data (CI, *m/z*): 498 [M]<sup>+</sup> (Found C, 64.91, H, 10.19, N, 8.32. C<sub>27</sub>H<sub>51</sub>N<sub>3</sub>OZn requires C, 64.97, H, 10.30, N, 8.42%).

# Ethyl zinc 4,6-di-*tert*-butyl-2-bis(2-methoxyethyl)aminomethylphenoxide, 7c

Complex 7c was formed in an analogous manner to 7a using 1c (3.00 g, 8.5 mmol) and diethyl zinc (1.11 g, 9 mmol). Recrystallisation from hot heptane afforded 8c as a white crystalline solid (4.71 g, 66%).

<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.57 (d, J = 2.7 Hz, 1H, ArH), 6.88 (d, J = 2.6 Hz, 1H, ArH), 3.32 (s, 1H, ArCH<sub>2</sub>N), 2.97 (ddd, J = 3.7 Hz, J = 8.9 Hz, J = 10.0 Hz, 2H, NCH<sub>2</sub>CH<sub>2</sub>O), 2.85 (s, 6H, OCH<sub>3</sub>), 2.82 (ddd, 1H, J = 4.5 Hz, J = 10.1 Hz, 2H, NCH<sub>2</sub>CH<sub>2</sub>O), 2.42 (ddd, 1H, J = 4.5 Hz, J = 4.4 Hz, J = 8.8 Hz, J = 13.3 Hz, 2H, NCH<sub>2</sub>CH<sub>2</sub>O), 2.18 (ddd, 1H, J = 4.1 Hz, J = 4.1 Hz, J = 13.4 Hz, 2H, NCH<sub>2</sub>CH<sub>2</sub>O), 1.86 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.62 (t, J = 8.1 Hz, 3H, ZnCH<sub>2</sub>CH<sub>3</sub>), 1.45 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.57 (q, J = 8.1 Hz, 2H, NCH<sub>2</sub>CH<sub>3</sub>), 1.45 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.57 (q, J = 8.1 Hz, 2H, 35.0, 125.2, 124.1, 122.4, 68.5, 59.5, 58.6, 56.5, 35.8, 34.2, 32.4, 30.2, 13.5, -1.9. MS data (CI, m/z): 444 [M + H]<sup>+</sup> (Found: C, 62.00, H, 9.18, N, 3.14. C<sub>23</sub>H<sub>41</sub>NO<sub>3</sub>Zn requires C, 62.08, H, 9.29, N, 3.15%).

### 4,6-Di-*tert*-butyl-2-bis(2-diethylamino)ethyl)aminomethylphenoxide chromium dichloride, 8a

**2a** (3.14 g, 6.7 mmol) in THF (20 cm<sup>3</sup>) was added to a solution of  $CrCl_3(THF)_3$  (2.49 g, 6.7 mmol) in THF (20 cm<sup>3</sup>). The mixture was stirred for 16 h and then filtered and concentrated under reduced

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 Table 9
 Crystal data, data collection and refinement parameters for compounds 2a, 3b, 6c, 7a, 7c, 8a, 9c and 10c

	2a	3b	6c	7a	7b	8a	96	10c
Formula	$C_{54}H_{100}K_2N_6O_2$	C <sub>28</sub> H <sub>53</sub> MgN <sub>3</sub> O	$C_{23}H_{42}AINO_3$	$C_{29}H_{55}N_3OZn$	$C_{27}H_{51}N_3OZn$	$C_{27}H_{50}Cl_2CrN_3O$	$C_{42}H_{72}Cl_2Fe_2N_2O_6$	C <sub>21</sub> H <sub>36</sub> ClCoNO <sub>3</sub>
Solveilt M.	943.60	472.04	— 407.56	527.13	499.08	555.60	2С7П <sub>8</sub> 1067.88	
Colour, habit	Colourless blocks	Colourless	Colourless blocky	Colourless blocks	Colourless blocks	Pale green needles	Colourless needles	Lilac platy needles
		hexagonal plates	needles			1		
Crystal size/mm	$0.37 \times 0.28 \times 0.21$	$0.30 \times 0.29 \times 0.18$	$0.29 \times 0.22 \times 0.10$	$0.36 \times 0.35 \times 0.33$	$0.38 \times 0.32 \times 0.17$	$0.19 \times 0.02 \times 0.01$	$0.31 \times 0.08 \times 0.05$	$0.39 \times 0.32 \times 0.02$
T/K	173	173	173	173	173	173	173	173
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\overline{1}$ (no. 2)	$P2_1/n$ (no. 14)	<i>P</i> 1 (no. 2)	<i>P</i> 1 (no. 2)	<i>Pbca</i> (no. 61)	C2/c (no. 15)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14)	$P2_1/c$ (no. 14)
a/Å	11.0251(6)	12.9731(4)	10.3132(4)	14.7846(16)	11.6696(3)	28.367(4)	10.6902(4)	11.9832(5)
$b/ m \AA$	16.2531(7)	12.3098(4)	11.9611(5)	15.365(2)	19.4177(6)	13.2626(18)	13.6702(4)	12.9061(7)
$c/ m \AA$	17.4691(8)	19.0286(6)	20.6126(9)	17.136(2)	25.5282(8)	16.275(2)	19.5952(6)	15.6009(7)
$a/^{\circ}$	77.252(4)		86.978(3)	67.774(13)		:	:	
$\beta/^{\circ}$	77.205(4)	96.436(3)	86.976(3)	72.413(10)		98.509(11)	94.272(3)	106.512(4)
y./°	84.064(4)		89.506(3)	71.161(12)				
$V/Å^3$	2972.4(2)	3019.64(17)	2535.60(18)	3337.8(8)	5784.6(3)	6055.5(14)	2855.63(16)	2313.28(19)
Z	5	4	4ª	4ª	8	8	2 <sup>b</sup>	4
$D_{ m c}/{ m g~cm^{-3}}$	1.054	1.038	1.068	1.049	1.146	1.219	1.242	1.277
Radiation used	Mo-Ka	$Mo-K\alpha$	Mo-Ka	Mo-Ka	Mo-Ka	Cu-Ka	Mo-Ka	Μο-Κα
$\mu/\mathrm{mm}^{-1}$	0.200	0.081	0.100	0.757	0.870	4.896	0.649	0.877
$2\theta \max/^{\circ}$	65	65	65	65	66	142	99	65
No. unique refins								
measured	19557	10268	16761	22006	10193	5728	9871	7904
obs., $ F_{\circ}  > 4\sigma( F_{\circ} )$	17872	9666	10237	12530		3537	6715	6268
No. variables	651	323	546	663	289	307	308	246
$R_1, wR_2^c$	0.071, 0.166	0.077, 0.161	0.074, 0.206	0.081, 0.241	0.049, 0.126	0.052, 0.065	0.041, 0.097	0.036, 0.094
CCDC	293279	293280	293281	293282	293283	293285	293284	293286
" There are two crystal.	lographically independ	dent molecules in the	e asymmetric unit. <sup>b</sup>	The molecule has cr	stallographic C <sub>i</sub> syn	nmetry. ${}^{c}R_{1} = \sum   F_{1} $	$   -   F_{c}  /\sum   F_{o}  $	$wR_2 = \{\sum [w(F_o^2 -$
$F_{\rm c}^{\ 2})^2]/\sum[w(F_{\rm o}^{\ 2})^2]\}^{1/2}; w$	$\sigma^{-1} = \sigma^2(F_o^2) + (aP)^2 + i$	bP.						ļ

