Bidentate salicylaldiminato tin(II) complexes and their use as lactide polymerisation initiators†

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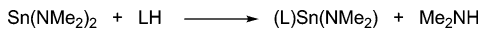
A study of the reactions of several salicylaldimines (*ortho*-iminophenols) with $Sn(NMe_2)_2$ reveals that the sterics and electronics of the *N*-substituent play a principal role in determining the product mixture. Thus mono(chelate) tin(II) amides have only been isolated with bulky *N*-anilido substituents, including $[2,4\text{-}X_2\text{-}6\text{-}\{CH{=}N\text{-}2,6\text{-}^{i}Pr_2C_6H_3\}\text{-}C_6H_2O]Sn(\mu\text{-}NMe_2)]_2$, X = Cl, **1**; X = I, **2** and $[2,4\text{-}Cl_2\text{-}6\text{-}\{CH{=}N\text{-}2,4,6\text{-}^{t}Bu_3C_6H_2\}\text{-}C_6H_2O]Sn(NMe_2)$, **3**. With smaller *N*-aryl and *N*-alkyl substituted salicylaldimines, mixtures of mono- and bis- chelate complexes are formed, even if the phenoxide ring bears large *tert*-butyl substituents. Further, when the anilido group bears electron-withdrawing substituents, the imino carbon is activated towards nucleophilic attack (as demonstrated by the formation of $[2,4\text{-}^{t}Bu_2\text{-}6\text{-}\{CH(NMe_2)N\text{-}2,4,6\text{-}Br_3C_6H_2\}\text{-}C_6H_2O]Sn$, **4**); no such reactivity has been observed when the halo substituents are located on the phenolic ring. The abilities of complexes **1–4** to initiate the ring-opening polymerisation of *rac*-lactide have also been studied. Complexes **1**, **2** and **4** possess comparitively similar activities, but propagation with **3** is at least one order of magnitude slower, an observation rationalised in terms of steric congestion.

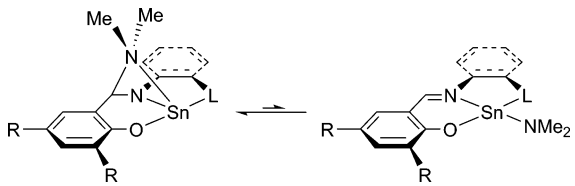
Introduction

Several single-site tin(II)-based initiators for the well-controlled polymerisation of lactide, LA, have been reported.[1–6] Initiation *via* nucleophilic attack at the carbonyl carbon may be performed by either alkoxide (LSnOR) or amido ($LSnNR_2$) complexes[7–10] and although chain termini differ (ester *versus* amide), subsequent propagation steps proceed in an identical manner. We have therefore found $Sn(NMe_2)_2$ to be a particularly useful precursor: this compound may be readily isolated as crystalline blocks from the reaction of $SnCl_2$ with $LiNMe_2$,[11] and usually reacts in an effectively irreversible and highly predictable manner (Scheme 1) with acidic pro-ligands including β-diketimines[4] and amidines.[5]



Scheme 1

An exception to this behaviour is the reaction of $Sn(NMe_2)_2$ with potentially tridentate salicylaldiminines (*ortho*-iminophenols with Lewis basic *N*-substituents): following deprotonation of the phenol, the remnant NMe_2 ligand attacks the imino carbon to generate a tetradentate, dianionic aminoamidophenoxide ligand.[3,6] These species may still be used to initiate the polymerisation of lactide as they exist in equilibria with their terminal amide tautomers (Scheme 2).



Scheme 2

We describe here a related study into the divalent tin coordination chemistry of bidentate salicylaldimines, with the aim of producing less congested tin(II) coordination spheres with high activities for LA polymerisation. Our original decision to study tridentate analogues was based upon the known tendency of even sterically bulky bidentate iminophenols to form bischelate products with a range of divalent metals,[12–17] but we suspected that Sn(II) might prove an exception to this behaviour given the usual stereochemical activity of its lone $5s^2$ electron pair. Here, we shall show that: (i) if steric conditions are met, then this supposition is largely correct; and (ii) the amine migration reaction shown in Scheme 2 is not restricted to the tridentate salicylaldiminato family.

Results and discussion

Synthetic and crystallographic studies

As summarised in Scheme 3, ten salicylaldimines were chosen for this study and these are abbreviated to $[_{R}ON_{R'}]H$, where R and R′ are the 2,4-phenoxy- and imino substituents respectively. In a series of NMR scale experiments each of the salicylaldimines was reacted with *ca.* 10 mg of $Sn(NMe_2)_2$ in C_6D_6. Despite our initial hopes of circumventing bischelation, the reactions of $[_{tBu}ON_{iPr}]H$, $[_{tBu}ON_{tBu}]H$, $[_{tBu}ON_{Bn}]$ and $[_{Me}ON_{DIPP}]H$ all led to mixtures of the mono(chelate) tin(II) dimethylamides, $[_{R}ON_{R'}]Sn(NMe_2)$,

