

# Titanium, zinc and alkaline-earth metal complexes supported by bulky *O,N,N,O*-multidentate ligands: syntheses, characterisation and activity in cyclic ester polymerisation

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The reactions of the bulky amino-bis(phenol) ligand Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>N{CH<sub>2</sub>-3,5-Bu<sup>t</sup>-C<sub>6</sub>H<sub>2</sub>OH-2}<sub>2</sub> (**1-H<sub>2</sub>**) with Zn[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (**4**), [Mg{N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (**5**) and Ca[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(THF)<sub>2</sub> (**6**) yield the complexes **1-Zn**, **1-Mg** and **1-Ca** in good yields. The X-ray structure of **1-Ca** showed the complex to be dimeric, with calcium in a distorted octahedral coordination geometry. Five of the positions are occupied by an N<sub>2</sub>O<sub>3</sub> donor set, while the sixth is taken up by an intramolecular close contact to an *o*-Bu<sup>t</sup> substituent, a rare case of a Ca...H-C agostic interaction (Ca...H distances of 2.37 and 2.41 Å). Another sterically hindered calcium complex, Ca{2-Bu<sup>t</sup>-6-(C<sub>6</sub>F<sub>5</sub>N=CH)C<sub>6</sub>H<sub>3</sub>O}<sub>2</sub>(THF)<sub>2</sub>·(C<sub>7</sub>H<sub>8</sub>)<sub>2/3</sub> (**7**), was prepared by reaction of **6** with the iminophenol 2-Bu<sup>t</sup>-6-(C<sub>6</sub>F<sub>5</sub>N=CH)C<sub>6</sub>H<sub>3</sub>OH (**3-H**). According to the crystal structure, **7** is monomeric and octahedral, with *trans* THF ligands. The complex Ti[N{CH<sub>2</sub>-3-Bu<sup>t</sup>-5-Me-C<sub>6</sub>H<sub>2</sub>O-2}<sub>2</sub>{CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>}]<sub>2</sub>(OPr<sup>i</sup>)<sub>2</sub> (**2-Ti**) was prepared by treatment of Ti(OPr<sup>i</sup>)<sub>4</sub> with the new amino-bis(phenol) Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>N{CH<sub>2</sub>-3-Bu<sup>t</sup>-5-Me-C<sub>6</sub>H<sub>2</sub>OH-2}<sub>2</sub> (**2-H<sub>2</sub>**). The reduction of **2-Ti** with sodium amalgam gave the titanium(III) salt Ti[N{CH<sub>2</sub>-3-Bu<sup>t</sup>-5-Me-C<sub>6</sub>H<sub>2</sub>O-2}<sub>2</sub>{CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>}]<sub>2</sub>·Na(THF)<sub>2</sub> (**8**). A comparison of the X-ray structures of **2-Ti** and **8** showed that the additional electron in **8** significantly reduced the intensity of the π-bonding from the oxygen atoms of the isopropoxide groups to titanium. **1-Ca** and **8** were active initiators for the ring-opening polymerisation of ε-caprolactone (up to 97% conversion of 200 equivalents in 2 hours) and yielded polymers with narrow molecular weight distributions.

## Introduction

The interest in biodegradable and biocompatible polymers, based on environmentally friendly monomers, has increased considerably in the past decade.<sup>1</sup> The polymerisation of cyclic esters such as ε-caprolactone (CL) and especially lactide (LA), a renewable resource derived from corn, has attracted the attention of many research groups.<sup>2,3</sup> Aliphatic polyesters such as poly(ε-caprolactone) (PCL) and poly(lactide) (PLA) are very conveniently prepared by ring-opening polymerisation (ROP) of CL or LA. They and their copolymers are now frequently used in pharmaceutical and medical applications, for instance as drug delivery media or surgical sutures.<sup>4-6</sup> Although remarkably simple and efficient in principle, the anionic polymerisation of these monomers initiated by alkali-metal alkyls or alkali-metal alkoxides is not without problems due to side reactions.<sup>7,8</sup> By contrast, homoleptic metal alkoxide catalysts based on Sn, Fe, Al, Y or Ln allow a much improved control of the polymerisation parameters and give high molecular weight polymers in very good yields, and as a result have been commonly employed.<sup>9-24</sup> However, a great deal of attention has been paid in the past few years to the development of single-site catalysts bearing sterically hindered ancillary ligands (Chart 1) since they are capable of offering a better control over the

stereoselectivity of LA polymerisation. Early work by Inoue on metalloporphyrins proved very promising.<sup>25</sup> Many catalysts based on Al,<sup>26-35</sup> Mg,<sup>36-39</sup> or Zn,<sup>40-43</sup> supported by various multidentate ligands have now been shown to give excellent molecular weight polymers, with very good stereocontrol and polymerisation rates.

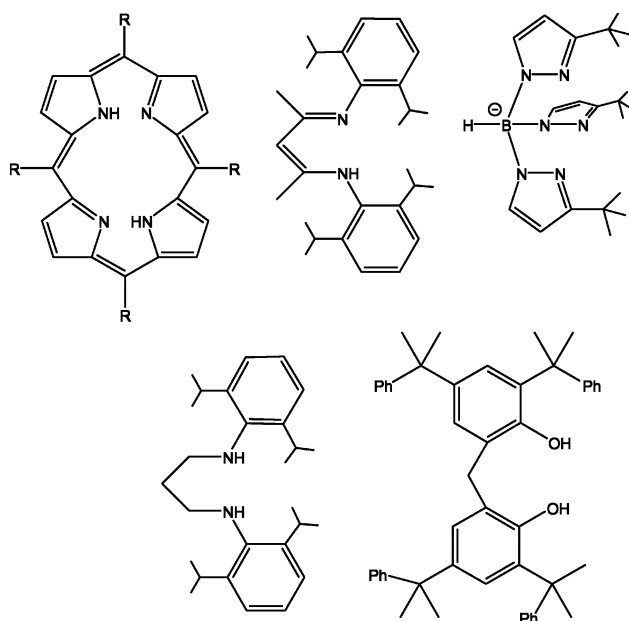


Chart 1

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These metals are especially attractive, since they do not impart any colour to the polymers, and are inexpensive and are non-toxic, an essential criterion for any medical application. Other metals used for the polymerisation of CL and LA include Ti, Y, Ln, and Sn.<sup>2,3,44</sup>

A literature survey indicated that remarkably few discrete complexes of calcium and titanium had been reported for the ring-opening polymerisation of CL and LA. Very recently Chisholm described some calcium complexes supported by bulky tris-pyrazolyl borate ligands which were among the most active catalysts reported to date.<sup>45,46</sup> Efficient Ti(IV) catalysts bearing bulky chelating aryloxy ligands are also uncommon.<sup>47-50</sup> To the best of our knowledge there is no report of single-site Ti(III) complexes for CL- or LA-polymerisations. Moreover, whereas  $\beta$ -diketiminates<sup>38,40,41</sup> and tris(pyrazolyl)borate<sup>36,45-46,51</sup> ligands have been widely employed, there are only few literature reports of bulky amino-bis(phenolate) complexes, primarily of trivalent metals.<sup>33-35,44</sup> Following our earlier reports on the polymerisation of polar monomers with zinc,<sup>52,53</sup> magnesium<sup>54</sup> and lanthanide catalysts,<sup>55-58</sup> we describe in this paper the syntheses of well-defined Ti(IV), Ti(III), Zn, Mg and Ca complexes bearing chelating iminophenolate and amino-bis(phenolate) ligands, and their activity in the polymerisation of  $\epsilon$ -caprolactone.

## Results and discussion

### Syntheses

The substituted amino-bis(2-hydroxyarylmethyl) ligands  $\text{Me}_2\text{NCH}_2\text{CH}_2\text{N}\{\text{CH}_2\text{-}3,5\text{-Bu}^t\text{-C}_6\text{H}_3\text{OH-}2\}_2$  (**1-H<sub>2</sub>**) and  $\text{Me}_2\text{NCH}_2\text{CH}_2\text{N}\{\text{CH}_2\text{-}3\text{-Bu}^t\text{-}5\text{-Me-C}_6\text{H}_3\text{OH-}2\}_2$  (**2-H<sub>2</sub>**) (Chart 2) were prepared following the modified Mannich reaction between *N,N*-

dimethylethylenediamine, formaldehyde and a substituted phenol as described in the literature.<sup>59</sup> In particular, **2-H<sub>2</sub>**, which was prepared by addition of *N,N*-dimethylethylenediamine and formaldehyde to a solution of 2-Bu<sup>t</sup>-4-Me-C<sub>6</sub>H<sub>3</sub>OH in refluxing methanol, is reported here for the first time. The iminophenol 2-Bu<sup>t</sup>-6-(C<sub>6</sub>F<sub>5</sub>N=CH)C<sub>6</sub>H<sub>3</sub>OH (**3-H**) was also prepared according to a known route previously reported by our group (Chart 2).<sup>60</sup>