pressure to yield a dark green solid. Recrystallisation from layered toluene–pentane afforded **8a** (1.15 g, 31%).

 $\mu_{\text{eff}} = 3.9 \ \mu_{\text{B}}$ . MS data (FAB +ve, m/z): 555 (4%, [M]<sup>+</sup>), 519 (100%, [M - Cl]<sup>+</sup>) (Found: C, 58.27, H, 8.98, N, 7.64%. C<sub>27</sub>H<sub>50</sub>Cl<sub>2</sub>CrN<sub>3</sub>O requires C, 58.37, H, 9.07, N, 7.56%).

# 4,6-Di-*tert*-butyl-2-bis(2-methoxyethyl)aminomethylphenoxide iron(II) chloride, 9c

A solution of **2c** (0.83 g, 2.4 mmol) in THF (20 cm<sup>3</sup>) was added to a THF solution (20 cm<sup>3</sup>) of FeCl<sub>2</sub>(THF)<sub>1.5</sub> (0.50 g, 2.4 mmol). The mixture was stirred for 16 h and then filtered and concentrated under reduced pressure to yield a light blue solid. Recrystallisation from hot toluene afforded **9c** as colourless crystals (0.51 g, 49%).

 $\mu_{\text{eff}} = 8.7 \ \mu_{\text{B}}$ . MS data (FAB +ve, m/z): 441 (38%, [M]<sup>+</sup>), 406 (47%, [M - Cl]<sup>+</sup>), 352 (100% [M - Cl - Fe]<sup>+</sup>) (Found: C, 56.95, H, 8.28, N, 3.08. C<sub>42</sub>H<sub>72</sub>Cl<sub>2</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>6</sub> requires C, 57.09, H, 8.21, N, 3.17%).

# 4,6-Di-*tert*-butyl-2-bis(2-methoxyethyl)aminomethylphenoxide cobalt(II) chloride, 10c

A solution of **2c** (0.94 g, 2.4 mmol) in THF (20 cm<sup>3</sup>) was added to a THF solution (20 cm<sup>3</sup>) of CoCl<sub>2</sub> (0.31 g, 2.4 mmol). The solution was stirred for 16 h and then filtered and concentrated under reduced pressure to yield a blue solid. Recrystallisation from layered toluene–pentane gave **10c** (0.51 g 49%).

 $\mu_{\text{eff}} = 3.7 \ \mu_{\text{B}}$ , MS data (FAB +ve, m/z): 444 (8%, [M]<sup>+</sup>), 408 (16%, [M - Cl]), 352 (100%, [M - Cl - Co]<sup>+</sup>) (Found: C, 56.61, H, 8.21, N, 3.24. C<sub>21</sub>H<sub>36</sub>NClCoO<sub>3</sub> requires C, 56.69, H, 8.16, N, 3.15%).

#### X-Ray crystallography

Table 9 provides a summary of the crystallographic data for compounds 2a, 3b, 6c, 7a, 7c, 8a, 9c and 10c. Analogous data for 4c and 5a may be found in Table S1 (ESI†). Data were collected using Oxford Diffraction Xcalibur 3 (2a, 3b, 6c, 7a, 7c, 9c and 10c) and PX Ultra (8a) diffractometers, and the structures were refined based on  $F^2$  using the SHELXTL and SHELX-97 program systems.<sup>10</sup>

CCDC reference numbers 293279–293286, 293483 and 293484. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b607753f

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