Inorganic Chemistry

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Bis(phosphinic)diamido Yttrium Amide, Alkoxide, and Aryloxide Complexes: An Evaluation of Lactide Ring-Opening Polymerization Initiator Efficiency

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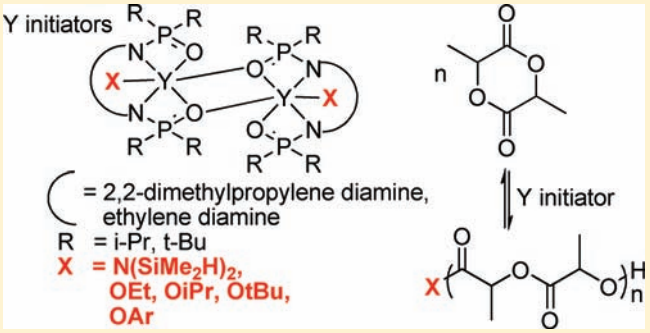
Supporting Information

ABSTRACT: The synthesis and characterization of a series of bis(phosphinic)diamido yttrium alkoxide, amide, and aryloxide initiators are reported. The new complexes are characterized using multinuclear nuclear magnetic resonance (NMR) spectroscopy, elemental analysis, and, in some cases, X-ray crystallography. The alkoxide complexes are all dimeric in both the solid state and in solution, as are the amide complexes substituted with *iso*-propyl or phenyl groups on the phosphorus atoms. On the other hand, increasing the steric hindrance of the phosphorus substituents (*tert*-butyl), enables isolation of mononuclear yttrium amide complexes with either 2,2-dimethylpropylene or ethylene diamido ligand backbones. The complex of 2,6-di-*tert*-butyl-4-methylphenoxide is also mononuclear. All the new complexes are efficient initiators for *rac*-lactide ring-opening polymerization. The polymerization kinetics are compared and pseudo first order rate constants, k_{obs}, determined. The polymerization control is also discussed, by monitoring the number-averaged molecular weight, M_n, and polydispersity index, PDI, obtained using gel permeation chromatography (GPC). The alkoxide complexes are the most efficient initiators, showing very high rates and good polymerization control, behavior consistent with rapid rates of initiation. The phenoxide and amide complexes are less efficient as manifest by nonlinear regions in the kinetic plots, lower values for k_{obs}, and reduced polymerization control. One of the mononuclear yttrium amide complexes shows heteroselectivity in the polymerization of *rac*-lactide; however, this effect is reduced on changing the initiating group to phenoxide or on changing the ancillary ligand diamido backbone group.



INTRODUCTION

Polylactide (PLA) is an aliphatic polyester comprising lactic acid repeat units which derives from renewable resources and which can be degraded after use to metabolites.[1−3] The polymer has suitable thermal and mechanical properties to be considered as a replacement for some commodity polymers.[1] In contrast to such conventional polymers, PLA is degradable and can be hydrolyzed to produce lactic acid, which can be metabolized, ultimately yielding carbon dioxide and water. Lactic acid is currently obtained via the fermentation of D-glucose, derived from corn or sugar beet.[1] Therefore PLA has the potential to show a renewable life cycle, as some of the CO_2 released during its degradation is photosynthesized by the plant; however, it should be noted that the production of the polymer does require significant energy input. PLA is currently manufactured by the ring-opening polymerization of lactide, a process initiated by metal complexes (Figure 1).[2]

The driving force for the reaction is the relief of ring strain: for a 1 M solution of lactide at 25 °C, $\Delta H = 22.1$ kJ mol^{-1}.[4] The ring-opening polymerization is proposed to occur via a coordination−insertion reaction mechanism, a hypothesis supported by polymer chain end-group analyses and theoretical analyses.[2] The mechanism proposes coordination of the lactide to the Lewis acidic metal center, followed by attack/insertion of the labile metal alkoxide/amide bond leading to acyl bond ring-opening of the lactide and formation of a propagating metal alkoxide species. Propagation occurs by repetition of the coordination and insertion steps until all the monomer is consumed. Chain terminations occur by exposure of the reaction mixture to moisture or dilute acid which cleaves the metal alkoxide bond. Thus, the chain end-groups are an ester/amide and a hydroxyl group, respectively.

Various Lewis acidic metal alkoxide and amide complexes have been shown to be initiators for lactide polymerization.[2] Of these, yttrium complexes show some of the fastest rates and even the potential for stereochemical control and polymerization control. Some of the earliest reports of yttrium initiators focused on homoleptic alkoxide complexes; these were, however, found to form clusters of the form $Y_5(\mu\text{-O})(OR)_{13}$ which were rather slow initiators.[5,6] One strategy to overcome the low rates was to prepare homoleptic yttrium alkoxides

Received: April 15, 2011
Published: July 13, 2011

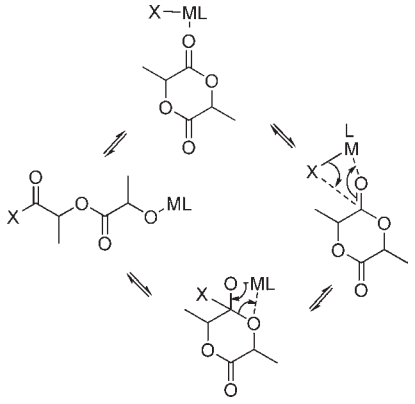


Figure 1. Ring-opening polymerization of lactide, where ML = metal center, for example, Y(III) with ancillary ligand, X = O-polymer for propagation steps and X = NR_2, OR for initiation, where R = alkyl, aryl.

in situ by addition of alcohol to more stabilized yttrium precursors; this led to some very high active initiating systems.[5,7] While homoleptic yttrium alkoxides generally display excellent rates, the requirement for in situ addition of alcohol complicated the characterization of the active species.[5−7] Research has focused on the preparation of heteroleptic complexes; these have generally been of the form $LY(NR_2)$, where L represents a sterically hindered dianionic ancillary ligand and R is a sterically hindered alkyl or, more commonly, a trialkylsilyl group. Notable among these are the 1,-ω-dithiaalkandiyl bridged bis(phenolate) yttrium complexes, reported by Okuda, which showed excellent activities and high heteroselectivity for *rac*-lactide or syndioselectivity for *meso*-lactide polymerization.[8,9] Independently, the groups of Carpentier and Mountford, and others, have extensively investigated amine bridged bis(phenolate) yttrium amido/alkyl/borohydride/alkoxide complexes.[10−12] Many of these complexes show good polymerization rates and excellent heteroselectivity; in particular improved polymerization control is frequently observed on addition of exogeneous alcohol as a chain transfer agent.[13] Recently, Arnold et al. reported a chiral alcohol which formed homochiral yttrium complexes, by a ligand recognition process, and which showed high isoselectivity in the polymerization of *rac*-lactide.[14] Alternative ligand systems not containing phenolate groups remain under-explored,[13,15−17] presenting an opportunity to understand the factors which influence the behavior at the yttrium active site.

Our research group have focused on diamido ligand systems; in particular, bis(phosphinic)diamido and bis(thiophosphinic)diamido) yttrium amido complexes have shown excellent rates.[18−22] The rate shows a first order dependency on both monomer and initiator concentration; the pseudo first order rate constants, k_{obs}, have been among the highest reported.[19] Herein, a series of bis(phosphinic)-diamido yttrium amido and alkoxide complexes are reported, and comparisons drawn between the catalytic activity (quantified by a pseudo first order rate constant, k_{obs}), the rates of initiation versus propagation (quantified by kinetic analysis, M_n, and PDI), and the potential for this initiator class to exert stereocontrol.

RESULTS AND DISCUSSION

Yttrium Alkoxide Complexes. Our research group have previously reported a series of bis(phosphinic)diamido yttrium bis-(dimethylsilyl)amido complexes as initiators for the ring-opening polymerization of *rac*-lactide. It was observed that addition of

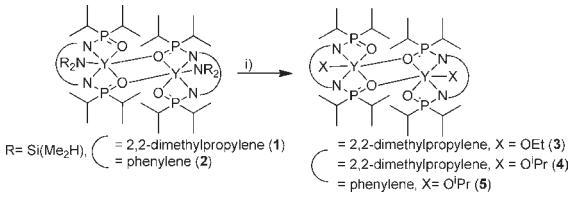


Figure 2. Synthesis of Complexes **3**−**5**. Reagents and Conditions: (i) 2 ROH (R = Et, *i*Pr), toluene, 298 K, 24 h, - 2 HNR_2.

iso-propyl alcohol to the polymerization enabled improved rates and control.[21] The isolation and characterization of a series of bis(phosphinic)diamido yttrium alkoxide complexes was targeted to enable more detailed studies of the influence of an alkoxide initiating group during lactide ring-opening polymerization.

We have already established, using $^{31}P\{^1H\}$ NMR spectroscopy, that addition of *iso*-propyl alcohol to the $[LYN(SiMe_2H)_2]$ complexes does not protonate the ancillary ligand,[21] thereby providing a route to prepare and isolate various other yttrium alkoxide complexes. Isolated heteroleptic yttrium alkoxide complexes have not been extensively examined for lactide ROP,[16,17] in contrast to the amido groups. We have previously reported the synthesis, characterization, and polymerization activity of a series of bis(phosphinic diamido)yttrium amido complexes, where the phosphorus substituents have been *iso*-propyl or phenyl and where the diamine groups have been propylene, ethylene, cyclohexylene, or phenylene. Two of these amido complexes (**1**, **2**) were selected for further study (Figure 2)

The complexes were prepared by reaction between the bis(phosphinic)diamine pro-ligands and $[Y\{N(SiMe_2H)_2\}_3(THF)_2]$.[20,21] The complexes formed dimeric structures, both in the solid state and in solution. The complexes were specifically chosen as they represent extremes in initiator activity, with complex **1** showing the highest rates and complex **2** showing the lowest.[20,21] Each complex was reacted with 2 equivalents of alcohol, in toluene/benzene solution, over 24 h at 298 K. This enabled isolation of the alkoxide complexes **3**−**5**, in 66−80% yields (Figure 2).

