

Unprecedented Reversible Migration of Amide to Schiff Base Ligands Attached to Tin: Latent Single-Site Initiators for Lactide Polymerization

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Schiff base ligands represent one of the most widely utilized classes of ligand in metal coordination chemistry.¹ Their complexes find many important catalytic applications, ranging from asymmetric epoxidation,² Lewis acid assisted organic transformations,³ to various types of polymerization,^{4–7} as well as their widespread use as model compounds for the study of the active sites of metalloenzymes.⁸ While an attractive feature of Schiff base ligands is their relative inertness to ligand-centered reaction chemistry, the partially positively charged imine unit can sometimes render them susceptible to nucleophilic attack. This usually arises from irreversible intramolecular attack by donors incorporated within the Schiff base ligand leading to macrocyclic ring contractions.⁹ Radical mediated alkylations are also known to occur.^{10,11} Herein, we describe an unprecedented attack by amide at the imine carbon atoms of tridentate Schiff base ligands to give unusual tetradentate ligand systems. A reverse process disassembles the so-formed tetradentate ligands to afford single-site initiators for lactide polymerization.

The iminophenols **1–3** containing O, S, and P donor arms were synthesized by condensation of 3,5-Bu^t₂-salicylaldehyde with the appropriate amine and reacted with Sn(NMe₂)₂ to give the crystalline products **1a–3a** in good yields (Scheme 1). The same products could also be obtained, first by treatment of SnCl₂ with the in-situ-generated lithium salts derived from **1–3** to afford the monochloride complexes **1b–3b**, followed by their reactions with LiNMe₂.

NMR spectra for **1a–3a** revealed chemical shifts in the range δ 5.35–5.60, considerably upfield of the usual region for the imine HC=N resonances of salicylaldiminato ligands (typically ca. δ 7.50–8.50) while the ¹³C NMR spectrum showed corresponding upfield shifts for the associated carbon nuclei, at δ 87–90 (cf. ca. δ 165–170 for salicylaldiminato complexes). These are indicative of a saturated carbon center rather than an unsaturated imino moiety. In addition, a 2D HMBC NMR spectrum¹² showed the presence of coupling between the methyl hydrogens of the dimethylamino unit and the carbon of the ligand CH moiety implying a close association of these two groups.

It proved possible to obtain crystals of **3a** suitable for an X-ray structure determination. A view of the structure is shown in Figure 1; selected bond lengths and angles are given in the figure caption. The tin amide group is found to have attacked the imine carbon of the salicylaldimine to give a new dianionic tetradentate ligand in which the O, N, and P donors of the original salicylaldimine ligand and the nitrogen of the dimethylamino group are bonded to the tin(II) center. As a result, the original C=N double bond is now a C–N single bond, with a length of 1.467(17) Å. The Sn–N bond lengths reflect the changes in bonding that have occurred upon generating the new ligand system. The Sn–N(2) bond length, at

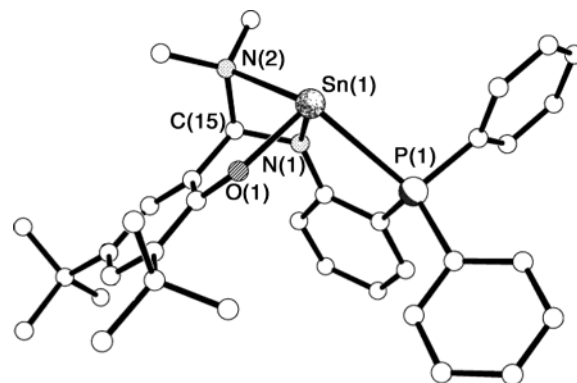
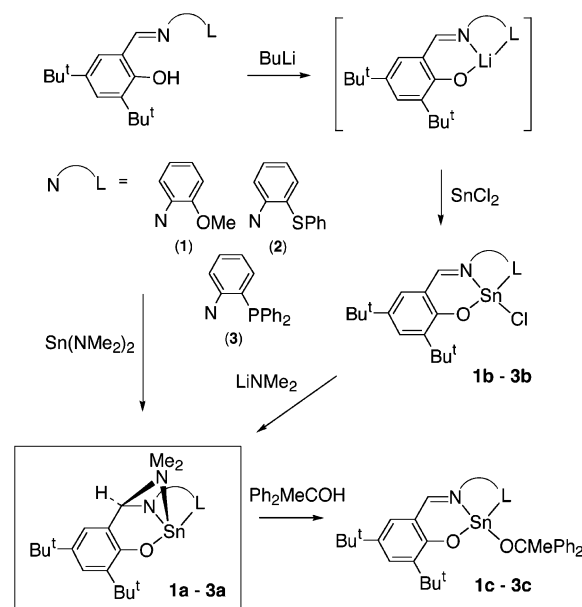


Figure 1. Crystal structure of **3a** with H atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn(1)–P(1) 2.8400(4), Sn(1)–N(1) 2.1649(12), Sn(1)–N(2) 2.4490(13), Sn(1)–O(1) 2.0628(9), N(1)–C(15) 1.4672(17), N(2)–C(15) 1.4948(19), P(1)–Sn(1)–N(2) 130.10(3), N(1)–Sn(1)–N(2) 59.40(4), N(2)–Sn(1)–O(1) 82.54, N(1)–C(15)–N(2) 101.82(11), Sn(1)–N(1)–C(15) 98.16(8), Sn(1)–N(2)–C(15) 86.16(7).