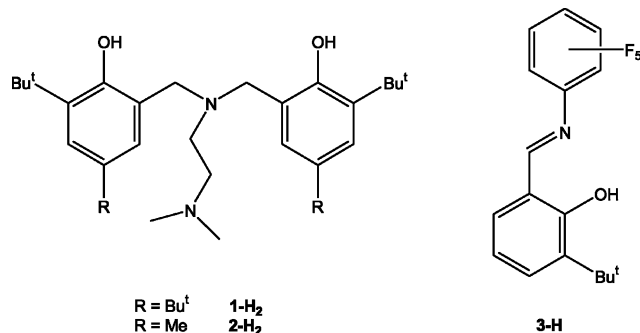
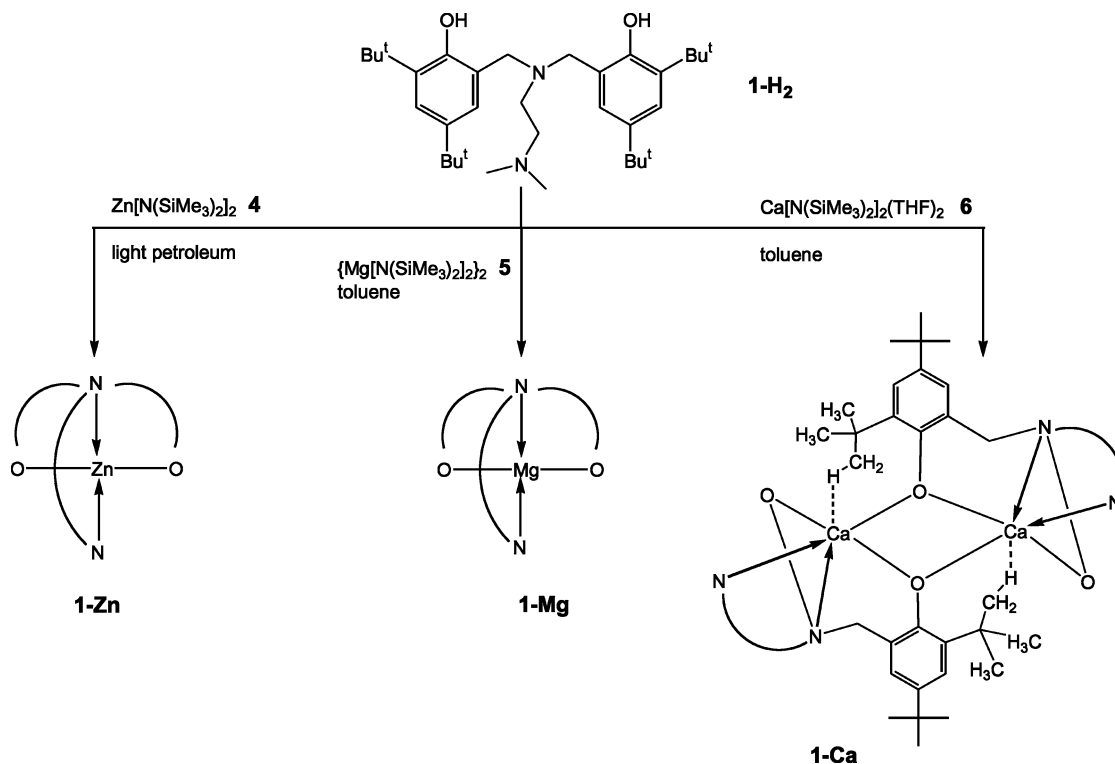


Chart 2

**1-H<sub>2</sub>** was reacted with various metal bis(trimethylsilyl)amides (Scheme 1). The addition of  $\text{Zn}\{\text{N}(\text{SiMe}_3)_2\}_2$  (**4**) to a solution of **1-H<sub>2</sub>** in light petroleum resulted in a colourless solution, which rapidly became cloudy upon stirring. After 16 h a large amount of white precipitate had formed which was isolated by filtration, washed with light petroleum and dried *in vacuo*. NMR spectroscopic data and elemental analysis were consistent with the formulation  $\text{Zn}\{\text{Me}_2\text{NC}_2\text{H}_4\text{N}(\text{CH}_2\text{-}3,5\text{-Bu}^t\text{-C}_6\text{H}_3\text{O-}2)_2\}$  (**1-Zn**). **1-Zn** was only sparingly soluble in light petroleum, but was fully soluble in toluene, Et<sub>2</sub>O, THF and dichloromethane.

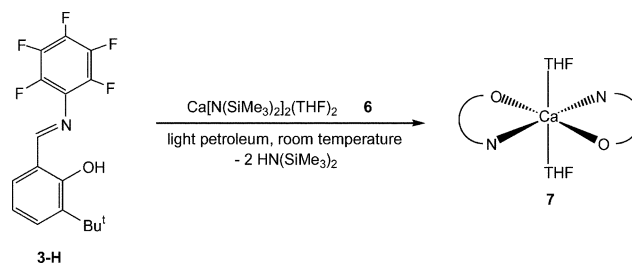


Scheme 1

Similarly, slow addition of a toluene solution of **1-H<sub>2</sub>** to a solution of  $[\text{Mg}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$  (**5**) and recrystallisation from toluene at  $-26^\circ\text{C}$  gave  $\text{Mg}\{\text{Me}_2\text{NC}_2\text{H}_4\text{N}(\text{CH}_2\text{-3,5-Bu}^t\text{C}_6\text{H}_2\text{O-2})_2\}$  (**1-Mg**) as colourless crystals. The composition of **1-Mg** was confirmed by elemental analysis and NMR spectroscopy. The excellent solubility of **1-Mg** in toluene,  $\text{Et}_2\text{O}$ , THF and  $\text{CH}_2\text{Cl}_2$  precluded the existence of a polymeric structure. Needle-shaped crystals of **1-Mg** were grown from diethyl ether/light petroleum at  $+6^\circ\text{C}$ , but were only poorly diffracting, and the molecular structure of **1-Mg** could not be determined.

The dimeric calcium complex  $[\text{Ca}\{\text{Me}_2\text{NC}_2\text{H}_4\text{N}(\text{CH}_2\text{-3,5-Bu}^t\text{C}_6\text{H}_2\text{O-2})_2\}]_2$  (**1-Ca**) was obtained upon treatment of  $\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2$  (**6**) with **1-H<sub>2</sub>** in toluene. The compound was very poorly soluble in light petroleum, sparingly soluble in aromatic solvents but showed good solubility in ethers and chlorinated solvents. The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **1-Ca** were unexpectedly complicated. In the  $^1\text{H}$  NMR spectrum, the four protons from the  $\text{Ar-CH}_2\text{-N}$  methylene bridges were diastereotopic and gave rise to four doublets with coupling constants of 12.0–12.4 Hz; four different singlets were also found for the  $\text{Bu}^t$  substituents. The heteronuclear  $^1\text{H-}^{13}\text{C}$  and homonuclear  $^1\text{H-}^1\text{H}$  correlation spectra allowed the complete assignment of all signals. The dimeric structure of **1-Ca** was elucidated by X-ray crystallography (see below).

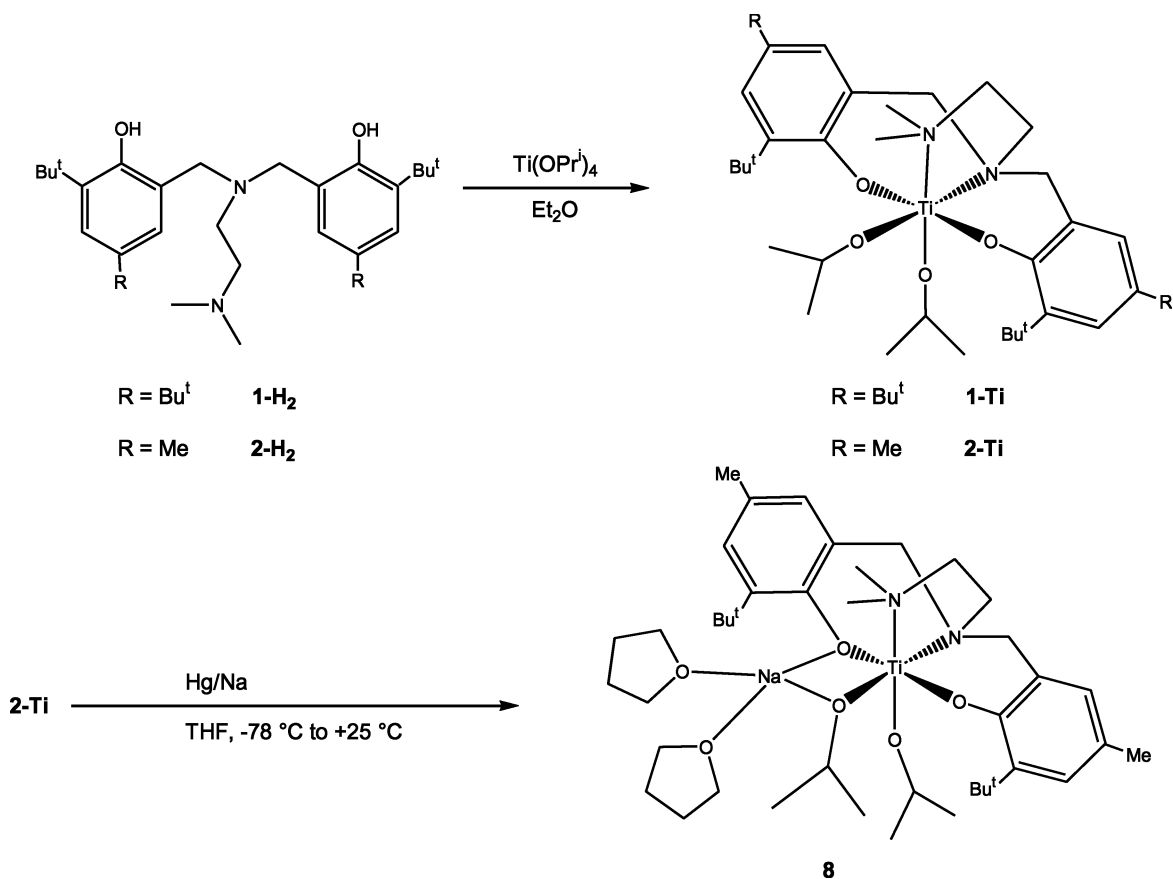
In an attempt to prepare a calcium complex related to **1-Ca** for structural and reactivity studies, **6** was reacted with one equivalent of the bidentate ligand 2- $\text{Bu}^t$ -6-( $\text{C}_6\text{F}_5\text{N}=\text{CH}$ ) $\text{C}_6\text{H}_3\text{OH}$  (**3-H**) in light petroleum (Scheme 2). A yellow solid precipitated



Scheme 2

from the reaction mixture, which was isolated by filtration and washed with light petroleum. Single crystals suitable for X-ray diffraction were grown by recrystallisation in a 4 : 1 toluene/light petroleum mixture at  $-26^\circ\text{C}$ . NMR spectroscopy and elemental analysis indicated the composition  $\text{Ca}\{2\text{-Bu}^t\text{-6-(C}_6\text{F}_5\text{N}=\text{CH})\text{C}_6\text{H}_3\text{O}\}_2(\text{THF})_2\cdot(\text{C}_7\text{H}_8)_{2/3}$  (**7**). The toluene of crystallisation could not be removed, even upon heating up to  $60^\circ\text{C}$  under vacuum. **7** was sparingly soluble in light petroleum but showed good solubility in aromatic and polar solvents.

