Inorganic Chemistry

Article

pubs.acs.org/IC

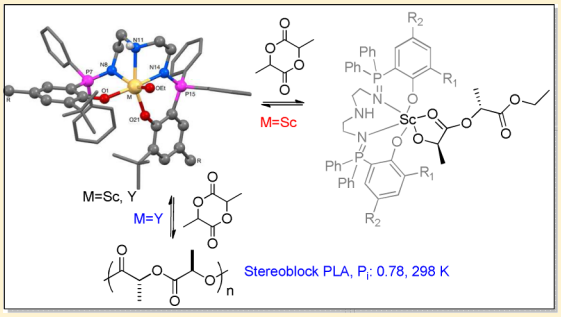
Scandium and Yttrium Phosphasalen Complexes as Initiators for Ring-Opening Polymerization of Cyclic Esters

Clare Bakewell, Andrew J. P. White, Nicholas J. Long,* and Charlotte K. Williams*

Department of Chemistry, Imperial College London, London SW7 2AZ, United Kingdom

Supporting Information

ABSTRACT: The synthesis and characterization of novel scandium and yttrium phosphasalen complexes is reported, where phosphasalen refers to two different bis(iminophosphorane) derivatives of the more ubiquitous salen ligands. The activity of the complexes as initiators for the ring-opening polymerization of cyclic esters is presented. The scandium complexes are inactive for lactide polymerization but slow and controlled initiators for ε-caprolactone polymerization. The lack of activity toward lactide exhibited by these compounds is probed, and a rare example of single-monomer insertion product, unable to undergo further reactions with lactide, is identified. In contrast, the analogous yttrium phosphasalen complex is a very active initiator for the ring-opening polymerization of *rac*-lactide (k_{obs} = 1.5 × 10^{-3} s^{-1} at 1:500 [yttrium initiator]:[*rac*-lactide], 1 M overall concentration of lactide in THF at 298 K). In addition to being a very fast initiator, the yttrium complex also maintains excellent levels of polymerization control and a high degree of isoselectivity, with the probability of isotactic enchainment being P_i = 0.78 at 298 K.



INTRODUCTION

The long-standing environmental and economic issues surrounding current, petrochemically derived, polymers have prompted the investigation of more sustainable and, in some cases, degradable alternatives. Polylactide (PLA) is currently a leading bioderived polymer, being produced on a 140 000 tonne scale annually by Natureworks in the United States and by a range of other suppliers worldwide.[1] Polylactide and related aliphatic polyesters such as polycaprolactone (PCL) are formed by the ring-opening polymerization (ROP) of the cyclic ester, e.g., lactide (LA) or ε-caprolactone (CL).[2] The ROP process requires an initiator, with a range of Lewis-acidic metals and complexes having precedent in catalysis. Furthermore, by careful selection of the initiator and using the racemic lactide precursor it is possible to control the ROP stereochemistry leading to PLA with defined tacticities.[3] The production of isotactic PLA, using racemic lactide, is attracting particular attention as it can lead to stereoblock or stereocomplex PLA, both of which show superior thermal and mechanical properties compared to atactic PLA.[4] Isoselective initiators remain of high interest but are rather unusual; so far the most selective initiators are complexes of Al(III), In(III), Zn(II), or Y(III).[4c,e,5]

Yttrium complexes are particularly interesting as they have shown fast rates and, in many cases, afford good polymerization control.[3e,5a,m,n,y,6] As mentioned, the control the initiator exerts over the polymer microstructure remains critical; currently, the majority of yttrium initiators lead to heterotactic, or more often, atactic PLA. Arnold and co-workers reported the first example of an isoselective initiator in 2008: a homochiral yttrium complex (Figure 1) which showed high selectivity (P_i = 0.81, 262 K).[5y] Since 2012, we have also reported various yttrium

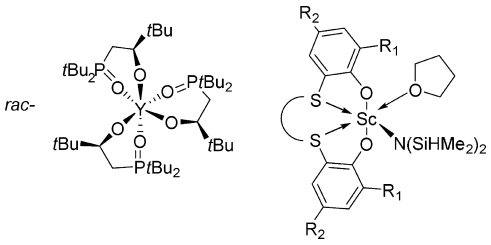


Figure 1. (Left) Isoselective yttrium initiator reported by Arnold and co-workers.[5y] (Right) General representation of the series of scandium complexes reported by Okuda and co-workers,[6am] where R_1 and R_2 = alkyl/aryl groups (P_s = 0.95).

complexes, including complex **A** (Figure 2) which showed good isoselectivity (P_i = 0.84, 258 K).[5n] In contrast to the attention focused on yttrium complexes, scandium initiators have been less studied. The first report of a scandium initiator was the use of a scandium(III) trifluoromethanesulfonate complex [Sc(OTf)$_3$].[7] Furthermore, in this field Okuda and co-workers pioneered discrete scandium initiating systems for the controlled, highly heteroselective ring-opening polymerization of *rac*-lactide (Figure 1).[6am] Analogous yttrium and lutetium complexes afforded PLA with a significantly reduced heterotactic microstructure, leading to the overall trend Sc > Y > Lu.[6o]

Received: November 10, 2014
Published: February 18, 2015

DOI: 10.1021/ic5027015
Inorg. Chem. 2015, 54, 2204−2212

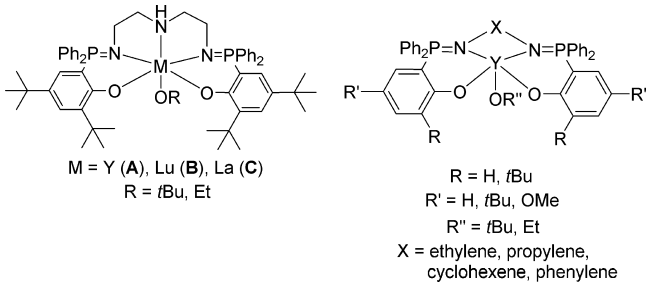


Figure 2. Structures of previously reported phosphasalen complexes for the ROP of lactide; if M = Y, then an isoselective (left) or a heteroselective (right) initiator is prepared.[5a,m,n]

Group 3 and rare-earth phosphasalen complexes are interesting initiators for the ring-opening polymerization of *rac*-lactide, offering both high rates of reaction and good levels of stereocontrol (Figure 2).[5a,m,n] Indeed, the phosphasalen ligand scaffold is of general interest due to its strong σ- and π-donor abilities, making it a relevant ancillary ligand for a range of catalytic transformations.[5a,m,n,8] The hexacoordinate yttrium phosphasalen complex, **A**, showed good isoselectivity for the ROP of *rac*-LA (P_i = 0.74, 298 K).[5n] The stereocontrol occurs by a chain-end control mechanism, implying that the coordination chemistry of the growing polymer chain plays a significant role in influencing the overall stereochemistry. The nature of the metal center, in the phosphasalen complex, can be used to moderate the degree of isotacticity, with the smaller lutetium complex **B** showing enhanced isoselectivity compared to the yttrium complex **A** (**B** shows P_i = 0.82, 298 K). It was also possible to completely change the stereocontrol by coordinating the larger lanthanum which resulted in **C** showing high selectivity for heterotactic PLA (P_i = 0.28, 298 K).[5a] The increase in isoselectivity from the yttrium phosphasalen initiator, **A**, to the lutetium phosphasalen, **B**, is large compared with a relatively small change in covalent radius. Thus, it was reasoned that targeting significantly smaller metals could lead to a further increase in the isoselectivity. Here, the investigations of more sterically constrained metal phosphasalen complexes, particularly of scandium and yttrium, are presented.

RESULTS AND DISCUSSION

The investigations into other metal complexes were somewhat limited by the relative size of the ligand, for instance, the aluminum complexes of the pentadentate phosphasalen ligand were not attainable, presumably due to steric requirements. Scandium was, however, an obvious choice due to its smaller covalent radius (1.70 Å)[9] relative to yttrium and lutetium (1.90 and 1.87 Å, respectively)[9] and the proven activity of scandium initiators for the ring-opening polymerization of cyclic esters.[6h,o,w,am] In addition to stereocontrol, it was also anticipated that a smaller metal center would lead to a more sterically constrained coordination site and thereby decrease the rate of polymerization. To this end, a methoxy-substituted (R = OMe) phosphasalen scandium complex was targeted, in addition to the *tert*-butyl-substituted phosphasalen complex. Previous observations with pentacoordinate yttrium phosphasalen initiators showed an increase in rate when the *tert*-butyl group at the para position was replaced with a methoxy substituent.[5m] This is proposed to lead to an increase in electron density at the metal center, reducing its Lewis acidity and increasing the lability of the metal−alkoxide bond, favoring lactide insertion.

The new methoxy-substituted pro-ligand, **L2**, was synthesized by the reaction of 2-*tert*-butyl-4-methoxy-6-phosphinophenol with bromine and 0.5 equiv of diethylenetriamine, a modified version of the Kirsanov reaction, in reasonable yields (Figure S1, Supporting Information, 50% yield after purification). A single peak was observed in the phosphorus NMR spectrum at 40.9 ppm, and the compound was fully characterized by NMR spectroscopy, with the purity being confirmed by elemental analysis.