The $^{31}P\{^1H\}$ NMR spectra of **3**−**5** did not show any signals for the yttrium amide precursor (**1** or **2**, respectively) or the free ligand. Thus, ligand redistribution reactions with concomitant formation of the homoleptic yttrium alkoxide complexes can be ruled out. The $^{31}P\{^1H\}$ NMR spectrum, at 293 K, of **3** showed a broad signal at 62.7 ppm, with a relative integral value of 25, as well as several low intensity peaks. On cooling the sample to 183 K, the broad peak (62.7 ppm) split into four peaks: a pair at 68.5 and 59.1 ppm, with relative integrals of 2.5, and another pair at 68.2 and 58.3 ppm, with relative integrals of 1 (Supporting Information, Figure S1). The complex is assigned a dimeric structure, whereby for each ligand, one oxygen atom bridges between two yttrium centers (leading to the resonances at ∼68 ppm) and the other is coordinated to a single yttrium center (resonances at 58−9 ppm). The appearance of four resonances at lower temperatures suggests there are two isomeric dimeric complexes; the isomerization could be due to the LY chelate ring conformation, and/or changes to the yttrium coordination geometry. The appearance of two isomers, both of which are dimeric, was also observed for complex **1** (in a relative ratio of 13:1). In contrast to complex **1**, whose spectrum is well resolved at 293 K, complex **3** has an alkoxide coligand, and it is proposed that the smaller size of this group increases the fluxionality of the

dx.doi.org/10.1021/ic200773x |*Inorg. Chem.* 2011, 50, 7718–7728

complex. At lower temperatures, the fluxional processes are sufficiently slowed enabling the phosphorus atoms attached to the bridging oxygen atoms and the phosphorus atoms attached to the terminally bound oxygen atoms to be distinguished. The ^{1}H NMR spectrum of **3** shows broadened resonances; a quartet and a triplet, due to the methylene and methyl protons of the ethoxide group, were shifted downfield compared to free ethanol.[23] Satisfactory elemental analyses results for compound **3** could not be obtained despite multiple attempts; the structure is therefore assigned on the basis of NMR spectroscopic data and the solid state structure. The analogous *iso*-propyl alkoxide complex **4** gave similar spectra; at 293 K the ^{31}P{^{1}H} NMR spectrum showed a broad multiplet, and at 188 K a closely related spectrum to **3** was obtained, with four peaks, two of relative integral 2 and two with relative integral 1, assigned to two isomeric dimeric complexes (Supporting Information, Figure S1).

Crystals of complex **3** suitable for X-ray crystallographic analysis were grown from a toluene solution. The compound crystallized with two independent C_i-symmetric complexes (**3**-A and **3**-B) in the asymmetric unit, each having essentially the same geometry; complex **3**-A is shown in Figure 3, complex **3**-B in Supporting Information, Figure S8, and selected bond lengths and angles for both complexes are in given in Table 1. The complex is dimeric with a center of symmetry in the middle of the Y_2O_2 ring, and the coordination geometry at the yttrium center is distorted pentagonal bipyramidal with the ancillary ligand occupying the basal positions and the ethoxide coligand in the apical site. The distorted basal plane is only coplanar to about 0.23 Å [0.23 Å] with the yttrium atom lying about 0.64 Å [0.62 Å] out of this plane in the direction of O(30). (The initial values refer to complex **3**-A and those in square parentheses refer to complex **3**-B.) Interestingly, the ethoxide groups lie anti to each other, which is in contrast to the yttrium amido complexes, for example, **1**, whose amido groups were arranged syn to each other.

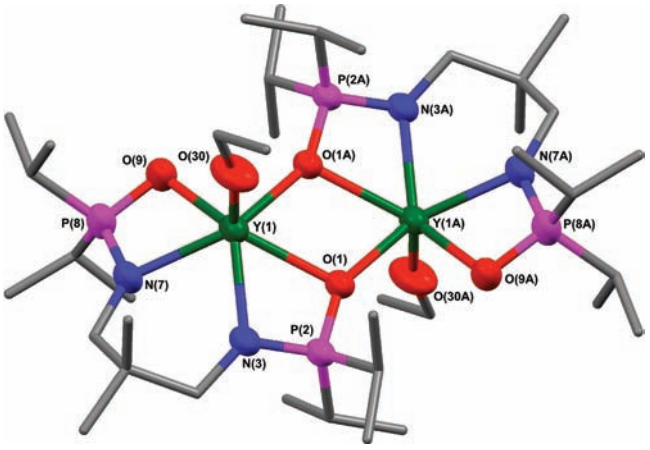


Figure 3. Molecular structure of one (**3**-A) of the two crystallographically independent C_i-symmetric complexes present in the crystals of **3**. The labeled hetereoatoms have been drawn with 50% probability ellipsoids.

The use of a more rigid ancillary ligand enabled isolation of yttrium alkoxide complexes which did not show any isomerization on the NMR time scale at ambient temperature. Thus, complex **5** showed a single resonance at 59.5 ppm in the ^{31}P{^{1}H} NMR spectrum in CD_2Cl_2 at 293 K. Upon reducing the temperature, this signal broadened, splitting to two broad signals of equal integration at 183 K, at 64.7 and 55.8 ppm, as well as other, sharper signals (Supporting Information, Figure S3). The corresponding ^{1}H NMR spectrum at 273 K showed the broadening of all resonances compared to the amido complex **2** and new signals 4.39, 1.09, and 1.05 ppm corresponding to the *iso*-propyl alkoxide protons.

Phosphorus Substituents. We have previously established that by changing the steric hindrance of the substituents on the phosphorus atoms it is possible to control the nuclearity of the resulting complex.[20−22] Thus, less sterically hindered substituents such as *iso*-propyl or phenyl resulted in formation of dimeric yttrium complexes.[20,21] In contrast, more sterically hindered *tert*-butyl phosphorus substituents enabled isolation of a monomeric yttrium amido complex, **6** (Figure 4).[22] Complex **6** enabled the heteroselective polymerization of *rac*-lactide (P_r: 0.85). The reaction of **6** with 2 equiv of *iso*-propyl alcohol led to the formation of a dimeric alkoxide complex, **7**. Complex **7**, in common with all other dimeric complexes, showed very little stereocontrol in the polymerization of *rac*-lactide. Therefore, it was of interest to establish whether mononuclear yttrium alkoxide complexes could be prepared as these might be expected to exert stereocontrol; thus **6** was reacted with more sterically

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Two Crystallographically Independent C_i-Symmetric Complexes (3-A and 3-B) Present in the Crystals of 3

	3-A	3-B		3-A	3-B
Y(1)−O(1)	2.405(2)	2.436(2)	Y(1)−N(3)	2.372(3)	2.368(3)
Y(1)−N(7)	2.342(3)	2.342(3)	Y(1)−O(9)	2.334(2)	2.344(3)
Y(1)−O(30)	2.028(3)	2.033(2)	Y(1)−O(1A)	2.312(2)	2.305(2)
Y(1)···Y(1A)	3.9124(5)	3.9593(6)			
O(1)−Y(1)−N(3)	61.61(8)	61.03(9)	O(1)−Y(1)−N(7)	125.97(9)	127.86(10)
O(1)−Y(1)−O(9)	132.46(8)	133.19(9)	O(1)−Y(1)−O(30)	110.46(11)	109.51(11)
O(1)−Y(1)−O(1A)	67.92(8)	66.77(9)	N(3)−Y(1)−N(7)	74.96(9)	76.03(11)
N(3)−Y(1)−O(9)	134.10(9)	134.15(10)	N(3)−Y(1)−O(30)	104.28(11)	103.57(12)
N(3)−Y(1)−O(1A)	129.16(8)	127.52(9)	N(7)−Y(1)−O(9)	62.99(9)	62.70(10)
N(7)−Y(1)−O(30)	110.12(12)	108.08(12)	N(7)−Y(1)−O(1A)	136.94(9)	139.52(10)
O(9)−Y(1)−O(30)	106.65(12)	107.34(11)	O(9)−Y(1)−O(1A)	78.44(8)	80.48(8)
O(30)−Y(1)−O(1A)	98.21(10)	98.05(10)	Y(1)−O(1)−Y(1A)	112.08(8)	113.23(9)

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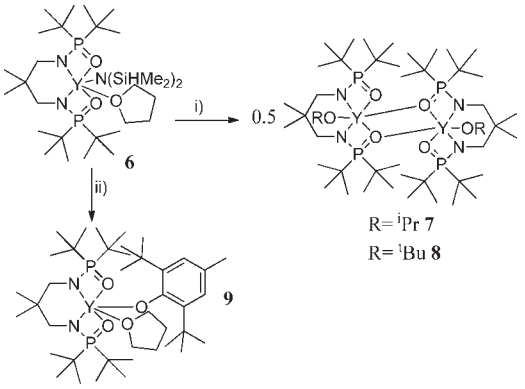

Figure 4. Preparation of complexes **7**−**9**. Reagents and Conditions: (i) ROH, toluene, 298 K, - $HN(SiHMe_2)$. (ii) 2,6-di-*tert*-butyl-4-methyl-phenol, C_6D_6, 298 K, - $HN(SiHMe_2)$.

