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Synthesis and structural characterisation of heavy alkaline earth *N*,*N′*-bis(aryl)formamidinate complexes

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Received 14th February 2006, Accepted 13th April 2006
First published as an Advance Article on the web 27th April 2006
DOI: 10.1039/b602210c

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Treatment of calcium or strontium with 2.0 equivalents of *N*,*N′*-bis(*o*-methylphenyl)formamidine (*o*-TolFormH), *N*,*N′*-bis(2,6-dimethylphenyl)formamidine (XylFormH) or *N*,*N′*-bis(*o*-phenylphenyl)-formamidine (*o*-PhPhFormH) in the presence of 1.0 equivalent of $Hg(C_6F_5)_2$ in tetrahydrofuran (thf) affords the bis(formamidinate) complexes $[Ca(o\text{-TolForm})_2(thf)_2]$ (**1**), $[Ca(XylForm)_2(thf)_2]$ (**2**), $[Ca(o\text{-PhPhForm})_2(thf)_2]\cdot thf$ (**3**), $[Sr(o\text{-TolForm})_2(thf)_3]$ (**4**), $[Sr(XylForm)_2(thf)_3]\cdot 3thf$ (**5**) and $[Sr(o\text{-PhPhForm})_2(thf)_3]\cdot 2thf$ (**6**). Analogous reactions with barium were generally unsatisfactory but $[Ba(o\text{-PhPhForm})_2(thf)_3]\cdot 2thf$ (**7**) was successfully prepared. Compounds **1–7** have been characterised by various spectroscopic methods (^1H, $^{13}C\{^1H\}$ NMR and IR), elemental analyses and, for **1**, **2** and **4–6**, X-ray crystallography. The calcium complexes are monomeric and six-coordinate with either *transoid* octahedral or trigonal prismatic geometry, whilst the larger radius of strontium accommodates an additional thf solvent donor to give seven-coordinate structures with two types of coordination polyhedra.

Introduction

The challenge of preparing and characterising highly reactive heavy alkaline earth organometallics and organoamides is attracting increasing attention.[1–5] Commonly used synthetic methods are metathesis from the anhydrous halides and protolysis of suitable reactants,[1–5] most usually the bis(trimethylsilyl)amides, which also pose a synthetic challenge.[1,4] For metathesis reactions the anhydrous chlorides and bromides have the disadvantage of low solubility in common polar organic solvents, whilst the more suitable high purity anhydrous iodides are extremely expensive.[1]

Syntheses based on the highly reactive metals analogous to reactions of lanthanoid metals[6] offer an alternative approach, and the metals in liquid ammonia have been particularly successful,[1–3] for example giving bis(trimethylsilyl)amides.[7] More recently the direct reaction of the metals with phenols[8] and pyrazoles[9] at elevated temperatures has provided a number of phenolate and pyrazolate complexes. Redox transmetallation/ligand exchange between a metal, a diarylmercurial, and a protonated ligand (eqn (1)), a route notably successful for the lanthanoid elements,[6,10–13] offers particular promise for the more electropositive alkaline earth metals.

$$M + HgR_2 + 2\,HL \rightarrow ML_2 + 2\,RH + Hg \qquad (1)$$

Alkaline earth 3,5-diphenylpyrazolates have been obtained as both thf and dme (1,2-dimethoxyethane) complexes employing this method,[14] as have complexes of the very bulky *N*,*N′*-bis(2,6-diisopropylphenyl)formamidinate ligand[15] and pentafluorophenyl complexes stabilised by 'super' bulky and π-bonding triazenide ligands.[16]

Herein we report the use of redox transmetallation/ligand exchange reactions for the synthesis of some heavy alkaline earth species with the moderately bulky organoamide ligands *N*,*N′*-bis(*o*-methylphenyl)formamidine (*o*-TolFormH), *N*,*N′*-bis(2,6-dimethylphenyl)formamidine (XylFormH) and *N*,*N′*-bis(*o*-phenylphenyl)formamidine (*o*-PhPhFormH). Formamidinate ligands ($[R^1NC(H)NR^2]^-$, where R^1 and R^2 = alkyl or aryl) have demonstrated excellent coordination flexibility with transition and alkali metals[17–24] but have experienced only limited application to the alkaline earths.[15] We have shown that the extremely bulky formamidinate with 2,6-diisopropylphenyl *N*-substituents (DippForm) produces complexes with the alkaline earth metal in a sterically frustrated environment, in this instance $[M(DippForm)_2(thf)_n]$; M = Ca, $n = 1$; M = Sr or Ba, $n = 2$.[15] In principle, use of the moderately bulky ligands *o*-TolFormH and XylFormH will give the metal greater control of coordination number and geometry, and will therefore allow us to probe whether two *ortho*-methyl groups (XylForm) do indeed provide greater steric hindrance than a single *ortho*-methyl substituent (*o*-TolForm). This is of interest as we have recently observed that XylForm adopts a conformation in binding to lithium and sodium where the xylyl groups lie perpendicular to the plane of the MNCN metallacycle to avoid disfavourable buttressing with the formamidinate backbone methine.[17g] By contrast, the *o*-tolyl groups of *o*-TolForm can and sometimes do adopt co-planarity with the MNCN metallacycle permitting the *o*-methyl to project towards the metal.[17b,25] As the latter conformation is inaccessible to the XylForm ligand, it is conceivable that the *o*-TolForm ligand can exert greater steric influence on the metal coordination environment. The hitherto neglected *N*,*N′*-bis(*o*-phenylphenyl)formamidinate ligand,[26,27] with the potential for different conformations (owing to the planarity of the phenyl group) and π-phenyl binding, has been explored with calcium, strontium and barium. Accordingly, its coordination chemistry is reported here for the first time.

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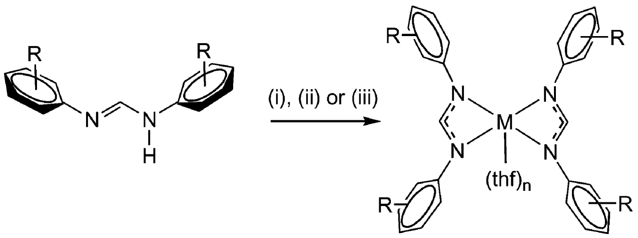
Results and discussion

Freshly filed calcium and strontium metal react cleanly with two equivalents of *o*-TolFormH, XylFormH or *o*-PhPhFormH in thf in the presence of one equivalent of bis(pentafluorophenyl)mercury to afford the compounds [M(*o*-TolForm)$_2$(thf)$_n$], where M = Ca; n = 2 (**1**) and M = Sr; n = 3 (**4**), [M(XylForm)$_2$(thf)$_n$]·$m$thf, where M = Ca; n = 2; m = 0 (**2**) and M = Sr; n = 3; m = 3 (**5**), and [M(*o*-PhPhForm)$_2$(thf)$_n$]·$m$thf, where M = Ca; n = 2; m = 1 (**3**) and M = Sr; n = 3; m = 2 (**6**), in good yield (see Scheme 1). By contrast, reactions of *o*-TolFormH and XylFormH with barium were unsatisfactory but [Ba(*o*-PhPhForm)$_2$(thf)$_3$]·2thf (**7**) was successfully isolated. The absence of a ν(N–H) absorption in the infrared spectra and the lack of a NH resonance in the ^{1}H NMR spectra of the bulk vacuum dried materials in C_6D_6 indicated complete deprotonation of the formamidine reagents in the isolated complexes. The methine proton resonance (NC(H)N) in the spectra of **1** and **4** is shifted significantly to higher frequencies from those of the neutral ligand (7.72 ppm for *o*-TolFormH to 8.39 ppm (**1**) and 8.80 ppm (**4**)). The same trend is observed for XylForm complexes **2** and **5** and *o*-PhPhForm complexes **3**, **6** and **7** (see Experimental section). The change in chemical shift is typical of deprotonation of the formamidine.[17a] Analogous appropriate shifts of the methine carbons were observed for all complexes.