Titanium(IV) amino-bis(phenolato) bis(isopropoxide) complexes were similarly prepared from the reaction of the neutral ligands with  $\text{Ti}(\text{OPr}^i)_4$  to give  $\text{Ti}(\text{OPr}^i)_2(\mathbf{1})$  (**1-Ti**) and  $\text{Ti}(\text{OPr}^i)_2(\mathbf{2})$  (**2-Ti**), respectively (Scheme 3). The synthesis of **1-Ti** has been described elsewhere.<sup>59</sup> **2-Ti** was isolated as a yellow powder in good yield and recrystallised from diethyl ether to give crystals adequate for X-ray diffraction.



Scheme 3

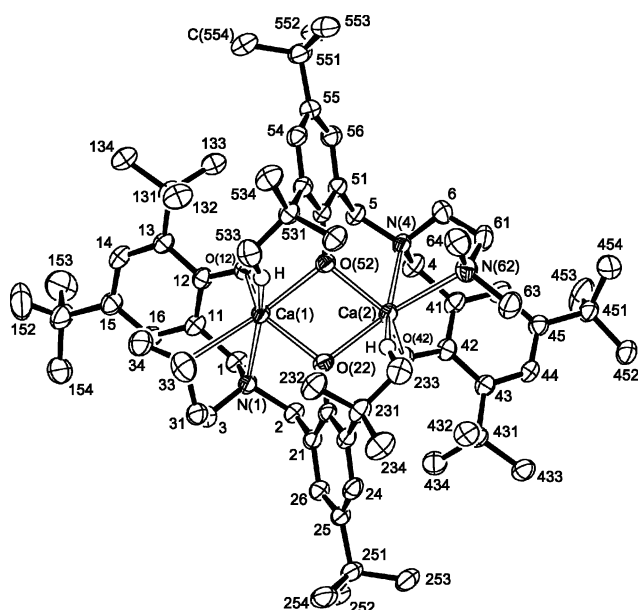
Treatment of **2-Ti** with sodium amalgam in THF at  $-78\text{ }^{\circ}\text{C}$  led to a colour change from yellow to pale green which changed to very dark green on warming to room temperature. The Ti(III) reduction product,  $\text{Ti}\{\text{Me}_2\text{NC}_2\text{H}_4\text{N}\{\text{CH}_2\text{-3-Bu}^i\text{-5-Me-C}_6\text{H}_2\text{O-2}\}_2(\text{OPr}^i)_2\cdot\text{Na}(\text{THF})_2$  (**8**) was isolated as a green solid and recrystallised from light petroleum. The composition was confirmed by elemental analysis.

### Structural characterisation

Crystals of **1-Ca** $\cdot\text{Et}_2\text{O}$  were obtained as colourless blocks from a  $\text{Et}_2\text{O}$ /light petroleum mixture (10 : 3) at  $+6\text{ }^{\circ}\text{C}$ . All attempts to grow crystals from toluene proved unsuccessful. Selected bond lengths and angles are collected in Table 1. The compound is a dimer, with two phenolate-oxygens bridging the two calcium atoms (Fig. 1). The presence of one molecule of  $\text{Et}_2\text{O}$  per dimer

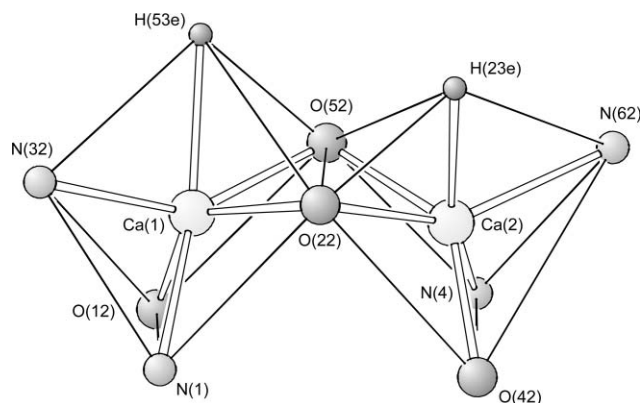
**Table 1** Selected dimensions in compound  $\{\mathbf{1-Ca}\}_2$ . Bond lengths are in Ångstroms, angles in degrees. E.s.d.s are in parentheses

Ca(1)⋯Ca(2)	3.4653(6)		
Ca(1)–N(1)	2.5115(19)	Ca(2)–O(22)	2.2904(15)
Ca(1)–O(12)	2.1817(16)	Ca(2)–N(4)	2.4981(19)
Ca(1)–O(22)	2.2488(15)	Ca(2)–O(42)	2.1842(16)
Ca(1)–N(32)	2.551(2)	Ca(2)–O(52)	2.2682(15)
Ca(1)–O(52)	2.3170(16)	Ca(2)–N(62)	2.552(2)
Ca(1)–H(53e)	2.41	Ca(2)–H(23e)	2.37
O(12)–Ca(1)–N(1)	82.74(6)	O(22)–Ca(2)–N(4)	136.43(6)
O(22)–Ca(1)–N(1)	80.37(6)	O(42)–Ca(2)–O(22)	92.73(6)
N(1)–Ca(1)–N(32)	72.32(6)	O(52)–Ca(2)–O(22)	72.71(5)
O(52)–Ca(1)–N(1)	136.32(6)	O(22)–Ca(2)–N(62)	146.34(6)
O(12)–Ca(1)–O(22)	134.13(6)	O(42)–Ca(2)–N(4)	82.46(6)
O(12)–Ca(1)–N(32)	112.01(7)	O(52)–Ca(2)–N(4)	80.13(6)
O(12)–Ca(1)–O(52)	92.05(6)	N(4)–Ca(2)–N(62)	73.28(7)
O(22)–Ca(1)–N(32)	102.84(7)	O(42)–Ca(2)–O(52)	134.39(6)
O(22)–Ca(1)–O(52)	72.56(5)	O(42)–Ca(2)–N(62)	109.52(6)
O(52)–Ca(1)–N(32)	146.39(7)	O(52)–Ca(2)–N(62)	105.19(6)



**Fig. 1** View of a molecule of  $\{\text{Ca}[\text{N}\{\text{CH}_2\text{-2-O-3,5-(Bu}^i\text{)}_2\text{-C}_6\text{H}_2\}_2\text{-}\{\text{CH}_2\text{CH}_2\text{NMe}_2\}]\}_2$  (**1-Ca**). Ellipsoids are drawn at the 50% probability level. All hydrogen atoms except H(53e) and H(23e), labelled 'H', are omitted for clarity. The major conformations for each disordered  $\text{CH}_2\text{NMe}_2$  unit are displayed.

complex is also observed, but there is no interaction between the solvent molecules and the metal centres. Remarkably, the position of the solvent in the lattice is perfectly defined. The  $\text{Ca}_2\text{O}_2$  core forms a shallow biplane, the angle between the normals of the two  $\text{CaO}_2$  planes is  $39.0^\circ$ . The two halves of the molecule are related by a pseudo-two-fold symmetry axis. Each Ca atom is coordinated by the ONNO atoms of one ligand, and the bridging O atom of the other ligand. The coordination pattern of these five atoms is quite irregular. A sixth coordination position is occupied by a CMe<sub>3</sub> methyl group situated close to each Ca atom,  $\text{Ca}(1)\cdots\text{H}(53e) = 2.41\text{ }\text{Å}$ ,  $\text{Ca}(2)\cdots\text{H}(23e) = 2.37\text{ }\text{Å}$ , *i.e.* closer than the nitrogen atoms and shorter than the sum of the van der Waals radius of H (1.4 Å) and the ionic radius of six-coordinate  $\text{Ca}^{2+}$  (1.14 Å). To the best of our knowledge, this represents a unique example of intramolecular  $\text{Ca}\cdots\text{H-C}$  agostic interactions. A similar close interionic contact (2.41 Å) was found between a calcium cation and a hydrogen atom on one of the  $\alpha$ -carbons of its  $\text{HB}(\text{CH}_2\text{CH}_3)_3$  counter anion.<sup>61</sup> Taking these H atoms into consideration, the six-coordinate pattern resembles a skew-trapezoidal bipyramid, as described by Kepert,<sup>62</sup> in this arrangement, there is a square-planar base [*viz* N(1), O(12), O(22), O(52) for Ca(1) and N(4), O(42), O(22), O(52) for Ca(2)] and a pair of ligand atoms lying over a diagonal of the base-plane [*viz* N(32), H(53e) over the N(1)⋯O(52) line and N(62), H(23e) over the N(4)⋯O(22) line] (Fig. 2).