The scandium phosphasalen complexes, compounds **1** and **2**, were synthesized by a similar route to that previously reported (Figure 3).[5a] First, the ligands were deprotonated, using 5 equiv

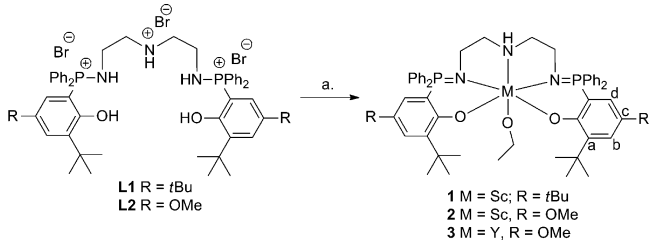


Figure 3. Synthesis and structure of initiators **1** and **2**. Reaction conditions: (1) $KN(SiMe_3)_2$ (5 equiv), THF, 2 h, 298 K; (2) $ScCl_3$, THF, 24 h, 348 K or YCl_3, THF, 4 h, 298 K; (3) KOEt, THF, 4 h, 298 K.

of potassium bis(trimethylsilyl)amide, leading to quantitative conversion to the salts, as observed by upfield shifts in the $^{31}P\{^1H\}$ NMR spectra (R′ = *t*Bu, 23.4 ppm; R′ = OMe, 22.4 ppm). The scandium phosphasalen chloride complexes were synthesized by reaction with $ScCl_3$, under reflux at 348 K for 24 h, with the resultant complexes being formed but not isolated. The species showed two peaks in the $^{31}P\{^1H\}$ NMR spectrum (R′ = *t*Bu, 32.7 and 32.2 ppm; R′ = OMe, 32.3 and 31.7 ppm), indicating that the two phosphorus environments in the complexes are not equivalent. Scandium ethoxide complexes were targeted as the ethoxide group is known from previous studies using yttrium complexes to be a better initiator than more sterically hindered alkoxides.[5m,n] Additionally, it is possible that carrying out salt metathesis reactions using bulkier alkoxide groups may be problematic. Indeed, clean formation of product could not be achieved when potassium *tert*-butoxide was used. In contrast, the addition of 1 equiv of potassium ethoxide to the scandium chloride complexes led to the formation of the scandium phosphasalen alkoxide compounds **1** and **2**. A slight upfield shift was again observed in the $^{31}P\{^1H\}$ NMR spectra for both complexes (**1**, 32.3 and 31.1 ppm; **2**, 31.7 and 30.9 ppm). Compounds **1** and **2** were isolated in good yields after recrystallization (66% and 58%, respectively).

Compounds **1** and **2** were characterized by multinuclear NMR techniques. As previously stated, the presence of two singlet phosphorus signals in the $^{31}P\{^1H\}$ NMR spectrum of both the scandium chloride complexes and the scandium ethoxide complexes indicates a significant degree of rigidity in the complexes resulting in different phosphorus environments. Such rigidity is not apparent in yttrium, lutetium, or lanthanum analogues of this complex, which typically show a single peak in the $^{31}P\{^1H\}$ NMR spectra.[5a] The increased rigidity of the scandium complexes is also observed in the phosphorus-

DOI: 10.1021/ic5027015
Inorg. Chem. 2015, 54, 2204−2212

decoupled ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra, where all proton/carbon environments are observed as separate signals (i.e., indicative of C_1-symmetric complexes). The NH resonances were confirmed by $^{1}H-^{15}N$ HSQC NMR spectrometry (Figures S10 and S11, Supporting Information). The purity of the complexes was also confirmed by elemental analysis.

The yttrium phosphasalen complex, compound **3**, was also synthesized in order to confirm the effect of an electron-donating methoxy group attached to the pentadentate ligand (Figure 3). The complex was formed using an analogous route to compounds **1** and **2**, which resulted in the isolation of compound **3** as a white crystalline solid in good yield (66%). A single peak was observed in the $^{31}P\{^{1}H\}$ NMR spectrum at 32.7 ppm, which is in line with analogous yttrium compounds and suggests equilibration or equivalence of the phosphorus environments in the complex.[5a]

X-RAY CRYSTALLOGRAPHY DATA

Single crystals of compounds **1**, **2**, and **3**, suitable for X-ray crystallography, were grown from solutions of either THF/hexane or THF/cyclohexane. The crystal structures of **1** (M = Sc, R = *t*-Bu), **2** (M = Sc, R = OMe), and **3** (M = Y, R = OMe) all show a severely distorted octahedral geometry at the metal center with trans angles in the ranges 153.95(7)−166.08(6)°, 154.12(11)−166.07(12)°, 154.42(12)−166.42(12)°, and 138.95(13)−155.99(12)° for **1**, **2-A**, **2-B**, and **3**, respectively (complex **2** crystallized with two independent molecules, **2-A** and **2-B**). In each case the pentacoordinate ligand occupies one hemisphere, leaving the ethoxide ligand isolated in the other hemisphere (Figure 4). The geometries of **1**, **2-A**, and **2-B** are

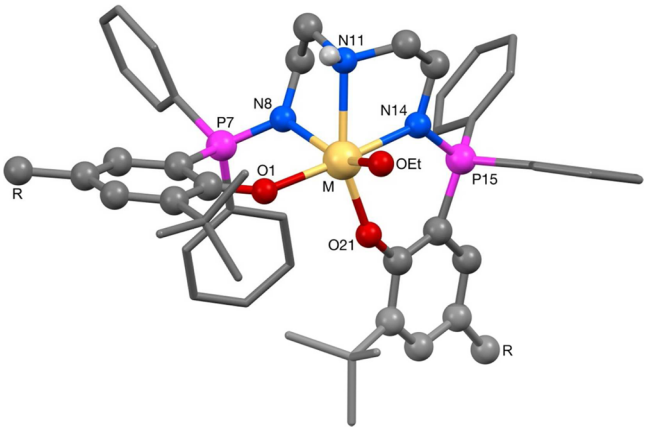


Figure 4. Schematic representation of the crystal structures of **1** (M = Sc, R = *t*-Bu), **2** (molecules **A** and **B**, M = Sc, R = OMe), and **3** (M = Y, R = OMe).

quite similar, as would be expected with the only difference being a change from *t*-Bu to OMe for the phenyl substituent R. The yttrium structure **3**, however, shows marked differences from **1** and **2**, mainly associated with the larger size of the metal atom, cf. the scandium present in **1** and **2**. In addition to the expected lengthening of all of the M−X bonds (Table 1) and the even greater distortion from ideal octahedral coordination angles at the metal center (see above), the O(1)···O(21) phenoxide···phenoxide separation is markedly increased [2.9752(17), 2.894(3), 2.944(3), and 3.117(4) Å in **1**, **2-A**, **2-B**, and **3**, respectively]. A similar pattern was seen for the previously reported structures of the related lanthanum and lutetium complexes where the coordination of the pentadentate ligand was more distorted in the complexes with the larger metal atom (lanthanum) than in those of the smaller metal (lutetium).[5a] Again, similar to the lanthanum and lutetium complexes, all four structures reported here adopt asymmetric conformations that place one phenyl ring of one of the two PPh_2 units—that based on P(15)—much closer to the ethoxide than the other three phenyl rings.

There is some evidence for an N−H···O hydrogen bond between the N(11)−H hydrogen atom and the O(80) oxygen of the major (ca. 63%) occupancy orientation of the disordered included THF solvent molecule in the structure of **1** [N···O 3.009(4) Å, H···O 2.119(6) Å, N−H···O 170(2)°, N−H distance fixed at 0.90 Å), though the disordered nature of the solvent molecule means that this interaction should be treated with caution. This is relevant as the NH group has the potential to form H bonds with both solvent and monomer during polymerization reactions. Interestingly, recent investigations of bimetallic indium complexes by Mehrkhodavandi and co-workers have indicated that H bonding, from secondary amines, may be a factor implicated in controlling the activity for the ROP of LA.[5b]

Despite the asymmetry observed in compounds **1** and **2** using multinuclear NMR techniques, vide supra, comparison of the single-crystal X-ray structures does not highlight any significant deviation from related lutetium and yttrium complexes. In other words, all analogous complexes, **1**, **2**, **3**, **A**, and **B**, show very distorted octahedral solid state geometries.

POLYMERIZATION OF CYCLIC ESTERS

Compounds **1** and **2** were investigated as possible initiators for the ring-opening polymerization of a series of cyclic esters including *rac*-lactide, *rac*-*β*-butyrolactone, and *ε*-caprolactone. As previously highlighted, it was anticipated that the reduced covalent radius of scandium, 1.70 Å,[9] might lead to a more sterically congested coordination environment and thus have a positive influence on the level of isoselectivity. With this in mind, compound **1** was investigated as an initiator for the ROP of lactide under the standard conditions employed for the series of phosphasalen complexes: 1:500 [I]:[LA], 1 M [LA], THF, 298 K. However, after 24 h, no conversion of *rac*-LA was observed. Conducting the polymerization at elevated temperature (343 K) also proved unsuccessful, with no conversion observed after 24 h. Carrying out polymerizations under melt conditions also led to no conversion after 1.5 h, at which point the polymerization solution turned brown, indicating some degradation of the initiator. Previous observations using scandium{amino-alkoxy-bis(phenolate)} complexes have shown limited polymerization activity when THF was used as the solvent presumably due to competitive coordination of the solvent.[6b] However, in the case of compound **1**, even when the solvent was switched to toluene (353 K) no conversion was observed after 20 h, indicating that in this case the solvent choice is not activity limiting. Compound **2** was expected to show an increased rate versus compound **1**, based on previous observations of *para*-methoxy groups on yttrium initiators.[5n] However, under the same range of polymerization conditions described above, compound **2** also showed no polymerization activity.