Scheme 1 *Reagents and conditions*: (i) R = *o*-Me, 2.0 eq. *o*-TolFormH, 1.0 eq. Hg(C_6F_5)$_2$, 1.0 eq. M, thf, room temperature, 48 h, −2 C_6F_5H, **1**; M = Ca, n = 2, **4**; M = Sr, n = 3. (ii) R = 2,6-Me$_2$, 2.0 eq. XylFormH, 1.0 eq. Hg(C_6F_5)$_2$, 1.0 eq. M, thf, room temperature, 48 h, −2 C_6F_5H, **2**; M = Ca, n = 2, **5**; M = Sr, n = 3. (iii) R = 2-Ph, 2.0 eq. *o*-PhPhFormH, 1.0 eq. Hg(C_6F_5)$_2$, 1.0 eq. M, thf, room temperature, 48 h, −2 C_6F_5H, **3**; M = Ca, n = 2, **6**; M = Sr, n = 3, **7**; M = Ba, n = 3.

For compounds **1**, **2** and **4** the ^{1}H NMR spectra and microanalyses support the ratio of solvent to ligand observed in the crystal structure (see below), but for **5** the lattice thf is removed by drying of the bulk material *in vacuo* to give a thf to formamidinate ratio of 3 : 2 as confirmed by metal analysis and ^{1}H NMR data. In the case of **6**, a microanalysis on single crystals was consistent with their composition as [Sr(*o*-PhPhForm)$_2$(thf)$_3$]·2thf but the sample prepared for acquisition of ^{1}H NMR data showed loss of lattice thf. Compound **3**, which was not obtained as single crystals, had microanalyses and a ^{1}H NMR spectrum indicative of a thf to formamidinate ratio of 3 : 2. For **7**, also not obtained as single crystals, both microanalyses and ^{1}H NMR data suggest a thf to formamidinate ratio of 5 : 2. Only a single, symmetrical formamidinate environment is evident in the ^{1}H NMR spectra of **1–7**, indicating either symmetrically bound ligands or a rapidly exchanging system.[28] Variable-temperature ^{1}H and ^{13}C{^{1}H} NMR spectra of arguably the most sterically crowded compound, **2**, in C_7D_8 over the regime −60 to +80 °C exhibit no significant differences.

X-Ray crystallographic studies

Colourless crystalline samples of compounds **1**, **2** and **4–6** of suitable quality for X-ray structure determination were grown from thf and proved to be extremely air-sensitive and prone to solvent loss. However, satisfactory X-ray data were obtained and the structure solutions show all compounds to be mononuclear species with two chelating formamidinate ligands (see Fig. 1–5, POV-RAY illustrations, 40% thermal ellipsoids). Table 1 contains a summary of crystallographic data for all compounds characterised by X-ray methods, while Table 2 provides selected bond lengths (Å), angles and interplanar angles (°).

Table 1 Summary of crystallographic data for all compounds characterised by single-crystal X-ray structure determination

	[Ca(*o*-TolForm)$_2$(thf)$_2$] (**1**)	[Ca(XylForm)$_2$(thf)$_2$] (**2**)	[Sr(*o*-TolForm)$_2$(thf)$_3$] (**4**)	[Sr(XylForm)$_2$(thf)$_3$]·3thf (**5**)	[Sr(*o*-PhPhForm)$_2$(thf)$_3$]·2thf (**6**)
Mol. formula	$C_{38}H_{46}CaN_4O_2$	$C_{42}H_{54}CaN_4O_2$	$C_{42}H_{54}N_4O_3Sr$	$C_{58}H_{86}N_4O_6Sr$	$C_{70}H_{78}N_4O_5Sr$
M	630.87	686.98	750.51	1022.93	1142.98
T/K	123(2)	123(2)	123(2)	123(2)	123(2)
Space group	$P2_1/c$	$C2/c$	Cc	$P2_1/c$	$Pccn$
a/Å	11.2249(3)	19.3852(3)	21.4128(8)	10.9388(3)	26.6486(4)
b/Å	16.7282(9)	11.1831(2)	9.8514(4)	33.5561(10)	10.17120(10)
c/Å	19.6462(10)	18.1765(4)	18.7930(8)	16.2284(5)	21.9266(3)
α/°	90	90	90	90	90
β/°	105.930(3)	101.7590(10)	100.313(3)	109.591(2)	90
γ/°	90	90	90	90	90
V/Å^3	3547.3(3)	3857.73(12)	3900.3(3)	5612.0(3)	5943.17(13)
Z	4	4	4	4	4
D_c/g cm^{-3}	1.181	1.183	1.278	1.211	1.277
μ/mm^{-1}	0.214	0.202	1.425	1.012	0.962
Reflections collected	23008	12570	15560	34805	49571
Unique reflections	8358	4599	7223	12813	6710
Parameters varied	411	226	455	640	390
R_{int}	0.0665	0.0572	0.1114	0.0880	0.1274
R_1	0.0510	0.0574	0.0605	0.0763	0.0783
wR_2	0.1357	0.1331	0.1159	0.1458	0.1374

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Table 2 Selected bond lengths (Å), angles and interplanar angles (°) for compounds **1**, **2** and **4–6**

