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Aluminium, gallium and indium complexes supported by a chiral phenolato-prolinolato dianionic ligand

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Abstract: Congeneric complexes (S)-{O^ˆO}MCH₂SiMe₃ (M=Al, **3**; Ga, **5**; In, **6**) of the triel metals supported by an enantiomerically pure phenolato-alkoxo {O^ˆO}²⁻ dianionic tridentate ligand derived from prolinol, along with their chloro derivatives, have been prepared and characterised. The aluminium-alkyl species (S)-{O^ˆO}AlMe and **3** form four-coordinate complexes with slightly distorted tetrahedral geometries, whereas the geometry in the Lewis acidic five-coordinate (S)-{O^ˆO}GaCl·THF is a distorted trigonal bipyramid. These alkyl complexes do not react cleanly, if at all, with protic sources. The indium(III) compound **6**, which is for instance inert towards *i*PrOH or BnOH even after hours at 70°C, catalyses at 95°C the controlled, immortal ring-opening polymerisation of racemic lactide (up to 1000 equivalents) in the presence of excess BnOH as a chain transfer agent. It affords atactic, monodisperse polylactides with predictable molecular weights.

Keywords: aluminium; gallium; indium; phenolato-alkoxo ligand; ring-opening polymerisation (ROP).

Introduction

Dianionic tetradentate bis(phenolate)s derived from salen (Jacobsen, 1993; Atwood and Harvey, 2001; Cozzi, 2004; Katsuki, 2004; Larrow and Jacobsen, 2004; Baleizao and Garcia, 2006; Gupta and Sutar, 2008; Wezenberg and Kleij, 2008), salan (Atwood, 1997; Matsumoto et al., 2008) and salalen (Matsumoto et al., 2007) proteo-ligands (**A**, **B** and **C**, respectively, in Figure 1) constitute ubiquitous ligand platforms that are readily amenable to the tuning of their steric and electronic properties. As a result, they have been used in the past decades to generate a plethora of well-defined main-group and transition metal complexes. These have in turn been utilised for a variety of purposes, and have for instance demonstrated overall excellent performances as homogeneous catalysts in metal-mediated asymmetric organic transformations such as olefin epoxidation and polymerisations (Bellemin-Laponnaz and Dagonne, 2014). Of particular interest, unsymmetrical salen ligands, where the two salicylidene moieties bear different substituents, can feature original catalytic behaviour (Kleij, 2009). On the other hand, surprisingly little has been reported on the stabilisation of discrete complexes using mixed phenol/alcohol proteo-ligands bridged by amino or imino moieties (Figure 1D).

In 2009, our group reported (Alaaeddine et al., 2009) on aluminium compounds bearing an unsymmetrical fluorinated alkoxo-phenolato-diimino dianionic ligand that competently mediated the isoselective ($P_m = 0.87$) ring-opening polymerisation (ROP) of racemic lactide (Figure 2E). During the course of the work presented here, it was shown (Qian et al., 2014) that an ytterbium(III) ‘ate’ complex supported by two chiral phenolate/ α,α -diphenylalcoholate ligands $\{_{Ar}O^{\hat{N}}CPh_2^{\hat{O}}_{Alc}\}^-$ promoted the asymmetric epoxidation of α,β -unsaturated ketones with *ees* up to 99% (Figure 2F); excellent results were also obtained by mixing *in situ* the proteo-ligand with $[(Me_3Si)_2N]_3Ln(\mu-Cl)Li\cdot(THF)_3$ (Zeng et al., 2015). Moreover, related chiral tridentate, dianionic ligands $\{_{Ar}O^{\hat{N}}O_{Alc}\}^-$ have afforded zirconium precatalysts (Figure 2G) which display good performances in the asymmetric

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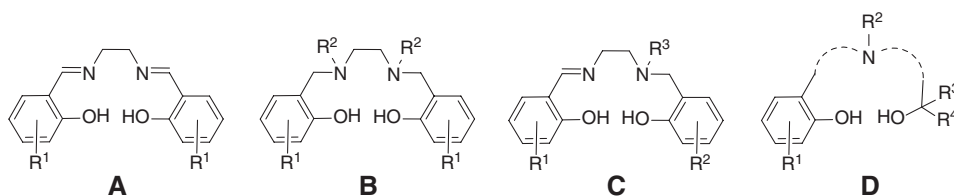


Figure 1: Examples of salen, salen, hemisalen and mixed phenol/alcohol proteo-ligands.

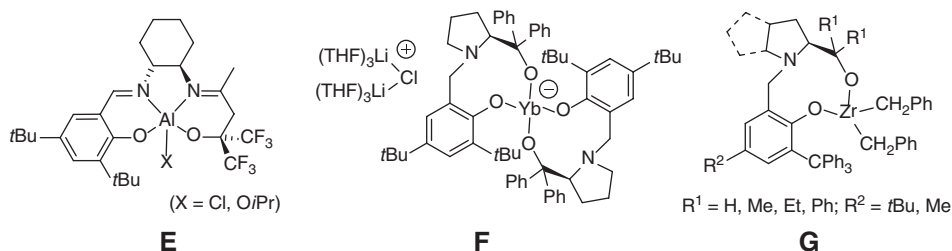


Figure 2: Examples of complexes bearing mixed phenolate/alcoholate dianionic ligands.

hydroamination of terminal aminoalkenes, with *ee* values reaching up to 94% (Zhou et al., 2015).

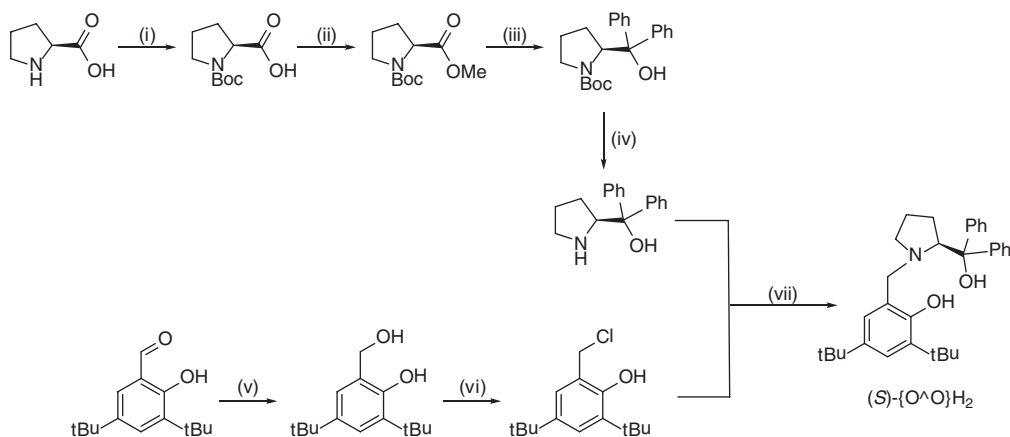
We have long maintained a keen interest in the implementation of the triel metals aluminium, gallium and indium in homogeneous catalysis. The ROP of cyclic esters is a field where aluminium-salen (Le Borgne et al., 1993; Ovitt and Coates, 1999, 2002; Nomura et al., 2002; Zhong et al., 2002, 2003; Majerska and Duda, 2004; Hormnirun et al., 2006; Nomura et al., 2007), -salan (Hormnirun et al., 2004; Alaaeddine et al., 2009; Du et al., 2009; Maudoux et al., 2014; Pang et al., 2014; Press et al., 2015; McKeown et al., 2016), -salalen (Whitelaw et al., 2011; Hancock et al., 2013; Pilone et al., 2015) and -hemisalen (Darensbourg et al., 2011; Normand et al., 2013; Li et al., 2014) complexes, and also more recently indium (Douglas et al., 2008; Peckermann et al., 2009; Normand et al., 2012; Yu et al., 2012; Aluthge et al., 2013; Maudoux et al., 2014) and gallium (Horeglad et al., 2010, 2012; Bakewell et al., 2013; Hild et al., 2013; Maudoux et al., 2014; Horeglad et al., 2015) ones, have been prolific (Dagorne et al., 2013). Aluminium complexes in particular still are the precatalysts of choice for the isoselective ROP of racemic lactide (Stanford and Dove, 2010; Dijkstra et al., 2011). They have also proved useful catalysts for a range of asymmetric reactions, e.g. the Meerwein-Ponndorf-Verley reduction of prochiral ketones (Ooi et al. 1998; Campbell et al., 2001, 2002), the cyanosilylation of ketones affording chiral cyanohydrins (Hamashima et al., 1999; Baeza et al., 2003; Alaaeddine et al., 2008), aldol reactions (Evans et al., 2001), and ketone and aldehyde hydrophosphonylations (Saito and Katsuki, 2005; Saito et al., 2007). As part of our ongoing program aimed at developing triel complexes in molecular

catalysis, we embarked on the preparation of Al, Ga and In complexes supported by the chiral ligand $\{_{Ar}O^{\wedge}N^{\wedge}CPh_2^{\wedge}O_{Alc}\}^-$ derived from (*S*)-proline. Their syntheses, characterisation and performances in ROP catalysis are presented here.

