Inorg. Chem. **2008**, *47*, 6840−6849

A Series of *Bis*(phosphinic)diamido Yttrium Complexes As Initiators for Lactide Polymerization

Rachel H. Platel, Andrew J. P. White, and Charlotte K. Williams*

Department of Chemistry, Imperial College London, London, SW7 2AZ, U.K.

Received March 10, 2008

A series of new *bis*(phosphinic)diamido yttrium complexes have been synthesized and fully characterized. The complexes adopt dimeric structures, both in solution and in the solid state, where one phosphinic group bonds to one yttrium center and the other bonds to two yttrium centers. The complexes have all been tested as initiators for the ring-opening polymerization of lactide; they are all highly active. The rate of polymerization is controlled by the diamine backbone substituent with the rate depending on the backbone flexibility. The order of decreasing rates were 2,2-dimethyl-1,3-propylene > *trans*-1,2-cyclohexylene > 1,2-ethylene ≫ 1,2-phenylene. The polymerization kinetics showed, in most cases, an initiation period, during which the percentage conversion and the rate of polymerization were much lower than during propagation. This was attributed to relatively slow initiation by the bulky amido group. The initiator structure was probed using $^{31}P\{^{1}H\}$ NMR spectroscopy, which showed that the dimeric structure was maintained throughout the polymerization. The initiators give rise to controlled ring-opening polymerization as shown by the linear relationship between the percentage conversion and the number-average molecular weight.

Introduction

Polylactide is a commercially produced polyester derived from renewable resources.[1] It degrades in vivo, or in the environment, to yield metabolites.[2] It has long been used in medicine, but recently applications in packaging and fiber technology have widened its scope.[3] It is prepared by the ring-opening polymerization of lactide (Scheme 1); the polymerization is initiated by a variety of species, including metal complexes or organo-catalysts.[4–6] Metal complexes are applied industrially and are proposed to operate via a coordination-insertion mechanism.[4] Yttrium complexes are particularly useful initiators because of their very high rates, low toxicity (the initiator frequently contaminates the product), good control and in some cases the ability to control the stereochemistry.[7–35]

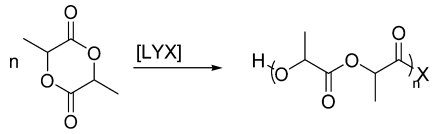
The initiator should be a well-defined complex of the general structure [LYX], where L is an ancillary ligand and X is an amido/alkoxide group. The synthesis of such heteroleptic yttrium complexes requires ancillary ligands which are dianionic and sufficiently sterically protected to prevent complex redistribution reactions.[36] *Bis*(phosphinic)diamido ligands have previously been used to prepare yttrium and zirconium complexes in situ; these species have shown good activity and stereoselectivity for hydroamination reactions.[37,38] The requirements for the hydroamination catalysts (high Lewis acidity but with a labile metal-amido bond) parallel those of initiators for lactide ring-opening polymerization. Therefore, we have previously discovered that [{*N,N′*-1,3-*bis*(*P,P′*-di-isopropyl thiophosphinic)-2,2-dimethylamido}{*bis*(trimethylsilyl)amido}yttrium] was a highly active initiator for lactide ring-opening polymerization.[24] The oxo-analogue complex was also an excellent initiator.[27] This study builds upon these results and investigates the relationship between the ancillary ligand substituents and the polymerization rate and control.

* To whom correspondence should be addressed. E-mail: c.k.williams@imperial.ac.uk.

(1) Ragauskas, A. J.; Williams, C. K.; Davison, B. H.; Britovsek, G.; Cairney, J.; Eckert, C. A., Jr.; Hallett, J. P.; Leak, D. J.; Liotta, C. L.; Mielenz, J. R.; Murphy, R.; Templer, R.; Tschaplinski, T. *Science* **2006**, *311*, 484.
(2) Amass, W.; Amass, A.; Tighe, B. *Polym. Int.* **1998**, *47*, 89.
(3) Albertsson, A. C.; Varma, I. K. *Biomacromolecules* **2003**, *4*, 1466.
(4) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147.
(5) Platel, R. H.; Hodgson, L. M.; Williams, C. K. *Polym. Rev.* **2008**, *48*, 11.
(6) Kamber, N. E.; Jeong, W.; Waymouth, R. M.; Pratt, R. C.; Lohmeijer, B. G. G.; Hedrick, J. L. *Chem. Rev.* **2007**, *107*, 5813.