	1	**2**	**4**	**5**	**(6)**
M–N(1)	2.415(2)	2.415(2)	2.595(5)	2.631(3)	2.661(4)
M–N(2)	2.442(2)	2.442(2)	2.666(5)	2.642(3)	2.704(3)
M–N(3)	2.4244(19)	2.415(2)[b]	2.623(5)	2.652(3)	2.661(4)[c]
M–N(4)	2.425(2)	2.442(2)[b]	2.674(5)	2.657(3)	2.704(3)[c]
M–O(1)	2.3668(16)	2.4013(19)	2.585(4)	2.571(3)	2.565(3)
M–O(2)	2.3688(17)	2.4013(19)[b]	2.640(4)	2.586(3)	2.622(4)
M–O(3)	—	—	2.654(4)	2.630(3)	2.565(3)[c]
N(1)–$\mathrm{C_{NCN}}$[a]	1.332(3)	1.327(3)	1.330(8)	1.322(5)	1.326(5)
N(2)–$\mathrm{C_{NCN}}$[a]	1.317(3)	1.319(3)	1.320(8)	1.321(5)	1.325(5)
N(3)–$\mathrm{C_{NCN'}}$[a]	1.319(3)	1.327(3)[b]	1.311(8)	1.319(5)	1.326(5)[c]
N(4)–$\mathrm{C_{NCN'}}$[a]	1.330(3)	1.319(3)[b]	1.327(8)	1.317(5)	1.325(5)[c]
N(1)–M–N(2)	56.41(6)	56.58(7)	52.22(17)	51.97(10)	51.17(10)
N(3)–M–N(4)	56.29(6)	56.58(7)[b]	51.65(16)	51.65(11)	51.17(10)[c]
$\mathrm{C_{NCN}}$–M–$\mathrm{C_{NCN'}}$[a]	169.87(7)	129.20(11)[b]	116.66(18)	144.25(11)	152.29(14)[c]
$\mathrm{C_{NCN}}$–M–O(1)[a]	93.69(6)	118.54(7)	141.88(16)	90.70(11)	103.04(10)
$\mathrm{C_{NCN}}$–M–O(2)[a]	91.48(6)	100.36(7)[b]	83.32(15)	93.30(11)	103.86(7)
$\mathrm{C_{NCN}}$–M–O(3)[a]	—	—	105.93(15)	108.99(10)	82.85(10)[c]
$\mathrm{C_{NCN'}}$–M–O(1)[a]	89.67(6)	100.36(7)[b]	101.41(16)	91.17(11)	103.04(10)[c]
$\mathrm{C_{NCN'}}$–M–O(2)[a]	85.73(6)	118.54(7)[b]	128.92(16)	87.93(11)	103.86(7)[c]
$\mathrm{C_{NCN'}}$–M–O(3)[a]	—	—	94.27(16)	106.75(10)	82.85(10)[c]
O(1)–M–O(2)	174.04(6)	79.90(9)	70.58(15)	174.33(10)	77.79(7)
O(1)–M–O(3)	—	—	71.40(14)	85.53(10)	155.58(14)[c]
O(2)–M–O(3)	—	—	126.62(17)	89.37(10)	77.79(7)[c]
N(1)–M–O(1)	94.90(7)	145.42(7)	121.15(17)	95.27(11)	89.74(10)
N(1)–M–O(2)	91.06(7)	94.52(7)[b]	85.06(16)	86.62(11)	79.74(7)
N(1)–M–O(3)	—		83.91(15)	83.80(10)	85.94(10)[c]
N(2)–M–O(1)	89.60(6)	92.48(7)	152.10(15)	87.88(11)	111.85(10)
N(2)–M–O(2)	93.58(6)	108.13(7)[b]	81.59(16)	97.47(10)	128.58(7)
N(2)–M–O(3)	—	—	127.55(15)	134.40(10)	83.78(9)[c]
N(3)–M–O(1)	87.34(6)	94.52(7)[b]	110.10(16)	84.67(11)	85.94(10)[c]
N(3)–M–O(2)	90.37(6)	145.42(7)[b]	154.24(16)	92.12(11)	79.74(7)[c]
N(3)–M–O(3)	—	—	75.02(16)	81.30(10)	89.74(10)[c]
N(4)–M–O(1)	88.95(6)	108.13(7)[b]	88.24(16)	95.76(10)	83.78(9)[c]
N(4)–M–O(2)	85.20(6)	92.48(7)[b]	103.37(15)	85.85(10)	128.58(7)[c]
N(4)–M–O(3)	—	—	111.44(15)	132.37(10)	111.85(10)[c]
MNCN–MNCN[d]	7.92(11)	71.07(7)[b]	89.62(14)	20.14(24)	32.68(11)[c]
MNCN–N(1)Ar[d]	39.25(7)	74.39(7)	49.06(20)	69.46(15)	40.09(13)
MNCN–N(2)Ar[d]	57.00(7)	80.44(8)	42.41(21)	65.55(12)	43.60(12)
N(1)Ar–N(2)Ar[d]	86.36(7)	64.60(8)	83.18(16)	73.52(14)	51.98(11)
MNCN–N(3)Ar[d]	48.66(6)	74.39(7)[b]	27.73(27)	66.06(12)	40.09(13)[c]
MNCN–N(4)Ar[d]	23.95(8)	80.44(8)[b]	35.38(23)	65.37(14)	43.60(12)[c]
N(3)Ar–N(4)Ar[d]	65.56(6)	64.60(8)[b]	35.84(26)	68.73(12)	51.98(11)[c]

[a] $\mathrm{C_{NCN}}$ and $\mathrm{C_{NCN'}}$ refer to the lowest numbered and highest numbered "NCN" methine carbon, respectively. [b] N(3), N(4), O(2) and $\mathrm{C_{NCN'}}$ are symmetry generated equivalents of N(1)#, N(2)#, O(1)# and $\mathrm{C_{NCN}}$#, respectively. Symmetry transformation used to generate equivalent atoms: $1 - x, y, \frac{3}{2} - z$. [c] N(3), N(4), O(3) and $\mathrm{C_{NCN'}}$ are symmetry generated equivalents of N(1)#, N(2)#, O(1)# and $\mathrm{C_{NCN}}$#, respectively. Symmetry transformation used to generate equivalent atoms: $\frac{3}{2} - x\ \frac{3}{2} - y, z$. [d] MNCN refers to a metallacyclic plane directly associated with an aryl ring (N(#)Ar).

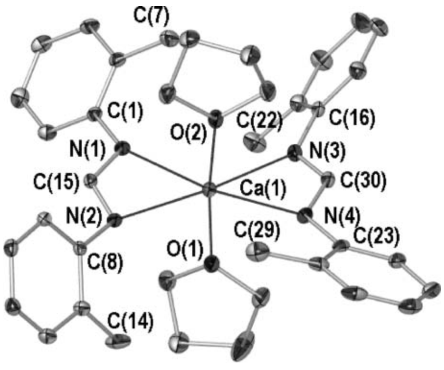

Fig. 1 Molecular structure of [Ca(*o*-TolForm)$_2$(thf)$_2$] (**1**) (40% thermal ellipsoids). All hydrogen atoms omitted for clarity.