Results and discussion

The enantiomerically pure proteo-ligand (*S*)- $\{_{Ar}O^{\wedge}N^{\wedge}CPh_2^{\wedge}O_{Alc}\}H_2$ (labelled (*S*)- $\{O^{\wedge}O\}H_2$ hereafter) was selected as a platform for the production of chiral complexes of aluminium, gallium and indium. Our attempts to synthesise it on a multi-gram scale following a reported three-step procedure (Shen et al., 2004) were unsuccessful. It was instead obtained as a colourless powder in a seven-step protocol (overall 29% yield, Scheme 1) taking advantage of the synthesis of α,α -diphenyl-(*S*)-prolinol described by Schore and co-workers (Price et al., 2002). X-ray quality single-crystals of (*S*)- $\{O^{\wedge}O\}H_2$ were grown by slow evaporation of a methanol solution, and its molecular structure was determined (Figure 3); it shows that the configuration of (*S*)-proline and α,α -diphenyl-(*S*)-prolinol is retained at C14 in the proteo-ligand. Its NMR data recorded in $CDCl_3$ essentially matched those reported elsewhere (Shen et al., 2004).

Reacting $AlEt_2Cl$ with (*S*)- $\{O^{\wedge}O\}H_2$ in toluene at 70°C yielded the chloro complex (*S*)- $\{O^{\wedge}O\}AlCl$ (**1**) as a colourless solid in 92% yield upon double protonolysis and release of two equivalents of ethane (Scheme 2). By contrast, attempts to react $AlCl_3$ with (*S*)- $\{O^{\wedge}O\}Li_2$ or (*S*)- $\{O^{\wedge}O\}Na_2 \cdot THF$ (which was structurally characterised; upon recrystallisation from THF, the sodium salt forms the



Scheme 1: Seven-step synthesis of $(S)\text{-}\{O^{\wedge}N^{\wedge}CPh_2^{\wedge}O_{Alc}\}H_2$ ($\equiv(S)\text{-}\{O^{\wedge}O\}H_2$). (i) Boc_2O , NEt_3 , CH_2Cl_2 , $0^\circ C$, 3 h, 95%; (ii) MeI , K_2CO_3 , DMF , $25^\circ C$, 12 h, 99%; (iii) $PhMgBr$, Et_2O , 3 h, $25^\circ C$, 50%; (iv) KOH , $MeOH$, $DMSO$, $65^\circ C$, 4 h, 78%; (v) $NaBH_4$, $EtOH$, $0^\circ C$, 1 h, 99%; (vi) $SOCl_2$, CH_2Cl_2 , $25^\circ C$, 1 h, 100%; (vii) NEt_3 , CH_2Cl_2 , $25^\circ C$, 12 h, 79%.

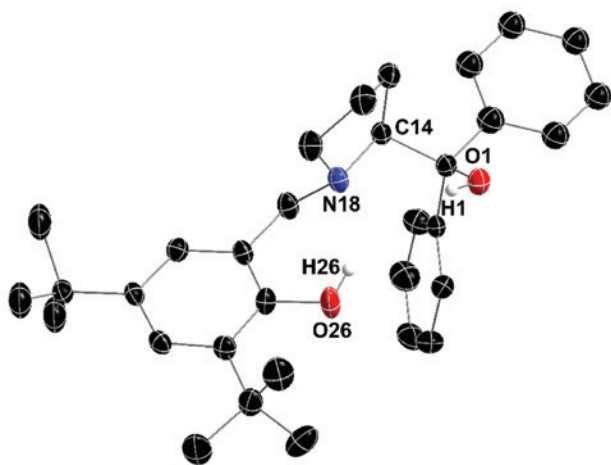


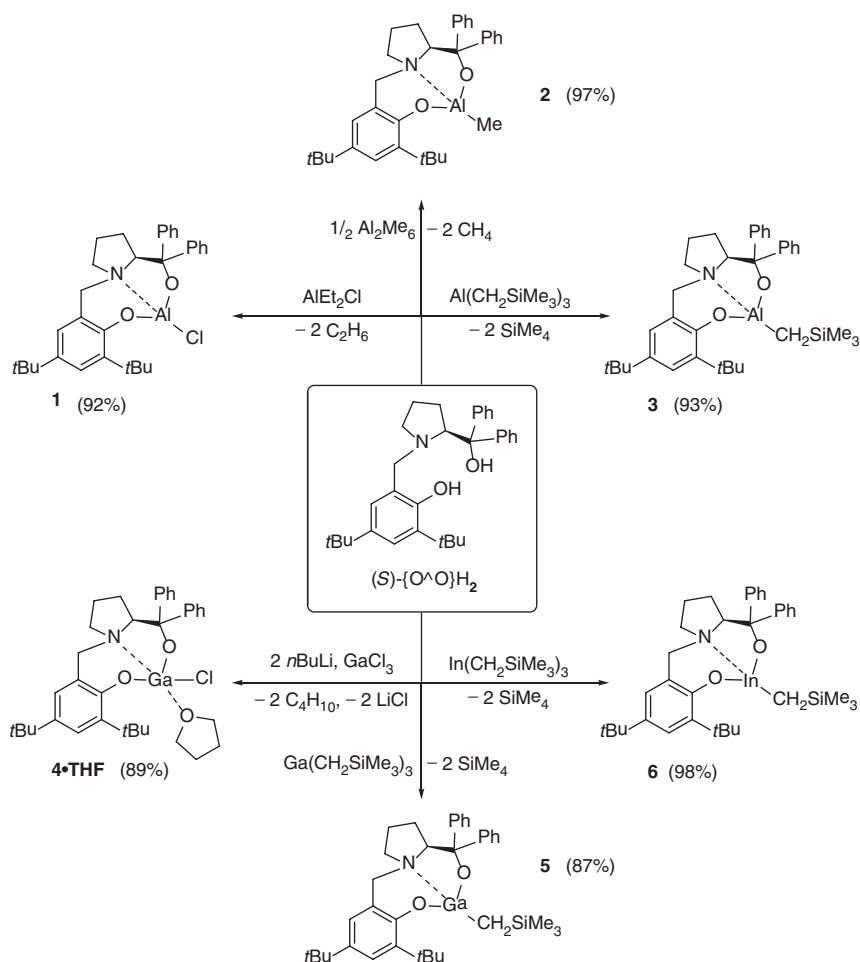
Figure 3: ORTEP representation of the molecular solid-state structure of the enantiomerically pure proteo-ligand $(S)\text{-}\{O^{\wedge}O\}H_2$, showing only the main component of the disordered *p*-*t*Bu group. H atoms other than those on oxygen atoms omitted for clarity. Ellipsoids drawn at the 50% probability level.

tetranuclear $[(S)\text{-}\{O^{\wedge}O\}Na_2\cdot THF]_2$, with a distorted cubane Na_4O_4 central core featuring bridging $O_{phenolate}$ and $O_{alcoholate}$ atoms, see Figure 4) failed to deliver **1**.

The identity of **1** was established based on its NMR spectroscopic data recorded in $THF-d_8$ and combustion analysis. The 1H NMR data for **1** feature two doublets at 2.75 and 3.88 ppm for diastereotopic hydrogen atoms in the methylene unit bridging the aromatic and prolinol moieties (AB spin system, $^3J_{HH} = 12.2$ Hz). The colourless methyl complex $(S)\text{-}\{O^{\wedge}O\}AlMe$ (**2**) was isolated in quantitative yield following the reaction of $(S)\text{-}\{O^{\wedge}O\}H_2$ with stoichiometric amounts of Al_2Me_6 ; the diagnostic

resonance for $[Al]\text{-}CH_3$ hydrogen atoms was located at $\delta_{1H} = -0.44$ ppm in the 1H NMR spectrum of this complex. The equimolar reactions of $(S)\text{-}\{O^{\wedge}O\}H_2$ with $M(CH_2SiMe_3)_3$ in toluene at $80^\circ C$ afforded the corresponding alkyl complexes $(S)\text{-}\{O^{\wedge}O\}MCH_2SiMe_3$ ($M = Al$, **3**; Ga , **5**; In , **6**) in excellent yields upon consecutive protonolysis reactions and release of two equivalents of $SiMe_4$. These three complexes were obtained as analytically pure, colourless powders. For each of them, the resonances in the 1H NMR spectra for the two diastereotopic $[M]\text{-}CH_2SiMe_3$ hydrogen atoms appeared as a pair of doublets ($^3J_{HH} = 12.0\text{--}12.6$ Hz) in the region $\delta_{1H} = 0.0$ to -1.0 ppm. $GaCl_3$ and $(S)\text{-}\{O^{\wedge}O\}Li_2$ reacted smoothly in THF at room temperature to give $(S)\text{-}\{O^{\wedge}O\}GaCl\cdot THF$ (**4**·**THF**). The presence of coordinated THF in this complex was unambiguously confirmed by spectroscopic, combustion and crystallographic analyses. Attempts to prepare the analogous, THF-free complex by carrying out the synthesis in hydrocarbons returned intractable mixtures. As a result of the binding of the N_{amine} atom onto the metal centre M , both the N_{amine} and M atoms become chiral in **1–6**, taking the total to three optically active centres in these complexes. Yet, the simple 1H and $^{13}C\{^1H\}$ NMR spectra for **1–6**, with single sets of narrow resonances, were consistent with the existence of a single diastereoisomer in solution, and this agreed with the crystallographic data. For instance, the examples of the 1H NMR spectra of the *in situ* generated **1** and **5** (reactions in J-Young NMR tubes) are shown in Figures 5 and 6.