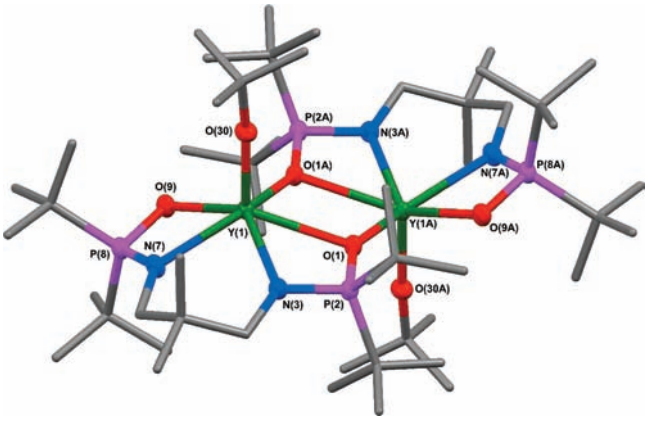

Figure 5. Molecular structure of the C_i-symmetric complex **8**. The labeled hetereoatoms have been drawn with 50% probability ellipsoids.

hindered alcohols including *tert*-butyl alcohol and 2,6-di-*tert*-butyl-4-methylphenol.

The *tert*-butoxide complex, **8**, had a dimeric structure as evidenced by the $^{31}P\{^1H\}$ NMR spectrum which consisted of two resonances, of equal integration, at 59.3 and 67.1 ppm, a doublet and a triplet, respectively. The doublet arises because of the phosphorus attached to the terminally bound oxo group which couples with a single yttrium center. The triplet signal was maintained even when the spectrum was collected at higher frequency and with a greater number of data points and was assigned to the phosphorus atom attached to the bridging oxygen atom, which couples with two, equivalent yttrium centers. Complex **7** showed a closely related spectrum, with a doublet and triplet resonances. The high symmetry of these alkoxide complexes renders the yttrium atoms equivalent; thus the phosphorus bonded to the bridging oxygen resonates as a triplet. The corresponding ^1H NMR spectrum, of complex **8**, shows four doublets for the *tert*-butyl phosphorus substituents, each integrating to 18 protons. The alkoxide methyl groups resonate as a singlet at 1.14 ppm.

Crystals suitable of complex **8** suitable for X-ray crystallographic analysis were grown from a benzene solution, and the molecular structure is illustrated in Figure 5. The structure is similar to that previously reported for complex **7** and shows a C_i-symmetric dimeric complex with a pentagonal pyramidal yttrium coordination geometry. The distorted basal plane is coplanar to about 0.12 Å with the yttrium atom lying about 0.67 Å out of this plane in the direction of O(30). The bond lengths (Table 2) are unexceptional and are closely related to those previously found for the yttrium amide and alkoxide complexes. It is also notable that all the dimeric amide complexes have the amide groups on the same face of the molecule (i.e., syn to one another) whereas the alkoxide complexes **4**, **7**, and **8** have the alkoxide groups anti to one another.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 8

Y(1)−O(1)	2.4881(12)	Y(1)−N(3)	2.3696(14)
Y(1)−N(7)	2.3921(15)	Y(1)−O(9)	2.3293(12)
Y(1)−O(30)	2.0647(13)	Y(1)−O(1A)	2.3803(12)
Y(1)···Y(1A)	4.0187(3)		

O(1)−Y(1)−N(3)	60.74(4)	O(1)−Y(1)−N(7)	129.12(5)
O(1)−Y(1)−O(9)	134.04(4)	O(1)−Y(1)−O(30)	106.50(5)
O(1)−Y(1)−O(1A)	68.75(4)	N(3)−Y(1)−N(7)	74.83(5)
N(3)−Y(1)−O(9)	130.95(5)	N(3)−Y(1)−O(30)	105.14(5)
N(3)−Y(1)−O(1A)	127.54(5)	N(7)−Y(1)−O(9)	62.49(5)
N(7)−Y(1)−O(30)	108.01(5)	N(7)−Y(1)−O(1A)	135.96(5)
O(9)−Y(1)−O(30)	109.94(5)	O(9)−Y(1)−O(1A)	77.23(4)
O(30)−Y(1)−O(1A)	101.59(5)	Y(1)−O(1)−Y(1A)	111.25(4)

Table 3. Comparison of the Hydrodynamic Radii (r) of 7 and 8 Calculated Both in the Solid State and in Solution

complex	r (crystal structure) /Å	r (^{1}H PGSE NMR) /Å
7	5.97	5.81
8	5.93	5.47

To further investigate the nuclearity of the complexes, comparisons were made between the hydrodynamic radii, calculated from the molecular structure obtained by X-ray crystallography, and from an NMR PGSE experiment, according to the method previously described.[20,24] The hydrodynamic radii are listed in Table 3; there is a good agreement between the values calculated from the solid state structures and those from solution measurements. This agreement, together with the $^{31}P\{^1H\}$ NMR data, strongly suggest that the complexes maintain the dimeric structures in solution.

Since dimeric products were obtained using aliphatic alcohols, bulkier aryl alcohols (2,4,6-trimethylphenol and 2,6-di-*tert*-butyl-4-methyl-phenol) were also investigated. The reactions between the aryl alcohols and complex **6** were slower than for aliphatic alcohols, typically taking 24 h at 343 K to completely consume **6**. The reaction with 2,4,6-trimethyl phenol led to a mixture of products, the major species was monomeric, as evidenced by a doublet at 58.6 ppm in the $^{31}P\{^1H\}$NMR spectrum; however, low intensity multiplets, at 71.4 and 60.7 ppm and broad resonances at 64.3 and 59.3 ppm, indicated dimeric complexes were also present. As any catalytic studies would be likely to be complicated by such monomer−dimer mixtures, this aryl alcohol was not further investigated. The reaction with 2,6-di-*tert*-butyl-4-methylphenol led exclusively to a mononuclear complex, **9**. This was established by the presence of a single doublet at 58.7 ppm in the $^{31}P\{^1H\}$ NMR spectrum and by the presence of only one doublet signal for the *tert*-butyl phosphorus substituents, at 1.16 ppm, in the ^1H NMR spectrum. In the ^1H NMR spectrum,

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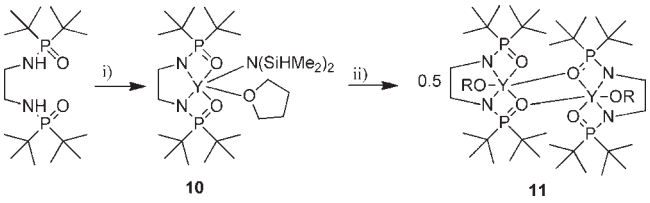

Figure 6. Synthesis of yttrium complexes **10** and **11**, where R = *tert*-butyl. Reagents and Conditions: (i) $[Y\{N(SiHMe_2)_2\}_3(THF)_2]$, THF, 298 K, (ii) ^tBuOH, 298 K.

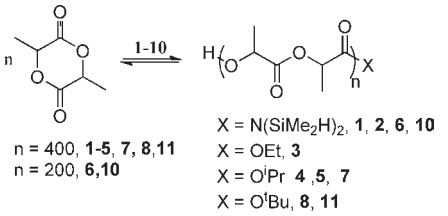

Figure 7. Polymerization of *rac*-lactide by complexes **1**−**11**. Conditions: CH_2Cl_2 or THF, 298 K, $[LA]_0/[I]_0$ = 400 for **1**−**5**, **7**, **8**, **11**, $[LA]_0/[I]_0$ = 200 for **6**, **9**, **10**.

the signals for the ancillary ligand methylene protons are two well-defined doublets of doublets, each with a $^2J_{HH}$ coupling of 11.4 Hz and a $^3J_{HP}$ coupling of 3.2 Hz. This coupling was also observed in the ^{1}H NMR spectrum of **6**, but was quite different in the ^{1}H NMR spectra of dimeric complexes, where the methylene group resonated as multiplets. Furthermore, the 2,6-*tert*-butyl groups on the phenol were equivalent, resonating as a singlet, integrating to 18, at 1.78 ppm, indicating that this group had free rotation.

The *tert*-butyl substituents on the phosphorus atoms were only sufficiently sterically hindered to enable isolation of monomeric complexes when sterically hindered coligands were applied, for example, amido or aryl oxide. It was also of interest to investigate the influence, if any, of the diamido backbone group; therefore, a bis(di-*tert*-butyl-phosphinic)ethylene diamine pro-ligand was prepared. The pro-ligand was prepared by reacting ethylene diamine with 2 equiv of di(*tert*-butyl)chlorophosphine and base, followed by a one-pot oxidation, using aqueous hydrogen peroxide; the product was isolated in 89% yield. The new ligand was reacted with yttrium precursors and alcohols, as illustrated in Figure 6.