Calcium formamidinates

Compound **1** exhibits two *transoid* thf donor molecules complementing two formamidinate ligands, giving the calcium metal centre a coordination number of six (Fig. 1). The calcium atom and the four formamidinate nitrogen atoms lie in a plane with the two thf ligands normal to this plane. Compound **1** can be described as having a distorted octahedral geometry, with the NCN backbones in the equatorial plane and the two *transoid* thf molecules in axial positions (O(1)–Ca(1)–O(2) 174.04(6)°). The *ortho*-methyl groups are placed to avoid clash with the methine hydrogen, and occupy the space on either side of the two thf ligands. This produces close Ca(1)···C(Me) distances (3.6467(23)–4.2372(23) Å) that are nevertheless too long to be considered bonding/agostic interactions (*ca.* 3.0 Å).[1,3,4,5b] Compound **1** displays a similar

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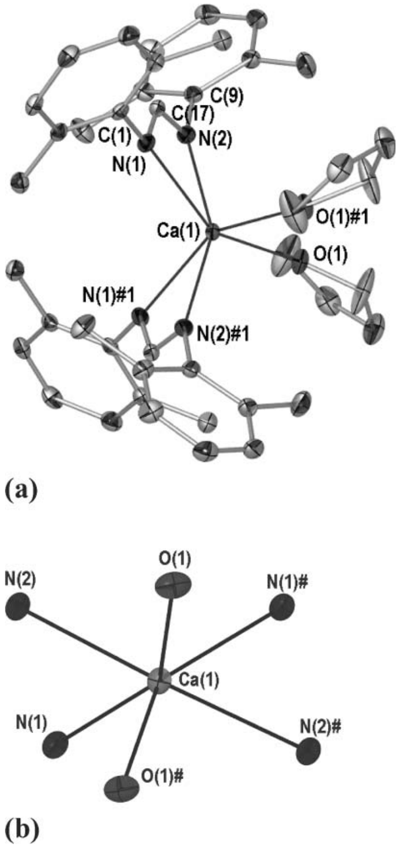

Fig. 2 (a) Molecular structure of $[Ca(XylForm)_2(thf)_2]$ (**2**) (40% thermal ellipsoids). All hydrogen atoms omitted for clarity. (b) Orientation of **2** depicting the distorted trigonal prismatic geometry of the central CaN_4O_2 unit (40% thermal ellipsoids). Selected distances (Å), interplanar and twist angles (°): N(1)–N(2)/N(1)#–N(2)# 2.2999(27), O(1)–O(1)# 3.0800(35), N(2)O(1)N(1)#:N(2)#O(1)#N(1) interplanar; 17.49(5), twist; 24.47(47), centroid–Ca(1)–centroid' (centroid = centre of each trigonal face) 175.26(71). Symmetry transformation used to generate '#' atoms: $1 - x, y, \frac{3}{2} - z$.

arrangement to its magnesium analogue[25] despite the larger ionic radius of Ca^{2+} (six-coordinate; 0.28 Å increase).[29]

Compound **2**, which crystallises with half a molecule in the asymmetric unit and the calcium on a two-fold rotation axis, also exhibits six-coordination about its metal centre (Fig. 2). Unlike the *transoid* octahedral geometry of **1**, the metal centre of **2** is considered *cisoid* octahedral owing to its O(1)–Ca(1)–O(1)# angle of 79.90(9)°. However, closer inspection of the bond angles about Ca(1) suggests the geometry of **2** is best described as a distorted trigonal prism (Fig. 2(b)). The two triangular faces of this prism, composed of O(1)#, N(1) and N(2)# and N(2), O(1) and N(1)#, are twisted by 24.47(47)° and are not parallel (17.49(5)°) due to the small bite angles of the two XylForm ligands. The two centroids of the triangular faces and Ca(1) are approximately linear (175.26(71)°).

A calcium amidinate complex closely related to **1** is octahedral $[Ca\{C(Ph)\{N(SiMe_3)\}_2\}_2(thf)_2]$, where the thf molecules are *trans* and the benzamidinate ligands chelate to calcium in the equatorial positions.[30] The average Ca–O and Ca–N bond lengths of this compound (⟨Ca–O⟩ 2.38 Å, ⟨Ca–N⟩ 2.43 Å) are similar to those of compound **1** and the Ca–N bond length of **2** (**1**; ⟨Ca–O⟩ 2.37 Å, ⟨Ca–N⟩ 2.43 Å; **2** ⟨Ca–N⟩ 2.43 Å), however the Ca–O bond lengths of both $[Ca\{C(Ph)\{N(SiMe_3)\}_2\}_2(thf)_2]$ and **1** are marginally shorter than those of **2** (2.401(2) Å) due to the increased bulk of XylForm.

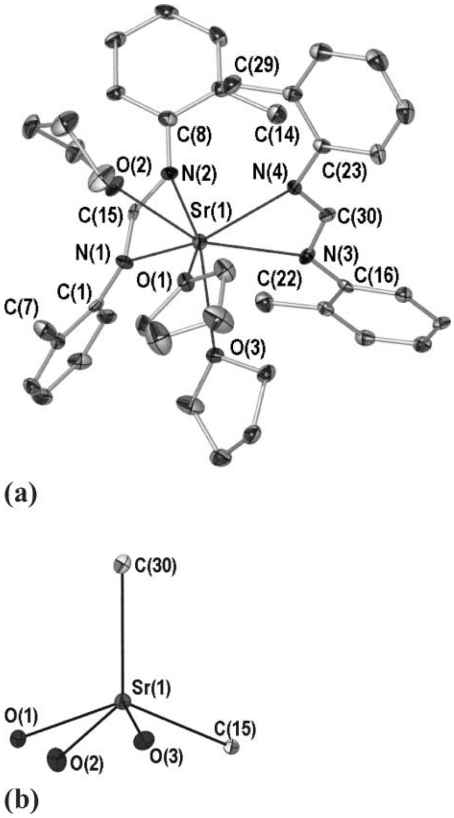

Fig. 3 (a) Molecular structure of $[Sr(o\text{-}TolForm)_2(thf)_3]$ (**4**) (40% thermal ellipsoids). All hydrogen atoms omitted for clarity. (b) Orientation of **4** depicting the pseudo-square based pyramidal geometry of the central C_2O_3Sr unit (40% thermal ellipsoids). Refer to Table 2 for selected angles.

A proposal for the structure of compound **3**, which has the empirical formulation $Ca(o\text{-}PhPhForm)_2(thf)_3$, can be made on the basis of the coordination numbers of both **1** and **2**, which have two coordinated thf molecules. Further, comparison of the strontium compounds $[Sr(XylForm)_2(thf)_3]$ (**5**) and $[Sr(o\text{-}PhPhForm)_2(thf)_3]$ (**6**) *vide infra* suggests the coordination geometries adopted by complexes bearing these particular formamidinates are similar. Accordingly, compound **3** is reasonably formulated as $[Ca(o\text{-}PhPhForm)_2(thf)_2]\cdot thf$.