Attempts to prepare the aluminium alkoxide(S)- $\{O^{\wedge}O\}Al(OiPr)$ by treatment of $(S)\text{-}\{O^{\wedge}O\}H_2$ with stoichiometric amounts of $\{Al(OiPr)_3\}_4$ or $AlMe_2(OiPr)$ only returned mixtures of species which could not be purified or characterised. The reaction of **2** with *i*PrOH did



Scheme 2: Syntheses of mononuclear aluminium (1–3), gallium (4–5) and indium (6) complexes supported by the chiral ligand $(S)\text{-}\{O^{\wedge}O\}^{2-}$.

trigger the rapid release of methane (vigorous bubbling was observed); the ^1H NMR spectrum of the crude product indicated that the starting material **2** had been consumed, but it was not consistent with the formation of a putative $(S)\text{-}\{O^{\wedge}O\}\text{Al}(\text{O}i\text{Pr})$ species. By contrast, the indium complex **6** remained entirely unreacted in the presence of BnOH or $i\text{PrOH}$, even after several hours at 25°C or 70°C .

Single-crystals of **2**, **3** and **4·THF** suitable for X-ray diffraction crystallography were grown by recrystallisation of the purified products, and their structures were established. The 4-coordinate aluminium complex **2** crystallises in the orthorhombic $P2_12_12_1$ space group. Upon coordination of the N_{amine} atom (N18), the geometry about the metal forms a distorted tetrahedral (Figure 7), with the geometry index $\tau_4 = 0.87$ (Yang et al., 2007). As a result, the aluminium atom lies only 0.34 \AA above the mean plane defined by the O1, O2 and C34 atoms. The asymmetric unit contains a single stereoisomer (together with one molecule of non-interacting toluene), with the

configurations S, S and R at C14, Al1 and N18, respectively; this is consistent with the NMR spectroscopic data for this complex. The Al-O1 ($1.747(2) \text{ \AA}$) and Al-O2 ($1.763(2) \text{ \AA}$) bond lengths to the $\text{O}_{\text{alkoxide}}$ and $\text{O}_{\text{phenolate}}$ atoms in **2** resemble those in a five-coordinate aluminium chloride supported by a alcoxophenolato-diimino $\{(3,5\text{-}t\text{Bu}_2\text{-1-OC}_6\text{H}_4)\text{CH}=\text{N}(\text{trans}\text{-}1,2\text{-cyclo-C}_6\text{H}_{10})\text{N}=\text{C}(\text{Me})\text{CH}_2\text{C}(\text{CF}_3)_2\text{O}\}^{2-}$ ligand ($1.763(2)$ and $1.791(2) \text{ \AA}$, respectively) (Alaaeddine et al., 2009), and in the four-coordinate aluminium- β -oxy enolate $\{\text{BHT}\}\text{AlEt}\{\text{O}=\text{C}(t\text{Bu})\text{CH}_2\text{C}(\text{Me})(t\text{Bu})\text{O}\}$ ($1.720(5)$ and $1.732(5)$, respectively) (Power et al., 1990). The Al-C bond distances in this complex ($1.962(9) \text{ \AA}$) and in **2** ($1.950(3)$) are also very similar.

The molecular structure of **3** depicted in Figure 8 matches closely that of **2**. It crystallises in the monoclinic space group $P2_1$. Each asymmetric unit contains two independent and very similar molecules, with four coordinate aluminium atoms sitting in a distorted tetrahedral arrangement ($\tau_4 = 0.86$ and 0.89 ; Yang et al., 2007). Each molecule presents S, S and R configurations at the chiral

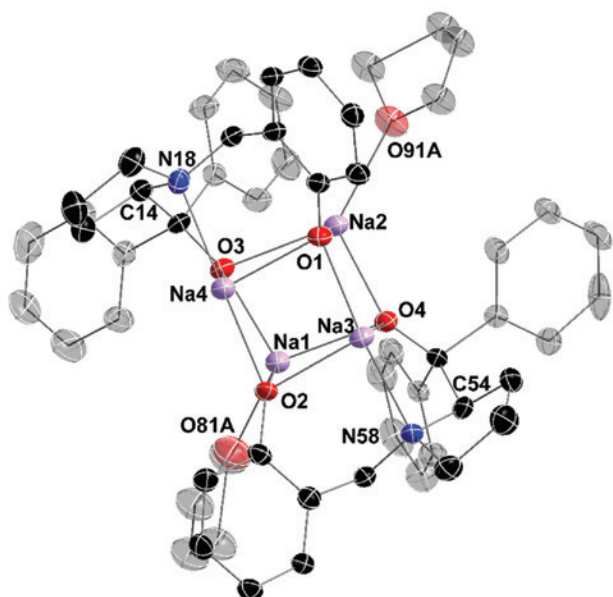


Figure 4: ORTEP representation of the molecular solid-state structure of $[(S)-(O^-O)Na_2 \cdot THF]_2$. Ellipsoids drawn at the 30% probability level. H atoms and *t*Bu groups omitted and THF molecules and C_6H_5 substituents in shaded tone for clarity. Selected bond lengths (Å): Na1-O2=2.376(6), Na1-O3=2.252(5), Na1-O4=2.421(6), Na1-O81A=2.347(8), Na2-O1=2.380(6), Na2-O3=2.522(6), Na2-O4=2.246(5), Na2-O91A=2.437(7), Na3-O1=2.280(5), Na3-O2=2.296(6), Na3-O4=2.297(6), Na4-O2=2.307(5), Na4-O1=2.324(6), Na4-O3=2.256(6).

carbon, aluminium and nitrogen atoms, respectively, and therefore a single stereoisomer is found in the crystalline material. The main metric parameters in **3** compare very well with those for **2**. In the molecule represented in Figure 8, the metal atom Al2 rests 0.38 Å above the mean plane defined by O51, O73 and C91. The Al2-C91 bond length of 1.937(5) Å in **3** is somewhat shorter than in $[(Me_3SiCH_2)_2AlOCH_2CH_2OMe]_2$ (1.983(1) and 1.969(1) Å) (Westerhausen et al., 1999), in $Al(CH_2SiMe_3)_3 \cdot NMe_3$ (1.984(3) Å) (Feighery et al., 1994) and in the enantiomerically pure (1,2)-diphenylethylene-salen complex $\{(R,R)-(MeONNO^Me)\}AlCH_2SiMe_3$ (1.976(3) Å) (Maudoux et al., 2014).

Owing to the presence of the coordinated THF molecule, the five-coordinate gallium atom in **4·THF** sits in a slightly distorted trigonal bipyramid environment ($\tau_5 = 0.62$) (Addison et al., 1984), with the O_{THF} and N_{amine} atoms in the apical positions ($\angle O1-Ga1-N31 = 165.37(19)^\circ$), and the O11, O37 and Cl1 occupying the equatorial sites (Figure 9). The bond distances Ga1-O11 to the alkoxide and Ga1-O37 to the phenolate, 1.830(4) and 1.836(4), are almost identical, and much smaller than that to O1 (2.107(4)) belonging to the coordinated THF molecule. They are comparable to those in the five coordinate gallium complexes $\{Me_2NCH_2CH_2O\}_2GaCl$ (1.841(2) and 1.842(3) Å) and $\{Me_2NCH(CH_3)CH_2O\}_2GaCl$ (1.8373(12) and 1.8389(12) Å) (Basharat et al., 2008).

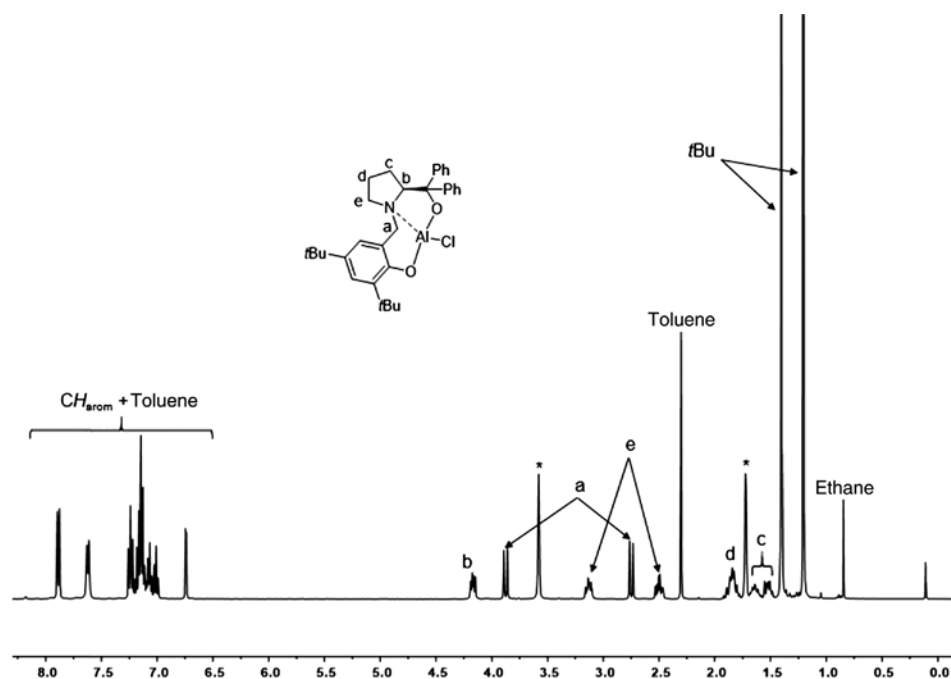


Figure 5: 1H NMR spectrum ($THF-d_8$, 500.1 MHz, 298 K) of $(S)-(O^-O)AlCl$ (**1**) generated *in situ* upon reaction of $(S)-(O^-O)H_2$ and $AlEt_2Cl$ at 343 K for 3 h. * $THF-d_8$.