Compounds **1** and **2** were next investigated as initiators for the ROP of other cyclic esters. Attempts to polymerize *rac*-*β*-butyrolactone under high monomer concentration conditions likely to favor polymerization (1:100 [I]:[*β*-BL], 8 M [*β*-BL]) using either THF or toluene as the solvent led to no

DOI: 10.1021/ic5027015
Inorg. Chem. 2015, 54, 2204−2212

Table 1. Selected Bond Lengths (Angstroms) and angles (degrees) for 1, 2-A, 2-B, and 3

	1 [M = Sc, R = *t*-Bu]	2-A [M = Sc, R = OMe]	2-B [M = Sc, R = OMe]	3 [M = Y, R = OMe]
M−O(1)	2.0458(13)	2.052(2)	2.054(3)	2.196(3)
M−N(8)	2.3083(15)	2.267(3)	2.265(3)	2.412(4)
M−N(11)	2.3367(17)	2.397(3)	2.378(3)	2.571(4)
M−N(14)	2.2567(16)	2.271(3)	2.269(3)	2.423(4)
M−O(21)	1.9921(13)	2.001(2)	1.995(2)	2.194(3)
M−OEt	1.9829(16)	1.985(3)	1.979(3)	2.078(3)
O(1)···O(21)	2.9752(17)	2.894(3)	2.944(3)	3.117(4)
O(1)−M−N(8)	80.26(5)	80.10(10)	80.59(10)	75.77(12)
O(1)−M−N(11)	108.01(6)	113.49(11)	111.06(11)	120.94(12)
O(1)−M−N(14)	166.08(6)	166.07(12)	166.42(12)	155.99(12)
O(1)−M−O(21)	94.91(5)	91.09(10)	93.24(10)	90.48(11)
O(1)−M−OEt	95.90(6)	95.19(11)	94.80(12)	100.08(12)
N(8)−M−N(11)	73.27(6)	71.93(11)	72.71(12)	67.77(13)
N(8)−M−N(14)	87.22(6)	90.10(11)	88.23(12)	89.94(12)
N(8)−M−O(21)	105.52(6)	106.41(11)	104.89(12)	114.75(12)
N(8)−M−OEt	153.95(7)	149.53(12)	150.60(12)	138.95(13)
N(11)−M−N(14)	73.70(6)	72.09(11)	72.39(11)	68.70(12)
N(11)−M−O(21)	156.24(6)	154.12(11)	154.42(12)	146.61(12)
N(11)−M−OEt	83.68(7)	82.81(12)	82.19(13)	81.05(13)
N(14)−M−O(21)	82.54(5)	82.15(10)	82.13(10)	77.93(11)
N(14)−M−OEt	98.02(7)	98.24(12)	98.71(13)	103.30(13)
O(21)−M−OEt	100.47(7)	103.74(11)	104.36(12)	106.03(12)

Table 2. Polymer Data Obtained Using Initiators 1, 2, and 3 for the ROP of ε-CL or *rac*-LA

I	solvent	time (h)	convn. (%)[c]	$M_{n\,calc}$	$M_{n\,exp}$[d]	PDI[d]
1[a]	THF	19	21	2200	3200	1.05
1[a]	toluene	19	40	4600	5000	1.04
1[a]	toluene	48	84	9600	9350	1.06
2[a]	toluene	48	98	11 300	15600	1.03
3[b]	THF	0.5	88	67 500	48 600	1.08
A[b]	THF	0.8	85	61 200	61 700	1.04

[a]298 K, 1:100 [I]:[ε-CL], [ε-CL] 8 M. [b]298 K, 1:500 [I]:[*rac*-LA], [*rac*-LA] 1 M. [c]Determined by integration of the methine region of the ^{1}H NMR spectrum (*rac*-LA, 4.98−5.08 ppm; PLA, 5.09−5.24 ppm; ε-CL, 2.52−2.60 ppm; PCL, 2.30−2.36 ppm). [d]Determined by GPC in THF vs PS standards (M_n values are corrected by factors of 0.56 (PCL) and 0.58 (PLA) as described in ref 10).

polymerization at 298 K. In contrast, both compounds **1** and **2** were found to be active, albeit slow, initiators for the ROP of ε-caprolactone under high monomer concentration conditions (1:100 [I]:[ε-CL], 8 M [ε-CL], 298 K).[11] After 48 h, in toluene, the polymerizations proceed to high conversions, 84% and 98% for **1** and **2**, respectively. The polymerizations were significantly faster in toluene compared to those run in THF, presumably due to the ability of THF to coordinate to the scandium metal center. A good agreement between the theoretical and experimental M_n values was observed, in addition to narrow PDI values (<1.06 in all cases). These are both characteristics indicative of a controlled polymerization.

In contrast to the results using scandium, the yttrium compound **3** was an active initiator for the ring-opening polymerization of *rac*-lactide under the standard set of conditions employed (1:500 [I]:[*rac*-LA], 1 M [*rac*-LA], THF, 298 K). Polymerizations proceeded to high conversions in less than 0.5 h, with the observed rate constant, $k_{obs} = 1.5 \times 10^{-3}$ s^{-1}, being approximately twice that of the analogous previously reported compound, **A**, $k_{obs} = 6.9 \times 10^{-4}$ s^{-1}.[5n] This result is in line with previous observations regarding electron-donating ligand substitutions accelerating polymerizations. Despite the increase in rate, the level of stereocontrol was maintained, producing a polymer with a significant isoselective bias (P_i = 0.78, Figure S7, Supporting Information). The initiator also showed good polymerization control, demonstrating a linear evolution of molecular weight with percentage conversion and narrow dispersities throughout the reaction (Figure S8, Supporting Information). It is difficult to compare the performance of **3** against other isoselective catalysts reported in the literature as each is tested under different conditions (including concentrations, solvents, mol % loading, and temperature). Aluminum catalysts are known to show the best isoselectivities but are generally slow.[5e,z−ac,12] Recently, a number of very promising zinc catalysts showing high isoselectivities have been reported.[5f,13] Complex **3** shows equivalent, or slightly lower, isoselectivity ($P_i \approx 0.80$) to these systems but has a qualitatively faster rate, for example, the chiral zinc phenolate diamine catalysts take >180 min to reach 86% conversion (200:1:1, lactide:catalyst:isopropyl alcohol, in THF at 25 °C),[13a] the zinc heteroscopionate catalysts take ∼8 h to reach 96% conversion (400:1, lactide:zinc, in toluene at 30 °C),[5f] and the chiral zinc oxazolinates took 44 h to reach 96% conversion (200:1 lactide:zinc, 23 °C in toluene).[13b]

The reason for the lack of polymerization activity observed with the scandium phosphasalen complexes was not immediately obvious; thus, the reactivity of compounds **1** and **2** with stoichiometric amounts of lactide was probed. One equivalent of *rac*-lactide was added to a solution of compounds **1** and **2**, respectively, in benzene-d_6. Immediate ^{1}H NMR analysis revealed quantitative conversion of both compounds **1** and **2** to new products. In both cases, the new compounds formed showed distinctive ^{1}H NMR spectra, and in particular, they showed two diagnostic sets of quartets, resonating at 5.63 and 5.63 ppm for compound **1′** (Figure 5) and at 5.59 and 5.29 ppm for compound **2′**, which correspond to the methine protons of a lactide-containing product (versus the single quartet, at 3.67 ppm in d_6-benzene, observed for free lactide in

DOI: 10.1021/ic5027015
Inorg. Chem. 2015, 54, 2204−2212

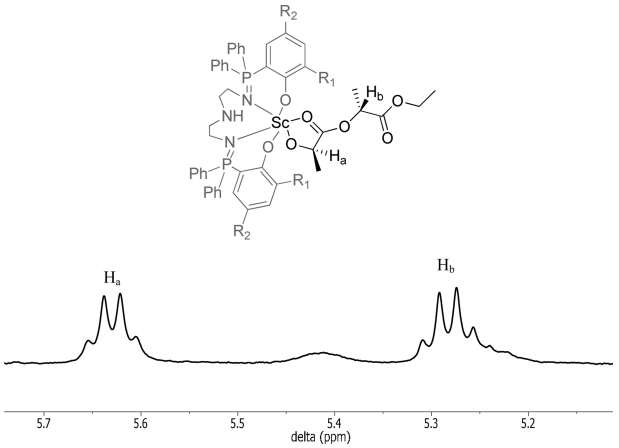


Figure 5. Proposed structure of compounds **1**′ and **2**′, where R_1 = *t*Bu, R_2 = *t*Bu (**1**′), OMe (**2**′), and the expanded region of the ^{1}H NMR spectrum of compound **1**′ (benzene-d_6), attributed to the methine lactate signals (H_a and H_b, respectively).

benzene-d_6). Neither compound reacts further if additional lactide is added, as seen by the presence of excess LA in the ^{1}H NMR spectrum of **1**′ (Figure S14, Supporting Information). It is also notable that the N*H* resonance experiences a significant downfield shift upon formation of **1**′ and **2**′, from 2.48 to 4.49 ppm and from 2.47 to 4.44 ppm, respectively. While no ^{1}H−^{15}N correlation signal could be observed in HSQC experiments, the assignment of the signals as N*H* groups could be confirmed by correlations between it and the signals due to the protons of the diimine bridge via TOCSY NMR. Such significant shifts in the NH signals might be indicative of hydrogen bonding, and it might be inferred that the lactide monomer is interacting with the N*H* functionality (note, a weak interaction between the NH group and residual solvent, THF, was observed in the X-ray crystal structure of compound **1**). However, further investigations using NMR spectroscopy suggest that the complexes are more likely single-insertion products, proposed to form stable chelates with the scandium (the proposed structure of such species is illustrated in Figure 5). This proposed intermediate structure is supported by through-space interactions observed using ROESY NMR spectroscopy, where cross-peaks between one of the methine protons, at 5.59 ppm, and the *tert*-butyl group of phosphasalen ligand, at 1.78 ppm, indicate close proximity. Such interactions are either only weakly observed or not observed at all for the other methine proton, suggesting that it is further from the metal center. No through-space interactions are observed between the protons of the OCH_2CH_3 group and the ligand, whereas such interactions are present in the spectra of compounds **1** and **2**, thereby indicating that the alkoxide is no longer coordinated to the scandium center. Additionally, no through-space interactions are observed between the lactide unit and any protons of the diimine bridge, which would be expected if a lactide molecule were hydrogen bonding with the N*H* group on the ligand. It is proposed that the significant shift of the N*H* proton resonance may be due to hemilabile coordination chemistry upon formation of the lactate−scandium chelate. Other characterization data supporting the formation of a single-insertion product includes the DOSY NMR spectrum which shows the signals corresponding to the methine protons of the "lactate" unit diffuse at the same rate as those for the ligand, indicating the formation of a single product containing both lactate and complex. Furthermore, a molecular ion peak, corresponding to the ring-opened lactide, was detected when CIMS was conducted on a sample of **2**′ exposed to air (Figure S18, Supporting Information). Attempts to isolate crystals of **1**′ and **2**′, suitable for single-crystal X-ray diffraction experiments, have thus far been unsuccessful.