The monomeric complex, **10**, was prepared as the sole product when reacting the pro-ligand and $[Y\{N(SiHMe_2)_2\}_3(THF)_2]$ in tetrahydrofuran (THF) in situ on an NMR scale. Thus, equimolar quantities of the pro-ligand and $[Y\{N(SiHMe_2)_2\}_3(THF)_2]$ were dissolved in the minimum of THF-d_8; after 16 h the $^{31}P\{^1H\}$ NMR spectrum showed exclusive formation of **10**, as evidenced by a doublet at 54.3 ppm, with a $^2J_{PY}$ of 4.05 Hz, in excellent agreement with the data obtained for **6**.[22] The ^{1}H NMR spectrum showed a doublet at 1.25 ppm for the *tert*-butyl groups and a multiplet at 3.56 ppm for the methylene protons on the amine backbone of the ligand. One molecule of bound THF was also observed (with peaks at 3.62 and 1.78 ppm), the signals of which were shifted downfield compared to free THF (3.58 and 1.73 ppm), although presumably this is undergoing rapid exchange with free THF in the bulk solvent. Thus, the structure of complex **10** (prepared and characterized in situ) was mononuclear. On removal of the THF and analysis of the product in d_6-benzene, a mixture of **10** and dimeric analogues were observed. The $^{31}P\{^1H\}$NMR spectrum showed the major species was complex **10** (a doublet at 54.4 ppm, with a relative integration of 4 and a $^2J_{PY}$ coupling constant of 3.56 Hz). However, the spectrum also showed other low intensity signals including two doublets of doublets of doublets at approximately 60 ppm and two doublets of doublets at approximately 55 ppm. These multiplets, and the associated coupling constants, are consistent with the presence of two dimeric isomers, in a relative ratio of 2:1. It is interesting to note the influence that the diamido group and solvent exert over the complex nuclearity: the complex **6** was mononuclear in all solvents, yet complex **10** was more susceptible to removal of coordinated THF and formation of monomer−dimer mixtures in noncoordinating solvents.

Addition of 1 equiv of *tert*-butanol to either complex **10** (formed in situ in d_8-THF) or to the monomer−dimer mixture (in d_6-benzene), yielded a single dimeric yttrium alkoxide product, **11** (Figure 6). The $^{31}P\{^1H\}$ NMR spectrum showed a doublet of doublets at 61.4 ppm and a doublet at 53.4 ppm. The ^{1}H NMR spectrum showed four doublet signals for the *tert*-butyl groups on the phosphorus atoms and four multiplets for the backbone methylene groups. In addition, a singlet at 1.49 ppm was assigned to the *tert*-butoxide group. The dimeric structure of **11** highlights the dependency of nuclearity of these yttrium complexes on the steric bulk of the ligand, the initiating group, and the nature of the solvent.

Polymerization of *rac*-Lactide. All the complexes were tested as initiators for the ring-opening polymerization of *rac*-lactide (Figure 7, Table 4)

The polymerizations were carried out either in CH_2Cl_2 (initiators **1**−**6**) or in THF (initiators **6**−**11**). The polymerizations conducted in THF were somewhat slower than those in CH_2Cl_2, an effect which has previously been observed and which is ascribed to competitive binding of THF versus lactide at the active site.[12,17,19,20,22] Thus, it is not possible to directly compare the rates of polymerization in the two solvents; however, it is still feasible to uncover some structure−activity relationships. The polymerizations were all conducted so that the concentration of initiating group was the same; thus dimeric complexes (with two amido/alkoxide initiating groups) were used at $[LA]_0/[I]_0$ = 400, while the monomeric complexes (**6**, **9**, **10** with one amido initiating group) were used at $[LA]_0/[I]_0$ = 200. Therefore, the expected number averaged molecular weight, at high (>95%) monomer conversion, is approximately 28,000 g/mol. All polymerizations were analyzed by taking aliquots, quenching them by precipitation in cold hexanes, and analyzing the crude product to determine the conversion of lactide and molecular number of the polylactide.

Polymerization Rates. Semilogarithmic plots of $\ln\{[LA]_0/[LA]_t\}$ versus time were constructed (Figures 8−10, where $[LA]_0$ = 0.5 M). The plots generally showed linear fits, with *x*-intercepts at the origin, consistent with rapid initiation; the gradients of the linear fits correspond to the pseudo first order rate constants. The kinetic data for initiators **1** and **2** shows rather more complex behavior, with two different regimes in the polymerization: a slower initiation regime leading to a region where the data can be fit in a linear fashion, corresponding to a propagation regime (Supporting Information, Figures S3, S4).[20,21] It is believed that the relatively low nucleophilicity of a metal-amide bond and the steric hindrance of the bis(dimethylsilyl)amido nucleophile hinder the initiation reaction and complicate the kinetic analysis. However, the isolation of the alkoxide complexes, **3**−**5**, led to a distinct improvement in the linear fits to the

dx.doi.org/10.1021/ic200773x |*Inorg. Chem.* 2011, 50, 7718–7728

Table 4. Polymerization of *rac*-LA Using Initiators 1−11[a]

initiator	$[LA]_0/M$	time/s	percentage conversion[b]	$k_{obs} \times 10^{-3}$ [c] $/s^{-1}$	M_n /g mol^{-1} [d]	PDI[d]	P_r[f]
1	1.0	221	99	24.3	66,409	1.66	0.62
2	1.0	8515	99	0.66	147,900	1.66	
3	0.5	150	98	32.3	32,550	1.34	
4	0.5	240	99	17.6	26,820	1.12	
5	0.5	390	98	17.3	29,060	1.15	
6	0.5	300	98	17.8	99,590	1.30	0.62
6	0.5[e]	480	96	8.36	81,390	1.38	0.85
7	0.5[e]	120	94	38.8	23,180	1.77	0.62
8	0.5[e]	59	96	39.5	35,670	1.31	0.63
9	1[e]	1800	91	1.93	64,700	1.23	0.71
10	0.5[e]	180	79	15.6	43,900	1.26	0.61
11	0.5[e]	62	99	68.6	37,200	1.19	0.62

[a] Polymerization conditions: CH_2Cl_2, 298 K, $[LA]_0/[I]_0 = 400$ for **1**−**5**, $[LA]_0/[I]_0 = 200$ for **6**; THF, 298 K, $[LA]_0/[I]_0 = 400$ for **7**, **8**, **11**, $[LA]_0/[I]_0 = 200$ for **9**, **10**. [b] Determined by integration of the methine region of the ^1H NMR spectrum. [c] Determined from the gradients of the plots of $\ln\{[LA]_0/[LA]_t\}$ versus time. [d] Determined by SEC in THF, using multiangle laser light scattering (GPC-MALLS). [e] Polymerizations conducted in THF. [f] Determined by analysis of all the tetrad signals in the methyne region of the homonuclear decoupled ^1H NMR spectrum and comparison with the signal intensities predicted by Bernouillan statistics.[25]

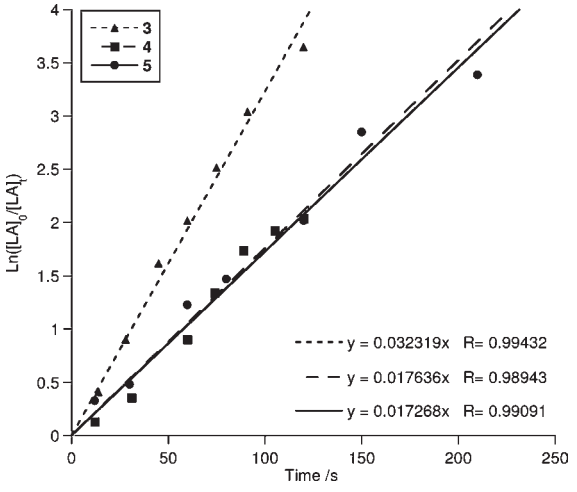

Figure 8. Plot of $\ln\{[LA]_0/[LA]_t\}$ against time, for initiators **3**−**5**. Conditions: $[LA]_0 = 0.5$ M, $[LA]_0/[I]_0 = 400$, CH_2Cl_2, 298 K.

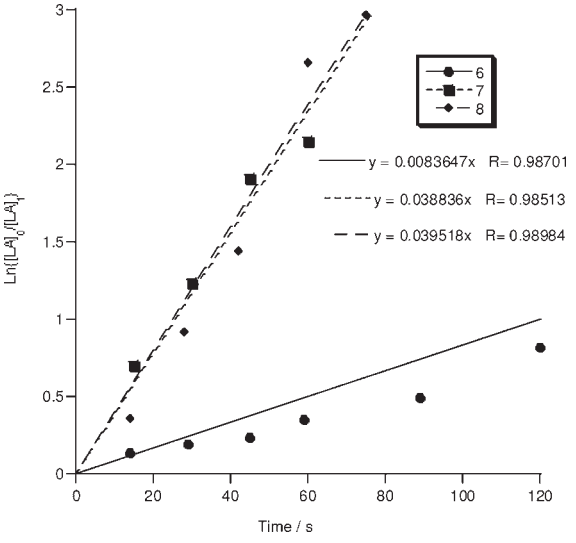

Figure 9. Semilogarithmic plot for polymerizations using initiators **6**−**8**. Conditions: $[LA]_0 = 0.5$ M; $[LA]_0/[I] = 200$ for **6** and $[LA]_0/[I] = 400$ for **7**, **8**; 298 K; THF.

data and an increase in the value of the pseudo first order rate constant, k_{obs} (Figure 8). While the values cannot be directly compared with those obtained for **1** and **2**, as the latter were obtained at monomer concentrations of 1 M; it can be seen that even on decreasing the monomer concentration by 0.5, the value of k_{obs} increases indicative of significantly improved activity. The linearity of the fits also corresponds well with the notion that the yttrium-alkoxide is more nucleophilic than the yttrium-amide.