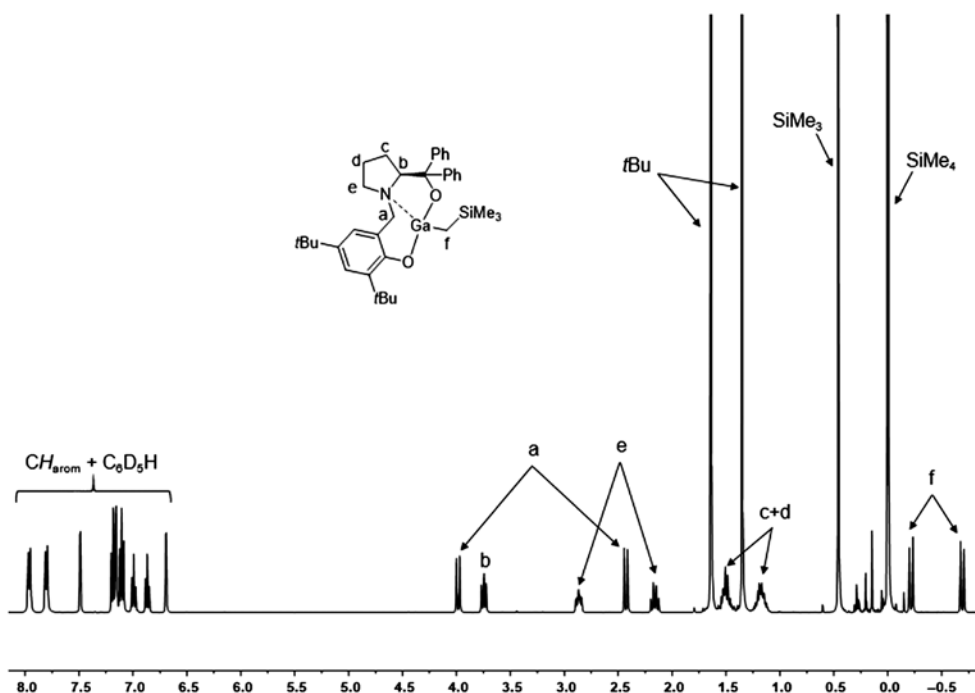


Figure 6: ^1H NMR spectrum (benzene- d_6 , 500.1 MHz, 298 K) of $(S)\text{-[O}^{\text{O}}\text{]GaCH}_2\text{SiMe}_3$ (**5**) generated *in situ* upon reaction of $(S)\text{-[O}^{\text{O}}\text{]H}_2$ and $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ at 343 K for 3 h.

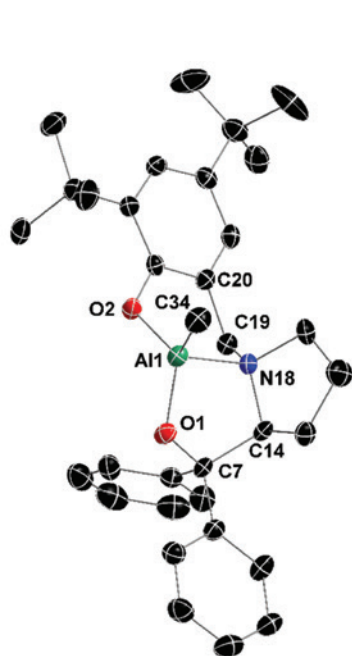


Figure 7: ORTEP representation of the molecular solid-state structure of $(S)\text{-[O}^{\text{O}}\text{]AlMe}$ (**2**).

Ellipsoids drawn at the 50% probability level. H atoms and non-interacting toluene lattice molecule omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$): Al1-O1=1.747(2), Al1-O2=1.763(2), Al1-C34=1.950(3), Al1-N18=2.0082; O1-Al1-O2=116.69(10), O1-Al1-C34=120.01(13), O2-Al1-C34=112.89(12), O1-Al1-N18=89.48(10), O2-Al1-N18=99.07(9), C34-Al1-N18=113.95(11).

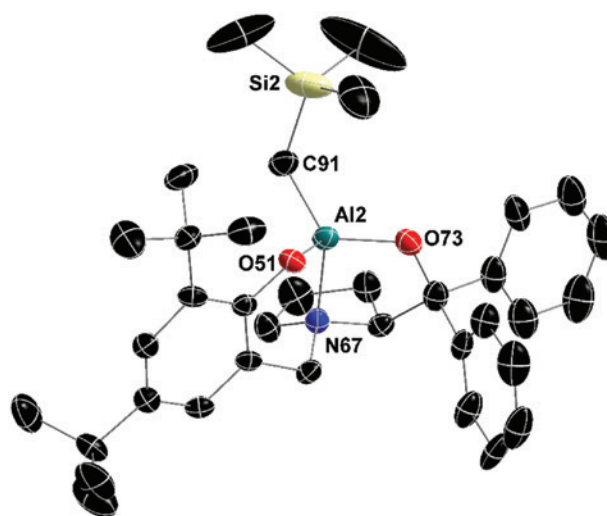


Figure 8: ORTEP rendering of the molecular solid-state structure of $(S)\text{-[O}^{\text{O}}\text{]AlCH}_2\text{SiMe}_3$ (**3**).

One of the two independent molecules in the asymmetric unit is represented. Ellipsoids drawn at the 50% probability level. H atoms and non-interacting benzene lattice molecules omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$): Al1-O23=1.742(3), Al1O1-1.749(3), Al1-C41=1.949(5), Al1-N17=2.007(5), Al2-O73=1.731(4), Al2-O51=1.765(3), Al2-C91=1.937(5), Al2-N67=1.989(5); O23-Al1-O1=117.32(16), O23-Al1-C41=115.7(2), O1-Al1-C41=112.7(2), O23-Al1-N17=89.28(17), O1-Al1-N17=98.36(17), C41-Al1-N17=120.6(2), O73-Al2-O51=116.95(17), O73-Al2-C91=116.9(2), O51-Al2-C91=112.8(2), O73-Al2-N67=90.17(18), O51-Al2-N67=100.05(17), C91-Al2-N67=116.9(2).

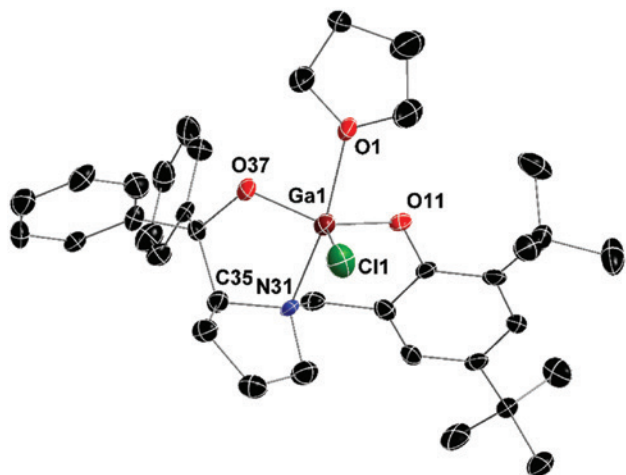


Figure 9: ORTEP representation of the molecular solid-state structure of (S)-{O[∘]O}GaCl·THF (**4·THF**). Ellipsoids drawn at the 50% probability level. H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ga1-O11=1.830(4), Ga1-O37=1.836(4), Ga1-O1=2.107(4), Ga1-N31=2.113(5), Ga1-Cl1=2.206(2); O11-Ga1-O37=127.9(2), O11-Ga1-O1=85.69(17), O37-Ga1-O1=83.97(17), O11-Ga1-N31=94.59(18), O37-Ga1-N31=84.35(18), O1-Ga1-N31=165.37(19), O11-Ga1-Cl1=111.02(15), O37-Ga1-Cl1=120.26(15), O1-Ga1-Cl1=91.97(15), N31-Ga1-Cl1=101.53(15).