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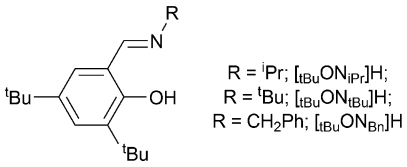
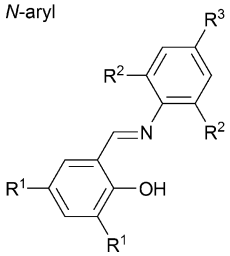
† Electronic supplementary information (ESI) available: ^1H NMR spectra for complexes **2** and **3**; crystallographic data for complexes **2** and **4**. CCDC reference numbers 696308 and 696309. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b812877d

N-alkyl:



R = ^{i}Pr; [$_{tBu}$ON$_{iPr}$]H;
R = ^{t}Bu; [$_{tBu}$ON$_{tBu}$]H;
R = CH_2Ph; [$_{tBu}$ON$_{Bn}$]H

N-aryl



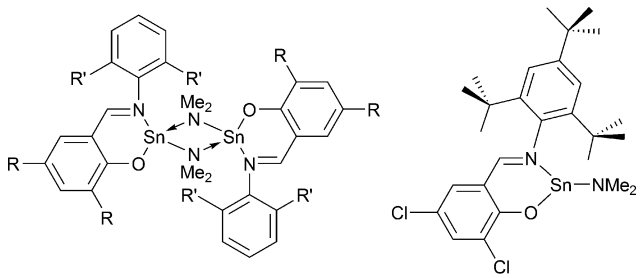
R^1 = Me, R^2 = ^{i}Pr, R^3 = H; [$_{Me}$ON$_{DIPP}$]H;
R^1 = ^{t}Bu, R^2 = Me, R^3 = H; [$_{tBu}$ON$_{DMP}$]H;
R^1 = ^{t}Bu, R^2 = ^{i}Pr, R^3 = H; [$_{tBu}$ON$_{DIPP}$]H;
R^1 = ^{t}Bu, R^2 = R^3 = Br; [$_{tBu}$ON$_{TBP}$]H;
R^1 = Cl, R^2 = ^{i}Pr, R^3 = H; [$_{Cl}$ON$_{DIPP}$]H;
R^1 = Cl, R^2 = R^3 = ^{t}Bu; [$_{Cl}$ON$_{TTBP}$]H;
R^1 = I R^2 = ^{i}Pr, R^3 = H; [$_{I}$ON$_{DIPP}$]H;

Scheme 3 DIPP = 2,6-di-isopropylphenyl; DMP = 2,6-dimethylphenyl; TBP = 2,4,6-tribromophenyl; TTBP = 2,4,6-tris(*tert*-butyl)phenyl.

contaminated to varying degrees with the bis(chelate) species, [$_{R}$ON$_{R'}$]$_2$Sn. However, bis(chelate) species were not observed in any other case.

Thus, the 2,4-dihalophenols, [$_{Cl}$ON$_{DIPP}$]H, [$_{I}$ON$_{DIPP}$]H and [$_{Cl}$ON$_{TTBP}$]H, were cleanly transformed into their mono(chelate) tin(II) amides and when repeated on a larger scale, [$_{Cl}$ON$_{DIPP}$]-Sn(NMe$_2$), **1**, [$_{I}$ON$_{DIPP}$]Sn(NMe$_2$), **2**, and [$_{Cl}$ON$_{TTBP}$]Sn(NMe$_2$), **3**, were all successfully recrystallised from toluene in yields of *ca.* 65, 45 and 60% respectively. The two di-*tert*-butylphenol salicylaldimines were also converted into [$_{tBu}$ON$_{DMP}$]Sn(NMe$_2$) and [$_{tBu}$ON$_{DIPP}$]Sn(NMe$_2$); however, when synthesised on a preparative scale, the high solubility of both complexes in a range of solvents precluded purification (via washing or recrystallisation) in our hands.

The ^{1}H and ^{13}C NMR spectra of **1–3** are consistent with mono(iminophenoxide) mono(amide) formulations with no suggestion of the migration of the NMe$_2$ unit to the imino carbon. However, while the ^{119}Sn NMR spectra of **1** and **2** feature singlets consistent with four-coordinate centres at δ –634 and –639 respectively, the metal nuclei in complex **3** resonate at δ –108, indicative of a lower coordination number.[18] We therefore propose that both **1** and **2** exist as amide-bridged dimers in solution whereas the 2,4,6-tri-*tert*-butyl anilino component of **3** occupies sufficient space to confer mononuclearity (Scheme 4). Consistent with this hypothesis, broadening of the 2,6-di-isopropylphenyl



R = Cl, R' = ^{i}Pr; **1**;
R = I, R' = ^{i}Pr; **2**

3

Scheme 4 Postulated solution state structures of **1–3**.

^{1}H NMR signals in the room temperature spectra of **1** and **2** is observed consistent with hindered rotation of the aryl rings due to their proximity to the bridging NMe$_2$ ligands. By contrast, all resonances in the ^{1}H NMR spectrum of **3** are sharp (see ESI Fig. S1–S3†). An alternative argument may be advanced which is also consistent with the spectroscopic solution data, namely that **3** also adopts a dimeric structure with bridging amides, but the salicylaldiminato ligands bind in an η^1 manner. However, lactide polymerisation activities (*vide infra*) suggest this is not the case.