For the series of initiators tested in THF, it was also noted that yttrium-alkoxides showed higher k_{obs} values and linear fits to the semilogarithmic data. Figure 9 illustrates the increase in rate on changing the initiating group from di(methylsilyl amido) (**6**) to *iso*-propyl alkoxide (**7**) and *tert*-butyl alkoxide (**8**). Figure 10 shows that on substituting di(methylsilylamido) (**10**) group for a *tert*-butyl alkoxide group (**11**) the values of k_{obs} increase approximately 4-fold. Initiator **9** displays somewhat different behavior, showing a more complex data set where a linear fit can only be applied after an initiation period of approximately 4 min and giving a significantly lower value of k_{obs} (Supporting Information, Figure S5). This is closely related behavior to that observed with (dimethylsilyl)amido initiators and is consistent with a relatively poor initiating behavior for the sterically hindered aryl oxide group.

It can be seen that there is some influence of the backbone diamido linker group on the overall rate. For example, complexes **6** and **10** differ by having 2,2-dimethylpropylene and ethylene backbone linker groups, respectively. Complex **6** shows slower polymerization than **10**; the same effect is observed for complexes **8** and **11**. Thus for the series of complexes with *tert*-butyl substituents on the phosphorus atoms, it appears that the ethylene diamido ligand fragment leads to greater rates. It is proposed that the shorter ethylene diamido linker leaves the yttrium atom more exposed than for the complexes with a C-3 backbone diamido group, resulting in an increase in polymerization activity for the former. It should be noted that overall the

dx.doi.org/10.1021/ic200773x |*Inorg. Chem.* 2011, 50, 7718–7728

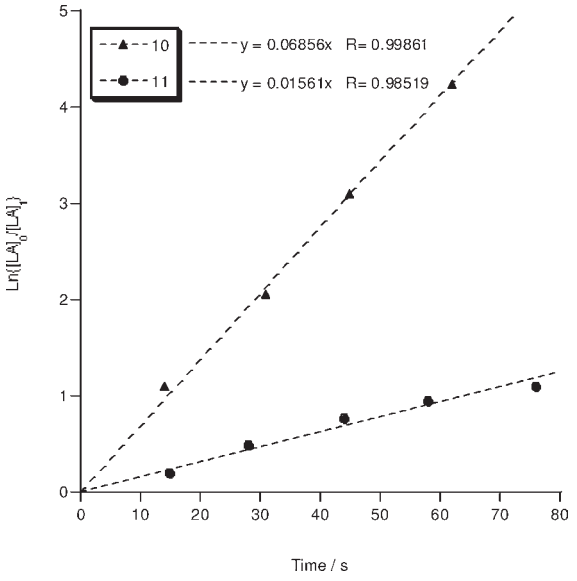

Figure 10. Semilogarithmic plots for polymerizations using initiators **10** and **11**. Conditions: $[LA]_0 = 1.0$ M, $[LA]_0/[I]_0 = 200$ (**10**), 400 (**11**); 298 K; THF.

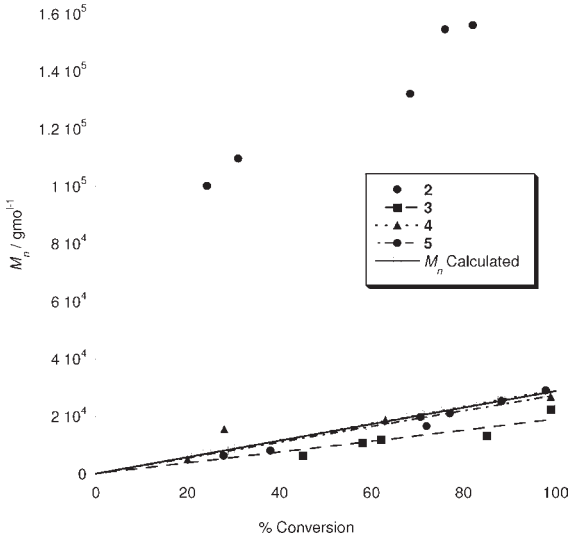

Figure 11. Evolution of M_n versus % conversion for polymerizations using initiators **2**−**5**. Conditions: $[LA]_0$ = 1 M (**2**), 0.5 M (**3**−**5**), $[LA]_0/[I]_0$ = 400 (**2**−**5**); 25 °C; CH_2Cl_2.

rates of polymerization of this type of yttrium initiator are high and compete with some of the best literature systems.[5]

The polymerizations were all conducted so that the concentration of initiating group was the same and such that the calculated number averaged molecular weight, at high (>95%) monomer conversions, should be approximately 28,000 g/mol. The correlation between experimentally determined and calculated values for M_n was poor for the amido initiators, for example, compare the values for **1**−**2** versus **3**−**5** (Figure 11) or **6** and **10** versus **7**−**9**, **11**. The poor correlation is proposed to be due to relatively slow initiation versus propagation reactions. In contrast, the alkoxide initiators gave values for M_n that matched the predicted values well.

Other yttrium initiating systems have also displayed improved control for alkoxide versus amide initiating groups, although these are generally prepared in situ rather than isolated, as in this case.[9,11,13] It is proposed that the improved properties of the alkoxide initiators result from both a reduction in steric hindrance and an increase in nucleophilicity (initiating ability) versus amide analogues. The M_w/M_n values are also narrower (1.12−1.39) for the alkoxide initiators, supporting the notion that they enable rapid initiation followed by controlled polymerization of lactide.

Tacticity Control. The stereochemistry of *rac*-lactide enchainment can be evaluated by comparing the integrals in the homonuclear decoupled ^{1}H NMR spectrum, at the tetrad level, with calculated values (using Bernouillan statistics).[25] Most of the yttrium initiators display little stereocontrol, leading to PLA with a slight heterotactic bias (∼0.6). However, we have previously observed that complex **6** shows reasonable heteroselectivity (0.85), when used in THF.[22] This has been attributed to a chain end control mechanism enhanced by solvent coordination at the active site. The alkoxide analogues of complex **6**, showed much reduced heteroselectivity, even when used in coordinating solvents. This is proposed to be due to the dinuclear nature of these complexes which prohibits efficient stereoselecontrol. The mononuclear aryloxide complex, **9**, shows slightly enhanced heteroselectivity (0.71) compared to dinuclear analogues, although the value is lower than for the amido analogue **6**. The initiating group would not be expected to influence polymer tacticity in such a manner. MALDI-ToF spectra of the polymers produced during the early stages of polymerization (e.g., 10% conversion) showed that significant transesterification had occurred in both cases. These reactions reduce the level of stereocontrol observed as they can scramble the stereochemistry of the polymers. It is possible that the slower rate of propagation for **9** causes the rate of transesterification to become competitive with propagation, and transesterification becomes more significant as a reaction pathway, causing the observed decrease in stereocontrol, this would also be consistent with increased values for the PDI of PLA produced using complex **9**. On the other hand, mononuclear complex **10**, which has an ethylene diamido backbone group, also shows much reduced heteroselectivity. These findings highlight the central importance of the coordination environment in enabling chain end control. Thus, the more open coordination geometry at complex **10**, versus complex **6**, enhances the rate of polymerization but reduces the stereoselectivity. The open coordination site is implicated in the finding that in noncoordinating solvents approximately half of complex **10** dimerizes, a finding not observed for complex **6**.

■ CONCLUSIONS

A series of yttrium alkoxide and amide complexes, ligated by various bis(phosphinic)diamido ancillary ligands, have been prepared. The alkoxide complexes were prepared by alcoholysis of the amide precursors and were fully characterized, including using multinuclear NMR spectroscopies to confirm the solution structures. The alkoxide complexes were all dimeric both in the solid state and in solution, a finding supported by the multiplicity of the peaks in the $^{31}P\{^1H\}$ NMR spectra. An aryloxide complex was also isolated using 2,6-di-*tert*-butyl-4-methyl-phenol, and had a mononuclear structure in solution. The use of bulky *tert*-butyl substituents on the phosphorus atoms in the ancillary ligand enables isolation of monomeric amide complexes with either

2,2-dimethylpropylene or ethylene diamido linkers. In contrast, alcoholysis reactions yield dimeric alkoxide complexes regardless of the nature of the phosphorus substituents. The new complexes are all viable initiators for lactide ring-opening polymerization, showing very high rates and values of k_{obs}. The alkoxide complexes all showed superior rates and improved polymerization control compared to the amido analogues. The aryloxide complex showed rather slower polymerization and reduced polymerization control. These findings are consistent with the sterically hindered amido and aryl oxide initiators showing poor initiation efficiencies. This is likely to be due to the reduced nucleophilicity of the amido groups compared to the alkoxide counterparts and also influenced by the steric hindrance of the amide and aryl oxide groups. The amide complex with *tert*-butyl phosphorus substituents shows good stereocontrol, yielding heterotactic PLA, and this is proposed to be due to its monomeric structure. Further investigations show that related monomeric amido complex (**10**) shows much reduced heteroselectivity. This underscores the importance of the active site coordination environment in controlling the stereochemistry. The monomeric amido complex with an ethylene diamine backbone results in a more open coordination environment at the yttrium center, as evidenced by the finding that in noncoordinating solvents this complex has a tendency to dimerize.