The observed lactate chelate signals correspond well with the few other examples of isolated ring-opened lactate−metal complexes reported in the literature.[14] To date, there has been just one such complex isolated crystallographically, a cationic aluminum complex reported by Dagorne and co-workers, in which the lone pair of electrons of the carbonyl are observed to be bonding to the metal center.[14b] Using Sn(II) initiators, Carpentier and co-workers recently established that precisely such a characteristic lactate chelate complex was present during polymerization.[14d,15]

The likely formation of compounds **1**′ and **2**′ sheds some light on the inactivity of the two scandium phosphasalen complexes. It is conceivable that the formation of the chelate prevents further reactivity by two possible methods: (i) the formation of the chelate prevents the coordination/insertion of another lactide monomer due to steric congestion, (ii) the stability of the chelate prevents the insertion of another lactide monomer. The comparable activity of ε-caprolactone may be explained by its inability to form such a chelate; this being said, the overall ε-CL ROP activity of the scandium complex is slow; thus, electronic parameters are also likely to be influential. The increased Lewis acidity of the scandium complexes, versus active analogous yttrium, lutetium, and lanthanum derivatives, and reduced covalent radii are both potential contributing factors to the inactivity. The scandium chelates **1**′ and **2**′ may offer some insight into potential polymerization reaction intermediates of analogous active compounds and are almost certainly indicative active site models for the stereospecific Y/Lu initiators.[5a]

■ CONCLUSIONS

Three scandium and yttrium phosphasalen complexes have been synthesized and fully characterized. The new complexes were tested as initiators for the ring-opening polymerization of cyclic esters. The scandium phosphasalen complexes were inactive for lactide ring-opening polymerization. Stoichiometric NMR-scale experiments revealed the formation of an intermediate, likely a chelating single-lactide insertion product, which was unreactive toward further monomer addition. The stability of the intermediate in part explains the complexes failure as polymerization initiators, at least using lactide. The scandium complexes were, however, active initiators for the ROP of ε-caprolactone, perhaps due to the inability of ring-opened caprolactone to form a chelate with the active metal center.

A novel yttrium phosphasalen complex was also presented, which has a methoxy group at the para position of the phenoxide ring. The introduction of this electron-donating moiety is hypothesized to increase the electron donation from the ligand to metal, thus decreasing the Lewis acidity of the metal. Indeed, the rate of *rac*-lactide polymerization increased 2-fold compared to an analogue with a *t*Bu substituent while maintaining reasonable polymerization control and most importantly stereocontrol. The presence of the methoxy group in the analogous scandium complex did not render the complex active.

DOI: 10.1021/ic5027015
Inorg. Chem. 2015, 54, 2204−2212

These results highlight both the versatility and the limitations within the same phosphasalen complex family. The ligand scaffold, discussed here and in previous work, has demonstrated that simple modifications have dramatic effects on the polymerization rate and control. However, care must be taken when choosing suitable metal centers with which to prepare initiators; here, the limitations associated with a smaller and more Lewis-acidic metal center are demonstrated.

EXPERIMENTAL SECTION

Materials and Methods. All reactions were conducted under an atmosphere of dry nitrogen or argon using standard Schlenk line and glovebox techniques. Solvents and reagents were obtained from commercial sources. Tetrahydrofuran, toluene, and hexane were distilled from sodium/benzophenone under dry nitrogen. Cyclohexane was dried over 3 Å molecular sieves. Dichloromethane was distilled from CaH_2 under dry nitrogen. *rac*-Lactide was recrystallized from anhydrous toluene and sublimed under vacuum three times prior to use. Scandium(III) chloride and yttrium (III) chloride were obtained from Strem Chemicals. The phosphasalen pro-ligand **L1** was prepared according to previously reported literature procedures.[5n,8b]

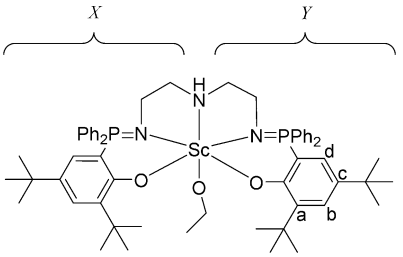
Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Av400 instrument or a Av500 instrument equipped with a z-gradient bbo/5 mm tunable probe and a BSMS GAB 10 A gradient amplifier providing a maximum gradient output of 5.35 G/cmA. Solvent peaks were used as internal references for ^{1}H and ^{13}C chemical shifts (ppm). The following abbreviations are used: b, broad; s, singlet; d, doublet; dd, doublet of doublets; t, triplet; q, quartet; m, multiplet. Advanced NMR experiments were conducted by Peter Haycock. Rotating frame nuclear Overhauser effect spectroscopy (ROESY) was conducted on a Bruker 500 MHz AVANCE III HD spectrometer running TopSpin 3.2 and equipped with a z-gradient bbo/5 mm tunable SmartProbe and a GRASP II gradient spectroscopy accessory providing a maximum gradient output of 53.5G/cm (5.35G/cmA). The Bruker pulse program roesyetgp was employed.[16] Total correlation spectroscopy (TOCSY) were measured at 298 K on a Bruker 500 MHz AVANCE III HD spectrometer running TopSpin 3.2 and equipped with a z-gradient bbo/5 mm tunable SmartProbe and a GRASP II gradient spectroscopy accessory providing a maximum gradient output of 53.5G/cm (5.35G/cmA).[17] CI mass spectrometry spectra were meatured by Dr. Lisa Haigh using a Micromass Autospec Premier in low resolution mode CI using ammonia gas.

Elemental analyses were determined by Stephen Boyer at London Metropolitan University. PCL number-averaged molecular weight, M_n, and the polydispersity index (M_w/M_n; PDI) were determined using gel permeation chromatography (GPC). Two Polymer Laboratories Mixed D columns were used in series, with THF as the eluent, at a flow rate of 1 mL min^{-1}, on a Polymer Laboratories PL GPC-50 instrument at 40 °C. Polycaprolactone and polylactide molecular numbers (M_n) were determined by comparison against polystyrene standards using correction factors of 0.56 and 0.58, respectively, as reported by Penczek and Duda.[10] PLA stereochemistry was determined by comparison of the normalized integrals for all the tetrad signals in the homonuclear proton-decoupled NMR spectrum. The tetrad signals' integrals were compared against the values predicted by Bernoullian statistics,[18] so as to enable determination of the probability of an isotactic diad (P_i) to be determined for each tetrad signal. The average P_i value from all 5 signals is reported. The peaks were integrated using peak deconvolution and the values normalized; deconvolution was achieved using Mestrenova software.

Compound ***L2***. Bromine (197 μL, 3.8 mmol) was added dropwise to a solution of 2-*tert*-butyl-4-methoxy-6-phosphinophenol (1.4 g, 3.8 mmol) in methylene chloride (40 mL) at −78 °C. The solution was allowed to warm to atmospheric temperature and stirred for 2 h before cooling to −78 °C. Tributylamine (456 μL, 1.92 mmol) was added dropwise to the reaction solution, followed by diethylenetriamine (207 μL, 1.92 mmol). The reaction was allowed to warm to atmospheric temperature and stirred for 16 h, after which time the methylene chloride was removed in vacuo. Tetrahydrofuran (15 mL) was added, and the reaction was allowed to stir; after a few minutes a white powder was produced and isolated by filtration. The powder was washed with THF (3 × 15 mL) until no coloration remained and dried in vacuo (2.0 g, 1.9 mmol, 50%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 9.76 (bs, 2H, N*H* or O*H*), 7.76−7.70 (m, *p*-CH(PPH$_2$)), 7.70−7.60 (m, *o*- and *m*-CH(PPH$_2$)), 7.22 (d, 2H, C$_b$*H*, $^4J_{HH}$ = 3.2 Hz), 6.70 (bs, 2H, N*H* or O*H*), 6.15 (dd, 2H, C$_d$*H*, $^3J_{P,H}$ = 16.0 Hz, $^4J_{HH}$ = 2.8 Hz), 3.70 (m, 4H, P═NCH$_2$C*H*$_2$), 3.58 (s, 6H, OC*H*$_3$), 3.54 (m, 4H, P═NC*H*$_2$), 1.44 (s, 18H, *t*Bu). ^{13}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, 298 K) δ (ppm): 40.9 (s). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 154.7 (d, $^{2/3}J_{P,C}$ = 19.1 Hz, $C_{a/c}^{IV}$), 151.7 (s, C^{IV}−O), 144.9 (d, $^{2/3}J_{P,C}$ = 7.8 Hz, $C_{a/c}^{IV}$), 134.8 (s, *p*-CH(PPh$_2$)), 133.5 (d, $^{2/3}J_{P,C}$ = 11.0 Hz, *m*- or *o*-CH(PPh$_2$)), 130.1 (d, $^{2/3}J_{P,C}$ = 13.3 Hz, *m*- or *o*-CH(PPh$_2$)), 121.7 (s, C$_b$H), 121.3 (d, $^1J_{P,C}$ = 104.0 Hz, C^{IV}−PPh$_2$)), 115.4 (d, $^2J_{P,C}$ = 13.3 Hz, C$_d$H), 114.7 (d, $^1J_{P,C}$ = 116.0 Hz, C^{IV}−P), 55.7 (s, OCH$_3$), 48.9 (d, $^2J_{P,C}$ = 15.6 Hz, P^{IV}−N--CH$_2$), 48.3 (s, P^{IV}−N−CH$_2$−CH$_2$), 35.2 (s, C^{IV}(CH$_3$)$_3$), 30.4 (s, CH$_2$CH$_3$). Anal. Calcd for $C_{50}H_{62}Br_3N_3O_4P_2$: C, 56.09; H, 5.84; N,3.92. Found: C, 55.92; H, 5.92; N, 3.91.