**Fig. 2** Coordination geometry around the calcium atoms in the dimeric **1-Ca**.

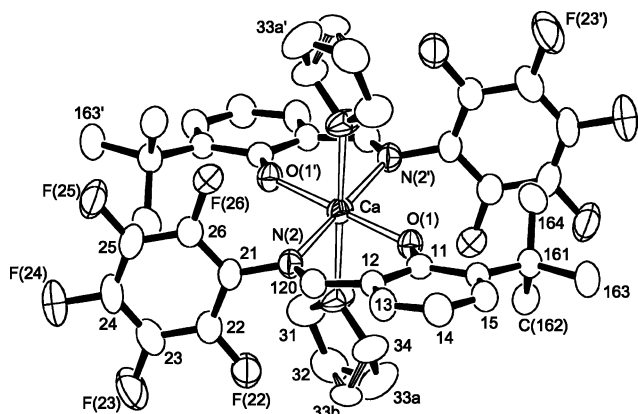
Although clearly non-bonding, the  $\text{Ca}(1)\cdots\text{Ca}(2)$  distance is significantly shorter in **1-Ca** [3.4653(6) Å] than in  $[\text{Ca}_2(\text{tmdh})_4(\text{OAr})_4(\text{HOEt})_2]$  [tmdh-H = 2,2,6,6-tetramethylheptane-3,5-dione; 3.926(2) Å].<sup>63</sup> The Ca–O (terminal aryloxy) bond lengths in **1-Ca** [Ca(1)–O(12), 2.1817(16) Å; Ca(2)–O(42), 2.1842(16) Å] are a little shorter than in  $[\text{Ca}\{\text{salen}(\text{Bu}^i)\}(\text{HOEt})_2(\text{THF})]$  (average 2.30 Å),<sup>64</sup> but compare well with that of  $[(\text{C}_5\text{Me}_5)\text{Ca}(\text{O-2,6-Pr}^i\text{-C}_6\text{H}_3)(\text{THF})_3]$  [Ca–OAr, 2.177(2) Å].<sup>65</sup> As expected, the Ca–O (bridging aryloxy) bond distances in **1-Ca** are longer than those involving terminal oxygen atoms; they range between 2.2488(15) and 2.3170(16) Å and are shorter than in  $[\text{Ca}_2(\text{tmdh})_4(\text{OAr})_4(\text{HOEt})_2]$  (2.332(3)–2.408(3) Å).<sup>63</sup> The Ca–N distances for the nitrogens linking the two aryl groups [Ca(1)–N(1), 2.5115(19) Å; Ca(2)–N(4), 2.4981(19) Å] are shorter than those for the sidearm nitrogens [Ca(1)–N(32), 2.551(2) Å; Ca(2)–N(62), 2.552(2) Å], confirming weaker bonding in the latter case; the former ones are comparable to those

**Table 2** Selected dimensions in compound **7**. Bond lengths are in Ångstroms, angles in degrees. E.s.d.s are in parentheses

(a) About the calcium atom			
Ca–O(1)	2.2229(18)	O(1)–Ca–O(3)	91.02(7)
Ca–O(3)	2.3369(19)	O(1)–Ca–N(2)	74.08(7)
Ca–N(2)	2.479(2)	O(3)–Ca–N(2)	85.83(8)

described above for  $[\text{Ca}\{\text{salen}(\text{Bu}^i)\}(\text{HOEt})_2(\text{THF})]$ .<sup>64</sup> There is disorder in both of the  $\text{CH}_2\text{-NMe}_2$  fragments; alternative sites for the  $\text{CH}_2$  and  $\text{CH}_3$  units were found and refined satisfactorily. In non-coordinating solvents (benzene, toluene, dichloromethane), there is no indication that **1-Ca** does not retain its dimeric structure.

After recrystallisation in toluene/light petroleum at  $-26^\circ\text{C}$ , single crystals of **7** were isolated as pale yellow square prisms. The X-ray crystal structure of **7** (Fig. 3) displays a centrosymmetric, slightly distorted octahedral arrangement around the metal; the pairs of oxygen atoms and nitrogen atoms of the Schiff-base ligands are located in mutually *trans* positions about the centre of symmetry. Selected bond lengths and angles are in Table 2.



**Fig. 3** A molecule of  $\{2\text{-Bu}^i\text{-6-(C}_6\text{F}_5\text{-N=CH)C}_6\text{H}_3\text{O}\}_2\text{Ca}(\text{THF})_2$  (**7**) with thermal ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity.

The coordinated THF molecules were disordered; alternative sites for a  $\beta$ -carbon atom of the THF were identified and refined satisfactorily. The Ca–OAr bond distance in complex **7** [Ca–O(1), 2.223(2) Å] is slightly longer than the analogous distance observed in **1-Ca** and in  $[(\text{C}_5\text{Me}_5)\text{Ca}(\text{O}-2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)(\text{THF})_3]$  [Ca–OAr, 2.177(2) Å],<sup>65</sup> but shorter than in the related complex reported previously  $[\text{Ca}(\text{salen}(\text{Bu}^i))(\text{HOEt})_2(\text{THF})]$  where the Ca–O(aryloxide) bond length is on average 2.30 Å.<sup>64</sup> The Ca–O(THF) bond distance in **7** [Ca–O(3), 2.337(2) Å] is significantly shorter than the corresponding distances in  $[(\text{C}_5\text{Me}_5)\text{Ca}\{\text{O}-2,6\text{-Pr}^i_2\text{-C}_6\text{H}_3\}(\text{THF})_3]$  [2.466(3), 2.408(3), 2.454(2) Å] and  $[\text{Ca}\{\text{salen}(\text{Bu}^i)\}(\text{HOEt})_2(\text{THF})]$  [2.390(2) Å]. The Ca–N bond length in **7** [Ca–N(2), 2.479(2) Å] compares well to that of the salen complex (average 2.52 Å) and **1-Ca**, but is considerably shorter than in the dimer  $[\text{Ca}_2(\text{tmdh})_4(\text{OAr})_4(\text{HOEt})_2]$  [Ca–N, 2.706(4)–2.746(4) Å].<sup>65</sup> Finally, the chelate bite-angle in **7** (O(1)–Ca–N(2), 74.08(7)°) is only slightly different from the equivalent angle in  $[\text{Ca}\{\text{salen}(\text{Bu}^i)\}(\text{HOEt})_2(\text{THF})]$  (71.79(18) and 72.34(18)°).<sup>64</sup>

Complex **2-Ti** crystallised as very pale yellow cube-like blocks from a concentrated solution in  $\text{Et}_2\text{O}$  stored at  $-26^\circ\text{C}$ . The

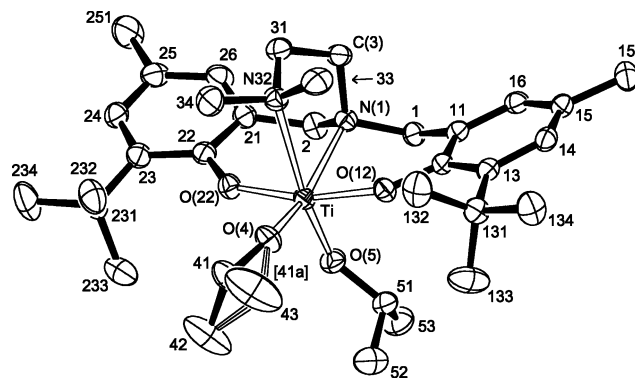
**Table 3** Selected dimensions in compound **2-Ti**. Bond lengths are in Ångstroms, angles in degrees. E.s.d.s are in parentheses

(a) About the titanium atom			
Ti–N(1)	2.335(2)	Ti–N(32)	2.400(2)
Ti–O(12)	1.9034(15)	Ti–O(4)	1.8025(17)
Ti–O(22)	1.9009(15)	Ti–O(5)	1.8321(17)
O(12)–Ti–N(1)	82.23(7)	O(5)–Ti–O(12)	92.68(7)
O(22)–Ti–N(1)	83.82(7)	O(22)–Ti–N(32)	84.24(7)
N(1)–Ti–N(32)	74.44(7)	O(4)–Ti–O(22)	97.37(7)
O(4)–Ti–N(1)	163.36(8)	O(5)–Ti–O(22)	92.12(7)
O(5)–Ti–N(1)	90.51(7)	O(4)–Ti–N(32)	89.13(7)
O(22)–Ti–O(12)	165.27(7)	O(5)–Ti–N(32)	164.79(8)
O(12)–Ti–N(32)	87.51(7)	O(4)–Ti–O(5)	106.00(8)
O(4)–Ti–O(12)	94.67(7)		

(b) In the O <sup>i</sup> Pr <sup>−</sup> ligands			
O(4)–C(41)	1.407(4)	C(41)–O(4)–Ti	162.8(2)
O(4)–C(41A)	1.429(11)	C(41A)–O(4)–Ti	147.1(6)
O(5)–C(51)	1.418(3)	C(51)–O(5)–Ti	135.95(15)

titanium atom is six-coordinate, with an octahedral coordination pattern (Fig. 4). A selection of bond lengths and angles is given in Table 3. One of the isopropyl groups is disordered, with two possible orientations, while the rest of the structure is well ordered. In the ONNO ligand, the two oxygen atoms are mutually *trans* about the Ti atom, whereas each of the nitrogen atoms is *trans* to an isopropoxide ligand. The orientation of the ligands around the metal is identical to that of  $\text{Ti}(\text{OPr}^i)_2\{\text{Me}_2\text{NC}_2\text{H}_4\text{N}(\text{CH}_2\text{-3,5-Me}_2\text{C}_6\text{H}_2\text{O-2})_2\}$ ,<sup>66</sup> and all the distances from the metal to the nitrogen and oxygen atoms [Ti–OAr average 1.902(2) Å; Ti–OPr<sup>i</sup> average 1.82(2) Å; Ti–N(32) 2.400(2) Å; Ti–N(1) 2.335(2) Å] are also very similar.