Strontium formamidinates

In compound **4** the strontium atom is seven-coordinate and bound to two formamidinate and three thf ligands (Fig. 3). The increase in coordination number from **1** is consistent with the increase in ionic radius (0.21 Å) of Sr^{2+} relative to Ca^{2+}.[29] The corresponding lengthening of the Sr–O bonds in compound **4** (⟨Sr–O⟩ 2.63 Å; *cf.* **1** ⟨Ca–O⟩ 2.37 Å) is 0.05 Å larger than expected on the basis of ionic radii and coordination number differences.[29] Further, the coordination geometry of **4**, though irregular, can be described as a pseudo-square-based pyramid (Fig. 3(b)), formed by the thf oxygen atoms and the methine carbons of the NCN fragments, with C(30) as the apex. The square

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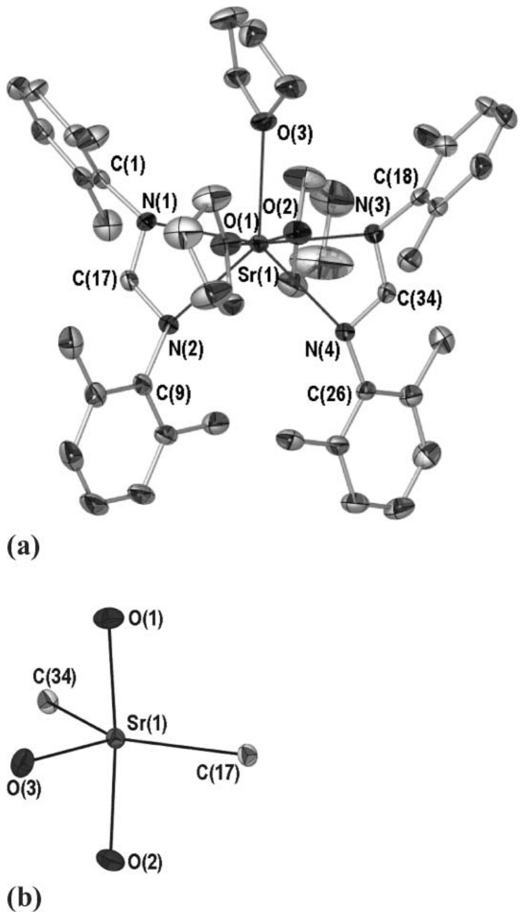

Fig. 4 (a) Molecular structure of [Sr(XylForm)$_2$(thf)$_3$] (**5**) (40% thermal ellipsoids). All hydrogen atoms and lattice thf omitted for clarity. (b) Orientation of **5** depicting the distorted trigonal pyramidal C_2O_3Sr polyhedron (40% thermal ellipsoids). Refer to Table 2 for selected angles.

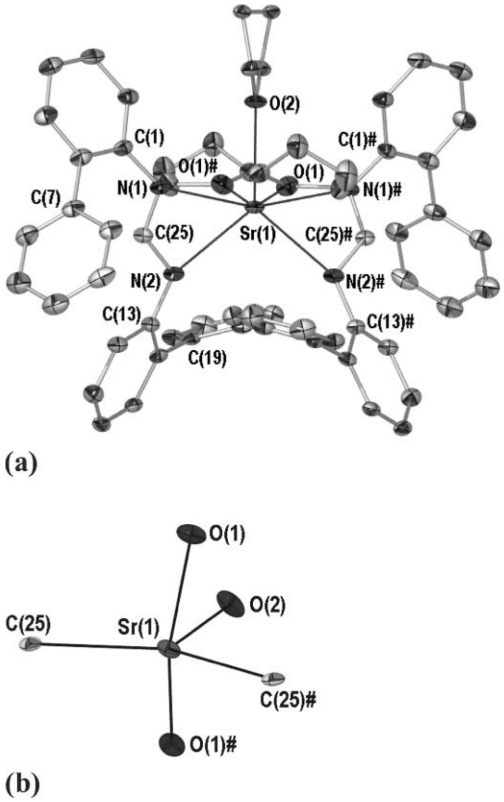

Fig. 5 (a) Molecular structure of [Sr(PhPhForm)$_2$(thf)$_3$] (**6**) (40% thermal ellipsoids). All hydrogen atoms and lattice thf omitted for clarity. (b) Orientation of **6** depicting the distorted trigonal pyramidal C_2O_3Sr polyhedron (40% thermal ellipsoids). Refer to Table 2 for selected angles. Symmetry transformation used to generate '#' atoms: $\frac{3}{2} - x, \frac{3}{2} - y, z$.

base places O(2) and O(3), and C(15) and O(1), *trans* to one another, with Sr–O(2,3) bond distances significantly longer (*ca* 0.06 Å) than Sr–O(1). The increased average Sr–O bond length (2.63 Å) over the average reported Sr–O bond length for seven coordination (2.59 Å)[31] suggests significant steric crowding in **4** owing to the positioning of the *ortho*-methyl groups (see below). The Sr–N bond lengths of **4** (⟨2.64 Å⟩) are expectedly longer than the Ca–N bond lengths of compound **1** (⟨2.43 Å⟩). Two related benzamidinate compounds, *trans*-[Sr{C(Ph){N(SiMe$_3$)}$_2$}$_2$(thf)$_2$] (six-coordinate) and [Sr{C(Ph){N(SiMe$_3$)}$_2$}$_2$(diglyme)] (seven-coordinate),[32] have mean Sr–N bond lengths (2.58 Å, 2.60 Å) shorter than the mean of analogous bonds in **4**.

Mononuclear **5** and **6** (Fig. 4, 5), which crystallise with one and one half molecule in the asymmetric unit, respectively (the latter with the strontium on a two-fold rotation axis), differ only in the number of lattice thf molecules, and have seven coordinate (two chelating formamidinates and three thf ligands) strontium metals with distorted trigonal bipyramidal arrangements (Fig. 4(b) and 5(b)) of oxygen atoms and NCN methine carbon atoms. In both, two thf molecules are apical and two NCN methine carbons and one thf oxygen are equatorial. This contrasts with the square pyramidal arrangement in **4** (Fig. 3(b)) suggesting, at least for strontium, that the replacement of the methyl of *o*-TolForm with a phenyl group (giving *o*-PhPhForm) has a similar effect to the addition of an *o*-methyl to *o*-TolForm (giving XylForm). The most striking difference between **5** and **6** is the greater bending of the O_{apical}–Sr–O_{apical} angle (**5**; 174.3(1)°, **6**; 155.6(1)°), which presumably arises from the differing steric effects of planar *o*-phenyl and the 2,6-dimethyl substituents (Fig. 4, 5). The phenyl substituents are somewhat directed towards the metal, but the closest approach at 3.7050(38) Å (Sr(1)–C(20)/C(20)#) is far too distant to be considered a bonding interaction.[1,3,4,5b] Accordingly, exploration of π-phenyl···M interactions with *o*-PhPhForm, where M = Ca, Sr or Ba, would appear to require the preparation of homoleptic complexes.