EXPERIMENTAL SECTION

Materials and Methods. All reactions were conducted under a nitrogen atmosphere, using either standard Schlenk techniques or in a nitrogen filled glovebox, unless stated otherwise. All solvents and reagents were obtained from commercial sources (Aldrich and Strem) and used as received unless stated otherwise. Ethylene diamine was stirred over CaH_2, distilled, and stored under nitrogen; *tert*-butanol was stirred over CaH_2, distilled, degassed and stored under nitrogen. THF and pentane were distilled from sodium and stored under nitrogen. Dichloromethane was distilled from CaH_2 and stored under nitrogen. Benzene-d_6 and THF-d_8 were dried over potassium; in each case, performing three freeze−thaw cycles under vacuum, refluxing them for 1−2 days, distilling them under vacuum, and storing them under nitrogen. *Rac*-lactide was donated by Purac Plc. and was recrystallized from anhydrous ethyl acetate or toluene and sublimed at 50 °C three times under vacuum prior to use. [Tris{*N,N*′-bis(dimethylsilyl)-amido}bis(tetrahydrofurano)]yttrium, [Y{N(SiHMe$_2$)$_2$}$_3$(THF)$_2$], complexes **1**, **2**, and **6** were prepared according to the literature procedure.[20−22,26]

Measurements. ^{1}H and ^{13}C{^{1}H} NMR spectra were performed on a Bruker Av-400 instrument, unless otherwise stated. ^{31}P{^{1}H} NMR experiments were performed on a Bruker Av500 spectrometer 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. To observe the complex P−Y coupling patterns, ^{31}P{^{1}H} spectra were collected at a frequency of 202.47 MHz using a 30 degree pulse, a spectral width of 8082 Hz (centered on 57.5 ppm), and 65536 data points with a relaxation delay of 2 s. The spectra were zero filled (0.12 Hz/point resolution) and processed with no apodization. Spectra were processed and analyzed using Mestrenova software. Elemental analyses were determined by Mr. Stephen Boyer at London Metropolitan University, North Campus, Holloway Road, London, N7. Mass spectra were performed on a Micromass Autospec Premier machine, using LSIMS (FAB) ion sources. Melting points were determined using a Reichert apparatus. IR spectra were acquired on a Perkin-Elmer Spectrum 100 FT-IR spectrometer, and the data was processed using Spectrum Express software. Polylactide molecular weights and polydispersity indices were determined from gel permeation chromatography with multiangle laser light scattering (GPC-MALLS). 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. The light scattering detector was a triple-angle detector (Dawn 8+, Wyatt Technology), and the data were analyzed using Astra V version 5.3.1.4. The refractive angle increment for polylactide in THF, was taken as 0.042 mL g^{-1}.[27]

***N,N*′-1,2-bis(*P,P*′-di-*tert*-butylphosphinoyl)ethylenediamine.** To a 250 mL round bottomed flask, equipped with a stirrer bar, was added 1,2-ethylenediamine (0.26 mL, 4 mmol), triethylamine (2.80 mL, 20 mmol), and dichloromethane (40 mL). The flask was cooled to 0 °C, in an ice bath, and chlorodi-*tert*-butylphosphine (1.60 mL, 8.4 mmol) was added dropwise, via a syringe. The mixture was warmed to room temperature and stirred for 20 h. The flask was opened to air, and the mixture cooled to 0 °C, in an ice bath. Hydrogen peroxide (2.06 mL of a 30% w/v soln., 16 mmol) was added cautiously to the mixture. Stirring was continued at 0 °C for 10 min and then at 25 °C for a further 30 min. Sodium thiosulphate (40 mL of a 1 M soln., 40 mmol) was then added slowly. The aqueous and organic layers were separated, and the aqueous layer washed with dichloromethane (2 × 10 mL). The organic layers were collected, dried ($MgSO_4$), and the solvents were removed under reduced pressure, to leave a colorless residue. Recrystallization from dichloromethane and hexane gave the title product as colorless needles (1.35 g, 89%).

M. Pt. °C: 190−193 (sublimes) ^{1}H NMR (400 MHz, $CDCl_3$,) δ ppm: 3.13 (m, 4H, CH_2), 2.94 (m, 2H, NH), 1.21 (d, 36 H, $^3J_{PH}$ = 13.6 Hz, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$,) δ ppm: 44.0 (s, CH_2), 36.5 (d, $^1J_{PC}$ = 76.4, $C(CH_3)_3$), 26.7 (s, $C(CH_3)_3$). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ ppm: 56.1 (s). *m/z* (FAB$^+$): 381 [M+H]$^+$. IR (neat) υ cm^{-1}: 3262 (w, N−H), 3177 (w, N−H), 2970 (m, C−H), 2946 (m, C−H), 2893 (m, C−H), 2865 (m, C−H), 1474 (m), 1388 (w), 1357 (w), 1218 (w), 1153 (s, P═O), 1086 (s, P═O), 1017 (m), 935 (w), 825 (m), 818 (s), 759 (m), 656 (s). Anal. Calcd. for $C_{14}H_{34}N_2O_2P_2$: C, 56.82, H, 11.13, N, 7.36%. Found: C, 60.89, H, 11.21, N, 7.32%.

Di-μ-oxo-{[*N,N*′-1,3-bis(*P,P*′-di-*iso*-propylphosphinoyl)-2,2-dimethylpropanediamido](ethoxy)yttrium} 3. To a solution of di-μ-oxo-{[*N,N*′-1,3-bis(*P,P*′-di-*iso*-propylphosphinoyl)-2,2-dimethylpropanediamido][bis(dimethylsilyl)amido]yttrium}, **1** (0.058 g, 0.05 mmol) in toluene (3 mL), in a Schlenk tube, was added ethanol (5.8 μL, 0.1 mmol) via a micro syringe. The resulting colorless solution was stirred and heated at 70 °C for 24 h. The solvents were removed in vacuo to yield a colorless solid. The title product was obtained by recrystallization from the minimum volume of hexane at −35 °C (0.016 g, 32%).

^{1}H NMR (400 MHz, C_6D_6) δ ppm: 4.36 (q, $^3J_{HH}$ = 6.8 Hz, 6H, OCH_2), 2.97 (m, 8H, CH_2), 2.08 (m, 8H CH(CH$_3$)$_2$), 1.50 (t, $^3J_{HH}$ = 6.8 Hz, 4H, CH_3), 1.30 (m, 24H, CH(CH_3)$_2$), 1.15 (m, 24H, CH-(CH_3)$_2$), 0.87 (m, 12H, C(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ ppm: 63.1 (s, OCH_2), 57.3 (s, CH_2), 38.2 (t, $C(CH_3)_2$), 27.7 (br s, $CH(CH_3)_2$), 25.4 (br s, $CH(CH_3)_2$), 24.6 (br s, $CH(CH_3)_2$), 24.1 (br s, $CH(CH_3)_2$), 22.6 (s, $CH(CH_3)_2$), 17.3 (s, $CH(CH_3)_2$), 16.8 (s, CH-(CH_3)$_2$), 15.5 (s, CH_3). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ ppm: 56.3 (br s, 20P), 50.1 (1P), 49.3 (1P).

Crystal Data for ***3***. $C_{38}H_{86}N_4O_6P_4Y_2$, M = 996.81, triclinic, $P\bar{1}$ (no. 2), a = 10.8212(4), b = 13.0664(4), c = 20.2479(6) Å, α = 105.984(3), β = 101.401(3), γ = 101.061(3)°, V = 2604.17(17) Å^3, Z = 2 [two independent C_i symmetric molecules], D_c = 1.271 g cm^{-3}, μ(Cu−Kα) = 4.463 mm^{-1}, T = 173 K, colorless platy needles, Oxford Diffraction Xcalibur PX Ultra diffractometer; 9922 independent measured reflections (R_{int} = 0.0552), F^2 refinement, R_1(obs) = 0.0436, wR_2(all) = 0.1241, 8151 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$], $2\theta_{max}$ = 144°], 505 parameters. CCDC 812442.

Di-μ-oxo-{[*N,N*′-1,3-bis(*P,P*′-di-*iso*-propylphosphinoyl)-2,2-dimethylpropanediamido](*iso*-propoxy)yttrium} 4. To a solution of di-μ-oxo-{[*N,N*′-1,3-bis(*P,P*′-di-*iso*-propylphosphinoyl)-2,2-dimethylpropanediamido][bis(dimethylsilyl)amido]yttrium} **1** (0.058 g,

dx.doi.org/10.1021/ic200773x |*Inorg. Chem.* 2011, 50, 7718–7728

0.05 mmol) in toluene (3 mL), in a Schlenk tube, was added *iso*-propanol (7.8 μL, 0.1 mmol) via a micro syringe. The resulting colorless solution was stirred and heated at 70 °C for 24 h. The solvents were removed, in vacuo, to yield a colorless solid. The title product was obtained by recrystallization from the minimum volume of hexane at −35 °C (0.034 g, 66%).

^{1}H NMR (400 MHz, C_7D_8) δ ppm: 4.53 (sept, $^3J_{HH}$ = 6.0 Hz, 2H, OC*H*(CH$_3$)$_2$), 2.99 (dd, $^2J_{HH}$ = 11.0 Hz, $^3J_{PH}$ = 3.6 Hz, 4H, C*H*$_2$), 2.89 (br s, 4H, C*H*$_2$), 1.98 (br s, 8H, C*H*(CH$_3$)$_2$), 1.48 (s, 6H, C*H*$_3$), 1.42 (d, $^3J_{HH}$ = 6.0 Hz, 12H, OCH(C*H*$_3$)$_2$), 1.36−0.98 (br m, 48H, CH-(C*H*$_3$)$_2$), 0.87 (s, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, C_7D_8) δ ppm: 68.1 (d, $^2J_{CY}$ = 5.2 Hz, OCH(CH$_3$)$_2$), 57.4 (s, CH$_2$), 38.2 (t, $^3J_{CP}$ = 1.6, *C*(CH$_3$)$_2$), 29.4 (OCH(*C*H$_3$)$_2$), 27.9 (s, *C*H$_3$), 24.6 (br s, *C*H-(CH$_3$)$_2$), 24.4 (s, *C*H$_3$), 16.0 (s, CH(*C*H$_3$)$_2$), 15.9 (s, CH(*C*H$_3$)$_2$), 15.8 (s, CH(*C*H$_3$)$_2$), 15.7 (s, CH(*C*H$_3$)$_2$), 15.5 (s, CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (162 MHz, C_7D_8) δ ppm: 66.4 (br s, 20P), 56.9 (br s, 20P), 51.4 (1P). Anal. Calcd. for $C_{20}H_{45}N_2O_3P_2Y$: C, 46.88, H, 8.95, N, 5.47%; Found: C, 46.63, H, 8.88 N, 5.67%.