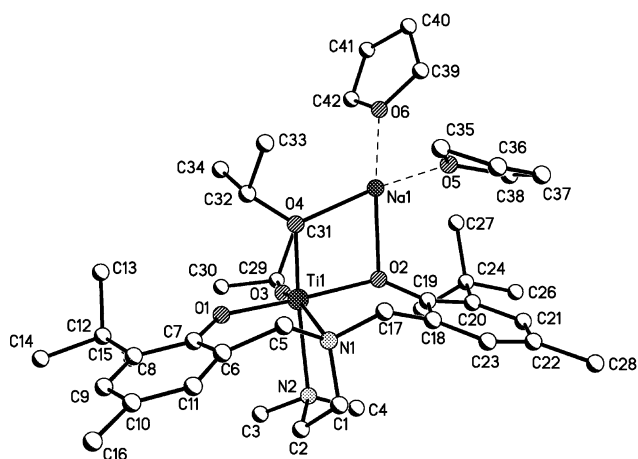


**Fig. 4** View of a molecule of  $\text{Ti}[\text{N}\{\text{CH}_2\text{-2-O-3-Bu}^i\text{-5-Me-C}_6\text{H}_2\}_2\text{-}\{\text{CH}_2\text{CH}_2\text{NMe}_2\}](\text{OPr}^i)_2$  (**2-Ti**). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Suitable red/green dichroic block-like crystals of complex **8** for X-ray analysis were obtained by recrystallisation from light petroleum at  $-26^\circ\text{C}$ , and the X-ray structure of the complex was determined (Fig. 5). Selected bond lengths and angles are collected in Table 4. There are two very similar, independent molecules in the crystal. Atoms of molecule 1 are numbered as in Fig. 4 but with a suffix “1”, e.g. Ti(11), O(11) etc.; atoms of molecule 2 have the suffix “2”, e.g. Ti(12), O(12) etc. The only significant difference between the molecules is in the orientation of the THF ligands. It can be seen from Fig. 5 that the titanium atom in **8** is six-coordinate, with a distorted octahedral arrangement and the same ligand orientations as in **2-Ti**. However, two oxygen atoms (one from an aryloxide and one from an isopropoxide

**Table 4** Selected dimensions in compound **8**. Bond lengths are in Ångstroms, angles in degrees. E.s.d.s are in parentheses

(a) About the Ti atoms			
Ti(11)–N(11)	2.354(5)	Ti(12)–N(12)	2.359(5)
Ti(11)–N(21)	2.413(5)	Ti(12)–N(22)	2.409(6)
Ti(11)–O(11)	2.013(4)	Ti(12)–O(12)	2.001(5)
Ti(11)–O(21)	2.076(4)	Ti(12)–O(22)	2.085(4)
Ti(11)–O(31)	1.828(4)	Ti(12)–O(32)	1.821(4)
Ti(11)–O(41)	1.999(4)	Ti(12)–O(42)	2.000(4)
Ti(11)···Na(11)	3.313(3)	Ti(12)···Na(12)	3.320(3)
N(11)–Ti(11)–N(21)	73.70(18)	N(12)–Ti(12)–N(22)	73.95(18)
O(11)–Ti(11)–N(11)	84.07(17)	O(12)–Ti(12)–N(12)	83.97(18)
O(21)–Ti(11)–N(11)	83.68(16)	O(22)–Ti(12)–N(12)	84.14(17)
O(31)–Ti(11)–N(11)	160.34(19)	O(32)–Ti(12)–N(12)	160.6(2)
O(41)–Ti(11)–N(11)	89.88(17)	O(42)–Ti(12)–N(12)	90.31(17)
O(11)–Ti(11)–N(21)	88.23(19)	O(12)–Ti(12)–N(22)	88.58(19)
O(21)–Ti(11)–N(21)	96.65(19)	O(22)–Ti(12)–N(22)	95.83(19)
O(31)–Ti(11)–N(21)	87.01(19)	O(32)–Ti(12)–N(22)	86.9(2)
O(41)–Ti(11)–N(21)	163.57(18)	O(42)–Ti(12)–N(22)	164.25(18)
O(11)–Ti(11)–O(21)	164.97(17)	O(12)–Ti(12)–O(22)	165.65(18)
O(31)–Ti(11)–O(11)	99.42(18)	O(32)–Ti(12)–O(12)	99.0(2)
O(41)–Ti(11)–O(11)	89.44(17)	O(42)–Ti(12)–O(12)	89.75(18)
O(31)–Ti(11)–O(21)	95.04(17)	O(32)–Ti(12)–O(22)	94.86(19)
O(41)–Ti(11)–O(21)	81.85(17)	O(42)–Ti(12)–O(22)	82.30(18)
O(31)–Ti(11)–O(41)	109.41(18)	O(32)–Ti(12)–O(42)	108.80(19)
(b) About the Na atoms			
Na(11)–O(21)	2.293(5)	O(22)–Na(12)	2.300(5)
Na(11)–O(41)	2.186(4)	Na(12)–O(42)	2.208(5)
Na(11)–O(51)	2.312(6)	Na(12)–O(52)	2.315(6)
Na(11)–O(61)	2.291(6)	Na(12)–O(62)	2.310(6)
O(41)–Na(11)–O(21)	73.12(17)	O(42)–Na(12)–O(22)	73.19(17)
O(21)–Na(11)–O(51)	108.8(2)	O(22)–Na(12)–O(52)	107.2(2)
O(61)–Na(11)–O(21)	137.5(2)	O(22)–Na(12)–O(62)	140.1(2)
O(41)–Na(11)–O(51)	123.3(2)	O(42)–Na(12)–O(52)	122.0(2)
O(41)–Na(11)–O(61)	121.4(2)	O(42)–Na(12)–O(62)	116.7(2)
O(61)–Na(11)–O(51)	95.5(2)	O(62)–Na(12)–O(52)	99.2(2)
Ti(11)–O(21)–Na(11)	98.5(2)	Ti(12)–O(22)–Na(12)	98.3(2)
Ti(11)–O(41)–Na(11)	104.6(2)	Ti(12)–O(42)–Na(12)	104.1(2)
(c) In the O <sup>i</sup> Pr <sup>−</sup> ligands			
C(291)–O(31)–Ti(11)	170.3(4)	C(292)–O(32)–Ti(12)	172.2(5)
C(321)–O(41)–Ti(11)	128.1(4)	C(322)–O(42)–Ti(12)	127.6(4)
C(321)–O(41)–Na(11)	124.5(4)	C(322)–O(42)–Na(12)	124.9(4)

**Fig. 5** View of one of the two very similar molecules of  $[\text{Ti}\{\text{N}[\text{CH}_2\text{-}2\text{-O-3-Bu}^1\text{-5-Me-C}_6\text{H}_2\text{]}_2\{\text{CH}_2\text{CH}_2\text{NMe}_2\}]\{\text{OPr}^i\}_2][\text{Na}(\text{THF})_2]$  (**8**). Hydrogen atoms are omitted for clarity.

ligand) are also involved in oxygen bridges between the sodium and titanium atoms. The sodium atom is four-coordinate, with two coordinated THF molecules added to the bridging oxygen atoms. The titanium–nitrogen bond lengths in **8** [mean of Ti(11)–

N(11) and Ti(12)–N(12) = 2.357(3) Å; mean of the Ti(1)–N(2) bonds = 2.411(2) Å] are very similar to those in the neutral Ti(IV) complex **2-Ti**. On the other hand, the titanium–oxygen distances Ti(11)–OAr [mean of Ti(1)–O(1) and Ti(1)–O(2) type bonds = 2.007(6) and 2.081(5) Å] and Ti(11)–OPr<sup>i</sup> [mean of Ti(1)–O(3) and Ti(1)–O(4) bonds = 1.825(4) and 2.000(1) Å] in **8** are noticeably longer than the corresponding bond lengths in **2-Ti**. The short Ti–O bond lengths in **2-Ti** are characteristic of significant  $\pi$ -bonding, while the presence of the extra electron in the Ti(III) species **8** reduces the extent of the  $\pi$ -bonding, thus resulting in longer Ti–O distances. This is corroborated by a much wider Ti–O–C angle in **8** in the case of the terminal OPr<sup>i</sup> ligand [mean Ti(1)–O(3)–C(29) is 171.3(10)° in **8** against Ti–O(4)–C(41A) 147.1(6)° and Ti–O(5)–C(51) 135.95(15)° in **2-Ti**]. The Ti–O bonds bridging to Na are significantly longer than terminal Ti–O bonds. All Ti–O and Na–O distances compare well with those reported for Ti{OC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>–2,6}<sub>4</sub>Na(THF)<sub>2</sub>.<sup>67</sup>

### Polymerisation studies

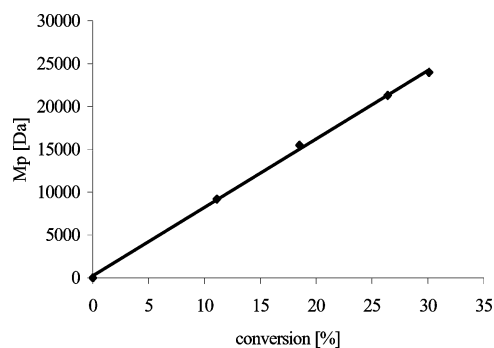
The efficiency of **1-Zn**, **1-Mg**, **1-Ca**, **7**, **1-Ti**, **2-Ti** and **8** as initiators for the ring-opening polymerisation of CL was assessed. The results are given in Table 5. Complexes of **1**<sup>2−</sup>, *i.e.* **1-Zn**, **1-Mg** and **1-Ca**, exhibited remarkably different behaviours under

**Table 5** CL polymerisation data<sup>a</sup>

Entry	Initiator	Time/h	Conversion/mol%	$M\bar{I}_w$ /Da	$M\bar{I}_w/M\bar{I}_n$	$M\bar{I}_p$ /Da
1	<b>1-Zn</b>	24	Trace	—	—	—
2	<b>1-Mg</b>	24	5.0	—	—	—
3	{ <b>1-Ca</b> } <sub>2</sub>	1	12.6	11 300	1.1	11 800
4	{ <b>1-Ca</b> } <sub>2</sub>	4	22.2	17 500	1.2	15 500
5	{ <b>1-Ca</b> } <sub>2</sub>	7	29.8	20 000	1.2	19 300
6	{ <b>1-Ca</b> } <sub>2</sub>	12	40.1	26 000	1.3	24 000
7	<b>7</b>	24	Trace	—	—	—
8	<b>1-Ti</b>	4	Trace	—	—	—
9	<b>2-Ti</b>	4	Trace	—	—	—
10	<b>8</b>	0.5	52.0	22 500	2.3	—
11	<b>8</b>	1	91.1	28 500	1.6	—
12	<b>8</b>	2	97.4	32 000	2.5	—
13	<b>2-Ti/8</b>	4	23.6	—	Multimodal	—

<sup>a</sup> Polymerisation conditions: 40 ml of toluene, 60 °C, CL/initiator = 200 : 1, 85 μmol of initiator.

rigorously identical polymerisation conditions. While **1-Zn** yielded only traces of polymer and **1-Mg** afforded only a 5.0% conversion of 200 equivalents of monomer after 24 hours, **1-Ca** was much more active, with a conversion of 12.6% after 1 h (run 3) and more than 40% after 12 h (run 6) to give  $M\bar{I}_w$  values of up to 26 000 Da. The polydispersity index was initially close to 1.0 but increased with the conversion and eventually reached 1.3; this coincided with the formation of a shoulder next to the main peak in the gel permeation chromatography traces. Such broadening of the molecular weight distribution is indicative of back-biting and transesterification processes. The possibility of a living polymerisation mechanism suggested by the initial  $M\bar{I}_w/M\bar{I}_n$  value was not corroborated by the non-linear  $M\bar{I}_n$ -to-conversion relationship; however, if one takes into account the broadening of the polydispersity and considers the molecular weight at the peak  $M\bar{I}_p$  instead of  $M\bar{I}_w$ , then a perfectly linear relationship is obtained (Fig. 6). The reactivity order Ca >> Mg >> Zn possibly reflects a decrease of the Lewis acidity of the metal centre from Ca to Zn, and has already been documented for LA-polymerisation.<sup>45</sup> It is not clear at this stage why complex **7**, where CL substrate binding should, if anything, be easier than in **1-Ca**, was catalytically inactive (run 7).