Further support for our postulate is provided from a single crystal X-ray diffraction study on **2**, which reveals that the amide-bridged dimeric structure shown in Scheme 4 is adopted in the solid state, with the two halves of the molecule related by a centre of inversion (Fig. 1). The four-membered Sn$_2$N$_2$ ring is planar, with the amide ligands bridging in an asymmetric fashion (Sn(1)–N(2A) = 2.326(2) Å *vs.* Sn(1)–N(2) = 2.192(2) Å, Table 1). One of the more remarkable features of the molecular structure is the particularly weak interaction between the metal and the imino nitrogen (Sn(1)···N(1) = 2.698 Å), which is distinctly longer than a typical dative covalent Sn–N bond, though still appreciably shorter than the sum of the respective van der Waals radii (2.17 (Sn) + 1.55 (N) = 3.72 Å).[19] The long nature of this interaction is attributed in part to electronic repulsive forces arising from the tin 5s^2 lone pair (previously suggested as the origin of similarly lengthy Sn–O interactions[4]).

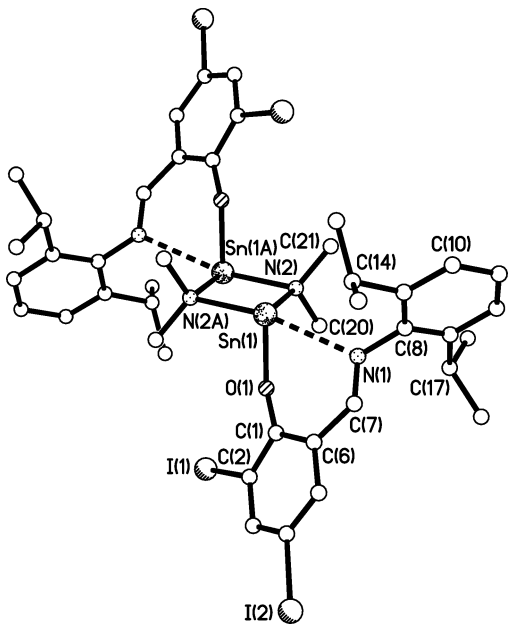
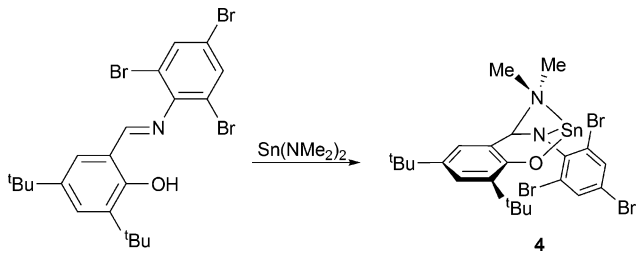


Fig. 1 The molecular structure of complex **2**. Symmetry operator A = 1 – *x*, 1 – *y*, 1 – *z*.

The reaction of Sn(NMe$_2$)$_2$ with the tenth salicylaldimine, [$_{tBu}$ON$_{TBP}$]H, also proceeds cleanly and again, bischelation is not observed. In this case, the ^{1}H NMR spectrum of the product (**4**) is noticeably different from those of complexes **1–3**, and is instead consistent with migration of the NMe$_2$ ligand to the imino carbon (Scheme 5), forming a tridentate dianionic aminoamidophenoxide ligand in a fashion analogous to that reported previously with tridentate salicylaldimines.[4] The ^{1}H NMR spectrum of **4** includes a methine singlet at δ 6.62 (*cf.* 7.49, 8.85 and 7.37 ppm for the

Table 1 Selected bond lengths (Å) and bond angles (°) for complex **2**

Sn(1)–N(2)	2.192(2)	Sn(1)–N(2A)	2.326(2)
Sn(1)–O(1)	2.103(2)	Sn(1)–N(1)	2.698(2)
O(1)–C(1)	1.314(3)	C(1)–C(6)	1.425(4)
C(6)–C(7)	1.466(4)	C(7)–N(1)	1.277(4)
Sn(1)–N(2)–Sn(1A)	99.25(9)	N(2)–Sn(1)–N(2A)	80.75(9)
N(2)–Sn(1)–O(1)	87.77(9)	N(2A)–Sn(1)–O(1)	90.11(8)
N(1)–Sn(1)–N(2)	92.43(8)	N(1)–Sn(1)–N(2A)	163.37(8)
N(1)–Sn(1)–O(1)	74.40(7)		



Scheme 5

C*H*=N resonances of **1–3** respectively), and a corresponding ^{13}C NMR chemical shift which is at odds with an unsaturated imino carbon environment (δ 88.44 *vs.* δ 165.54, 157.68 and 165.43 for **1–3**). In addition, two singlets at 2.34 and 1.84 ppm are attributed to inequivalent *N*-methyl groups, indicating that the Me_2N amino donor is strongly bound to the tin centre.[4]

The molecular structure of complex **4** is shown in Fig. 2 and Fig. 3. The *N*,*N*,*O* chelate adopts a tripodal geometry with the coordination sphere of the tin completed by weak inter- and intra- molecular interactions with the *N*-aryl *ortho*-bromine atoms (Sn(1)···Br(1) = 3.1469(6) Å; Sn(1)–Br(1A) = 3.850 Å). The conversion of the salicylaldimine nitrogen into an anionic amide ligand results in a Sn(1)–N(1) distance (2.153(2) Å) which is notably shorter than the neutral metal–amino interaction, Sn(1)–N(2) (2.354(2) Å, Table 2). The tin atom lies 1.307 Å out of the N(1)–C(7)–N(2) plane, in the direction of the phenoxide oxygen, and lies 1.439 Å above the O(1)–N(1)–N(2) plane. With the exception of the N(1)–Sn(1)–N(2) chelate [60.91(9)°] many of the angles at the metal formed between the ligand donor