Di-μ-oxo-{[*N*,*N*′-1,2-bis(*P*,*P*′-di-*iso*-propylphosphinoyl)-phenylenediamido](*iso*-propoxy)yttrium} 5. To a solution of di-μ-oxo-{[*N*,*N*′-1,2-bis(*P*,*P*′-di-*iso*-propylphosphinoyl)phenylene-diamido][bis(dimethylsilyl)amido]yttrium]} **2** (0.059 g, 0.05 mmol) in toluene (3 mL), in a Schlenk tube, was added *iso*-propanol (7.8 μL, 0.1 mmol) via a micro syringe. The resulting colorless solution was stirred and heated at 70 °C for 24 h. The solvents were removed in vacuo to yield a colorless solid. The title product was obtained by recrystallization from the minimum volume of hexane at −35 °C (0.041 g, 79%.).

^{1}H NMR (400 MHz, CD_2Cl_2) δ ppm: 6.50 (m, 8H, Ar*H*), 4.05 (sept, $^3J_{HH}$ = 6.0 Hz, 2H, OC*H*(CH$_3$)$_2$), 2.38 (sept, $^3J_{HH}$ = 7.2 Hz, 8H, C*H*(CH$_3$)$_2$), 1.27 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 15.2 Hz, 24H, CH(C*H*$_3$)$_2$), 1.14 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 16.4 Hz, 24H, CH(C*H*$_3$)$_2$), 0.98 (d, $^3J_{HH}$ = 6.0 Hz, 12H, OCH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2) δ ppm: 143.9 (d, $^2J_{CP}$ = 13.7 Hz, Ar*C*), 119.1 (s, Ar*C*), 118.8 (s, Ar*C*), 68.4 (s, OCH(CH$_3$)$_2$), 29.1 (s, OCH(*C*H$_3$)$_2$), 25.9 (d, $^1J_{CP}$ = 75.8 Hz, *C*H(CH$_3$)$_2$), 16.1 (s, CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ ppm: 59.5 (s). Anal. Calcd. for $C_{21}H_{39}N_2O_3P_2Y$: C, 48.65, H, 7.58, N, 5.40%; Found: C, 48.62, H, 7.63, N, 5.44%.

Di-μ-oxo-{[*N*,*N*′-1,3-bis(*P*,*P*′-di-*tert*-butylphosphinoyl)-2,2-dimethylpropanediamido](iso-propoxy)]yttrium} 7. To a solution of {[*N*,*N*′-1,3-bis(*P*,*P*′-di-*tert*-butylphosphinoyl)-2,2-dimethylpropanediamido][bis(dimethylsilyl)amido];(tetrahydrofurano)}yttrium, **6** -(0.071 g, 0.1 mmol) in toluene (0.2 mL), was added *iso*-propanol (7.6 μL, 0.1 mmol) via a microsyringe. The solution was stirred briefly, transferred to a tube, sealed and left to stand for 24 h, over which time colorless crystals formed. The mixture was filtered and the solid washed with cold toluene (0.1 mL) to give the title product as a colorless, crystalline solid (0.020 g, 35%).

^{1}H NMR (400 MHz, C_6D_6) δ ppm: 4.58 (sept, $^3J_{HH}$ = 5.6 Hz, 2H, OC*H*(CH$_3$)$_2$), 3.21 (m, 8H, C*H*$_2$), 1.59 (d, $^3J_{PH}$ = 13.6 Hz, 18H, C(C*H*$_3$)$_3$), 1.57 (s, 6H, C*H*$_3$), 1.48 (d, $^3J_{PH}$ = 13.2 Hz, 18H, C(C*H*$_3$)$_3$), 1.41 (d, $^3J_{HH}$ = 5.6 Hz, 6H, CH(C*H*$_3$)), 1.39 (d, $^3J_{HH}$ = 5.6 Hz, 6H, CH(C*H*$_3$)), 1.31 (d, $^3J_{PH}$ = 12.8 Hz, 18H, C(C*H*$_3$)$_3$), 1.25 (d, $^3J_{PH}$ = 12.8 Hz, 18H, C(C*H*$_3$)$_3$), 0.86 (s, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ ppm: 68.2 (s, OCH(CH$_3$)$_2$), 59.7 (s, *C*H$_2$), 58.8 (s, *C*H$_2$), 48.9 (s, *C*(CH$_3$)$_2$), 40.2 (d, $^1J_{CP}$ = 67.6 Hz, *C*(CH$_3$)$_3$), 37.9 (d, $^1J_{CP}$ = 65.1 Hz, *C*(CH$_3$)$_3$), 37.8 (d, $^1J_{CP}$ = 56.9 Hz, *C*(CH$_3$)$_3$), 36.8 (d, $^1J_{CP}$ = 61.3 Hz, *C*(CH$_3$)$_3$), 29.1 (s, OCH(*C*H$_3$)$_2$), 29.0 (s, OCH(*C*H$_3$)$_2$), 28.3 (s, *C*H$_3$), 28.1 (s, C(*C*H$_3$)$_3$), 27.6 (s, C(*C*H$_3$)$_3$), 27.3 (s, C(*C*H$_3$)$_3$), 23.7 (s, *C*H$_3$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ ppm: 67.0 (t, 1P, $^2J_{PY}$ = 4.37 Hz), 58.9 (d, 1P, $^2J_{PY}$ = 4.21 Hz). Anal. Calcd. for $C_{24}H_{53}N_2O_3P_2Y$: C, 50.70, H, 9.40, N, 4.93%. Found: C, 48.70, H, 7.61, N, 5.49%.

Di-μ-oxo-{[*N*,*N*′-1,3-bis(*P*,*P*′-di-*tert*-butylphosphinoyl)-2,2-dimethylpropanediamido](*tert*-butoxy)yttrium} 8. To a solution of {[*N*,*N*′-1,3-bis(*P*,*P*′-di-*tert*-butylphosphinoyl)-2,2-dimethylpropane-diamido][bis(dimethylsilyl)amido] (tetrahydrofurano)}yttrium **6** (0.071 g, 0.1 mmol) in toluene (0.2 mL), was added *tert*-butanol (9.5 μL, 0.1 mmol) via a microsyringe. The solution was stirred briefly, transferred to a tube, sealed, and left to stand for 24 h, over which time colorless crystals formed. The mixture was filtered and the solid washed with cold toluene (0.1 mL) to give the title product as a colorless, crystalline solid (0.031 g, 52%).

^{1}H NMR (400 MHz, C_7D_8) δ ppm: 3.16 (m, 8H, C*H*$_2$), 1.53 (d, $^3J_{HP}$ = 13.2 Hz, 18H, C(C*H*$_3$)$_3$), 1.42 (d, $^3J_{HP}$ = 10.4 Hz, 18H, C(C*H*$_3$)$_3$), 1.14 (s, 18H, OC(C*H*$_3$)$_3$), 1.40 (s, 6H, C*H*$_3$), 1.24 (d, $^3J_{HP}$ = 12.8 Hz, 18H, C(C*H*$_3$)$_3$), 1.20 (d, $^3J_{HP}$ = 12.4 Hz, 18H, C(C*H*$_3$)$_3$), 0.82 (s, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, C_7D_8) δ ppm: 72.6 (d, $^2J_{CY}$ = 5.8 Hz, OC(CH$_3$)$_3$), 59.5 (s, *C*H$_2$), 59.0 (d, $^2J_{CP}$ = 3.1 Hz, *C*H$_2$), 52.7 (s, *C*(CH$_3$)$_2$), 40.2 (d, $^1J_{CP}$ = 66.6 Hz, *C*(CH$_3$)$_3$), 38.2 (d, $^1J_{CP}$ = 41.7 Hz, *C*(CH$_3$)$_3$), 37.6 (d, $^1J_{CP}$ = 34.1 Hz, *C*(CH$_3$)$_3$), 36.8 (d, $^1J_{CP}$ = 60.7 Hz, *C*(CH$_3$)$_3$), 35.1 (s, OC(*C*H$_3$)$_3$), 28.6 (s, C(*C*H$_3$)$_3$), 28.3 (s, C(*C*H$_3$)$_3$), 27.9 (s, *C*H$_3$), 27.7 (s, C(*C*H$_3$)$_3$), 26.5 (s, *C*H$_3$). ^{31}P{^{1}H} NMR (202 MHz, C_7D_8) δ ppm: 67.2 (dt, 1P, $^2J_{PY}$ = 4.24 Hz, $^4J_{PP}$ = 0.8 Hz), 59.2 (dd, 1P, $^2J_{PY}$ = 4.24 Hz, $^4J_{PP}$ = 0.8 Hz). Anal. Calcd. for $C_{25}H_{55}N_2O_3P_2Y$: C, 51.54, H, 9.52, N, 4.81%. Found: C, 51.45, H, 9.51, N, 4.84%.