**Fig. 6** Relationship between  $M\bar{I}_p$  and monomer conversion for the polymerisation of CL promoted by **1-Ca**.

The coordinatively saturated titanium(IV) complexes **1-Ti** and **2-Ti** did not produce significant amounts of polymer (runs 8–9). By contrast, the zwitterionic complex **8** achieved almost complete

conversion of 200 equivalents of monomer over 2 h (runs 11–12). The polymers obtained with **8** had narrow polydispersities and  $M\bar{I}_w$  of up to 32 000 Da. However, no direct correlation could be found between molecular weight and conversion in this case.

## Conclusion

Several coordination complexes of magnesium, calcium, zinc and titanium supported by bulky amino-bis(phenolate) and iminophenolate ligands are described. The dimeric calcium amino-bis(phenolate) [Ca{Me<sub>2</sub>NC<sub>2</sub>H<sub>4</sub>N(CH<sub>2</sub>-3,5-Bu<sup>t</sup>C<sub>6</sub>H<sub>2</sub>O-2)<sub>2</sub>}<sub>2</sub>] (**1-Ca**) displays a very unusual case of a Ca...H-C agostic interaction and acts as an efficient initiator for CL-polymerisation. For complexes supported by identical ligands, activity for the polymerisation of ε-caprolactone decreases in the series Ca >> Mg >> Zn. The comparison of related octahedral Ti(III) and Ti(IV) alkoxo complexes bearing the same ancillary ligand shows that only the zwitterionic Ti(III) derivative is catalytically active. The polymerisations with **1-Ca** are well controlled, with narrow molecular weight distributions and a linear increase of the peak molecular weight with conversion.

## Experimental

### Generalities

All manipulations were performed under dry argon, using standard Schlenk techniques. Solvents were pre-dried over sodium wire (toluene, light petroleum, THF, diethyl ether) or calcium hydride (dichloromethane), and distilled under argon over sodium (toluene), sodium-potassium alloy (light petroleum, bp 40–60 °C), sodium-benzophenone (THF, diethyl ether) or calcium hydride (dichloromethane). Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze-thaw cycles. *N,N*-Dimethylethylenediamine, formaldehyde (37% aqueous solution), 2-Bu<sup>t</sup>-C<sub>6</sub>H<sub>4</sub>OH, CaI<sub>2</sub> and MgBu<sub>2</sub> (1.0 solution in heptane) were used as purchased (Aldrich). Ti(OPr<sup>i</sup>)<sub>4</sub> was distilled under vacuum and kept over activated molecular sieves prior to use. The amino-bis(phenol) **1-H**<sup>59</sup> and the phenoxy-imine **3-H**<sup>60</sup> ligand precursors, as well as zinc bis[bis(trimethylsilyl)amide]<sup>68</sup>

(4) and 1-Ti<sup>58</sup> were prepared according to literature methods. ε-Caprolactone was dried for a minimum of 24 hours over fresh calcium hydride, then distilled under vacuum and used immediately. NMR spectra were recorded using a Bruker DPX300 spectrometer. <sup>1</sup>H NMR spectra (300.1 MHz) were referenced to the residual solvent proton of the deuterated solvent used. <sup>13</sup>C NMR spectra (75.5 MHz) were referenced internally to the D-coupled <sup>13</sup>C resonances of the NMR solvent. Gel permeation chromatography (GPC) measurements were performed on a Polymer Laboratories PL-GPC 220 instrument equipped with a PLgel 5 Å MIXED-C column and a refractive index detector. The GPC column was eluted with THF at 40 °C at 1 ml min<sup>-1</sup> and was calibrated using 9 monodisperse polystyrene standards in the range 580–1 000 000 Da.

## Preparations

**Synthesis of Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>N-[CH<sub>2</sub>-2-HO-3-Bu<sup>1</sup>-5-Me-C<sub>6</sub>H<sub>2</sub>]<sub>2</sub>, 2-H<sub>2</sub>.** *N,N*-Dimethylethylenediamine (3.4 ml, 31.0 mmol) and formaldehyde (37% solution in water, 4.6 ml, 61.0 mmol) were sequentially added to a solution of 2-Bu<sup>1</sup>-4-Me-C<sub>6</sub>H<sub>3</sub>OH (10.0 g, 66.6 mmol) in methanol. The pale yellow solution was refluxed for 16 hours. Upon cooling, a white precipitate formed, which was isolated by filtration, washed with ice-cold methanol (3 × 20 ml) and dried *in vacuo* for 2 hours to yield a fine white powder (8.90 g, 66%). Anal. Calcd for C<sub>28</sub>H<sub>44</sub>N<sub>2</sub>O<sub>2</sub>: C 76.32, H 10.06, N 6.36. Found: C 76.41, H 10.20, N 6.15%. <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>, 25 °C): δ 9.66 (s, 2 H, OH), 6.95 (s, 2 H, Ar), 6.68 (s, 2 H, Ar), 3.53 (s, 4 H, Ar-CH<sub>2</sub>-N), 2.53 (s, 4 H, N-CH<sub>2</sub>-CH<sub>2</sub>-NMe<sub>2</sub>), 2.26 (s, 6 H, Ar-Me), 2.20 (s, 6 H, NMe<sub>2</sub>), 1.35 (s, 18 H, CMe<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (75.5 MHz, CDCl<sub>3</sub>, 25 °C): δ 153.8 (C-O), 137.7, 129.0, 127.2, 126.8, 121.4 (all Ar), 56.5 (ArCH<sub>2</sub>), 56.2 (CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>), 48.9 (CH<sub>2</sub>NMe<sub>2</sub>), 44.7 (NMe<sub>2</sub>), 34.7 (CMe<sub>3</sub>), 29.8 (CMe<sub>3</sub>), 20.8 (Ar-CH<sub>3</sub>).

**Synthesis of [Mg{N(SiMe<sub>3</sub>)<sub>2</sub>}]<sub>2</sub> (5).** The method for the synthesis of **5** was adapted from the literature.<sup>69</sup> MgBu<sub>2</sub> (5.0 ml of solution 1.0 M in heptane, 5.0 mmol) was added to 50 ml of neat HN(SiMe<sub>3</sub>)<sub>2</sub> in the absence of co-solvent. The reaction mixture was stirred at 70 °C for 24 h, after which time the large excess of amine was removed *in vacuo* (0.01 mm Hg) to afford a very clean white powder. Comparison of the <sup>1</sup>H NMR data with values reported elsewhere in the literature<sup>70</sup> indicated that the dimeric {Mg[N(SiMe<sub>3</sub>)<sub>2</sub>]}<sub>2</sub> had been isolated. Yield 1.64 g (95%).

**Synthesis of Ca{N(SiMe<sub>3</sub>)<sub>2</sub>}(THF)<sub>2</sub> (6).** The procedure for the preparation of Ca{N(SiMe<sub>3</sub>)<sub>2</sub>}(THF)<sub>2</sub> was adapted from the literature.<sup>71</sup> Freshly prepared NaN(SiMe<sub>3</sub>)<sub>2</sub> (22.0 g, 120 mmol) was dissolved in THF (175 ml) and cooled to -78 °C, and CaI<sub>2</sub> (16.1 g, 54.8 mmol) was added rapidly. The reaction mixture was allowed to warm slowly to room temperature, and then refluxed overnight. THF was removed under vacuum, and the product was separated from NaI by extraction with 2 × 150 ml of light petroleum. The resulting slightly yellow solution was concentrated to 50 ml, and a large amount of white crystals was obtained by recrystallisation at -26 °C. The spectroscopic data of the isolated material matched perfectly those reported in the literature for Ca{N(SiMe<sub>3</sub>)<sub>2</sub>}(THF)<sub>2</sub>.<sup>70</sup> Isolated yield 25.2 g (91%).

**Synthesis of Zn{Me<sub>2</sub>NC<sub>2</sub>H<sub>4</sub>N(CH<sub>2</sub>-3,5-Bu<sup>1</sup>-C<sub>6</sub>H<sub>2</sub>O-2)}<sub>2</sub> (1-Zn).** Zn[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (1.26 g, 3.26 mmol) was rapidly added to a solution of 1-H<sub>2</sub> (1.71 g, 3.26 mmol) in light petroleum. The resulting colourless solution was stirred at room temperature for 16 h, after which time a white precipitate had formed. The supernatant was filtered off. The remaining white solid was washed with light petroleum (8 ml) and dried under vacuum to afford a fine white powder, yield 1.45 g (76%). Anal. Calcd for C<sub>34</sub>H<sub>54</sub>O<sub>2</sub>N<sub>2</sub>Zn: C 69.43, H 9.25, N 4.76. Found: C 69.81, H 9.39, N 4.46%. <sup>1</sup>H NMR (300.1 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 7.60 (d, 2 H, J<sub>HH</sub> = 2.5 Hz, Ar), 6.87 (d, 2 H, J<sub>HH</sub> = 2.5 Hz, Ar), 3.76 (d, 2 H, J<sub>HH</sub> = 12.4 Hz, Ar-CH(H)-N), 3.16 (d, 2 H, J<sub>HH</sub> = 12.4 Hz, Ar-CH(H)-N), 2.15 (m, 2 H, CH<sub>2</sub>NMe<sub>2</sub>), 1.79 (s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>), 1.61 (m, 2 H, CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>), 1.48 (s, 6 H, NMe<sub>2</sub>), 1.44 (s, 18 H, CMe<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (75.5 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 164.5 (C-O), 138.9, 136.4, 126.3, 124.6, 122.3 (all Ar), 60.1 (ArCH<sub>2</sub>), 59.0 (CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>), 48.2 (CH<sub>2</sub>NMe<sub>2</sub>), 46.4 (NMe<sub>2</sub>), 35.4 (CMe<sub>3</sub>), 34.1 (CMe<sub>3</sub>), 32.2 (CMe<sub>3</sub>), 30.0 (CMe<sub>3</sub>).