The clearest evidence of a structural difference between **4** and compounds **5** and **6** is that the latter pair have a maximum O–Sr–O angle in excess of 150° (see above) while **4** possesses a maximum O–Sr–O angle of 126.6(2)°. Furthermore, the variation in Sr–N distances for **5** and **6** (0.03 and 0.04 Å, respectively) is much less than that of **4** (0.08 Å). Comparing Sr–O distances, **4** has one Sr–O bond significantly shorter than the other two (2.585(4), 2.640(4), 2.654(4) Å) whereas for **5** and **6** there is a significantly longer Sr–O distance for the equatorial thf of the SrO_3C_2 unit (**5**; 2.571(3), 2.586(3), 2.630(3) Å, **6**; 2.565(3), 2.565(3), 2.622(4) Å). Comparing **2** and **5**, with their common XylForm ligand, the average Ca–N (2.43 Å) and Sr–N (2.65 Å) bond lengths, and the average Ca–O (2.401(2) Å) and Sr–O (2.60 Å) bond lengths differ as expected (0.21 Å) for ionic radius differences.[29]

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A structural proposal for the sole barium complex, **7**, is speculative in the absence of a crystal structure. However, since the thf to formamidinate ratio of 5 : 2 is the same as that of the structurally characterised compound [Sr(*o*-PhPhForm)$_2$(thf)$_3$]·2thf (**6**) a similar structure is probable. It is noteworthy that the DippForm (see Introduction) complexes [M(DippForm)$_2$(thf)$_2$], M = Sr or Ba, are isostructural[15] despite the difference in six-coordinate Sr^{2+} and Ba^{2+} ionic radii (0.17 Å).[29]

Comparison of formamidinates

The bite angles of the formamidinate ligands appear unaffected by the addition of a CH_3 group in the *ortho*-phenyl position of *o*-TolForm to give Xylform (calcium compounds, **1**; 56.41(6), 56.29(6)°, **2**; 56.58(7)°, strontium compounds, **4**; 52.22(17), 51.65(16)°, **5**; 51.97(10), 51.65(11)°). Likewise, replacement of the *o*-methyl of *o*-TolForm with a phenyl group to give *o*-PhPhForm has only a marginal effect (**6**; 51.17(10)°). In contrast, the interplanar angles of the arene rings with respect to the MNCN metallacycle plane are significantly affected (Table 2). Whilst compounds **1** and **4** (with the *o*-TolForm ligand) show variable twisting of tolyl rings out of the MNCN plane (**1**; 23.95(8)–57.00(7)°, **4**; 27.73(27)–49.06(20)°) compounds **2** and **5** (with the XylForm ligand) exhibit consistently more substantial twisting of the arene rings (**2**; 74.39(7)–80.44(8)°, **5**; 65.37(14)–69.46(15)°). The analogous twisting exhibited for the *o*-PhPhForm compound **6** (40.09(13)–43.60(12)°) is less variable compared to the *o*-TolForm and XylForm compounds. This may be attributed to the ordered packing of the *o*-phenyl rings within the structure, which is also consistent with the low variation in biaryl C–C interplanar angles (54.35(16) and 55.19(14)°). The related magnesium complex *trans*-[Mg(*p*-TolForm)$_2$(thf)$_2$] (*p*-TolForm = *N*,*N*′-bis(*para*-tolyl)formamidinate),[25] with no *ortho* substituents, exhibits arene rings that are notably closer to coplanar with the MNCN metallacyclic plane (4.65(17)–38.49(11)°) than those of **1**, **2** and **4–6**.

All the present calcium complexes are six-coordinate and the strontium complexes are seven coordinate despite the contrasting formamidinate ligands. These are one higher than the respective DippForm complexes [M(DippForm)$_2$(thf)$_n$], where M = Ca, n = 1; M = Sr, n = 2; M = Ba, n = 2,[15] reflecting the lesser steric demand of the current ligands. All the calcium and strontium bis(formamidinate) compounds, including those containing the DippForm ligand, display longer M–N bonds to the anionically charged ligand than the corresponding M–O bonds to neutral thf. However, [Ba(DippForm)$_2$(thf)$_2$], which is both isostructural and isomorphous with the strontium analogue, displays Ba–N bond distances (⟨2.73 Å⟩) that are commensurate with the Ba–O lengths (⟨2.72 Å⟩), presumably because the larger Ba^{2+} relieves the steric strain within the six-coordinate complex.[15]

Conclusion

The redox transmetallation/ligand exchange reaction of the heavy alkaline earth metals Ca, Sr and Ba with bis(pentafluorophenyl)-mercury and the formamidines *o*-TolFormH, XylFormH and *o*-PhPhFormH provides a versatile route to a variety of new alkaline earth bis(formamidinate) complexes with limitations for barium. X-Ray crystallographic studies show exclusively *N*,*N*′-chelating formamidinate bonding with the residual coordination sphere occupied by thf, the extent of which is dependent on metal ionic radius. A variety of subtle steric effects are observed upon progression from *o*-TolForm to *o*-PhPhForm or XylForm without alteration of coordination number.

Experimental

N,*N*′-Bis(*o*-methylphenyl)formamidine (*o*-TolFormH) and *N*,*N*′-bis(2,6-dimethylphenyl)formamidine (XylFormH) were synthesised according to a modified published procedure.[33] The known ligand precursor *N*,*N*′-Bis(*o*-phenylphenyl)formamidine (*o*-PhPhFormH)[26,27] was prepared by the same procedure as *o*-TolFormH and XylForm. As this represents a new synthesis of *o*-PhPhFormH, details are given below. Calcium, strontium, barium, *o*-phenylaniline, 2,6-dimethylaniline, *o*-toluidine and triethyl orthoformate were purchased from Aldrich. The alkaline earth metals were stored under purified nitrogen and freshly filed prior to use. Bis(pentafluorophenyl)mercury was prepared as reported.[6,34] Tetrahydrofuran (thf) was pre-dried over sodium wire and freshly distilled over sodium benzophenone ketyl under nitrogen. All manipulations were performed using conventional Schlenk and glovebox techniques under an atmosphere of purified nitrogen. Infrared spectra (4000–500 cm^{-1}) of Nujol mulls were recorded with a Perkin Elmer 1600 Fourier transform infrared spectrometer. ^{1}H NMR spectra were recorded at 300.13 or 400.13 MHz, and ^{13}C{H} NMR spectra were recorded at 75.47 or 100.62 MHz using a Brüker AC 300 spectrometer or a Brüker AC 400 spectrometer, respectively. Chemical shifts were referenced to the residual ^{1}H and ^{13}C resonances of the solvent deuterobenzene or deuterotoluene. All microanalyses were conducted by the Campbell Microanalytical Laboratory, Chemistry Department, University of Otago, Dunedin, New Zealand. Metal analyses were determined according to a literature procedure[35] following acid digestion. Melting points were determined in sealed glass capillaries under nitrogen and are uncalibrated. The mass spectrometric analysis of *o*-PhPhFormH was conducted at low resolution electro spray ionisation (ESI) on a micromass platform spectrometer (QMS-Quadrupole Mass electrospray). The predominate ion peak (m/z) is reported [M] to denote the molecular ion.

ortho-PhPhFormH

Ten drops of acetic acid were added to a round bottom flask charged with *o*-phenylaniline (10.00 g, 59.1 mmol) and triethyl orthoformate (4.38 g, 29.6 mmol). The clear colourless solution was heated to reflux for 6 h and cooled to ambient temperature, whereupon crude *o*-PhPhFormH precipitated. Collection of the precipitate by filtration followed by recrystallisation from hot methanol gave pure *ortho*-PhPhFormH as a colourless powder (8.75–9.47 g, 85–92%), mp 163–165 °C (lit. 156.5–157.5 °C[26] and 162 °C[27]). IR (Nujol): $\tilde{\nu}$ 1661s, 1587m, 1488 sh w, 1461s, 1428m, 1309s, 1260m, 1202m, 1112w, 1074w, 1052w, 1000w, 910w, 827w, 763m, 743m, 726s, 694s cm^{-1}; ^{1}H NMR (300.13 MHz, C_6D_6, 300 K): δ 7.35 (br d, 4H; ArH), 7.21 (br d, 2H; ArH), 7.18–7.14 (m, 2H; ArH), 7.12 (br s, 2H; ArH), 7.09–6.95 (m, 7H; ArH + NC(H)N), 6.97 (br dd, 2H; ArH), 6.58 (br s, 1H; NH); ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6, 300 K) δ 147.3 (s, NC(H)N), 142.2 (s, Ar–C), 139.9 (s, Ar–CH), 133.5 (s, Ar–C), 130.7 (s, Ar–CH), 130.0 (s, Ar–CH),

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128.6 (s, Ar–CH), 127.2 (s, Ar–CH), 123.5 (s, Ar–CH), 119.5 (s, Ar–CH), 114.1 (s, Ar–C); ESMS: *m*/*z* 349 (100, $[M + H]^+$).