Attempts to prepare cationic Al-In complexes

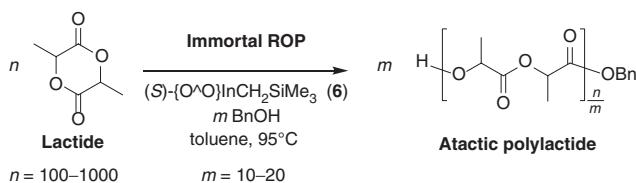
Well-defined cationic metal complexes associated to weakly-coordinating anions have proved very competent catalysts in a variety of catalysed organic transformations, for instance the hydroamination of alkenes (Zulys et al., 2005; Mukherjee et al., 2012) or the ROP of cyclic esters (Sarazin and Carpentier, 2015), and the role of cationic metallocenium in olefin polymerisation is also well established (Chen and Marks, 2000). Several cations of group 13 metals have been reported (Atwood, 1998; Dagorne and Atwood, 2008), and we were keen on probing whether complexes **1–6** would be amenable to cationisation.

Attempts to generate [(S)-{O[∘]O}M]⁺·[H₂N{B(C₆F₅)₃}₂]⁻ (M=Al-In), where the metallic cation is paired with Bochmann's amidodiborate anion (Lancaster et al., 2002), were carried out. The choice of this weakly coordinating anion was motivated by its usually excellent crystallisation properties, owing in particular to the presence of a dipolar moment (Bochmann, 2009; Sarazin and Carpentier, 2015). The equimolar treatment of **2**, **3**, **5** or **6** with [H(OEt)₂]₂⁺·[H₂N{B(C₆F₅)₃}₂]⁻ did not give the expected cationic complexes, but returned instead intractable mixtures in which the starting charge-neutral complexes were by a large margin the main components. Similarly, the

stoichiometric reaction of [(S)-{O[∘]O}H₃]⁺·[H₂N{B(C₆F₅)₃}₂]⁻, obtained quantitatively by treatment of the (S)-{O[∘]O}H₂ with [H(OEt)₂]₂⁺·[H₂N{B(C₆F₅)₃}₂]⁻, with the alkyl precursors M(CH₂SiMe₃)₃ gave a mixture of compounds which could not be purified by standard washing, stripping or recrystallisation procedures. This lack of reactivity of **6** towards these strong acids can be related to the inertness of the complex towards alcohols (see above), and it contrasts with the reactivity observed for aminotroponimate indium dialkyl complexes, which formed cations upon treatment with [PhNMe₂H]⁺·[B(C₆F₅)₄]⁻ (Delpech et al., 2002). It testifies to the robustness and high degree of covalence of the remaining [In]-CH₂SiMe₃ bond in **6**. The salt metathesis reactions between the chlorinated compounds **1** or **4·THF** and [Na(OEt)₄]₄⁺·[H₂N{B(C₆F₅)₃}₂]⁻ also failed to generate [(S)-{O[∘]O}M]⁺·[H₂N{B(C₆F₅)₃}₂]⁻. We thus sought to prepare triflate salts, reasoning that a more coordinating anion would perhaps encourage cleavage of the [M]-CH₂SiMe₃ bond. The reaction of the gallium alkyl **5** with triflic acid (TfOH) in Et₂O at room temperature afforded a single species, the NMR data of which were fully consistent with the formulation [(S)-{O[∘]O}Ga]⁺·[TfO]⁻ or (S)-{O[∘]O}GaOTf: quantitative release of CH₂(SiMe₃)₂ was observed in the ¹H NMR spectrum, while all resonances for aliphatic hydrogens other than those belonging to *t*Bu groups were substantially deshielded compared to the parent complex **5**; a sole singlet was found at δ_{19F} = -78.6 ppm in the ¹⁹F NMR spectrum. However, we did not manage to grow X-ray quality crystals of this product, and therefore the proposed formulation remains for now tentative.

Ring-opening polymerisation of lactide

The indium complex **6** catalysed competently the controlled ROP of racemic lactide under immortal conditions in toluene at 95°C (Ajellal et al., 2010; Sarazin and Carpentier, 2015), but without stereoselectivity as it only afforded atactic poly(lactides) (Scheme 3). It converted 500 equivalents of monomer in the presence of 10 equivalents of BnOH as chain transfer agent in 12 h, affording a polymer with a low molecular weight distribution ($M_w/M_n=1.12$) and an experimental molecular weight ($M_{n,exp}=8800$ g mol⁻¹ as determined by gel permeation chromatography) which matched reasonably well its theoretical value ($M_{n,exp}=7000$ g mol⁻¹) calculated on the basis of the [lactide]₀/[BnOH]₀ ratio. The reaction was equally well controlled when 1000 equivalents of lactide were used (conversion=100% in 6 h, $M_{n,exp}=12\,000$ g mol⁻¹,



Scheme 3: Immortal ROP of lactide catalysed by (S)-{O⁻O}InCH₂SiMe₃ (**6**).

$M_{n,theo} = 14\,500\text{ g mol}^{-1}$, $M_w/M_n = 1.03$). The polymerisation of the enantiomerically pure *L*-lactide was also catalysed by **6** in a controlled fashion, and occurred without epimerisation of the chiral centres. Considering the absence of reactivity between **6** and alcohols, it is very likely that these reactions follow an activated monomer mechanism (Ajellal et al., 2010). On the other hand, the gallium congener **5** did not afford controlled reactions, whereas the aluminium complex **3** required extremely forcing conditions to afford monomer conversion without suitable control over the polymerisation parameters; none of these systems displayed appreciable level of stereoselectivity in the polymerisation of racemic lactide.

Conclusions

The synthesis of mononuclear aluminium, gallium and indium alkyl complexes supported by a bulky, enantiomerically pure aminophenolate-alkoxo dianionic ligand has been achieved. Whereas the aluminium complex are four-coordinate distorted tetrahedra, the complex of the large gallium is five-coordinate and rests in a highly distorted trigonal pyramidal geometry. The *S* configuration of the chiral centre in the proteo-ligand is retained in the resulting triel heteroleptic complexes **1–6**. These compounds are fairly robust against hydrolysis, and do not react cleanly, if at all, with other protic reagents such as alcohols and Bochmann's acid. The indium-alkyl complex **6** is, upon association with benzyl alcohol, an efficient catalyst for the controlled ROP of lactides, afforded monodisperse polylactides with defined molecular weight and good end-group fidelity, albeit without significant stereocontrol. Based on the inability of **6** to react with alcohol to yield an alkoxo complex, we surmise that the polymerisations mediated by this complex follow an activated monomer mechanism where benzyl alcohol is the true initiator (Ajellal et al., 2010; Normand et al., 2013; Maudoux et al., 2014). The congeneric gallium and aluminium complexes lead to lower activity and less controlled polymerisations.

One can also seek to take advantage of the chiral centres in these complexes in other homogeneous enantioselective reactions. For instance, in a preliminary test, the aluminium-methyl complex **2** (10 mol% metal loading) quantitatively catalysed the Meerwein-Ponndorf-Verley reduction of acetophenone into enantiomerically enriched 1-phenyl-ethan-1-ol ($ee = 28\%$) in the presence of four equivalents of isopropanol in 17 h at 80°C (Ooi et al., 1998; Campbell et al., 2001, 2002). Future efforts should focus on taking advantage of these well-defined complexes for other enantio- or stereo-selective reactions.

Experimental section

General procedures

All manipulations were performed under inert atmosphere using standard Schlenk techniques or in a dry, solvent-free glove-box (Jacomex; O₂ < 1 ppm, H₂O < 5 ppm) for catalyst loading. Racemic and *L*-lactides were purified by recrystallisation from a hot (80°C), concentrated *i*PrOH solution, followed by two subsequent recrystallisations in hot (105°C) toluene; after purification, they were stored at –30°C under the inert atmosphere of the glove-box. Isopropanol (Aldrich) was dried and distilled over magnesium turnings and stored over 3 Å molecular sieves. InCl₃ (Strem), GaCl₃ (Strem), AlBr₃ (Strem), AlMe₃ (2.0 M solution in toluene; Aldrich), AlMe₂(*Oi*Pr) (Strem), AlEt₂Cl (0.9 M solution in toluene; Acros Organics) and Al(*Oi*Pr)₃ (Aldrich) were used as received. Solvents (THF, Et₂O, CH₂Cl₂, pentane and toluene) were purified and dried (water contents below 8 ppm) over columns alumina (MBraun SPS). THF was further distilled under argon from sodium/benzophenone ketyl. All deuterated solvents (Eurisotop, Saclay, France) were stored in sealed ampoules over activated 3 Å molecular sieves and were thoroughly degassed by several freeze-thaw-vacuum cycles. Al(CH₂SiMe₃)₃ (Beachley Jr. et al., 1982), Ga(CH₂SiMe₃)₃ (Beachley Jr. and Simmons, 1980) and In(CH₂SiMe₃)₃ (Beachley Jr. and Rusinko, 1979) were synthesised according to literature procedures.

NMR spectra were recorded on Bruker AM-400 and AM-500 spectrometers. All ¹H and ¹³C{¹H} chemical shifts were determined using residual signals of the deuterated solvents and were calibrated vs. SiMe₄. Assignment of the signals was carried out using 1D (¹H, ¹³C{¹H}) and 2D (COSY, HMBC, HMQC) NMR experiments.