Compound ***1***. Potassium bis(trimethylsilyl)amide (311 mg, 1.56 mmol) was added into a slurry of the phosphasalen pro-ligand **L1** (0.35 g, 0.31 mmol) in THF (15 mL). After 2 h, a cloudy suspension formed. The completion of the deprotonation reaction was verified by ^{31}P{^{1}H} NMR spectroscopy. The insoluble potassium salt was removed by centrifugation, and $ScCl_3$ (47 mg, 0.31 mmol) was added. The reaction was heated at reflux (348 K) for 24 h, after which time conversion to the metal chloride complex was again confirmed by ^{31}P{^{1}H} NMR spectroscopy. Potassium ethoxide (26 mg, 0.31 mmol) was added into the mixture, and stirring was continued for 4 h, after which time the solid was removed by centrifugation. The solvent was evaporated in vacuo, and the residue was crystallized or precipitated from a mixture of THF and cyclohexane (4 mL), giving compound **1** as colorless crystals (199 mg, 0.20 mmol, 66%).

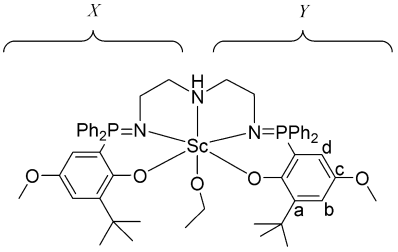


^{1}H{^{31}P} NMR (500 MHz, benzene-d_6, 298 K) δ (ppm): 8.09 (d, 2H, *o*-C*H*(PPh$_2$)^X, $^3J_{HH}$ = 7.0 Hz), 7.86 (d, 2H, *o*-C*H*(PPh$_2$)^Y, 7.71 (m, 3H, *o*-C*H*(PPh$_2$)^X and *p*-C*H*(PPh$_2$)), 7.47 (m, 3H, *o*-C*H*(PPh$_2$)^Y and *p*-C*H*(PPh$_2$)), 7.21−6.93 (bm, 14 H, *m*-C*H*(PPh$_2$), *p*-C*H*(PPh$_2$), C$_b$*H* and C$_d$*H*), 4.67 (q, 2H, OC*H*$_2$CH$_3$, $^3J_{HH}$ = 7.0 Hz), 3.57 (bm, 1H, P═N^X−CH$_2$C*H*$_2$), 3.35 (bm, 1H, P═N^Y−C*H*$_2$), 3.20 (bm, 1H, P═N^X−C*H*$_2$), 2.90 (bm, 1H, P═N^X−C*H*$_2$), 2.59 (bm, 1H, P═N^Y−C*H*$_2$), 2.48 (bs, 1H, N*H*), 2.17 (bm, 2H, P═N^X−C*H*$_2$ and P═N^Y−C*H*$_2$), 2.06 (bm, 1H, P═N^Y−C*H*$_2$), 1.84 (s, 9H, m-*t*Bu), 1.58 (t, 3H, OCH$_2$C*H*$_3$, $^3J_{HH}$ = 7.0 Hz), 1.25 (s, 27H, *t*Bu). ^{31}P{^{1}H} NMR (202.5 MHz, benzene-d_6, 298 K) δ (ppm): 32.39 (s, P^X), 31.60 (s, P^Y). ^{13}C{^{1}H} NMR (125 MHz, benzene-d_6, 298 K) δ (ppm): 169.1 (s, C^{IV}−$O^{X\text{ or }Y}$), 168.5 (s, C^{IV}−$O^{X\text{ or }Y}$), 140.4 (d, $C_{a/c}^{IV\ X\text{ or }Y}$, $^3J_{P,C}$ = 7.8 Hz), 140.3 (d, $C_{a/c}^{IV\ X\text{ or }Y}$, $^3J_{P,C}$ = 8.5 Hz), 134.6 (s, $C_{a/c}^{IV\ X\text{ or }Y}$), 134.4 (s, $C_{a/c}^{IV\ X\text{ or }Y}$), 133.8 (d, *o*-CH(PPh$_2$), $^2J_{P,C}$ = 9.0 Hz), 133.6 (d, *o*-CH(PPh$_2$), $^2J_{P,C}$ = 9.0 Hz), 133.5 (d, *o*-CH(PPh$_2$), $^2J_{P,C}$ = 9.0 Hz), 133.3 (d, *o*-CH(PPh$_2$), $^2J_{P,C}$ = 9.0 Hz), 132.5 (d, C^{IV}−PPh$_2$, $^1J_{P,C}$ = 49.7 Hz), 131.5−130.8 (m, *o*- and *p*-CH(PPH$_2$)), 128.9−128.0 (m, *o*- and *p*-CH(PPH$_2$)), 128.0 (s, C$_b$H$^{X\text{ or }Y}$), 127.8 (s, C$_b$H$^{X\text{ or }Y}$), 127.2 (d, C$_d$H$^{X\text{ or }Y}$, $^2J_{P,C}$ = 13.0 Hz), 126.5 (d, C$_d$H$^{X\text{ or }Y}$, $^2J_{P,C}$ = 12.1 Hz), 110.7 (d, C^{IV}−$P^{X\text{ or }Y}$, $^1J_{P,C}$ = 116.5 Hz), 110.6 (d, C^{IV}−$P^{X\text{ or }Y}$, $^1J_{P,C}$ = 115.4 Hz), 63.2 (s, OCH$_2$CH$_3$), 53.6 (d, P═N^Y−CH$_2$−CH$_2$, $^3J_{P,C}$ = 11.5 Hz), 53.2 (d, P═N^X−CH$_2$−CH$_2$, $^3J_{P,C}$ = 14.0 Hz), 48.6 (s, P═N^Y−CH$_2$), 48.1 (s, P═N^X−CH$_2$), 36.1 (s, C^{IV}(CH$_3$)$_3^{(X\text{ or }Y)}$), 35.7 (s, C^{IV}(CH$_3$)$_3^{(X\text{ or }Y)}$), 34.2 (s, C^{IV}(CH$_3$)$_3^{(X\text{ and }Y)}$), 31.9 (s, *t*Bu$^{X\text{ and }Y}$),

DOI: 10.1021/ic5027015
Inorg. Chem. 2015, 54, 2204−2212

30.4 (s, tBu$^{X\text{ or }Y}$), 29.6 (s, tBu$^{X\text{ or }Y}$), 23.1 (s, OCH_2CH_3). Anal. Calcd for $ScC_{58}H_{74}N_3O_3P_2$(THF): C, 71.59; H, 7.95; N, 4.04. Found: C, 71.43; H, 7.86; N, 4.16.

Compound **2**. Potassium bis(trimethylsilyl)amide (279 mg, 1.40 mmol) was added into a slurry of the phosphasalen pro-ligand **L2** (0.30 g, 0.28 mmol) in THF (15 mL). After 2 h, a cloudy suspension formed. The completion of the deprotonation reaction was verified by $^{31}P\{^1H\}$ NMR spectroscopy. The insoluble potassium salt was removed by centrifugation, and $ScCl_3$ (42 mg, 0.28 mmol) was added. The reaction was heated at reflux (348 K) for 24 h, after which time conversion to the metal chloride complex was again confirmed by $^{31}P\{^1H\}$ NMR spectroscopy. Potassium ethoxide (24 mg, 0.28 mmol) was added into the mixture, and stirring was continued for 4 h, after which time the solid was removed by centrifugation. The solvent was evaporated in vacuo, and the residue was crystallized or precipitated from a mixture of THF and cyclohexane (4 mL), giving compound **2** as colorless crystals (150 mg, 0.16 mmol, 58%).