**Synthesis of Mg{Me<sub>2</sub>NC<sub>2</sub>H<sub>4</sub>N(CH<sub>2</sub>-3,5-Bu<sup>1</sup>-C<sub>6</sub>H<sub>2</sub>O-2)}<sub>2</sub> (1-Mg).** A solution of 1-H<sub>2</sub> (1.51 g, 2.88 mmol) in toluene (20 ml) was added over 5 min to a solution of **5** (0.97 g, 1.40 mmol) in toluene (30 ml). The resulting colourless solution was stirred for 48 h at room temperature. The volatiles were removed *in vacuo*, yielding a white powder. After washing with light petroleum (10 ml), recrystallisation from 15 ml of toluene at -26 °C afforded a colourless crystalline solid, yield 0.99 g (63%). Anal. Calcd for C<sub>34</sub>H<sub>54</sub>O<sub>2</sub>N<sub>2</sub>Mg: C 74.64, H 9.95, N 5.12. Found: C 74.16, H 9.64, N 4.90%. <sup>1</sup>H NMR (300.1 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 7.53 (dd, 2 H, J<sub>HH</sub> = 2.5 and 5.2 Hz, Ar), 7.06 (d, 1 H, J<sub>HH</sub> = 2.5 Hz, Ar), 6.88 (d, 1 H, J<sub>HH</sub> = 2.5 Hz, Ar), 4.68 (m, 2 H, Ar-CH(H)-N), 2.98 (d, 1 H, J<sub>HH</sub> = 13.1 Hz, Ar-CH(H)-N), 2.75–2.48 (br, 2 H, CH<sub>2</sub>NMe<sub>2</sub>), 2.54 (d, 1 H, J<sub>HH</sub> = 12.1 Hz, Ar-CH(H)-N), 1.80–1.05 (br, 2 H, CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>), 1.69 (s, 9 H, CMe<sub>3</sub>), 1.55 (br s, 6 H, NMe<sub>2</sub>), 1.43 (s, 18 H, CMe<sub>3</sub>), 1.29 (s, 9 H, CMe<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (75.5 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 164.6 (C-O), 160.1 (C-O), 139.4, 137.5, 136.6, 133.7, 128.8, 126.4, 125.8, 125.1, 124.6, 122.6 (all Ar), 66.2 (ArCH<sub>2</sub>), 65.0 (ArCH<sub>2</sub>), 60.4 (CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>), 48.8 (CH<sub>2</sub>NMe<sub>2</sub>), 47.9 (NMe), 47.7 (NMe), 35.8 (CMe<sub>3</sub>), 35.5 (CMe<sub>3</sub>), 34.3 (CMe<sub>3</sub>), 34.2 (CMe<sub>3</sub>), 33.1 (CMe<sub>3</sub>), 32.5 (CMe<sub>3</sub>), 32.3 (CMe<sub>3</sub>), 30.7 (CMe<sub>3</sub>).

**Synthesis of [Ca{Me<sub>2</sub>NC<sub>2</sub>H<sub>4</sub>N(CH<sub>2</sub>-3,5-Bu<sup>1</sup>-C<sub>6</sub>H<sub>2</sub>O-2)}<sub>2</sub>]<sub>2</sub> (1-Ca).** A solution of 1-H<sub>2</sub> (1.15 g, 2.19 mmol) in toluene (20 ml) was added over 5 min to a solution of **6** (1.14 g, 2.26 mmol) in toluene (30 ml). The resulting colourless solution was stirred for 48 h at room temperature. The volatiles were removed *in vacuo*, yielding a white powder which was washed with light petroleum (5 × 10 ml), yield 0.93 g (75%). NMR and elemental analyses were performed at this point. Recrystallisation from Et<sub>2</sub>O/light petroleum (10:3) at +6 °C over a period of several days afforded a large amount of colourless crystals of 1-Ca-Et<sub>2</sub>O suitable for X-ray diffraction. Anal. Calcd for C<sub>68</sub>H<sub>108</sub>O<sub>4</sub>N<sub>4</sub>Ca<sub>2</sub>: C 72.55, H 9.67, N 4.98. Found: C 72.94, H 9.42, N 4.41%. <sup>1</sup>H NMR (300.1 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 7.48 (d, 4 H, J<sub>HH</sub> = 2.5 Hz, Ar), 7.09 (d, 4 H, J<sub>HH</sub> = 2.5 Hz, Ar), 5.19 (d, 2 H, J<sub>HH</sub> = 12.4 Hz, Ar-CH(H)-N), 4.62 (d, 2 H, J<sub>HH</sub> = 12.0 Hz, Ar-CH(H)-N), 3.03 (d, 2 H, J<sub>HH</sub> = 12.0 Hz, Ar-CH(H)-N), 2.94 (d, 2 H, J<sub>HH</sub> = 12.4 Hz, Ar-CH(H)-N), 2.41 (br, 4 H, CH<sub>2</sub>NMe<sub>2</sub>), 1.72 (br, 4 H, CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>),

1.58 (s, 18 H, CMe<sub>3</sub>), 1.46 (m, 36 H, CMe<sub>3</sub>), 1.41 (s, 18 H, CMe<sub>3</sub>), 1.37 (m, 6 H, NMe), 1.30 (m, 6 H, NMe). <sup>13</sup>C {<sup>1</sup>H} NMR (75.5 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 165.4 (C–O), 160.9 (C–O), 137.6, 136.4, 135.6, 133.2, 127.3, 126.5, 125.6, 124.5, 124.0, 123.4 (all Ar), 65.8 (ArCH<sub>2</sub>), 64.0 (ArCH<sub>2</sub>), 59.6 (CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>), 48.3 (CH<sub>2</sub>NMe<sub>2</sub>), 45.1 (NMe), 44.6 (NMe), 35.4 (CMe<sub>3</sub>), 35.0 (CMe<sub>3</sub>), 34.4 (CMe<sub>3</sub>), 34.3 (CMe<sub>3</sub>), 32.6 (CMe<sub>3</sub>), 32.4 (CMe<sub>3</sub>), 32.1 (CMe<sub>3</sub>), 30.2 (CMe<sub>3</sub>).

**Synthesis of {2-Bu<sup>1</sup>-6-(C<sub>6</sub>F<sub>5</sub>N=CH)C<sub>6</sub>H<sub>3</sub>O}<sub>2</sub>Ca(THF)<sub>2</sub>·(C<sub>7</sub>H<sub>8</sub>)<sub>2/3</sub> (7).** A solution of **3-H** (1.87 g, 5.35 mmol) in light petroleum (20 ml) was added dropwise over 20 min at room temperature to a solution of **6** (2.83 g, 5.60 mmol) in light petroleum (20 ml). After stirring overnight, a yellow precipitate had formed. The filtrate was removed, yielding a yellow powder which was washed with 2 × 20 ml of light petroleum and dried *in vacuo*. Yield 1.51 g, 29% (relative to Ca). Single crystals suitable for X-ray diffraction crystallography were isolated by recrystallisation in a 4 : 1 toluene/light petroleum mixture at –26 °C. NMR characterisation, elemental analyses and the X-ray structure all indicated the presence of 2/3 molecule of toluene per metal centre. The toluene could not be removed, even upon heating up to 60 °C under vacuum (0.01 mm Hg). Anal. Calcd C<sub>42</sub>H<sub>42</sub>F<sub>10</sub>N<sub>2</sub>O<sub>4</sub>Ca·<sup>2</sup>/<sub>3</sub>C<sub>7</sub>H<sub>8</sub>: C 60.13; H 5.08; N 3.00. Found: C 59.58; H 5.08; N 2.97%. <sup>1</sup>H NMR (300.1 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 7.82 (s, 2 H, Ar–CH=N), 7.38 (d, 2 H, *J*<sub>HH</sub> = 7.3 Hz, Ar), 7.14–7.09 (m, C<sub>6</sub>H<sub>5</sub>–CH<sub>3</sub>), 6.99 (d, 2 H, *J*<sub>HH</sub> = 7.7 Hz, Ar), 6.50 (t, 2 H, *J*<sub>HH</sub> = 7.8 Hz, Ar), 3.56 (t, 8 H, *J*<sub>HH</sub> = 6.4 Hz, CH<sub>2</sub>CH<sub>2</sub>O), 2.09 (s, C<sub>6</sub>H<sub>5</sub>–CH<sub>3</sub>), 1.41 (s, 18 H, CMe<sub>3</sub>), 1.24 (m, 8 H, CH<sub>2</sub>CH<sub>2</sub>O). <sup>13</sup>C {<sup>1</sup>H} NMR (75.5 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 176.1 (Ar–CH=N), 172.3 (C–O), 141.1, 136.7, 133.2, 129.5, 122.0, 112.9 (all Ar), 69.1 (CH<sub>2</sub>CH<sub>2</sub>O), 35.3 (CMe<sub>3</sub>), 29.5 (CMe<sub>3</sub>), 25.4 (CH<sub>2</sub>CH<sub>2</sub>O). <sup>19</sup>F NMR (282.4 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ –154.1 (d, 4 F, *J*<sub>FF</sub> = 19.8 Hz, *o*-F), –163.1 (t, 2 F, *J*<sub>FF</sub> = 19.8 Hz, *p*-F), –163.5 (t, 4 F, *J*<sub>FF</sub> = 19.8 Hz, *m*-F).