10.1021/ic800419t CCC: $40.75
Published on Web 06/25/2008

Scheme 1. Ring-Opening Polymerization of Lactide, Initiated by Yttrium Complexes, Where X = Alkoxide or Amido Group



Experimental Section

Materials and Methods. All reactions were conducted under a nitrogen atmosphere, using either standard anaerobic techniques or in a nitrogen filled glovebox. All solvents and reagents were obtained from commercial sources (Aldrich and Merck) and dried. Toluene, pentane, and hexane were distilled from sodium and stored under nitrogen. Methylene chloride was distilled from CaH_2 and stored under nitrogen. Deuterated solvents were dried over either CaH_2 (methylene chloride-d_2) or potassium (THF-d_8, toluene-d_8, benzene-d_6), 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 generously donated by Purac Plc. and was recrystallized from anhydrous ethyl acetate and sublimed three times under vacuum prior to use. *Tris*{*N,N′-bis*(dimethylsilyl)amido}*bis*(tetrahydrofurano)yttrium, [Y{N(SiHMe$_2$)$_2$}$_3$(THF)$_2$], was prepared according to the literature procedure.[39]

Measurements. ^{1}H and ^{13}C{^{1}H} NMR spectra were performed on a Bruker Av400 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 tuneable probe and a BSMS GAB 10 A gradient amplifier providing a maximum gradient output of 5.35 G/cmA. To observe the complex P−P 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.

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. The polymer's molecular weight and polydispersity index 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}.[40]

General Protocol for 1−5. Chloro di-isopropyl phosphine (2.67 mL, 16.80 mmol), was added dropwise, via a syringe, to a stirred solution of the appropriate diamine (8 mmol) and triethylamine (6.97 mL, 40 mmol) in CH_2Cl_2 (40 mL). The reaction mixture was stirred for 12 h, after which time it was opened to the atmosphere and cooled to 0 °C. H_2O_2 (30% aqueous soln., 4.10 mL, 32 mmol) was added, cautiously. After the addition, the reaction mixture was stirred for a further 10 min, at 0 °C, and at 25 °C, for 30 min, before being quenched with aqueous $Na_2S_2O_3$ (80 mL of a 1 M solution, 80 mmol). The layers were separated, and the aqueous layer extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were dried ($MgSO_4$) and the solvents removed under reduced pressure to give a colorless residue.

1.[27] Recrystallized from ethyl acetate to give colorless needles (1.47 g, 50%). ^{1}H NMR (400 MHz, $CDCl_3$,) δ ppm: 3.20 (m, 2H, N*H*), 2.81 (t, 4H, $^3J_{HH}$ = 8.0 Hz, CH_2), 1.96 (d sept, 4H, $^2J_{PH}$ = 9.2 Hz,$^3J_{HH}$ = 7.2 Hz, CH(CH$_3$)$_2$), 1.18 (dd, 12H, $^3J_{PH}$ = 5.6 Hz,$^3J_{HH}$ = 7.2 Hz, CH(CH_3)$_2$), 1.14 (dd, 12H, $^3J_{PH}$ = 5.6 Hz, $^3J_{HH}$ = 7.2 Hz, CH(CH_3)$_2$), 0.85 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$,) δ ppm: 46.2 (s, *C*H$_2$), 37.0 (s, *C*(CH$_3$)$_2$), 26.5 (d, $^1J_{PC}$ = 81.0 Hz, *C*H(CH$_3$)$_2$), 23.3 (s, *C*H$_3$), 16.2 (d, $^2J_{PC}$ = 2.1 Hz, CH(*C*H$_3$)$_2$), 15.9 (d, $^2J_{PC}$ = 2.3 Hz, CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ ppm: 54.0 (s). IR (nujol mull, NaCl) ν cm^{-1}: 3195 (m, N−H), 1294 (w), 1273 (m, *P* = O), 1180 (m), 1146 (s). *m*/*z* (FAB$^+$): 367 [M + H]$^+$. Anal. Calcd for $C_{17}H_{40}N_2O_2P_2$: C, 55.72; H, 11.00; N, 7.64%. Found: C, 55.66; H, 11.07; N, 7.56%.