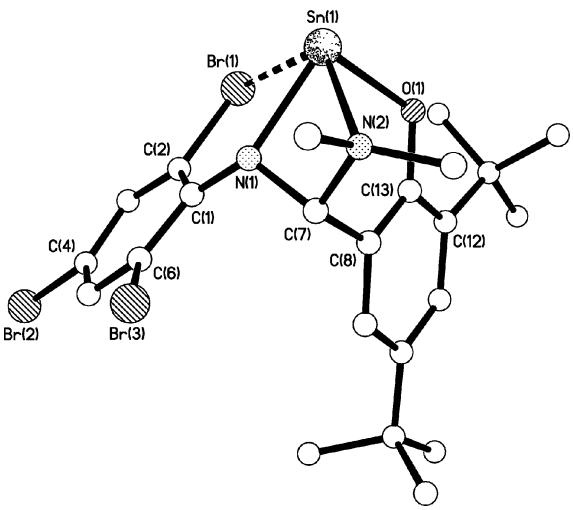


Fig. 2 The molecular structure of complex **4**.

Table 2 Selected bond lengths (Å) and bond angles (°) for complex **4**

Sn(1)–O(1)	2.073(2)	Sn(1)–N(1)	2.153(2)
Sn(1)–N(2)	2.354(2)	Sn(1)–Br(1)	3.1469(6)
C(7)–N(1)	1.481(4)	C(7)–N(2)	1.500(4)
O(1)–Sn(1)–N(1)	92.28(8)	O(1)–Sn(1)–N(2)	80.63(8)
N(1)–Sn(1)–N(2)	60.91(9)	N(1)–C(7)–N(2)	100.4(2)
Br(1)···Sn(1)–O(1)	81.01	Br(1)···Sn(1)–N(1)	69.56

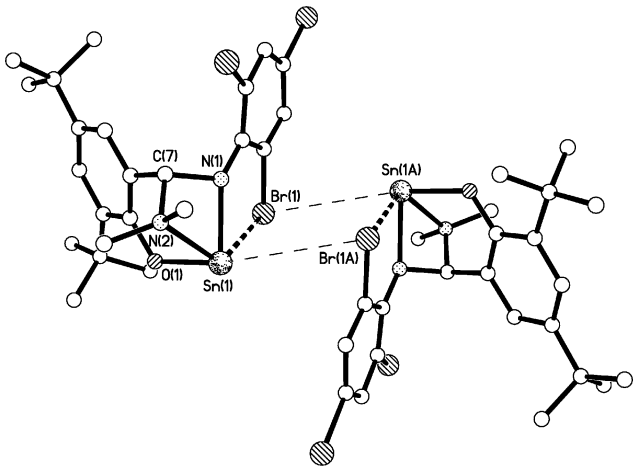


Fig. 3 Weak intermolecular interactions in the molecular structure of complex **4**. Sn(1)···Br(1A) = 3.850 Å. Symmetry operator A = 1 − *x*, 2 − *y*, 1 − *z*.

atoms approach 90°. As observed with several other divalent tin complexes, this bonding picture is consistent with the metal utilising orthogonally-aligned 4d and 5p orbitals to engage the ligand (on the basis of previous computational studies,[4] we assume that a relativistic contraction greatly precludes involvement of the 5s orbital).

Polymerisation studies

The three tin(II) amides **1–3**, and the amide tautomer **4**, have all been investigated as possible *rac*-lactide polymerisation initiators in toluene at 60 °C ($[LA]_0$ = 0.28 M; $[LA]_0$: [Sn] = 100; Table 3). The most reactive initiator, **1** promotes > 90% conversion in just 1 h but deviates slightly from ideal behaviour, resulting in a rather broad molecular weight distribution (*ca* 1.4). This most likely arises from transesterification (confirmed by an *rrr* tetrad *C*HMe ^{13}C resonance[20]) in line with the increased Lewis acidity of the metal in this complex; similar levels of molecular weight control have previously been reported with halo-substituted diketiminate-supported counterparts.[4] The polymerisations mediated by **2** and **4** are only slightly slower yet both are well-controlled chain growth processes, with linear relationships recorded between M_n and monomer conversion, molecular weights close to those calculated from the monomer : initiator stoichiometries, and relatively narrow polydispersities. A moderate heteroselectivity is observed with all four initiators, as reported for a number of tin(II)-based initiator families,[1–6] lending further credence to a lone pair assisted chain end mechanism.[4]

Despite the comparable activities of complexes **1**, **2** and **4** (Fig. 4), the mononuclear initiator **3** is far slower. No chain growth is observed during the first few hours and thereafter, propagation

Table 3 *rac*-LA polymerisation data[a]

Initiator	Time/min[b]	Conversion[c]	Induction period/min	k_{app}/h^{-1}	M_n[d]	M_w/M_n[d]	P_r[e]
1	60	92	—	2.56	15 400	1.37	0.65
2	100	92	—	1.55	20 700	1.19	0.65
3	1440	94	277	0.14	28 100	1.41	0.64
4	100	93	—	1.69	21 500	1.19	0.62

[a] Toluene, 60 °C, $[LA]_0 = 0.28$, $[LA]/[I] = 100$. [b] Time required for polymerisation to attain >90% LA consumption. [c] Determined by ^{1}H NMR ($CDCl_3$) by integration of monomer : polymer methine resonances. [d] Determined by GPC ($CDCl_3$). [e] P_r is the probability of racemic (heterotactic) enchainment, determined by homonuclear decoupled ^{1}H NMR ($CDCl_3$).