$^1H\{^{31}P\}$ NMR (500 MHz, benzene-d_6, 298 K) δ (ppm): 8.02 (d, 2H, o-CH(PPh$_2$)^X, $^3J_{HH}$ = 7.0 Hz), 7.77 (d, 2H, o-CH(PPh$_2$)^Y, $^3J_{HH}$ = 7.0 Hz), 7.66 (d, 2H, o-CH(PPh$_2$)^X, $^3J_{HH}$ = 7.0 Hz), 7.42 (d, 2H, o-CH(PPh$_2$)^Y, $^3J_{HH}$ = 7.0 Hz), 7.39 (d, 1H, C$_b$$H$, $^4J_{HH}$ = 3.0 Hz), 7.19 (d, 1H, C$_b$$H$, $^4J_{HH}$ = 3.0 Hz), 7.18 (m, 2H, m-CH(PPh$_2$) or p-CH(PPh$_2$)), 7.17−6.93 (m, 10H, m-CH(PPh$_2$) or p-CH(PPh$_2$)), 6.58 (d, 1H, C$_d$$H^X$, $^4J_{HH}$ = 2.5 Hz), 6.52 (d, 1H, C$_d$$H^Y$, $^4J_{HH}$ = 2.5 Hz), 4.64 (q, 2H, OCH_2CH$_3$, $^3J_{HH}$ = 7.0 Hz), 3.53 (bm, 1H, P═N^X−CH$_2$CH_2), 3.36 (s, 3H, OCH_3), 3.33 (s, 3H, OCH_3), 3.30 (bm, 1H, P═N^Y−CH_2), 3.17 (bm, 1H, P═N^X−CH_2), 2.89 (bm, 1H, P═N^X−CH_2), 2.59 (bm, 1H, P═N^Y−CH_2), 2.46 (bs, 1H, NH), 2.20 (bm, 1H, P═N^Y−CH$_2$CH_2), 2.16 (bm, 1H, P═N^X−CH$_2$CH_2), 2.06 (bm, 1H, P═N^Y−CH$_2$CH_2), 1.78 (s, 9H, tBu), 1.59 (t, 3H, OCH$_2$CH_3, $^3J_{HH}$ = 7.0 Hz), 1.25 (s, 9H, tBu). $^{31}P\{^1H\}$ NMR (202.5 MHz, benzene-d_6, 298 K) δ (ppm): 31.69 (s, P^X), 30.93 (s, P^Y). $^{13}C\{^1H\}$ NMR (125 MHz, benzene-d_6, 298 K) δ (ppm): 166.4 (s, C^{IV}−O$^{X\text{ or }Y}$), 166.7 (s, C^{IV}−O$^{X\text{ or }Y}$), 148.4 (d, $C_{a/c}^{IV\ X\text{ or }Y}$, $^3J_{P,C}$ = 20.5 Hz), 148.1 (d, $C_{a/c}^{IV\ X\text{ or }Y}$, $^3J_{P,C}$ = 19.0 Hz), 142.6 (s, $C_{a/c}^{IV\ X\text{ or }Y}$), 142.5 (s, $C_{a/c}^{IV\ X\text{ or }Y}$), 133.8 (d, o-CH(PPh$_2$), $^2J_{P,C}$ = 9.6 Hz), 133.7 (d, o-CH(PPh$_2$), $^2J_{P,C}$ = 10.0 Hz), 133.5 (d, o-CH(PPh$_2$), $^2J_{P,C}$ = 8.4 Hz), 133.4 (d, o-CH(PPh$_2$), $^2J_{P,C}$ = 9.0 Hz), 131.6 (d, C^{IV}−PPh$_2$, $^1J_{P,C}$ = 191.2 Hz), 131.4 (d, m-CH(PPh$_2$), $^3J_{P,C}$ = 12.2 Hz), 131.2 (d, C^{IV}−PPh$_2$, $^1J_{P,C}$ = 153.6 Hz), 131.1 (s, p-CH(PPh$_2$)), 128.8 (d, m-CH(PPh$_2$), $^3J_{P,C}$ = 11.5 Hz), 128.5 (d, m-CH(PPh$_2$), $^3J_{P,C}$ = 10.6 Hz), 128.3 (s, p-CH(PPh$_2$)), 128.2 (d, m-CH(PPh$_2$), $^3J_{P,C}$ = 11.9 Hz), 120.1 (s, C$_b$H), 114.1 (d, C$_d$$H^{X\text{ or }Y}$, $^2J_{P,C}$ = 13.7 Hz), 113.4 (d, C$_d$$H^{X\text{ or }Y}$, $^2J_{P,C}$ = 13.7 Hz), 110.5 (d, C^{IV}−P$^{X\text{ or }Y}$, $^1J_{P,C}$ = 116.9 Hz), 110.3 (d, C^{IV}−P$^{X\text{ or }Y}$, $^1J_{P,C}$ = 114.6 Hz), 63.2 (s, OCH$_2$CH$_3$), 55.6 (s, OCH$_3$), 53.6 (d, P═N^Y−CH$_2$−CH$_2$, $^3J_{P,C}$ = 9.8 Hz), 53.2 (d, P═N^X−CH$_2$−CH$_2$, $^3J_{P,C}$ = 15.0 Hz), 48.6 (s, P═N^Y−CH$_2$), 48.1 (s, P═N^X−CH$_2$), 35.9 (s, C^{IV}(CH$_3$)$_3^{(X\text{ or }Y)}$), 35.6 (s, C^{IV}(CH$_3$)$_3^{(X\text{ or }Y)}$), 30.1 (s, tBu$^{X\text{ or }Y}$), 29.5 (s, tBu$^{X\text{ or }Y}$), 23.1 (s, OCH$_2$CH$_3$). Anal. Calcd for $ScC_{52}H_{62}N_3O_5P_2$: C, 68.19; H, 6.82; N,4.59. Found: C, 68.05; H, 6.90; N, 4.58.

Compound **3**. Potassium bis(trimethylsilyl)amide (279 mg, 1.40 mmol) was added into a slurry of the phosphasalen pro-ligand **L2** (0.30 g, 0.28 mmol) in THF (15 mL). After 2 h, a cloudy suspension formed. The completion of the deprotonation reaction was verified by $^{31}P\{^1H\}$ NMR spectroscopy. The insoluble potassium salt was removed by centrifugation, and YCl_3 (55 mg, 0.28 mmol) was added. The reaction was stirred at 298 K for 4 h, after which time conversion to the metal chloride complex was again confirmed by $^{31}P\{^1H\}$ NMR spectroscopy. Potassium ethoxide (24 mg, 0.28 mmol) was added into the mixture, and stirring was continued for 4 h, after which time the solid was removed by centrifugation. The solvent was evaporated in vacuo, and the residue was crystallized or precipitated from a mixture of THF and cyclohexane (4 mL), giving compound **3** as colorless crystals (199 mg, 0.20 mmol, 66%).

^1H NMR (400 MHz, benzene-d_6, 298 K) δ (ppm): 7.71 (d, 4H, o-CH(PPh$_2$), $^3J_{HH}$ = 7.2 Hz), 7.68 (d, 4H, o-CH(PPh$_2$), $^3J_{HH}$ = 7.2 Hz), 7.31 (d, 2H, C$_b$$H$, $^4J_{HH}$ = 3.2 Hz), 7.13−6.95 (m, 12H, m- *and* p-CH(PPh$_2$)), 6.55 (dd, 2H, C$_d$$H$, $^3J_{P,H}$ = 14.8 Hz, $^4J_{HH}$ = 3.2 Hz), 4.54 (q, 2H, OCH$_2$CH_3, $^3J_{HH}$ = 6.8 Hz), 3.39 (s, 6H, OCH_3), 3.15 (m, 2H, P═N−CH_2), 2.77 (m, 4H, P═N−CH_2 and P═N−CH$_2$CH_2), 2.20 (bs, 1H, NH), 2.17 (m, 2H, P═N−CH$_2$CH_2), 1.56 (t, 3H, OCH$_2$CH_3, $^3J_{HH}$ = 6.8 Hz), 1.50 (s, 18H, tBu). $^{31}P\{^1H\}$ NMR (161.9 MHz, benzene-d_6, 298 K) δ (ppm): 32.65 (s, P^V). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6, 298 K) δ (ppm): 166.2 (s, C^{IV}−O), 148.2 (d, $C_{a/c}^{IV}$, $^3J_{P,C}$ = 19.0 Hz), 142.4 (d, $C_{a/c}^{IV}$, $^3J_{P,C}$ = 8.6 Hz), 133.4 (d, m- or o-CH(PPh$_2$), $^{2/3}J_{P,C}$ = 5.5 Hz), 133.3 (d, m- or o-CH(PPh$_2$), $^{2/3}J_{P,C}$ = 5.5 Hz), 131.4 (s, p-CH(PPh$_2$)), 131.3 (s, p-CH(PPh$_2$)), 131.3 (d, C^{IV}−PPh$_2$, $^1J_{P,C}$ = 90.0 Hz), 128.6 (d, m- or o-CH(PPh$_2$), $^{2/3}J_{P,C}$ = 12.0 Hz), 120.3 (s, C$_b$H), 114.2 (d, C$_d$H, $^2J_{P,C}$ = 13.6 Hz), 112.1 (d, C^{IV}−P, $^1J_{P,C}$ = 116.0 Hz), 62.7 (s, CH_2CH_3), 55.9 (s, OCH$_3$), 53.0 (d, P^{IV}−N−CH$_2$, $^2J_{P,C}$ = 15.6 Hz), 48.3 (d, P^{IV}−N−CH$_2$−CH$_2$, $^3J_{P,C}$ = 3.7 Hz,), 35.7 (s, C^{IV}(CH$_3$)$_3$), 29.8 (s, C^{IV}(CH$_3$)$_3$), 23.6 (s, CH_2CH_3). Anal. Calcd for $YC_{52}H_{62}N_3O_5P_2$: C, 65.06; H, 6.51; N, 4.38. Found: C, 65.13; H, 6.46; N, 4.45.

General Polymerization Proceedure (*rac*-Lactide). In a glovebox, a tube was loaded with *rac*-lactide (288 mg, 2 mmol), which was subsequently dissolved in THF (1.8 mL). A stock solution of initiator (0.2 mL, 0.02 M) was injected into the reaction, such that the overall concentration of lactide was 1 M and of initiator was 2 mM. Aliquots were taken from the reaction under a nitrogen atmosphere and quenched with wet hexane (1−2 mL), and the solvent was allowed to evaporate. The crude product was analyzed by ^1H NMR and homonuclear decoupled ^1H NMR spectroscopy and GPC. The conversion of LA to PLA was determined by integration of the methyne proton peaks of the ^1H NMR spectra, δ 5.00−5.30. The P_i value was determined by integration of the methyne region of the homonuclear decoupled ^1H NMR spectrum, δ 5.1−5.24. The methyne proton region was deconvoluted using MestReNova software. The PLA number-averaged molecular weight, M_n, and polydispersity index (M_w/M_n; PDI) were determined using gel permeation chromatography (GPC).

General Polymerization Proceedure (ε-Caprolactone). In a glovebox, a vial was loaded with catalyst (12.4 mg, 0.013 mmol) and toluene or THF solvent. ε-Caprolactone (0.15 mL, 1.3 mmol) was added; the vial was sealed and allowed to stir. After a given time the reaction was quenched directly into cold, wet, $CDCl_3$, and NMR analysis was immediately conducted to avoid any loss of the monomer. The crude product was analyzed by ^1H NMR and GPC. The conversion of ε-CL to PCL was determined by integration of the methene proton peaks of the ^1H NMR spectra, δ 2.1−2.5 ppm. The PLA number-averaged molecular weight, M_n, and polydispersity index (M_w/M_n; PDI) were determined using gel permeation chromatography against polystyrene standards with a correction factor of 0.56.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Supporting information containing synthetic procedures for L2, spectroscopic data for all new compounds, X-ray crystallographic CIF files, polymerization data and representative GPC chromagrams. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: n.long@imperial.ac.uk.
*E-mail: c.k.williams@imperial.ac.uk.

DOI: 10.1021/ic5027015
Inorg. Chem. 2015, 54, 2204−2212

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The EPSRC (EP/K014070/1, EP/K035274/1, Doctoral Prize Fellowship to C.B.) are acknowledged for funding.