Crystal data for ***8***. $C_{50}H_{110}N_4O_6P_4Y_2 \cdot C_6H_6$, M = 1243.23, monoclinic, $P2_1/n$ (no. 14), a = 10.6303(4), b = 19.9955(7), c = 15.6431(6) Å, β = 94.722(3)°, V = 3313.8(2) Å^3, Z = 2 [C_i symmetry], D_c = 1.246 g cm^{-3}, μ(Mo−Kα) = 1.885 mm^{-1}, T = 173 K, colorless blocks, Oxford Diffraction Xcalibur 3 diffractometer; 10912 independent measured reflections (R_{int} = 0.0631), F^2 refinement, R_1(obs) = 0.0379, wR_2(all) = 0.0949, 7645 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 65°], 323 parameters. CCDC 720129.

{[*N*,*N*′-1,3-bis(*P*,*P*′-di-*tert*-butylphosphinoyl)-2,2-dimethyl-propanediamido](tetrahydrofurano)(2,6-di-*tert*-butyl-4-methyl-phenoxy)}yttrium 9. To a solution of {[*N*,*N*′-1,3-bis(*P*,*P*′-di-*tert*-butylphosphinoyl)-2,2-dimethylpropanediamido][bis(dimethylsilyl)-amido] (tetrahydrofurano)}yttrium, **6** (0.071 g, 0.1 mmol) in toluene (0.2 mL) was added a solution of 2,6-di-*tert*-butyl-4-methylphenol (0.022 g, 0.1 mmol) in toluene. The resulting solution was stirred at 25 °C for 24 h. The solvents were removed in vacuo to leave a colorless solid. This was washed with pentane and the colorless residue dried in vacuo to give the title product (0.068 g, 85%).

^{1}H NMR (400 MHz, C_6D_6) δ ppm: 7.21 (br s, 2H, Ar*H*), 3.80 (m, 4H, OC*H*$_2$), 3.26 (dd, $^2J_{HH}$ = 11.4 Hz, $^3J_{HP}$ = 5.6 Hz, 2H, C*H*$_2$), 3.13 (dd, $^2J_{HH}$ = 11.4 Hz, $^3J_{HP}$ = 3.2 Hz, 2H, C*H*$_2$), 2.34 (s, 3H, Ar C*H*$_3$), 1.78 (s, 18H, Ar C(C*H*$_3$)$_3$), 1.42 (m, 4H, OCH$_2$C*H*$_2$), 1.38 (s, 3H, C-(C*H*$_3$)$_2$), 1.16 (d, $^3J_{HP}$ = 13.6 Hz, 36H, C(C*H*$_3$)$_3$), 0.88 (s, 3H, C(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ ppm: 160.8 (s, OAr*C*), 125.9 (s, Ar*C*C(CH$_3$)$_3$), 125.8 (s, Ar*C*H), 123.5 (s, Ar*C*(CH$_3$)), 68.7 (s, OCH$_2$), 58.4 (s, *C*H$_2$), 58.3 (s, *C*H$_2$), 39.0 (t, $^3J_{CP}$ = 14.9 Hz, *C*(CH$_3$)$_2$), 38.1 (d, $^1J_{CP}$ = 68.3 Hz, *C*(CH$_3$)$_3$), 36.7 (d, $^1J_{CP}$ = 59.2 Hz, *C*(CH$_3$)$_3$), 35.7 (s, ArC*C*(CH$_3$)$_3$), 33.8 (s, ArC*C*(CH$_3$)$_3$), 32.5 (br s, ArCC-(*C*H$_3$)$_3$), 32.3 (br s, ArCC(*C*H$_3$)$_3$), 30.5 (s, *C*H$_3$), 27.8 (s, *C*H$_3$), 27.7 (s, C(*C*H$_3$)$_2$), 27.2 (s, C(*C*H$_3$)$_2$), 25.5 (s, OCH$_2$*C*H$_2$), 21.6 (s, ArCCH$_3$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ ppm: 58.7 (d, $^2J_{PY}$ = 4.54 Hz). Anal. Calcd. for $C_{40}H_{77}N_2O_4P_2Y$: C, 59.99, H, 9.69, N, 3.50%. Found: C, 59.88, H, 9.62, N, 3.41%.

{[*N*,*N*′-1,2-bis(*P*,*P*′-di-*tert*-butylphosphinoyl)ethylene-diamido] [bis(dimethylsilyl)amido](tetrahydrofurano)} yttrium 10. To a Young's tap NMR tube was added **1** (0.038 g, 0.100 mmol) and [Y{N(SiHMe$_2$)$_2$}$_3$(THF)$_2$] (0.063 g, 0.100 mmol). THF-d_8 (0.25 mL) was added, and the tube shaken to form a colorless solution. The tube was left at room temperature for 24 h, or until a ^{31}P{^{1}H} NMR spectrum indicated the presence of one, yttrium-complexed species.

^{1}H NMR (400 MHz, THF-d_8) δ ppm: 4.60 (m, 2H, Si-*H*), 3.62 (m, 4H, OC*H*$_2$), 3.56 (m, 4H, C*H*$_2$), 1.78 (m, 4H, OCH$_2$C*H*$_2$), 1.25 (d, 36H, $^2J_{HP}$ = 13.2 Hz, C(C*H*$_3$)$_3$), 0.09 (d, 12H, $^2J_{HH}$ = 3.2 Hz, Si(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8) δ ppm: 49.2 (d, $^2J_{CP}$ = 12.6 Hz, CH$_2$), 36.9 (br m, *C*(CH$_3$)$_3$), 27.3 (br s, C(*C*H$_3$)$_3$), 3.6

dx.doi.org/10.1021/ic200773x |*Inorg. Chem.* 2011, 50, 7718–7728

(s, Si(CH_3)$_2$). ^{31}P{^{1}H} NMR (162 MHz, THF-d_8) δ ppm: 54.2 (d, $^2J_{PY}$ = 4.05 Hz).

Di-μ-oxo-{[*N*,*N*′-1,2-bis(*P*,*P*′-di-*iso*-propylphosphinoyl)-ethylenediamido](*tert*-butoxy)yttrium} 11. An NMR scale reaction was carried out. A solution of {[*N*,*N*′-1,2-bis(*P*,*P*′-di-*tert*-butylphosphinoyl)ethylenediamido] [bis(dimethylsilyl)amido](tetrahydrofurano)}yttrium, **10** (0.030 mg, 0.05 mmol) in benzene-d_6, in a Young's tap NMR tube, was prepared. To the resulting solution was added *tert*-butanol (4.75 μL, 0.05 mmol) via a microsyringe. The solution was left at room temperature for 2 h before NMR spectra were acquired.

^{1}H NMR (400 MHz, C_6D_6) δ ppm: 3.67 (m, 2H, CH_2), 3.55 (m, 2H, CH_2), 3.47 (m, 2H, CH_2), 3.38 (m, 2H, CH_2), 1.52 (d, $^3J_{HP}$ = 14.4 Hz, 18H, C(CH_3)$_3$), 1.49 (s, 18H, OC(CH_3)$_3$), 1.41 (d, $^3J_{HP}$ = 14.4 Hz, 18H, C(CH_3)$_3$), 1.33 (d, $^3J_{HP}$ = 14.4 Hz, 18H, C(CH_3)$_3$), 1.24 (d, $^3J_{HP}$ = 14.4 Hz, 18H, C(CH_3)$_3$), ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ ppm: 61.4 (dd, unresolved, 1P), 53.4 (d, 1P, $^2J_{PY}$ = 3.89 Hz).

General Polymerization Protocol. To a rapidly stirred solution of *rac*-lactide (144 mg, 1.0 mmol) in THF or CH_2Cl_2 (1.75 mL), in a small glass vial equipped with a lid, in the glovebox, was added a solution of the appropriate initiator in THF or CH_2Cl_2 (0.25 mL of a 0.02 M solution, 0.005 mmol for dimeric initiators and 0.125 mL of a 0.02 M solution, 0.0024 mmol for monomeric initiators), such that the total reaction volume was 2.0 mL, with [LA]$_0$ = 0.5 M and [**6**, **9**, **10**] = 2.5 mM, [**1**−**5**, **7**, **8**, **11**] = 1.25 mM. The lid was replaced on the vial, and aliquots of ∼0.1 mL were removed at known times via a syringe and quenched in 4−5 mL of cold hexane. Upon completion of the reaction, the quenched samples were dried in vacuo to yield colorless polymer. The polymerization conversion was determined by normalization and integration of the signals in the ^{1}H NMR spectrum ($CDCl_3$) due to the methyne proton in polylactide (δ = 5.30−5.00 ppm) and lactide (δ = 4.92 ppm). The polymer M_n and PDI were determined by SEC, using THF as the eluent, and triple detection was to determine the absolute molecular weight (see Measurements section). The polymer tacticity was determined from the homonuclear decoupled ^{1}H NMR spectrum and using the method described by Coudane et al. to analyze the tetrads.[25]

■ ASSOCIATED CONTENT

Supporting Information. Crystallographic data in CIF format. Further details are given in Figure S1−S10. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

The EPSRC are acknowledged for funding this research (EP/C544846/1 and EP/C544838/1). *Rac*-Lactide was donated by Purac Plc. Mr Peter Haycock, Imperial College London is thanked for his help with the ^{31}P NMR experiments.

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