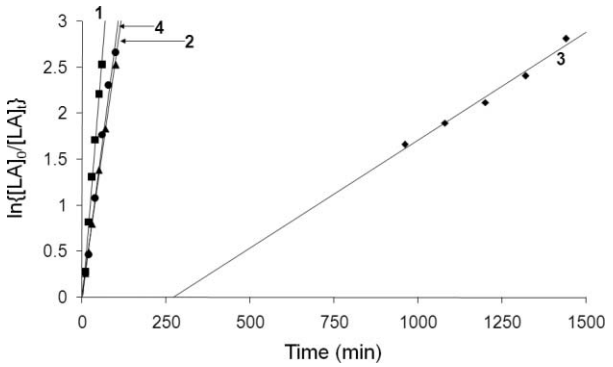


Fig. 4 Plots of $\ln\{[LA]_0/[LA]_t\}$ *versus* time (min) for the polymerisation of *rac*-LA with initiators **1**–**4** (toluene, 60 °C, $[LA]_0 = 0.28$ M, $[LA]_0/[I]_0 = 100$); ■ = **1**; ▲ = **2**; ◆ = **3**; ● = **4**.

proceeds at a rate which is at least one order of magnitude slower than for the other three complexes. Even though one might anticipate **3** to possess the most accessible active site, the relative reactivity of the four initiators is readily explained by comparing the nature of their propagating species. Examination of the solid state structure of **2** indicates that even in the dimeric form, the tin(II) centres are quite exposed, and we therefore propose that **1** and **2** rapidly insert one equivalent of lactide to give mononuclear four-coordinate active sites (Scheme 6). These would be analogous to the propagating species generated from **3**, but would be rather less bulky and hence more reactive. A similar argument justifies the potency of the latent amide initiator **4**: once initiation has occurred the propagating species is akin to those generated from **1–3** and the rate of propagation is therefore susceptible to similar steric and electronic effects. The large induction period witnessed with **3** has not been probed further, but we note that similar effects have been seen previously with sterically bulky diketiminate tin(II) initiators and have been subject to a recent theoretical study.[4]

Experimental

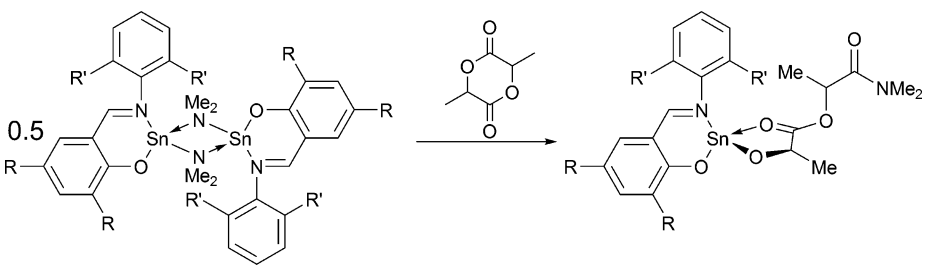
All solvents were dried by prolonged reflux over appropriate drying agents, except toluene, which was dried by passing through a column of Cu_2O/Al_2O_3 under a stream of nitrogen. All solvents were degassed thoroughly prior to use. $Sn(NMe_2)_2$ was prepared by an existing literature procedure.[10] The salicylaldimines were synthesised by the formic acid-catalysed condensation of amines or anilines with commercially available salicylaldimines in ethanol. Lactide (Aldrich) was purified by triple sublimation under vacuum.

NMR spectra were recorded on a Bruker AM500 or DRX400 instrument. Microanalyses were carried out at the University of North London. GPC measurements were performed in HPLC grade $CHCl_3$ at 1.0 ml min^{-1} using a Polymer Laboratories LC1220 HPLC pump and a Spark Midas autosampler connected to two 5 μm columns (300 × 7.5 mm) and a Shodex RI-101 differential refractometer. The columns were calibrated with polystyrene standards ranging in molecular weight from 1560 to 128 000 Da and chromatograms were analysed using Cirrus software (Polymer Laboratories) in order to establish molecular weights and polydispersities. Samples were passed through a 0.45 μm filter prior to injection.

[$_{Cl}$ON$_{DIPP}$]Sn(NMe$_2$), 1

[$_{Cl}$ON$_{DIPP}$]H (0.811 g, 2.32 mmol) was dissolved in 20 cm^3 toluene and added to a 20 cm^3 toluene solution of $Sn(NMe_2)_2$ (0.484 g, 2.34 mmol) chilled to −78 °C. After stirring for 2 h room temperature, volatiles were removed and the yellow solid was recrystallised (required several days at −30 °C) from warm (70 °C) toluene (0.769 g yellow crystals, 1.50 mmol, 65% yield).