Elemental analyses were performed on a Carlo Erba 1108 Elemental Analyser instrument at the London Metropolitan University by Stephen Boyer and were an average of a minimum of two independent measurements.

Size exclusion chromatography measurements were performed on an Agilent PL-GPC50 equipped with two PLgel 5 Å MIXED-C columns and a refractive index detector. The column was eluted with THF at 30°C at 1.0 mL·min⁻¹ and was calibrated using 11 monodisperse polystyrene standards in the range of 580–380 000 g·mol⁻¹. The molecular weights of all PLAs were corrected by a factor of 0.58 (Save et al., 2002).

(S)-{O⁻O}AlCl (1**):** (S)-{O⁻O}H₂ (350 mg, 0.74 mmol) was dissolved in toluene (4 mL) and added dropwise at –40°C to a solution of AlEt₂Cl

(0.83 mL of a 0.9 M solution in toluene, 0.75 mmol) in toluene (2 mL). The reaction mixture was warmed to room temperature over 30 min and was then heated at 70°C for 2 h. The volatiles were pumped off and the resulting solid was washed with pentane (2 × 2 mL) and dried under vacuum to afford **1** (365 mg, 92%) as a white powder. ¹H NMR (THF-*d*₈, 298 K, 400.16 MHz): δ = 7.90 (d, ³J_{HH} = 7.4 Hz, 2H, C_{arom}H), 7.62 (d, ³J_{HH} = 7.4 Hz, 2H, C_{arom}H), 7.30–6.99 (m, 7H, C_{arom}H), 6.75 (d, ⁴J_{HH} = 2.4 Hz, 1H, C_{arom}H), 4.17 (m, 1H, NCH), 3.88 (d, ²J_{HH} = 12.2 Hz, 1H, C_{arom}-CHHN), 3.13 (m, 1H, NCHHCH₂), 2.75 (d, ²J_{HH} = 12.2 Hz, 1H, C_{arom}-CHHN), 2.46 (m, 1H, NCHHCH₂), 1.84 (m, 2H, NCH₂CH₂), 1.58 (m, 1H, NCHHCH₂), 1.48 (m, 1H, NCHHCH₂), 1.40 (s, 9H, C(CH₃)₃), 1.21 (s, 9H, C(CH₃)₃) ppm. ¹³C{¹H} NMR (THF-*d*₈, 298 K, 100.25 MHz): δ = 155.9 (C_{arom}-OH), 151.9 (*i*-C₆H₅), 150.8 (*i*-C₆H₅), 139.2 (C_{arom}-C(CH₃)₃), 137.3 (C_{arom}-C(CH₃)₃), 128.6 (C_{arom}H), 127.9 (C_{arom}H), 126.6 (C_{arom}H), 126.2 (C_{arom}H), 126.1 (C_{arom}H), 126.0 (C_{arom}H), 124.9 (C_{arom}-CH₂N), 123.8 (C_{arom}H), 123.7 (C_{arom}H), 77.1 (C(Ph)₂), 74.5 (NCH), 62.0 (C_{arom}-CH₂N), 56.0 (NCH₂CH₂), 35.2 (C(CH₃)₃), 34.4 (C(CH₃)₃), 31.9 (C(CH₃)₃), 30.5 (NCHCH₂), 30.3 (C(CH₃)₃), 21.1 (NCH₂CH₂) ppm. Elem. Anal. For C₃₂H₃₉AlClNO₂ (532.09 g·mol⁻¹): Calcd, C, 72.2; H, 7.4; N, 2.6%; Found, C, 72.0; H, 7.5; N, 2.7%.

(S)-{O⁻O}AlMe (2): (S)-{O⁻O}H₂ (500 mg, 1.06 mmol) was dissolved in toluene (8 mL) and added dropwise at -40°C to a solution of trimethylaluminium (0.53 mL of a 2.0 M solution in toluene, 1.06 mmol) in toluene (2 mL). Then the reaction mixture was warmed to room temperature over 15 min and then stirred at 70°C for 2 h. The volatiles were pumped off and the resulting solid was washed with pentane (3 × 3 mL) and dried under vacuum to give **2** (525 mg, 97%) as a colourless powder. Crystals suitable for X-ray diffraction crystallography were grown from a concentrated toluene solution. ¹H NMR (C₆D₆, 298 K, 400.16 MHz): δ = 7.88 (d, ³J_{HH} = 7.6 Hz, 2H, C_{arom}H), 7.74 (d, ³J_{HH} = 7.6 Hz, 2H, C_{arom}H), 7.50 (d, ⁴J_{HH} = 2.4 Hz, 1H, C_{arom}H), 7.19–6.99 (m, 5H, C_{arom}H), 6.88 (t, ³J_{HH} = 7.3 Hz, 1H, C_{arom}H), 6.69 (d, ⁴J_{HH} = 2.4 Hz, 1H, C_{arom}H), 4.08 (d, ²J_{HH} = 12.5 Hz, 1H, ArCHHN), 3.68 (m, 1H, NCHCH₂), 2.75 (m, 1H, NCHHCH₂), 2.42 (d, ²J_{HH} = 12.5 Hz, 1H, ArCHHN), 2.00 (m, 1H, NCHHCH₂), 1.64 (s, 9H, C(CH₃)₃), 1.58–1.39 (m, 2H, NCH₂CH₂), 1.34 (s, 9H, C(CH₃)₃), 1.21–1.04 (m, 2H, NCHHCH₂), -0.44 (s, 3H, Al-CH₃) ppm. ¹³C{¹H} NMR (C₆D₆, 298 K, 100.25 MHz): δ = 155.8 (C_{arom}-OAl), 149.9 (*i*-C₆H₅), 149.7 (*i*-C₆H₅), 139.6 (C_{arom}-C(CH₃)₃), 138.9 (C_{arom}-C(CH₃)₃), 128.5 (C_{arom}H), 128.3 (C_{arom}H), 128.2 (C_{arom}H), 127.9 (C_{arom}-CH₂N), 126.8 (C_{arom}H), 125.9 (C_{arom}H), 125.8 (C_{arom}H), 125.0 (C_{arom}H), 123.5 (C_{arom}H), 79.3 (CHCO), 75.4 (NCHCO), 60.4 (ArCH₂N), 54.8 (NCH₂CH₂), 35.4 (C(CH₃)₃), 34.3 (C(CH₃)₃), 32.1 (NCH₂CH₂), 32.0 (C(CH₃)₃), 30.2 (C(CH₃)₃), 20.4 (NCHCH₂) ppm; Al-CH₃ was not detected. Elem. Anal. for C₃₃H₄₂AlNO₂ (511.69 g·mol⁻¹): Calcd, C, 77.5; H, 8.3; N, 2.7%; Found, C, 77.4; H, 8.2; N, 2.6%.

(S)-{O⁻O}Al(CH₂SiMe₃) (3): (S)-{O⁻O}H₂ (245 mg, 0.52 mmol) and Al(CH₂SiMe₃)₃ (150 mg, 0.52 mmol) were dissolved in C₆H₆ and the reaction mixture was stirred at 80°C overnight. The volatiles were removed under vacuum and the resulting solid was washed with pentane (3 × 2 mL) and subsequent drying under vacuum afforded **3** (282 mg, 93%) as a white powder. X-ray quality single-crystals were obtained by recrystallisation of the crude product at 25°C from a concentrated benzene solution. ¹H NMR (C₆D₆, 298 K, 500.13 MHz): δ = 7.86 (d, ³J_{HH} = 7.3 Hz, 2H, C_{arom}H), 7.75 (d, ³J_{HH} = 7.3 Hz, 2H, C_{arom}H), 7.48 (d, ⁴J_{HH} = 2.6 Hz, 1H, C_{arom}H), 7.08–7.06 (m, 3H, C_{arom}H), 7.02–6.99 (m, 2H, C_{arom}H), 6.83 (t, ³J_{HH} = 7.3 Hz, 1H, C_{arom}H), 6.67 (d, ⁴J_{HH} = 2.6 Hz, 1H, C_{arom}H), 4.08 (d, ²J_{HH} = 12.5 Hz, 1H, ArCHHN), 3.72 (m, 1H, NCHCH₂), 2.83 (m, 1H, NCHHCH₂), 2.43 (d, ²J_{HH} = 12.5 Hz, 1H, ArCHHN), 2.04 (m, 1H, NCHHCH₂), 1.63 (s, 9H,

C(CH₃)₃), 1.53–1.47 (m, 2H, NCH₂CH₂), 1.33 (s, 9H, C(CH₃)₃), 1.26–1.22 (m, 2H, NCHCH₂), 0.56 (s, 9H, Si(CH₃)₃), -0.57 (d, ²J_{HH} = 12.5 Hz, 1H, AlCHHSiMe₃), -0.97 (d, ²J_{HH} = 12.5 Hz, 1H, AlCHHSiMe₃) ppm. ¹³C{¹H} NMR (C₆D₆, 298 K, 125.75 MHz): δ = 155.8 (C_{arom}-OAl), 149.8 (*i*-C₆H₅), 149.7 (*i*-C₆H₅), 139.6 (C_{arom}-C(CH₃)₃), 138.8 (C_{arom}-C(CH₃)₃), 128.6 (C_{arom}H), 128.5 (C_{arom}H), 128.3 (C_{arom}H), 126.8 (C_{arom}H), 126.4 (C_{arom}H), 125.9 (C_{arom}H), 125.8 (C_{arom}H), 125.0 (C_{arom}H), 123.4 (C_{arom}-CH₂N), 79.3 (CHCO), 75.8 (NCHCO), 60.6 (ArCH₂N), 54.9 (NCH₂CH₂), 35.4 (C(CH₃)₃), 34.3 (C(CH₃)₃), 32.1 (C(CH₃)₃), 32.0 (NCH₂CH₂), 30.3 (C(CH₃)₃), 20.4 (NCHCH₂), 3.1 (Si(CH₃)₃) ppm; the resonance for Al-CH₂SiMe₃ was not detected. Elem. Anal. For C₃₆H₅₀AlNO₂Si (583.87 g·mol⁻¹): Calcd, C, 74.1; H, 8.6; N, 2.4%; Found, C, 73.9; H, 8.5; N, 2.4%.