■ REFERENCES

(1) (a) Ragauskas, A. J.; Williams, C. K.; Davison, B. H.; Britovsek, G.; Cairney, J.; Eckert, C. A.; Frederick, W. J.; Hallett, J. P.; Leak, D. J.; Liotta, C. L.; Mielenz, J. R.; Murphy, R.; Templer, R.; Tschaplinski, T. *Science* **2006**, *311*, 484−489. (b) Vink, E. T. H.; Davies, S.; Kolstad, J. J. *Ind. Biotechnol.* **2010**, *6*, 212−224.

(2) (a) Kamber, N. E.; Jeong, W.; Waymouth, R. M.; Pratt, R. C.; Lohmeijer, B. G. G.; Hedrick, J. L. *Chem. Rev.* **2007**, *107*, 5813−5840. (b) Kiesewetter, M. K.; Shin, E. J.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* **2010**, *43*, 2093−2107. (c) Platel, R. H.; Hodgson, L. M.; Williams, C. K. *Polym. Rev.* **2008**, *48*, 11−63. (d) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147−6176.

(3) (a) Stanford, M. J.; Dove, A. P. *Chem. Soc. Rev.* **2010**, *39*, 486−494. (b) Dijkstra, P. J.; Du, H.; Feijen, J. *Polym. Chem.* **2011**, *2*, 520−527. (c) Dagorne, S.; Normand, M.; Kirillov, E.; Carpentier, J. F. *Coord. Chem. Rev.* **2013**, *257*, 1869−1886. (d) Buffet, J.-C.; Okuda, J. *Polym. Chem.* **2011**, *2*, 2758−2763. (e) Ajellal, N.; Carpentier, J. F.; Guillaume, C.; Guillaume, S. M.; Helou, M.; Poirier, V.; Sarazin, Y.; Trifonov, A. *Dalton Trans.* **2010**, *39*, 8363−8376.

(4) (a) Rahaman, M. H.; Tsuji, H. *Polym. Degrad. Stab.* **2013**, *98*, 709−719. (b) Agatemor, C.; Shaver, M. P. *Biomacromolecules* **2013**, *14*, 699−708. (c) Zhao, W.; Wang, Y.; Liu, X. L.; Chen, X. S.; Cui, D. M. *Chem.—Asian J.* **2012**, *7*, 2403−2410. (d) Kakuta, M.; Hirata, M.; Kimura, Y. *Polym. Rev.* **2009**, *49*, 107−140. (e) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 1316.

(5) (a) Bakewell, C.; White, A. J. P.; Long, N. J.; Williams, C. K. *Angew. Chem., Int. Ed.* **2014**, *53*, 9226−9230. (b) Osten, K. M.; Aluthge, D. C.; Patrick, B. O.; Mehrkhodavandi, P. *Inorg. Chem.* **2014**, *53*, 9897−9906. (c) Aluthge, D. C.; Yan, E. X.; Ahn, J. M.; Mehrkhodavandi, P. *Inorg. Chem.* **2014**, *53*, 6828−6836. (d) Tabthong, S.; Nanok, T.; Kongsaeree, P.; Prabpai, S.; Hormnirun, P. *Dalton Trans.* **2014**, *43*, 1348−1359. (e) Pilone, A.; Press, K.; Goldberg, I.; Kol, M.; Mazzeo, M.; Lamberti, M. *J. Am. Chem. Soc.* **2014**, *136*, 2940−2943. (f) Mou, Z.; Liu, B.; Wang, M.; Xie, H.; Li, P.; Li, L.; Li, S.; Cui, D. *Chem. Commun.* **2014**, *50*, 11411−11414. (g) Fang, J.; Yu, I. S.; Mehrkhodavandi, P.; Maron, L. *Organometallics* **2013**, *32*, 6950−6956. (h) Aluthge, D. C.; Patrick, B. O.; Mehrkhodavandi, P. *Chem. Commun.* **2013**, *49*, 4295−4297. (i) Gao, B.; Duan, R. L.; Pang, X.; Li, X.; Qu, Z.; Tang, Z. H.; Zhuang, X. L.; Chen, X. S. *Organometallics* **2013**, *32*, 5435−5444. (j) Gao, B.; Duan, R. L.; Pang, X.; Li, X.; Qu, Z.; Shao, H. L.; Wang, X. H.; Chen, X. S. *Dalton Trans.* **2013**, *42*, 16334−16342. (k) Agatemor, C.; Arnold, A. E.; Cross, E. D.; Decken, A.; Shaver, M. P. *J. Organomet. Chem.* **2013**, *745*, 335−340. (l) Bakewell, C.; White, A. J. P.; Long, N. J.; Williams, C. K. *Inorg. Chem.* **2013**, *52*, 12561−12567. (m) Bakewell, C.; Thi-Phuong-Anh, C.; Le Goff, X. F.; Long, N. J.; Auffrant, A.; Williams, C. K. *Organometallics* **2013**, *32*, 1475−1483. (n) Bakewell, C.; Cao, T.-P.-A.; Long, N.; Le Goff, X. F.; Auffrant, A.; Williams, C. K. *J. Am. Chem. Soc.* **2012**, *134*, 20577−20580. (o) Bakewell, C.; Platel, R. H.; Cary, S. K.; Hubbard, S. M.; Roaf, J. M.; Levine, A. C.; White, A. J. P.; Long, N. J.; Haaf, M.; Williams, C. K. *Organometallics* **2012**, *31*, 4729−4736. (p) Yu, I.; Acosta-Ramirez, A.; Mehrkhodavandi, P. *J. Am. Chem. Soc.* **2012**, *134*, 12758−12773. (q) Osten, K. M.; Yu, I.; Duffy, I. R.; Lagaditis, P. O.; Yu, J. C. C.; Wallis, C. J.; Mehrkhodavandi, P. *Dalton Trans.* **2012**, *41*, 8123−8134. (r) Stopper, A.; Okuda, J.; Kol, M. *Macromolecules* **2012**, *45*, 698−704. (s) Chen, H.-L.; Dutta, S.; Huang, P.-Y.; Lin, C.-C. *Organometallics* **2012**, *31*, 2016−2025. (t) Wang, L. Y.; Ma, H. Y. *Dalton Trans.* **2010**, *39*, 7897−7910. (u) Qian, F.; Liu, K. Y.; Ma, H. Y. *Dalton Trans.* **2010**, *39*, 8071−8083. (v) Darensbourg, D. J.; Karroonnirun, O. *Organometallics* **2010**, *29*, 5627−5634. (w) Arnold, P. L.; Buffet, J.-C.; Blaudeck, R.; Sujecki, S.; Wilson, C. *Chem.—Eur. J.* **2009**, *15*, 8241−8250. (x) Douglas, A. F.; Patrick, B. O.; Mehrkhodavandi, P. *Angew.Chem. Int. Ed.* **2008**, *47*, 2290−2293. (y) Arnold, P. L.; Buffet, J.-C.; Blaudeck, R. P.; Sujecki, S.; Blake, A. J.; Wilson, C. *Angew. Chem., Int. Ed.* **2008**, *47*, 6033−6036. (z) Nomura, N.; Ishii, R.; Yamamoto, Y.; Kondo, T. *Chem.—Eur. J.* **2007**, *13*, 4433−4451. (aa) Zhong, Z.; Dijkstra, P. J.; Feijen, J. *J. Am. Chem. Soc.* **2003**, *125*, 11291−11298. (ab) Zhong, Z. Y.; Dijkstra, P. J.; Feijen, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 4510−4513. (ac) Nomura, N.; Ishii, R.; Akakura, M.; Aoi, K. *J. Am. Chem. Soc.* **2002**, *124*, 5938−5939. (ad) Maudoux, N.; Roisnel, T.; Dorcet, V.; Carpentier, J.-F.; Sarazin, Y. *Chem.—Eur. J.* **2014**, *20*, 6131−6147.