^{1}H NMR (400.1 MHz, C_6D_6): δ 8.21 (br, 2H, *H*C=N+/C_6H_3), 7.62 (br, 2H, *H*C=N+/C_6H_3), 7.49 (s, 1H, *H*C=N), 7.32 (d, 2H, $^4J_{HH}$ 2.4 Hz, C_6H_2), 7.14 (br s, 1H, C_6H_2), 7.14–6.99 (m, 3H, C_6H_3+*H*C=N), 6.78 (d, 1H, $^4J_{HH}$ 2.5 Hz, C_6H_2), 4.19 (br sept,



Scheme 6

1H, C*H*(CH$_3$)$_2$), 3.05 (br sept, 2H, C*H*(CH$_3$)$_2$), 2.80 (br sept, 1H, C*H*(CH$_3$)$_2$), 2.40 (br s, 12H, N(C*H*$_3$)$_2$), 1.40 (br d, 3H, $^3J_{HH}$ 5.8 Hz CH(C*H*$_3$)$_2$), 1.31 (br d, 3H, $^3J_{HH}$ 5.9 Hz CH(C*H*$_3$)$_2$), 1.11 (d, 12H, $^3J_{HH}$ 6.7 Hz CH(C*H*$_3$)$_2$), 1.00 (br d, 3H, $^3J_{HH}$ 5.9 Hz CH(C*H*$_3$)$_2$), 0.88 (br d, 3H, $^3J_{HH}$ 5.6 Hz CH(C*H*$_3$)$_2$); ^{13}C NMR (100.6 MHz, C_6D_6): δ 165.54 (H*C*=N), 162.45 (1/2/3/5-C_6H_2), 158.94 (1/2/3/5-C_6H_2), 148.93 (1-C_6H_3), 144.91 (1-C_6H_3), 141.17 (2/6-C_6H_3), 140.77 (2/6-C_6H_3), 138.48 (2 coincident resonances, 2/6-C_6H_3), 133.63 (4/6-C_6H_2), 133.03 (2 coincident resonances, 4/6-C_6H_2), 132.83 (4/6-C_6H_2), 127.23 (3/4/5-C_6H_3), 125.48 (3/4/5-C_6H_3), 123.71 (3 coincident resonances, 3/4/5-C_6H_3), 122.82 (3/4/5-C_6H_3), 121.78 (1/2/3/5-C_6H_2), 120.73 (1/2/3/5-C_6H_2), 41.22 (N(*C*H$_3$)$_2$), 28.48 (3 coincident resonances, *C*H(CH$_3$)$_2$), 27.72 (*C*H(CH$_3$)$_2$), 25.44 (CH(*C*H$_3$)$_2$), 25.28 (CH(*C*H$_3$)$_2$), 24.10 (5 coincident resonances, CH(*C*H$_3$)$_2$), 23.88 (CH(*C*H$_3$)$_2$); ^{119}Sn NMR (186.4 MHz, C_6D_6): δ −664. (Found: C, 49.00; H, 4.99; N, 5.60. $C_{21}H_{26}N_2OCl_2Sn$ requires C, 49.26; H, 5.12; N, 5.47%).

[$_{t}$ON$_{DIPP}$]Sn(NMe$_2$), 2

A diethyl ether solution (30 cm^3) of [$_{t}$ON$_{DIPP}$]H (1.1015 g, 1.91 mmol) was added dropwise to a solution of Sn(NMe$_2$)$_2$ (0.397 g, 1.92 mmol) in diethyl ether (20 cm^3) chilled to −78 °C. The mixture was then stirred for 2 h at room temperature, affording a yellow precipitate. The volatile components were removed under reduced pressure and yellow (X-ray diffraction quality) crystals of **2** were obtained by allowing a saturated toluene solution to cool from 70 °C to room temperature (0.815 g, 1.17 mmol, 61% yield).