General procedure

Tetrahydrofuran (40 cm^3) was added to a Schlenk flask charged with freshly filed alkaline earth metal (Ca; 0.035 g, 8.59 mmol, Sr; 0.035 g, 3.99 mmol, Ba; 0.035, 2.55 mmol), *o*-TolFormH (0.35 g, 1.60 mmol), XylFormH (0.35 g, 1.38 mmol) or *o*-PhPhFormH (0.35 g, 1.05 mmol) and bis(pentafluorophenyl)mercury (*o*-TolFormH; 0.42 g, 0.80 mmol $Hg(C_6F_5)_2$, XylFormH; 0.36 g, 0.69 mmol $Hg(C_6F_5)_2$, *o*-PhPhFormH; 0.28 g, 0.52 mmol $Hg(C_6F_5)_2$) under purified nitrogen. The slurry was stirred at ambient temperature for 48 h before the light brown solution was filtered from the deposit of elemental mercury and excess Ca, Sr or Ba metal. The solution was concentrated (to *ca.* 4 cm^3) and, after standing at ambient temperature for several hours, yielded colourless rectangular crystals (**1**, **2** and **4–6**) or a colourless powder (**3** and **7**).

[Ca(TolForm)$_2$(thf)$_2$] (1). (0.31 g, 61%), mp 166–170 °C, decomp. > 200 °C. Calc. (%) for $CaC_{38}H_{46}N_4O_2$: C 72.34, H 7.35, N 8.88, Ca 6.35. Found: C 71.02, H 7.05, N 8.99 Ca 6.77. IR (Nujol): $\tilde{\nu}$ 1668m, 1588m, 1304s, 1227s, 1183m, 1107m, 1034m, 987m, 953m, 883m, 838w, 776m, 752s, 721m, 700m, 671w, 611w cm^{-1}; ^1H NMR (300.13 MHz, C_6D_6, 300 K): δ 8.39 (s, 2H; NC(H)N), 7.13–6.67 (m, 16H; ArH), 3.52 (m, 8H; OCH_2, thf), 2.21 (s, 12H; CH_3), 1.23 (m 8H; CH_2, thf); $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6, 300 K) δ 162.1 (s, NC(H)N), 151.8 (s, Ar–C), 130.3 (s, Ar–CH), 129.4 (s, Ar–C), 125.9 (s, Ar–CH), 120.7 (s, Ar–CH), 117.4 (s, Ar–CH), 67.3 (s, OCH_2, thf), 24.2 (s, CH_2, thf), 17.4 (s, CH_3).

[Ca(XylForm)$_2$(thf)$_2$] (2). (0.34 g, 72%), mp 156–158 °C, decomp. 170 °C. Calc. (%) for $CaC_{42}H_{54}N_4O_2$: C 73.43, H 7.92, N 8.16, Ca 5.83. Found: C 72.59, H 8.07, N 8.35, Ca 6.20. IR (Nujol): $\tilde{\nu}$ 1651m, 1595m, 1531m, 1294s, 1200s, 1160m, 1090s, 1033s, 995m, 955m, 931m, 917 shw, 878s, 765s, 732w, 698m, 671w cm^{-1}; ^1H NMR (300.13 MHz, C_6D_6, 300 K): δ 7.75 (br s, 2H; NC(H)N), 7.09–6.71 (m, 12H; ArH), 3.53 (m, 8H; OCH_2, thf), 2.19 (s, 24H; CH_3), 1.31 (m, 8H; CH_2, thf); $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6, 300 K) δ 174.7 (s, NC(H)N), 154.2 (s, Ar–C), 127.6 (s, Ar–C), 127.4 (s, Ar–CH), 127.1 (s, Ar–CH), 66.8 (s, OCH_2, thf), 24.3 (s, CH_2, thf), 17.1 (s, CH_3); ^1H NMR (300.13 MHz, C_7D_8, 300 K): δ 7.79 (br s, 2H; NC(H)N), 6.95 (d, 8H; ArH, *J* 7.5 Hz), 6.85 (t, 4H; ArH, *J* 7.5 Hz), 3.57 (m, 8H; OCH_2, thf), 2.14 (s, 24H; CH_3), 1.37 (m, 8H; CH_2, thf); $^{13}C\{^1H\}$ NMR (75.47 MHz, C_7D_8, 300 K) δ 174.7 (s, NC(H)N), 152.5 (s, Ar–C), 133.7 (s, Ar–C), 127.6 (s, Ar–CH), 127.1 (s, Ar–CH), 68.5 (s, OCH_2, thf), 25.8 (s, CH_2, thf), 20.0 (s, CH_3).

[Ca(*o*-PhPhForm)$_2$(thf)$_2$]·thf (3). (0.30 g, 61%), mp 160–164 °C, decomp. 200 °C. Calc. (%) for $CaC_{62}H_{62}N_4O_3$: C 78.28, H 6.57, N 5.89. Found: C 78.59, H 6.67, N 5.95. IR (Nujol): $\tilde{\nu}$ 1663m, 1594w, 1522m, 1316s, 1210w, 1072w, 1034w, 934w, 882m, 764m, 742m, 696m cm^{-1}; ^1H NMR (400.13 MHz, C_6D_6, 300 K): δ 8.65 (br s, 2H; NC(H)N), 7.17–6.74 (m, 36H; ArH), 3.35 (br s, 12H; OCH_2, thf), 1.26 (br s, 12H; CH_2, thf); $^{13}C\{^1H\}$ NMR (100.62 MHz, C_6D_6, 300 K) δ 171.0 (s, NC(H)N), 150.9 (s, Ar–C), 144.0 (s, Ar–C), 134.6 (s, Ar–C), 131.5 (s, Ar–CH), 129.7 (s, Ar–CH), 129.5 (s, Ar–CH), 129.0 (s, Ar–CH), 126.9 (s, Ar–CH), 123.2 (s, Ar–CH), 121.7 (s, Ar–CH), 68.3 (s, OCH_2, thf), 25.9 (s, CH_2, thf).