**Synthesis of Ti(OPr<sup>i</sup>)<sub>2</sub>{Me<sub>2</sub>NC<sub>2</sub>H<sub>4</sub>N(CH<sub>2</sub>-3,5-Bu<sup>t</sup>C<sub>6</sub>H<sub>2</sub>O-2)<sub>2</sub>} (2-Ti).** Ti(OPr<sup>i</sup>)<sub>4</sub> (0.72 ml, 2.44 mmol) was added rapidly to a solution of **2-H<sub>2</sub>** (1.06 g, 2.40 mmol) in diethyl ether (20 ml), and the colour turned instantly bright yellow. The reaction mixture was stirred for 16 hours at room temperature, when a yellow precipitate had formed. The solid material was isolated by filtration and dried *in vacuo* to give a clean pale yellow powder. Yield 1.05 g (72%). Single crystals were obtained by recrystallisation from a diethyl ether solution at –26 °C. Anal. Calcd for C<sub>34</sub>H<sub>56</sub>N<sub>2</sub>O<sub>4</sub>Ti: C 67.53, H 9.33, N 4.63. Found: C 66.45, H 9.25, N 4.35%. <sup>1</sup>H NMR (300.1 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 7.26 (d, 2 H, *J*<sub>HH</sub> = 1.9 Hz, Ar), 6.71 (d, 2 H, *J*<sub>HH</sub> = 1.9 Hz, Ar), 5.21 (m, 1 H, O–CHMe<sub>2</sub>), 4.94 (m, 1 H, O–CHMe<sub>2</sub>), 4.23 (d, 2 H, *J*<sub>HH</sub> = 13.1 Hz, Ar–CH(H)–N), 2.96 (d, 2 H, *J*<sub>HH</sub> = 13.1 Hz, Ar–CH(H)–N), 2.33 (s, 6 H, Ar–CH<sub>3</sub>), 2.26 (m, 2 H, CH<sub>2</sub>NMe<sub>2</sub>), 2.08 (s, 6 H, NMe<sub>2</sub>), 1.80 (m, 2 H, CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>), 1.72 (s, 18 H, CMe<sub>3</sub>), 1.51 (d, 6 H, *J*<sub>HH</sub> = 6.0 Hz, OCHMe<sub>2</sub>), 1.06 (d, 6 H, *J*<sub>HH</sub> = 6.0 Hz, OCHMe<sub>2</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (75.5 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 161.1 (C<sub>ipso</sub>–O), 135.7, 125.3, 125.0 (all Ar), 77.4 (O–CHMe<sub>2</sub>), 77.3 (O–CHMe<sub>2</sub>), 65.1, 58.6, 52.3, 49.7, 35.3 (CMe<sub>3</sub>), 30.9 (CMe<sub>3</sub>), 27.2 (O–CHMe), 26.3 (O–CHMe), 21.1 (Ar–CH<sub>3</sub>).

**Synthesis of Ti(OPr<sup>i</sup>)<sub>2</sub>{Me<sub>2</sub>NC<sub>2</sub>H<sub>4</sub>N(CH<sub>2</sub>-3,5-Bu<sup>t</sup>C<sub>6</sub>H<sub>2</sub>O-2)<sub>2</sub>}Na(THF)<sub>2</sub>, 8.** THF (15 ml) was added at –78 °C to a freshly prepared sodium amalgam (mercury: 5.20 g, 25.9 mmol; sodium 0.05 g, 2.18 mmol). A solution of **2-Ti** (0.78 g, 1.29 mmol) in THF (50 ml) was cooled to –78 °C and added slowly to the Hg/Na amalgam. The colour changed rapidly from bright yellow to green. The mixture was allowed to warm to room temperature and was stirred overnight, when the colour gradually turned very dark green. The solution was filtered to remove the excess of Hg/Na, and the solvent was removed under vacuum to yield a green powder. Square-shaped, red/green dichroic X-ray quality crystals were grown by recrystallisation from a light petroleum solution stored at –26 °C. Yield 0.41 g (41%). Anal. Calcd for C<sub>42</sub>H<sub>72</sub>N<sub>2</sub>NaO<sub>6</sub>Ti: C 65.35, H 9.40, N 3.63. Found: C 64.86, H 9.42, N 3.71%. The paramagnetic nature of **8** precluded the acquisition of suitable NMR data.

### Polymerisation of ε-caprolactone

Polymerisations of ε-caprolactone were carried out in a Schlenk tube under inert gas. The flask was charged with the initiator in the glove-box and then attached to the vacuum line. The initiator was dissolved in the desired amount of toluene, and after temperature equilibration was ensured, CL was syringed in and the polymerisation time was measured from that point. Polymerisations were stopped by addition of a solution of acetic acid in methanol. The polymers were precipitated in methanol, filtered, and dissolved in THF. They were then re-precipitated in methanol, filtered again and dried *in vacuo* to constant weight.

### X-Ray crystallography

Crystals coated with perfluoropolyether oil or dry Nujol were mounted on glass fibres and fixed under a cold nitrogen stream. Intensity data for compound **7** were measured on a Rigaku R-Axis IIC image plate diffractometer equipped with a rotating-anode X-ray source (Mo-Kα radiation, λ = 0.71073 Å) and graphite monochromator, those for compounds **1-Ca**, **2-Ti** and **8** on a Nonius KappaCCD diffractometer equipped with Mo-Kα radiation and graphite monochromator.

All data were processed using the DENZO/SCALE-PACK programs.<sup>72</sup> The structures were determined by heavy atom methods (**2-Ti**) or direct methods in the SHELXS program<sup>73</sup> and refined by full-matrix least-squares methods, on *F*<sup>2</sup> values, in SHELXL.<sup>73</sup> The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealized positions, and their *U*<sub>iso</sub> values were set to ride on the *U*<sub>eq</sub> values of the parent carbon atoms. Scattering factors for neutral atoms were taken from reference 74. Crystal data and refinement details for the four complexes are collected in Table 6.

Computer programs used in these analyses have been noted above or in Table 4 of reference 75, and were run on a Silicon Graphics Indy at the University of East Anglia, or a DEC-AlphaStation 200 4/100 in the Biological Chemistry Department, John Innes Centre.

CCDC reference numbers 243644, 243645, 281712 and 281713.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b511851d

**Table 6** Crystal and structure refinement data for complexes **1-Ca**, **7**, **2-Ti** and **8**

Compound	1-Ca	7	2-Ti	8
Elemental formula	$C_{88}H_{108}Ca_{25}N_4O_4C_4H_{10}O$	$C_{42}H_{42}CaF_{10}N_2O_4 \cdot 2/3(C_7H_8)$	$C_{34}H_{56}N_2O_4Ti$	$C_{42}H_{72}N_2NaO_6Ti$
Formula weight	1199.9	930.3	604.7	771.9
Crystal system	Triclinic	Trigonal	Orthorhombic	Monoclinic
Space group	$P11$ (no. 2)	$R31$ (no. 148, hex. axes)	$Pbcm$ (no. 69)	$P2_1/c$ (no. 14)
$a/\text{\AA}$	9.7184(2)	28.728(4)	17.9796(4)	22.4176(4)
$b/\text{\AA}$	14.4919(2)	28.728(4)	16.7107(3)	15.6454(3)
$c/\text{\AA}$	27.3095(5)	13.871(3)	22.3627(4)	29.5745(6)
$a^\circ$	104.717(1)	90	90	90
$b^\circ$	90.064(1)	120	90	101.3821(7)
$\gamma^\circ$	105.413(1)	9914(3)	90	90
Cell volume, $V/\text{\AA}^3$	3576.51(11)	9	6718.9(2)	10168.7(3)
No. of formula units/cell, $Z$	2	9	8	8
$\rho_{\text{calc}}/\text{Mg m}^{-3}$	1.114	1.402	1.196	1.008
$F(000)$	1316	4350	2624	3352
Absorption coefficient, $\mu/\text{mm}^{-1}$	0.205	0.231	0.292	0.215
$T/\text{K}$	180(2)	140(2)	180(2)	180(2)
Crystal colour, shape	Colourless, block	Pale yellow, square prisms	Very pale yellow, cube-like blocks	Red/green, dichroic blocks
Crystal size/mm	$0.44 \times 0.42 \times 0.39$	$0.25 \times 0.10 \times 0.10$	$0.23 \times 0.14 \times 0.10$	$0.23 \times 0.12 \times 0.12$
Total no. of reflections measured (not including absences)	31350	18625	34498	42735
No. of unique reflections, and $R_{\text{int}}$ for equivalents	12430, 0.055	4044, 0.139	5924, 0.076	10744, 0.114
No. of 'observed' reflections ( $I > 2\sigma$ )	8912	2177	4482	6107
Data/restraints/parameters	12430/0/832	4044/0/301	5924/0/377	10744/0/937
Goodness-of-fit on $F^2$ , $S$	1.028	0.887	1.047	1.037
$R$ indices ('observed' data)	$R_1 = 0.052$ , $wR_2 = 0.110$	$R_1 = 0.053$ , $wR_2 = 0.124$	$R_1 = 0.050$ , $wR_2 = 0.111$	$R_1 = 0.087$ , $wR_2 = 0.223$
$R$ indices (all data)	$R_1 = 0.084$ , $wR_2 = 0.120$	$R_1 = 0.108$ , $wR_2 = 0.138$	$R_1 = 0.075$ , $wR_2 = 0.120$	$R_1 = 0.146$ , $wR_2 = 0.255$
Weighting parameters: $A$ , $B^a$	0.0445, 1.90	0.0686, 0	0.0498, 5.13	0.1434, 0
Largest diff. peak and hole/ $e \text{\AA}^{-3}$	0.27 and $-0.26$	0.64 and $-0.27$	0.28 and $-0.49$	0.69 and $-0.35$

<sup>a</sup> Reflection weighting scheme:  $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$  where  $P = (F_o^2 + 2F_c^2)/3$ .

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