^{1}H NMR (400.1 MHz, C_6D_6): δ 8.14 (d, 1H, $^4J_{HH}$ 2.3 Hz, C_6H_2), 8.04 (br, 1H, C_6H_2/*H*C=N), 7.95 (d, 1H, $^4J_{HH}$ 2.3 Hz, C_6H_2), 7.38 (s, 1H, *H*C=N), 7.27 (d, 1H, $^4J_{HH}$ 2.3 Hz, C_6H_2), 7.18–7.00 (m, 7H, C_6H_3+C_6H_2/*H*C=N), 4.17 (br sept, 1H, C*H*(CH$_3$)$_2$), 3.04 (br sept, 2H, C*H*(CH$_3$)$_2$), 2.69 (br sept, 1H, C*H*(CH$_3$)$_2$), 2.61 (br s, 12H, N(C*H*$_3$)$_2$), 1.39 (br d, 3H, $^3J_{HH}$ 5.6 Hz CH(C*H*$_3$)$_2$), 1.31 (br d, 3H, $^3J_{HH}$ 5.7 Hz CH(C*H*$_3$)$_2$), 1.12 (d, 12H, $^3J_{HH}$ 6.8 Hz CH(C*H*$_3$)$_2$), 0.93 (br d, 3H, $^3J_{HH}$ 6.4 Hz CH(C*H*$_3$)$_2$), 0.89 (br d, 3H, $^3J_{HH}$ 6.2 Hz CH(C*H*$_3$)$_2$); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ 165.43 (H*C*=N), 163.42 (1/2/3/5-C_6H_2), 162.70 (1/2/3/5-C_6H_2), 150.71 (4/6-C_6H_2), 150.38 (4/6-C_6H_2), 144.94 (4/6-C_6H_2), 144.47 (1-C_6H_3), 141.20 (2/6-C_6H_3), 140.86 (2/6-C_6H_3), 138.78 (2 coincident resonances, 2/6-C_6H_3), 127.13 (2 coincident resonances, 3/4/5-C_6H_3), 125.60 (2 coincident resonances, 3/4/5-C_6H_3), 123.75 (2 coincident resonances, 3/4/5-C_6H_3), 123.42 (1-C_6H_3/1-C_6H_2), 96.52 (1/2/3/5-C_6H_2), 96.14 (1/2/3/5-C_6H_2), 78.45 (1/2/3/5-C_6H_2), 76.72 (1/2/3/5-C_6H_2), 43.42 (N(*C*H$_3$)$_2$), 28.51 (3 coincident resonances, *C*H(CH$_3$)$_2$), 28.08 (*C*H(CH$_3$)$_2$), 26.08 (CH(*C*H$_3$)$_2$), 25.71 (CH(*C*H$_3$)$_2$), 24.17 (5 coincident resonances, CH(*C*H$_3$)$_2$), 23.63 (CH(*C*H$_3$)$_2$); ^{119}Sn NMR (186.4 MHz, C_6D_6): δ −639. (Found: C, 36.28; H, 3.81; N, 3.90. $C_{21}H_{26}N_2OI_2Sn$ requires C, 36.29; H, 3.77; N, 4.03%).

[$_{Cl}$ON$_{TTBP}$]Sn(NMe$_2$), 3

A 30 cm^3 diethyl ether solution of [$_{Cl}$ON$_{TTBP}$]H (0.802 g, 1.85 mmol) was added to Sn(NMe$_2$)$_2$ (0.385 g, 1.86 mmol, 20 cm^3 diethyl ether) at −78 °C. After allowing to warm to room temperature, the reaction was stirred for 2 h and volatiles removed *in vacuo* to give a yellow powder. Recrystallisation from a saturated toluene solution at −30 °C over several days afforded **3** as yellow crystals (0.501 g, 0.84 mmol, 45% yield).

^{1}H NMR (400.1 MHz, C_6D_6): δ 8.84 (s, 1H, *H*C=N), 8.57 (d, 1H, $^4J_{HH}$ 2.6 Hz, 6-C_6H_2), 7.55 (s, 2H, 3 + 5-C_6H_2^{t}Bu$_3$), 7.21 (d, 1H, $^4J_{HH}$ 2.7 Hz, 4-C_6H_2), 2.04 (s, 6H, N(C*H*$_3$)$_2$), 1.46 (s, 18H, 2 + 6-C(C*H*$_3$)$_3$), 1.34 (s, 9H, 4-C(C*H*$_3$)$_3$); ^{13}C NMR (100.6 MHz, C_6D_6): δ 158.47 (2-C_6H_2), 157.68 (H*C*=N), 151.44 (1-C_6H_2^{t}Bu$_3$), 144.63 (4-C_6H_2^{t}Bu$_3$), 138.86 (2 + 6-C_6H_2^{t}Bu$_3$), 132.09 (4-C_6H_2), 126.83 (6-C_6H_2), 124.13 (3/5-C_6H_2), 123.32 (3/5-C_6H_2), 121.90 (3/5-C_6H_2^{t}Bu$_3$), 40.40 (N(*C*H$_3$)$_2$), 36.22 (2 + 6-*C*(CH$_3$)$_3$), 34.84 (4-*C*(CH$_3$)$_2$), 32.08 (2 + 6-C(*C*H$_3$)$_3$), 31.81 (4-C(*C*H$_3$)$_3$), 1-C_6H_2 was not found; ^{119}Sn NMR (186.4 MHz, C_6D_6):δ −107. (Found: C, 54.56; H, 6.17; N, 4.60. $C_{27}H_{36}N_2OCl_2Sn$ requires C, 54.58; H, 6.11; N, 4.71%).

[2,4-^{t}Bu$_2$-6-{CH(NMe$_2$)N-2,4,6-Br$_3$C$_6$H$_2$}-C$_6$H$_2$O]Sn, 4

A 30 cm^3 diethyl ether solution containing 0.800 g [$_{tBu}$ON$_{TBP}$]H (1.46 mmol) was added to a diethyl ether solution (20 cm^3 of Sn(NMe$_2$)$_2$ (0.318 g, 1.54 mmol) at −78 °C. After allowing to stir for 2 h at room temperature the reaction was concentrated under reduced pressure to afford a yellow solid. Analytically pure **4** was then obtained by recrystallising from a minimum amount of diethyl ether stored at −30 °C for 18 h (0.599 g yellow crystals, 0.85 mmol, 58% yield). Crystals suitable for X-ray crystallography were grown by allowing a saturated diethyl ether solution to stand at room temperature for several days.