(S)-{O⁻O}GaCl-THF (4-THF): (S)-{O⁻O}H₂ (250 mg, 0.53 mmol) was dissolved in THF (20 mL) and *n*BuLi (0.3 mL of a 1.6 M solution in hexanes) was added dropwise at 0°C. The mixture was stirred at 0°C for 1 h, and it was then added to a suspension of GaCl₃ (93 mg, 0.53 mmol) in THF (10 mL). The reaction mixture was stirred overnight at room temperature, and the volatiles were pumped off. The resulting colourless solid was dissolved in dichloromethane (10 mL), the solution was filtered by cannula to remove insoluble impurities. Removal of the solvent under vacuum afforded a colourless powder. Recrystallisation from a mixture of dichloromethane and pentane at -26°C afforded crystals of **4-THF** (0.47 mmol, 89%) suitable for X-ray diffraction crystallography. ¹H NMR (500.13 MHz, 298 K, CD₂Cl₂): δ 7.90 (d, ³J_{HH} = 7.3 Hz, 2H, C_{arom}H), 7.69 (d, ³J_{HH} = 7.3 Hz, 2H, C_{arom}H), 7.39–7.27 (m, 5H, C_{arom}H), 7.22–7.15 (m, 2H, C_{arom}H), 6.79 (d, ⁴J_{HH} = 2.5 Hz, 1H, C_{arom}H), 4.39–4.25 (m, 1H, NCHCH₂), 4.06 (m, 4H, OCH₂CH₂), 3.91 (d, ³J_{HH} = 12.3 Hz, 1H, ArCHHN), 3.35 (m, 1H, NCHHCH₂), 2.97 (d, ³J_{HH} = 12.4 Hz, 1H, ArCHHN), 2.91–2.77 (m, 1H, NCHHCH₂), 2.01 (m, 4H, OCH₂CH₂), 1.94–1.71 (br m, 4H, NCH₂CH₂ and NCHCH₂), 1.43 (s, 9H, (CH₃)₃), 1.26 (s, 9H, (CH₃)₃) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 125.76 MHz, 298 K): δ = 156.9 (C_{arom}-OGa), 149.5 (*i*-C₆H₅), 139.1, 128.8, 128.3, 127.2, 126.6, 124.8, 124.5, 123.2 (all arom-C), 78.4 (CHCO), 73.7 (NCHCO), 69.6 (OCH₂CH₂), 60.7 (ArCH₂N), 56.8 (NCH₂CH₂), 35.3 (C(CH₃)₃), 34.3 (C(CH₃)₃), 31.7 (C(CH₃)₃), 30.0 (C(CH₃)₃), 29.3 (NCH₂CH₂), 26.0 (OCH₂CH₂), 20.8 (NCHCH₂) ppm. Elem. Anal. For C₃₆H₄₇ClGaNO₃ (646.95 g·mol⁻¹): Calcd, C, 66.8; H, 7.3; N, 2.2%; Found, C, 66.6; H, 7.3; N, 2.1%.

(S)-{O⁻O}Ga(CH₂SiMe₃) (5): (S)-{O⁻O}H₂ (245 mg, 0.52 mmol) and Ga(CH₂SiMe₃)₃ (172 mg, 0.52 mmol) were dissolved in toluene and the reaction mixture was stirred at 80°C for 2 h. The volatiles were removed under vacuum and the resulting solid was washed with pentane (3 × 2 mL). Subsequent drying under vacuum to constant weight afforded **5** (283 mg, 87%) as a white powder. ¹H NMR (C₆D₆, 298 K, 500.13 MHz): δ = 7.96 (d, ³J_{HH} = 7.7 Hz, 2H, C_{arom}H), 7.80 (d, ³J_{HH} = 7.7 Hz, 2H, C_{arom}H), 7.49 (d, ⁴J_{HH} = 2.5 Hz, 1H, C_{arom}H), 7.21–7.05 (m, 4H, C_{arom}H), 6.99 (t, ³J_{HH} = 7.3 Hz, 1H, C_{arom}H), 6.87 (t, ³J_{HH} = 7.3 Hz, 1H, C_{arom}H), 6.69 (d, ⁴J_{HH} = 2.5 Hz, 1H, C_{arom}H), 3.99 (d, ²J_{HH} = 12.0 Hz, 1H, ArCHHN), 3.77–3.72 (m, 1H, NCHCH₂), 2.90–2.84 (m, 1H, NCHHCH₂), 2.43 (d, ²J_{HH} = 12.0 Hz, 1H, ArCHHN), 2.20–2.12 (m, 1H, NCHHCH₂), 1.64 (s, 9H, C(CH₃)₃), 1.54–1.46 (m, 2H, NCH₂CH₂), 1.35 (s, 9H, C(CH₃)₃), 1.24–1.11 (m, 2H, NCHCH₂), 0.46 (s, 9H, Si(CH₃)₃), -0.22 (d, ²J_{HH} = 12.9 Hz, 1H, GaCHHSi), -0.69 (d, ²J_{HH} = 12.9 Hz, 1H, GaCHHSi) ppm. ¹³C{¹H} NMR (C₆D₆, 298 K, 125.76 MHz): δ = 158.5 (C_{arom}-OGa), 150.7 (*i*-C₆H₅), 149.7 (*i*-C₆H₅), 139.4 (C_{arom}-C(CH₃)₃), 138.9 (C_{arom}-C(CH₃)₃), 126.8 (C_{arom}H), 126.3 (C_{arom}H), 126.2 (C_{arom}H), 125.9 (C_{arom}H), 124.9 (C_{arom}H), 123.9 (C_{arom}-CH₂N), 80.9 (CHCO), 74.8 (NCHCH₂), 62.2 (ArCH₂N), 56.0 (NCH₂CH₂), 35.5 (C(CH₃)₃), 34.2 (C(CH₃)₃), 32.1 (C(CH₃)₃), 30.4 (C(CH₃)₃), 29.0 (NCH₂CH₂),

20.6(NCHCH₂), 2.2 (Si(CH₃)₃), -3.9 (GaCH₂) ppm. Elem. Anal. for C₃₆H₅₀GaNO₂Si (626.61 g.mol⁻¹): Calcd, C, 69.0; H, 8.0; N, 2.2%; Found, C, 68.9; H, 8.1; N, 2.3%.

(S)-{O⁻O}In(CH₂SiMe₃) (6): (S)-{O⁻O}H₂ (150 mg, 0.32 mmol) and In(CH₂SiMe₃)₂ (122 mg, 0.32 mmol) were dissolved in toluene and the reaction mixture stirred at 80°C for 2 h. The volatiles were pumped off. The resulting solid was dried overnight under dynamic vacuum to afford **6** (210 mg, 98%) as a white powder. ¹H NMR (C₆D₆, 298 K, 500.13 MHz): δ = 8.02 (d, ³J_{HH} = 7.3 Hz, 2H, C_{arom}H), 7.87 (d, ³J_{HH} = 7.3 Hz, 2H, C_{arom}H), 7.51 (d, ⁴J_{HH} = 2.6 Hz, 1H, C_{arom}H), 7.21–7.13 (m, 4H, C_{arom}H), 7.02 (t, ³J_{HH} = 7.3 Hz, 1H, C_{arom}H), 6.91 (t, ³J_{HH} = 7.3 Hz, 1H, C_{arom}H), 6.75 (d, ⁴J_{HH} = 2.6 Hz, 1H, C_{arom}H), 4.16 (d, ²J_{HH} = 11.8 Hz, 1H, ArCHHN), 3.74 (m, 1H, NCHCH₂), 2.79 (m, 1H, NCHHCH₂), 2.43 (d, ²J_{HH} = 11.8 Hz, 1H, ArCHHN), 2.14 (m, 1H, NCHHCH₂), 1.67 (s, 9H, C(CH₃)₃), 1.54–1.45 (m, 2H, NCH₂CH₂), 1.39 (s, 9H, C(CH₃)₃), 1.21–1.02 (m, 2H, NCHCH₂), 0.26 (s, 9H, Si(CH₃)₃), -0.02 (d, ²J_{HH} = 12.6 Hz, 1H, InCHHSi), -0.33 (d, ²J_{HH} = 12.6 Hz, 1H, InCHHSi) ppm. ¹³C{¹H} NMR (C₆D₆, 298 K, 125.76 MHz): δ = 160.8 (C_{arom}-OIn), 152.0 (*i*-C₆H₅), 150.7 (*i*-C₆H₅), 139.5 (C_{arom}-C(CH₃)₃), 137.9 (C_{arom}-C(CH₃)₃), 128.3 (C_{arom}H), 128.4 (C_{arom}H), 126.8 (C_{arom}H), 126.1 (C_{arom}H), 126.0 (C_{arom}H), 124.9 (C_{arom}H), 124.8 (C_{arom}H), 124.2 (ArCH₂N), 80.0 (CHCO), 73.7 (NCHCH₂), 60.0 (ArCH₂N), 56.3 (NCH₂CH₂), 35.6 (C(CH₃)₃), 34.2 (C(CH₃)₃), 32.1 (C(CH₃)₃), 30.4 (C(CH₃)₃), 28.3 (NCH₂CH₂), 20.6 (NCHCH₂), 2.1 (Si(CH₃)₃), -1.2 (InCH₂) ppm.