(6) (a) Maudoux, N.; Roisnel, T.; Carpentier, J.-F.; Sarazin, Y. *Organometallics* **2014**, No. 33, 5740−5748. (b) Chapurina, Y.; Klitzke, J.; Casagrande, O. d. L., Jr; Awada, M.; Dorcet, V.; Kirillov, E.; Carpentier, J.-F. *Dalton Transactions* **2014**, *43*, 14322−14333. (c) Rad'kov, V.; Roisnel, T.; Trifonov, A.; Carpentier, J. F.; Kirillov, E. *Eur. J. Inorg. Chem.* **2014**, *2014*, 4168−4178. (d) Bennett, S. D.; Core, B. A.; Blake, M. P.; Pope, S. J. A.; Mountford, P.; Ward, B. D. *Dalton Trans.* **2014**, *43*, 5871−5885. (e) Mou, Z.; Liu, B.; Liu, X.; Xie, H.; Rong, W.; Li, L.; Li, S.; Cui, D. *Macromolecules* **2014**, *47*, 2233−2241. (f) Yang, S.; Nie, K.; Zhang, Y.; Xue, M.; Yao, Y.; Shen, Q. *Inorg. Chem.* **2014**, *53*, 105−115. (g) Klitzke, J. S.; Roisnel, T.; Kirillov, E.; Casagrande, O. d. L.; Carpentier, J. F. *Organometallics* **2013**, *33*, 309−321. (h) Mazzeo, M.; Tramontano, R.; Lamberti, M.; Pilone, A.; Milione, S.; Pellecchia, C. *Dalton Trans.* **2013**, *42*, 9338−9351. (i) Pappalardo, D.; Bruno, M.; Lamberti, M.; Pellecchia, C. *Macromol. Chem. Phys.* **2013**, *214*, 1965−1972. (j) Nie, K.; Gu, W.; Yao, Y.; Zhang, Y.; Shen, Q. *Organometallics* **2013**, *32*, 2608−2617. (k) Zhang, W.; Liu, S.; Sun, W.-H.; Hao, X.; Redshaw, C. *New J. Chem.* **2012**, *36*, 2392−2396. (l) Zhang, J.; Qiu, J.; Yao, Y.; Zhang, Y.; Wang, Y.; Shen, Q. *Organometallics* **2012**, *31*, 3138−3148. (m) Li, W.; Zhang, Z.; Yao, Y.; Zhang, Y.; Shen, Q. *Organometallics* **2012**, *31*, 3499−3511. (n) Li, G.; Lamberti, M.; Mazzeo, M.; Pappalardo, D.; Roviello, G.; Pellecchia, C. *Organometallics* **2012**, *31*, 1180−1188. (o) Kapelski, A.; Buffet, J.-C.; Spaniol, T. P.; Okuda, J. *Chem.—Asian J.* **2012**, *7*, 1320−1330. (p) Shen, X.; Xue, M.; Jiao, R.; Ma, Y.; Zhang, Y.; Shen, Q. *Organometallics* **2012**, *31*, 6222−6230. (q) Platel, R. H.; White, A. J. P.; Williams, C. K. *Inorg. Chem.* **2011**, *50*, 7718−7728. (r) Sinenkov, M.; Kirillov, E.; Roisnel, T.; Fukin, G.; Trifonov, A.; Carpentier, J.-F. *Organometallics* **2011**, *30*, 5509−5523. (s) Broderick, E. M.; Thuy-Boun, P. S.; Guo, N.; Vogel, C. S.; Sutter, J.; Miller, J. T.; Meyer, K.; Diaconescu, P. L. *Inorg. Chem.* **2011**, *50*, 2870−2877. (t) Broderick, E. M.; Guo, N.; Vogel, C. S.; Xu, C. L.; Sutter, J.; Miller, J. T.; Meyer, K.; Mehrkhodavandi, P.; Diaconescu, P. L. *J. Am. Chem. Soc.* **2011**, *133*, 9278−9281. (u) Bouyahyi, M.; Ajellal, N.; Kirillov, E.; Thomas, C. M.; Carpentier, J.-F. *Chem.—Eur. J.* **2011**, *17*, 1872−1883. (v) Clark, L.; Cushion, M. G.; Dyer, H. E.; Schwarz, A. D.; Duchateau, R.; Mountford, P. *Chem. Commun.* **2010**, *46*, 273−275. (w) Grunova, E.; Kirillov, E.; Roisnel, T.; Carpentier, J. F. *Dalton Trans.* **2010**, *39*, 6739−6752. (x) Buchard, A.; Platel, R. H.; Auffrant, A.; Le Goff, X. F.; Le Floch, P.; Williams, C. K. *Organometallics* **2010**, *29*, 2892−2900. (y) Platel, R. H.; White, A. J. P.; Williams, C. K. *Chem. Commun.* **2009**, 4115−4117. (z) Otero, A.; Fernandez-Baeza, J.; Lara-Sanchez, A.; Alonso-Moreno, C.; Marquez-Segovia, I.; Sanchez-Barba, L. F.; Rodriguez, A. M. *Angew. Chem., Int. Ed.* **2009**, *48*, 2176−2179. (aa) Buchard, A.; Auffrant, A.; Ricard, L.; Le Goff, X. F.; Platel, R. H.; Williams, C. K.; Le Floch, P. *Dalton Trans.* **2009**, 10219−10222. (ab) Alaaeddine, A.; Thomas, C. M.; Roisnel, T.; Carpentier, J. F. *Organometallics* **2009**, *28*, 1469−1475. (ac) Platel, R. H.; White, A. J. P.; Williams, C. K. *Inorg. Chem.* **2008**, *47*, 6840−6849. (ad) Ma, H.; Spaniol, T. P.; Okuda, J. *Inorg. Chem.* **2008**, *47*, 3328−3339. (ae) Hodgson, L. M.; Platel, R. H.; White, A. J. P.; Williams, C. K. *Macromolecules* **2008**, *41*, 8603−8607. (af) Ajellal, N.; Lyubov, D. M.; Sinenkov, M. A.; Fukin, G. K.; Cherkasov, A. V.; Thomas, C. M.; Carpentier, J. F.; Trifonov, A. A. *Chem.—Eur. J.* **2008**, *14*, 5440−5448. (ag) Platel, R. H.; Hodgson, L. M.; White, A. J. P.; Williams, C. K. *Organometallics* **2007**, *26*, 4955−4963. (ah) Skvortsov, G. G.; Yakovenko, M. V.; Castro, P. M.; Fukin, G. K.; Cherkasov, A. V.; Carpentier, J. F.; Trifonov, A. A. *Eur. J. Inorg. Chem.* **2007**, 3260−3267.

DOI: 10.1021/ic5027015
Inorg. Chem. 2015, 54, 2204−2212

(ai) Amgoune, A.; Thomas, C. M.; Carpentier, J. F. *Pure Appl. Chem.* **2007**, *79*, 2013−2030. (aj) Liu, X.; Shang, X.; Tang, T.; Hu, N.; Pei, F.; Cui, D.; Chen, X.; Jing, X. *Organometallics* **2007**, *26*, 2747−2757. (ak) Heck, R.; Schulz, E.; Collin, J.; Carpentier, J. F. *J. Mol. Catal. A: Chem.* **2007**, *268*, 163−168. (al) Amgoune, A.; Thomas, C. M.; Carpentier, J. F. *Macromol. Rapid Commun.* **2007**, *28*, 693−697. (am) Ma, H.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7818−7821. (an) Amgoune, A.; Thomas, C. M.; Roisnel, T.; Carpentier, J. F. *Chem.—Eur. J.* **2006**, *12*, 169−179. (ao) Hodgson, L. M.; White, A. J. P.; Williams, C. K. *J. Polym. Sci., Polym. Chem.* **2006**, *44*, 6646−6651. (ap) Bonnet, F.; Cowley, A. R.; Mountford, P. *Inorg. Chem.* **2005**, *44*, 9046−9055. (aq) Amgoune, A.; Thomas, C. M.; Roisnel, T.; Carpentier, J. F. *Chem.—Eur. J.* **2006**, *12*, 169−179. (ar) Alaaeddine, A.; Amgoune, A.; Thomas, C. M.; Dagorne, S.; Bellemin-Laponnaz, S.; Carpentier, J.-F. *Eur. J. Inorg. Chem.* **2006**, 3652−3658. (as) Cai, C. X.; Amgoune, A.; Lehmann, C. W.; Carpentier, J. F. *Chem. Commun.* **2004**, 330−331.

(7) Möller, M.; Kånge, R.; Hedrick, J. L. *J. Polym. Sci. A: Polym. Chem.* **2000**, *38*, 2067−2074.

(8) (a) Thi-Phuong-Anh, C.; Nocton, G.; Ricard, L.; Le Goff, X. F.; Auffrant, A. *Angew. Chem., Int. Ed.* **2014**, *53*, 1368−1372. (b) Cao, T. P. A.; Buchard, A.; Le Goff, X. F.; Auffrant, A.; Williams, C. K. *Inorg. Chem.* **2012**, *51*, 2157−2169.

(9) Cordero, B.; Gomez, V.; Platero-Prats, A. E.; Reves, M.; Echeverria, J.; Cremades, E.; Barragan, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832−2838.

(10) Kowalski, A.; Duda, A.; Penczek, S. *Macromolecules* **1998**, *31*, 2114.

(11) (a) Labet, M.; Thielemans, W. *Chem. Soc. Rev.* **2009**, *38*, 3484−3504. (b) Arbaoui, A.; Redshaw, C. *Polym. Chem.* **2010**, *1*, 801−826.

(12) (a) Dijkstra, P. J.; Du, H. Z.; Feijen, J. *Polym. Chem.* **2011**, *2*, 520−527. (b) Du, H.; Velders, A. H.; Dijkstra, P. J.; Sun, J.; Zhong, Z.; Chen, X.; Feijen, J. *Chem.—Eur. J.* **2009**, *15*, 9836−9845.

(13) (a) Wang, H.; Yang, Y.; Ma, H. *Macromolecules* **2014**, *47*, 7750−7764. (b) Abbina, S.; Du, G. *ACS Macro Lett.* **2014**, *3*, 689−692.

(14) (a) Phomphrai, K.; Chumsaeng, P.; Sangtrirutnugul, P.; Kongsaeree, P.; Pohmakotr, M. *Dalton Trans.* **2010**, *39*, 1865−1871. (b) Dagorne, S.; Le Bideau, F.; Welter, R.; Bellemin-Laponnaz, S.; Maisse-François, A. *Chem.—Eur. J.* **2007**, *13*, 3202−3217. (c) Chisholm, M. H.; Delbridge, E. E. *New J. Chem.* **2003**, *27*, 1167−1176. (d) Wang, L.; Kefalidis, C. E.; Sinbandhit, S.; Dorcet, V.; Carpentier, J.-F.; Maron, L.; Sarazin, Y. *Chem.—Eur. J.* **2013**, *19*, 13463−13478.

(15) (a) Nimitsiriwat, N.; Gibson, V. C.; Marshall, E. L.; White, A. J. P.; Dale, S. H.; Elsegood, M. R. J. *Dalton Trans.* **2007**, 4464−4471. (b) Wang, L.; Poirier, V.; Ghiotto, F.; Bochmann, M.; Cannon, R. D.; Carpentier, J.-F.; Sarazin, Y. *Macromolecules* **2014**, *47*, 2574−2584. (c) Poirier, V.; Roisnel, T.; Sinbandhit, S.; Bochmann, M.; Carpentier, J.-F.; Sarazin, Y. *Chem.—Eur. J.* **2012**, *18*, 2998−3013.

(16) Bax, A.; Davis, D. G. *J. Magn. Reson.* **1985**, *63*, 207−213.

(17) Bax, A.; Davis, D. G. *J. Magn. Reson.* **1985**, *65*, 355−360.

(18) Coudane, J.; Ustariz-Peyret, C.; Schwach, G.; Vert, M. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 1651−1658.

DOI: 10.1021/ic5027015
Inorg. Chem. 2015, 54, 2204−2212