[Sr(*o*-TolForm)$_2$(thf)$_3$] (4). (0.42 g, 70%), mp 153–156 °C, decomp. > 200 °C. Calc. (%) for $C_{42}H_{54}N_4O_3Sr$: C 67.21, H 7.25, N 7.46, Sr 11.67. Found: C 65.81, H 6.90, N 7.72, Sr 11.39. IR (Nujol): $\tilde{\nu}$ 1667m, 1593m, 1573w, 1314s, 1224s, 1185m, 1154m, 1110s, 1039s, 990s, 926s, 884s, 838m, 796w, 778m, 755s, 722s, 698m, 666mw cm^{-1}; ^1H NMR (400.13 MHz, C_6D_6, 300 K): δ 8.80 (s, 2H; NC(H)N), 7.16–6.90 (m, 16H; ArH), 3.46 (m, 12H; OCH_2, thf), 2.26 (s, 12H; CH_3), 1.19 (m, 12H; CH_2, thf); $^{13}C\{^1H\}$ NMR (100.13 MHz, C_6D_6, 300 K): δ 162.5 (s, CN(H)N), 151.3 (s, Ar–C), 130.2 (s, Ar–CH), 129.3 (s, Ar–C), 126.9 (s, Ar–CH), 120.8 (s, Ar–CH), 117.9 (s, Ar–CH), 67.9 (s, OCH_2, thf), 25.0 (s, CH_2, thf), 18.9 (s, CH_3).

[Sr(XylForm)$_2$(thf)$_3$]·3thf (5). (0.31 g, 56% [Sr(XylForm)$_2$(thf)$_3$]), mp 155–158 °C, decomp. 200 °C. Calc. (%) for $C_{46}H_{62}N_4O_3Sr$: Sr 10.86. Found: Sr 11.07. IR (Nujol): $\tilde{\nu}$ 1651m, 1597m, 1538s, 1298s, 1201s, 1074s, 1043s, 982m, 914s, 823w, 759s, 732w, 667m, 598w, 500w cm^{-1}; ^1H NMR (300.13 MHz, C_6D_6,: 300 K) δ 7.72 (br s, 2H; NC(H)N), 6.99 (d, 8H; ArH, *J* 7.5 Hz), 6.90 (t, 4H; ArH, *J* 7.5 Hz), 3.45 (br s, 12H; OCH_2, thf), 2.21 (s, 24H; CH_3), 1.24 (br s, 12H; CH_2, thf); $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6, 300 K) δ 179.6 (s, NC(H)N), 154.7 (s, Ar–C), 133.9 (s, Ar–C), 129.3 (s, Ar–CH), 128.7 (s, Ar–CH), 68.4 (s, OCH_2, thf), 25.1 (s, CH_2, thf), 20.2 (s, CH_3).

[Sr(*o*-PhPhForm)$_2$(thf)$_3$]·2thf (6). (0.33 g, 56%), mp 135–140 °C, decomp. >300 °C. Calc. (%) for $C_{70}H_{78}N_4O_5Sr$: C 73.56, H 6.88, N 4.90. Found: C 73.46, H 7.34, N 5.01. IR (Nujol): $\tilde{\nu}$ 1662s, 1597m, 1567w, 1520s, 1310s, 1261m, 1202m, 1155w, 1108w, 1071s, 1039m, 1008w, 936w, 912w, 883m, 778m, 761m, 744s, 700s, 669w cm^{-1}; ^1H NMR (400.13 MHz, C_6D_6, 300 K): δ 9.14 (br s, 2H; NC(H)N), 7.36–6.85 (m, 36H; ArH), 3.62 (m, 12H; OCH_2, thf), 1.47 (m, 12H; CH_2, thf); $^{13}C\{^1H\}$ NMR (100.62 MHz, C_6D_6, 300 K) δ 161.0 (s, NC(H)N), 149.3 (s, Ar–C), 144.4 (s, Ar–C), 134.3 (s, Ar–C), 130.7 (s, Ar–CH), 129.6 (s, Ar–CH), 129.1 (s, Ar–CH), 128.7 (s, Ar–CH), 127.4 (s, Ar–CH), 120.8 (s, Ar–CH), 116.2 (s, Ar–CH), 67.8 (s, OCH_2, thf), 25.7 (s, CH_2, thf).

[Ba(*o*-PhPhForm)$_2$(thf)$_3$]·2thf (7). (0.35 g, 56%), mp 76–80 °C, decomp. >300 °C. Calc. (%) for $BaC_{70}H_{78}N_4O_5$: C 70.49, H 6.59, N 4.70. Found: C 70.21, H 6.48, N 4.79. IR (Nujol): $\tilde{\nu}$ 1662s, 1596m, 1565m, 1526s, 1306s, 1262w, 1208m, 1156w, 1112w, 1071m, 1047m, 1009w, 929w, 883m, 826w, 765m, 758m, 743s, 703s cm^{-1}; ^1H NMR (400.13 MHz, C_6D_6, 300 K): δ 9.26 (br s, 2H; NC(H)N), 7.31–6.72 (m, 36H; ArH), 3.57 (m, 20H; OCH_2, thf), 1.41 (m, 20H; CH_2, thf); $^{13}C\{^1H\}$ NMR (100.62 MHz, C_6D_6, 300 K) δ 159.8 (s, NC(H)N), 151.0 (s, Ar–C), 145.3 (s, Ar–C), 134.6 (s, Ar–C), 130.7 (s, Ar–CH), 130.0 (br s, 2 Ar–CH), 129.7 (br s, 2 Ar–CH), 120.7 (s, Ar–CH), 115.7 (s, Ar–CH), 68.1 (s, OCH_2, thf), 26.1 (s, CH_2, thf).

X-Ray structure determinations

Crystalline samples of compounds **1**, **2** and **4–6** were mounted on glass fibres in silicone oil at −150(2) °C (123 (2) K). A summary of crystallographic data can be found in Table 1. Data were collected on an Enraf-Nonius Kappa CCD diffractometer using graphite-monochromated Mo-Kα X-ray radiation ($\lambda = 0.71073$ Å). Data were corrected for absorption by the DENZO-SMN package.[36]

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Lorentz polarization and absorption corrections were applied. Structural solution and refinement was carried out using the SHELX suite of programs[37] with the graphical interface X-seed.[38]

Variata

For compound **1**, modelling of disorder for one thf methylene carbon (C(32)) was attempted but failed to give satisfactory thermal parameters.

For compound **4**, inversion of the structure gave a Flack parameter[39] of 0.943(15) suggesting the absolute configuration is that chosen (Flack parameter −0.004(9)).

For compound **5**, modelling of disorder for several thf methylene carbons (C(41), C(44), C(47), C(48) and C(49)) was attempted but only gave acceptable thermal parameters for C(44). The disorder of this atom was modelled over two sites of partial occupancy (62 : 38%) and the remaining atoms were left as is.

For compound **6**, the thf of solvation was found to reside over two partially coincident sites. These were modelled with partial occupancies of 60 : 40% (C(33) and O(3) : C(37) and C(39)).

CCDC reference numbers 298094–298098.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b602210c

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