Scheme 1

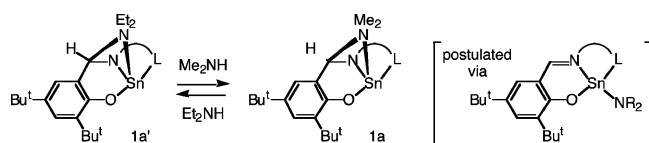


2.4490(13) Å, is consistent with a dative covalent interaction, while the Sn–N(1) bond distance, at 2.1649(12) Å, is indicative of an amide ligand containing a significant degree of lone pair donation to the tin center. Consistently, N(1) adopts an almost planar geometry. The overall outcome of the ligand rearrangement is a metal-centered geometry that is best viewed as being derived from a trigonal bipyramid in which one of the equatorial coordination sites is occupied by the stereochemically active lone pair of

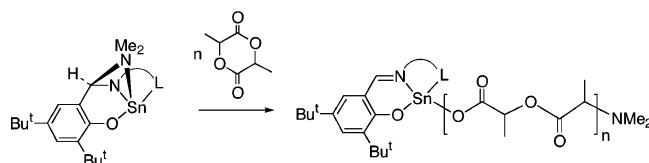
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Scheme 2



Scheme 3



	Time (min)	Conv. (%)	M_n	PDI	k_{app} (min^{-1})
1a	120	91	18600	1.29	0.0236
2a	120	95	19100	1.27	0.0263
3a	110	94	20400	1.25	0.0284

60°C, toluene, 100 equiv. LA.

electrons. Such a geometry is consonant with the predictions of the vibronic coupling model¹³ as well as simple valence shell electron pair repulsion (VSEPR) theory.

To learn more about the reactivity of the NR_2 -bridged species, the Et_2N derivative **1a'** was prepared and treated with excess Me_2NH . This led to clean formation of the Me_2N -bridged product **1a**. Conversely, treatment of **1a** with 12 equiv of Et_2NH led to a 1.6:1 mixture of **1a** and **1a'** (K_{298} 0.021) revealing the greater thermodynamic stability of products containing smaller amine bridges. A postulated pathway for this exchange process is via a terminal amide species (Scheme 2). That such terminal amide species are viable is supported by the observation that the N^iPr_2 and $\text{N}(\text{SiMe}_3)_2$ derivatives¹² contain terminal rather than bridging R_2N units. Related alkoxide derivatives, **1c–3c** (Scheme 1), obtained by treatment of **1a–3a** with Ph_2MeCOH , also have terminal alkoxide ligands.

$\text{Sn}(\text{II})$ alkoxide and amide complexes play a central role in the production of polylactide (PLA),¹⁴ a biosustainable material derived from lactic acid. The potential formation of terminal amide species from **1a–3a** suggested that they may act as latent single-site initiators for lactide polymerization. Treatment of **1a–3a** with *rac*-lactide afforded PLA with good control (see Scheme 3). The O, S, and P donor derivatives **1a–3a** gave quite similar rates (k_{app}) of polymerization. In all cases, a linear increase in molecular weight (M_n) with conversion was observed as well as a linear relationship between M_n and monomer/initiator ratio.¹² Examination of the ^1H NMR spectrum of a sample of **1a** treated with 10 equiv of lactide showed resonances attributable to the imine hydrogens of the salicylaldiminato ligand along with the dimethylamino moiety attached to the end of the growing polymer chains. For the isolated polymer, two singlet resonances, at δ 2.94 and 3.03 (CDCl_3), are

attributable to the diastereotopic methyl units of the NMe_2 end-group. Consistently, a MALDI-TOF mass spectrum on a sample of PLA prepared using **3a** and 20 equiv of *rac*-lactide revealed PLA chains bearing Me_2N end-groups.¹²

In summary, we have described an unprecedented migration of an amino group to the imine carbon atom of a family of tridentate salicylaldiminato complexes to give highly unusual tetradentate ligands. The so-formed complexes act as latent single-site initiators for the controlled polymerization of *rac*-lactide.

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Supporting Information Available: Full experimental details for the synthesis of all complexes, including crystallographic data for **3a** and polymerization data (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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