Elem. Anal. for C₃₆H₅₀InNO₂Si (671.70 g.mol⁻¹): Calcd, C, 64.4; H, 7.5; N, 2.1%; Found, C, 64.3; H, 7.6; N, 2.3%.

[(S)-{O⁻O}Na₂·THF]₂: (S)-{O⁻O}H₂ (276 mg, 0.5 mmol) was dissolved in THF (5 mL), NaH (30 mg, 1.25 mmol) was added in with a bent finger. The mixture was stirred at 25°C overnight and the residual insoluble material was eliminated by filtration. The volatiles were removed under vacuum and the resulting solid was washed with pentane (3 × 2 mL) and subsequent drying under vacuum afforded the title compound (267 mg, 91%) as a yellow powder. The crude product was dissolved in pentane. Green X-ray quality crystals were obtained after 2 days at 25°C. ¹H NMR (C₆D₆, 298 K, 500.13 MHz): δ = 8.06 (d, 2H, ³J_{HH} = 7.5 Hz, C_{arom}H), 7.40 (s, 1H, C_{arom}H), 7.20 (s, 3H, C_{arom}H), 7.09 (m, 4H, C_{arom}H), 6.98 (m, 1H, C_{arom}H), 6.89 (m, 1H, C_{arom}H), 4.00 (d, 1H, ²J_{HH} = 12.5 Hz, ArCHHN), 3.64 (m, 1H, NCHCH₂), 3.40 (m, 4H, OCH₂CH₂), 3.32 (m, 1H, NCHHCH₂), 2.95 (d, 1H, ²J_{HH} = 12.5 Hz, ArCHHN), 2.44 (m, 1H, NCHHCH₂), 1.46 (s, 9H, C(CH₃)₃), 1.53–1.47 (m, 2H, NCH₂CH₂), 1.34 (m, 4H, OCH₂CH₂), 1.30 (s, 9H, C(CH₃)₃), 1.05 (br s, 2H, NCHCH₂) ppm. ¹³C{¹H} NMR (C₆D₆, 298 K, 125.76 MHz): δ = 164.6 (C_{arom}-ONa), 157.8 (*i*-C₆H₅), 156.8 (*i*-C₆H₅), 135.4 (C_{arom}-C(CH₃)₃), 129.1 (C_{arom}-C(CH₃)₃), 127.6 (C_{arom}H), 127.5 (C_{arom}H), 126.6 (C_{arom}H), 126.4 (C_{arom}H), 126.2 (C_{arom}-CH₂N), 79.0 (CHCO), 68.6 (NCHCO), 67.9 (OCH₂CH₂), 54.2 (NCH₂CH₂), 34.5 (C(CH₃)₃), 34.0 (C(CH₃)₃), 32.4 (C(CH₃)₃), 29.9 (C(CH₃)₃), 29.1 (NCH₂CH₂), 25.6 (OCH₂CH₂), 20.3 (NCHCH₂) ppm. Satisfactory, reproducible

Table 1: Summary of the crystallographic data.

	[(S)-{O ⁻ O}Na ₂ ·THF] ₂	(S)-{O ⁻ O}AlMe (2)	(S)-{O ⁻ O}AlCH ₂ SiMe ₃ (3)	(S)-{O ⁻ O}GaCl·THF(4·THF)
Formula	C ₇₂ H ₉₄ N ₂ Na ₄ O ₆	C ₄₀ H ₅₀ AlNO ₂	C ₈₄ H ₁₁₂ Al ₂ N ₂ O ₄ Si ₂	C ₃₆ H ₄₇ ClGaNO ₃
CCDC	1503973	1503972	1503970	1503971
Mol. wt.	1175.45	603.79	1323.9	646.92
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	10.4386(12)	9.612(2)	10.7733(8)	9.0981(13)
<i>b</i> (Å)	17.390(2)	13.877(3)	26.8859(17)	13.1689(18)
<i>c</i> (Å)	19.033(3)	26.482(7)	14.0782(8)	27.314(5)
α(°)	90	90	90	90
β(°)	98.397(5)	90	90.026(4)	90
γ(°)	90	90	90	90
<i>V</i> (Å ³)	3418.0(8)	3532.3(14)	4077.7(5)	3272.5(9)
<i>Z</i>	2	4	2	4
Density (g/cm ³)	1.142	1.135	1.078	1.313
Abs. coeff. (mm ⁻¹)	0.093	0.091	0.112	0.958
<i>F</i> (000)	1264	1304	1432	1368
Crystal size, mm	0.6 × 0.3 × 0.27	0.6 × 0.59 × 0.22	0.43 × 0.17 × 0.12	0.22 × 0.09 × 0.05
θ range, deg	1.08–27.61	3.00–27.48	2.96–27.57	2.98–27.7
Limiting indices	-13 < <i>h</i> < 13 0 < <i>k</i> < 22 0 < <i>l</i> < 24	-12 < <i>h</i> < 12 -16 < <i>k</i> < 17 -34 < <i>l</i> < 34	-13 < <i>h</i> < 13 -34 < <i>k</i> < 34 -18 < <i>l</i> < 18	-11 < <i>h</i> < 10 -15 < <i>k</i> < 17 -34 < <i>l</i> < 35
<i>R</i> (int)	0.0000	0.0781	0.0525	0.1511
Reflections collected	8100	26 115	30 477	27 522
Reflec. Unique [<i>I</i> > 2σ(<i>I</i>)]	8100	8026	16 596	7478
Completeness to θ (%)	98.6	99.4	96.5	97.9
Data/restraints/param.	8100/61/736	8026/0/405	16596/1/818	7478/0/385
Goodness-of-fit	1.055	1.023	1.008	0.984
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] (all data)	0.0796 (0.1630)	0.0604 (0.1007)	0.0625 (0.1064)	0.0721 (0.1325)
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] (all data)	0.1962 (0.2451)	0.1256 (0.1441)	0.1222 (0.1441)	0.1441 (0.1704)
Largest diff. e·Å ⁻³	0.469 and -0.466	0.546 and -0.328	0.296 and -0.31	0.434 and -0.581

elemental analysis for $C_{72}H_{94}N_2Na_4O_6$ (1175.52 g·mol⁻¹) could not be obtained.

Typical Schlenk-scale polymerisation procedure

In the glove-box, the metal catalyst (ca. 5.0–15.0 mg) was placed in a Schlenk flask together with the monomer (ca. 0.1–1.0 g). The Schlenk flask was sealed and removed from the glove-box. All subsequent operations were carried out on a vacuum manifold using Schlenk techniques. The required amount of solvent (toluene) was added with a syringe to the catalyst and the monomer, followed when necessary by addition of alcohol (BnOH, 3–10 μ L). The resulting mixture was immersed in an oil bath pre-set at the desired temperature and the polymerisation time was measured from this point. The reaction was terminated by addition of MeOH and the polymer was precipitated in methanol or a methanol/pentane mixture. It was washed thoroughly and reprecipitated from dichloromethane/pentane. The polymer was then dried to constant weight in a vacuum oven at 55°C under dynamic vacuum ($< 5 \times 10^{-2}$ mbar).

X-ray diffraction crystallography

All crystals suitable for X-ray diffraction analysis were obtained by recrystallisation of the purified compounds. Diffraction data were collected at 150(2) K using a Bruker APEX CCD diffractometer with graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). A combination of ω and Φ scans was carried out to obtain at least a unique data set. The crystal structures were solved by direct methods, remaining atoms were located from difference Fourier synthesis followed by full-matrix least-squares refinement based on F2 (programs SIR97 and SHELXL-97) (Sheldrick, 1997a,b). Carbon- and oxygen-bound hydrogen atoms were placed at calculated positions and forced to ride on the attached atom. All non-hydrogen atoms were refined with anisotropic displacement parameters. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities were of no chemical significance. Relevant collection and refinement data are collated in Table 1. Crystal data, details of data collection and structure refinement for all complexes structurally characterised (CCDC 1503970–1503973) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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