^{1}H NMR (400.1 MHz, C_6D_6): δ 7.53 (d, 1H, $^4J_{HH}$ 2.6 Hz, 4-C_6H_2), 7.13 (s, 2H, 3 + 5-$C_6H_2Br_3$), 6.73 (d, 1H, $^4J_{HH}$ 2.7 Hz, 6-C_6H_2), 6.62 (s, 1H, *H*C-N), 2.34 (s, 3H, N(C*H*$_3$)$_2$), 1.84 (s, 3H, N(C*H*$_3$)$_2$), 1.80 (s, 9H, 3-C(C*H*$_3$)$_3$), 1.20 (s, 9H, 5-C(C*H*$_3$)$_3$); ^{13}C NMR (100.6 MHz, C_6D_6): δ 154.59 (2-C_6H_2), 146.17 (1-$C_6H_2Br_3$), 138.53 (5-C_6H_2), 138.17 (3-C_6H_2), 135.20 (2/4/6 + 3+5-$C_6H_2Br_3$), 125.24 (4-C_6H_2), 123.88 (6-C_6H_2), 118.98 (2/4/6-$C_6H_2Br_3$), 109.76 (2/4/6-$C_6H_2Br_3$), 88.44 (H*C*-N), 43.90 (N(*C*H$_3$)$_2$), 40.68 (N(*C*H$_3$)$_2$), 35.54 (3-*C*(CH$_3$)$_3$), 34.02 (5-*C*(CH$_3$)$_2$), 31.80 (5-C(*C*H$_3$)$_3$), 30.28 (3-C(*C*H$_3$)$_3$); ^{119}Sn NMR (186.4 MHz, C_6D_6): δ −194. (Found: C, 38.95; H, 4.06; N, 3.90. $C_{23}H_{29}N_2OBr_3Sn$ requires C, 39.02; H, 4.13; N, 3.96%).

Crystal data for 2. $C_{42}H_{52}I_4N_4O_2Sn_2$, M = 1389.86, triclinic, space group $P\bar{1}$, a = 8.6381(5), b = 10.0747(6), c = 14.7661(8) Å, α = 71.3596(9), β = 85.7434(10), γ = 79.4997(9)°, U = 1197.07(12) Å^3, T = 150(2) K, Z = 1, μ(Mo-Kα) = 3.659 mm^{-1}, λ = 0.71073 Å, 10669 reflections measured, 5538 unique (R_{int} = 0.0170) which were used in all calculations. The final wR^2 = 0.0556 (all data) and $R1$ = 0.0247 (for 4588 data with $F^2 > 2\sigma(F^2)$). CCDC 696308.

Crystal data for 4. $C_{23}H_{29}Br_3N_2OSn$, M = 707.90, triclinic, space group $P\bar{1}$, a = 9.0297(2), b = 10.2931(3), c = 14.0540(4) Å, α = 78.4205(12), β = 88.3895(17), γ = 80.8048(18)°, U = 1263.19(6) Å^3, T = 120(2) K, Z = 2, μ(Mo-Kα) = 5.773 mm^{-1}, λ = 0.71073 Å, 22501 reflections measured, 5749 unique (R_{int} = 0.0485). wR^2 = 0.0734 (all data); $R1$ = 0.0301 (for 4961 data with $F^2 > 2\sigma(F^2)$). CCDC 696309.

Polymerisation procedure

In a N$_2$ atmosphere glove box, 10 ml toluene was added to a solid mixture of *rac*-LA (0.4036 g, 0.28 mmol) and the tin-based initiator (0.0028 mmol), and a magnetic stirrer was added. This mixture

was then transferred immediately to a pre-warmed oil-bath and stirred at 60 °C. At appropriate time intervals, aliquots were removed and following termination with MeOH the conversion of monomer was determined by integration of the monomer *vs.* polymer methine resonances in the ^{1}H NMR spectrum ($CDCl_3$), and molecular weight data was determined by GPC.

Conclusions

Although four of the smaller salicylaldimines are susceptible to bischelation at divalent tin centres, this study shows that mono(iminophenoxide) counterparts are accessible. A fine balance between steric and electronic effects clearly operates; for example, while bischelation is observed with $[_{Me}ON_{DIPP}]H$, the sterically similar $[_{Cl}ON_{DIPP}]H$ yields **1** cleanly and in good yield. In this case, the mono(amide) complex may be stabilised by the formation of the bridged dimer, a possible repercussion of the Lewis acidic tin when supported by the halogenated ancillary ligand.

One of the most intriguing results emanating from this work is the isolation of complex **4** which confirms that the amide migration previously reported by us is apparently not limited to tridentate salicylaldimines. However, the weak coordination of the *ortho*-bromo substituent in the solid state structure of **4** could point towards a requirement for a third coordination site to be occupied by the ligand. It is interesting that this rearrangement is not observed in **1**–**3** with halogenated phenolic groups, indicating that electron withdrawing *N*-substituents are more likely to activate the imino carbon towards nucleophilic attack. Preliminary ^{1}H NMR scale experiments with the analogous *N*-2,4,6-trichlorophenyl salicylaldimine with $Sn(NMe_2)_2$ indicate that amide migration also occurs in this system too.

All four complexes isolated in this study are active for the polymerisation of *rac*-lactide, though the mononuclear terminal amide complex **3** is notably slower than **1**, **2** or **4**. This observation is attributed to a common propagating species structure in all four cases (Scheme 6), with the accessibility of the metal in **3** impeded by the *N*-2,4,6-tris(*tert*-butyl)phenyl substituent.

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