(7) McClain, S. J.; Ford, T. M.; Drysdale, N. E. *Polym. Prep.* **1992**, 463.
(8) Stevels, W. M.; Ankone, M. J. K.; Dijkstra, P. J.; Feijen, J. *Macromol. Chem. Phys.* **1995**, *196*, 1153.
(9) Stevels, W. M.; Ankone, M. J. K.; Dijkstra, P. J.; Feijen, J. *Macromolecules* **1996**, *29*, 3332.
(10) Stevels, W. M.; Ankone, M. J. K.; Dijkstra, P. J.; Feijen, J. *Macromolecules* **1996**, *29*, 6132.
(11) Simic, V.; Spassky, N.; Hubert-Pfalzgraf, L. G. *Macromolecules* **1997**, *30*, 7338.
(12) Simic, V.; Girardon, V.; Spassky, N.; Hubert-Pfalzfraf, L. G.; Duda, A. *Polym. Degrad. Stab.* **1998**, *59*, 227.
(13) Chamberlain, B. M.; Sun, Y.; Hagadorn, J. R.; Hemmesch, E. W., Jr.; Pink, M.; Hillmyer, M. A.; Tolman, W. B. *Macromolecules* **1999**, *32*, 2400.
(14) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 4072.
(15) Chamberlain, B. M.; Jazdzewski, B. A.; Pink, M.; Hillmyer, M. A.; Tolman, W. B. *Macromolecules* **2000**, *33*, 3970.
(16) Aubrecht, K. B.; Chang, K.; Hillmyer, M. A.; Tolman, W. B. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 284.
(17) Ma, H.; Spaniol, T. P.; Okuda, J. *Dalton Trans.* **2003**, 4770.
(18) Cai, C. X.; Amgoune, A.; Lehmann, C. W.; Carpentier, J. F. *Chem. Commun.* **2004**, 330.
(19) Ma, H.; Okuda, J. *Macromolecules* **2005**, *38*, 2665.
(20) Bonnet, F.; Cowley, A. R.; Mountford, P. *Inorg. Chem.* **2005**, *44*, 9046.
(21) Alaaeddine, A.; Amgoune, A.; Thomas, C. M.; Dagorne, S.; Bellemin-Laponnaz, S.; Carpentier, J.-F. *Eur. J. Inorg. Chem.* **2006**, 3652.
(22) Amgoune, A.; Thomas, C. M.; Roisnel, T.; Carpentier, J. F. *Chem.—Eur. J.* **2006**, *12*, 169.
(23) Patel, D.; Liddle, S. T.; Mungur, S. A.; Rodden, M.; Blake, A. J.; Arnold, P. L. *Chem. Commun.* **2006**, 1124.
(24) Hodgson, L. M.; White, A. J. P.; Williams, C. K. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 6646.
(25) Ma, H.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7818.
(26) Westmoreland, I.; Arnold, J. *Dalton Trans.* **2006**, 4155.
(27) Platel, R. H.; Hodgson, L. M.; White, A. J. P.; Williams, C. K. *Organometallics* **2007**, *26*, 4955.
(28) Yang, Y.; Li, S. H.; Cui, D. M.; Chen, X. S.; Jing, X. B. *Organometallics* **2007**, *26*, 671.
(29) Shang, X. M.; Liu, X. L.; Cui, D. M. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 5662.
(30) Miao, W.; Li, S. H.; Zhang, H. X.; Cui, D.; Wang, Y. R.; Huang, B. T. *J. Organomet. Chem.* **2007**, *692*, 4828.
(31) Miao, W.; Li, S. H.; Cui, D. M.; Huang, B. T. *J. Organomet. Chem.* **2007**, *692*, 3823.
(32) Liu, X. L.; Shang, X. M.; Tang, T.; Hu, N. H.; Pei, F. K.; Cui, D. M.; Chen, X. S.; Jing, X. B. *Organometallics* **2007**, *26*, 2747.
(33) Heck, R.; Schulz, E.; Collin, J.; Carpentier, J. F. *J. Mol. Catal. A: Chem.* **2007**, *268*, 163.
(34) Amgoune, A.; Thomas, C. M.; Carpentier, J. F. *Pure Appl. Chem.* **2007**, *79*, 2013.
(35) Amgoune, A.; Thomas, C. M.; Carpentier, J. F. *Macromol. Rapid Commun.* **2007**, *28*, 693.
(36) Piers, W. E.; Emslie, D. J. H. *Coord. Chem. Rev.* **2002**, *233*, 131.
(37) Kim, Y. K.; Livinghouse, T.; Horino, Y. *J. Am. Chem. Soc.* **2003**, *125*, 9560.
(38) Watson, D. A.; Chiu, M.; Bergman, R. G. *Organometallics* **2006**, *25*, 4731.
(39) Hermann, W. A.; Munck, F. C.; Artus, G. R. J.; Runte, O.; Anwander, R. *Organometallics* **1997**, *16*, 682.
(40) Dorgan, J. R.; Janzen, J.; Knauss, D. M.; Hait, S. B.; Limoges, B. R.; Hutchinson, M. H. *J. Polym. Sci., Part B: Polym. Phys.* **2005**, *43*, 3100.

2. Precipitated from ethyl acetate, filtered and washed with hexane (1.06 g, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 3.33 (m, 2 H, N*H*), 2.91 (m, 4 H, CH_2), 1.78 (d sept, 4 H, $^3J_{HH}$ = 7.2 Hz, $^2J_{PH}$ = 11.2 Hz, CH(CH_3)$_2$), 0.99 (dd, 12 H, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 13.6 Hz, CH(CH_3)$_2$), 0.95 (dd, 12 H, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 13.6 Hz, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ ppm: 43.0 (s, *C*H$_2$), 25.7 (d, $^1J_{PC}$ = 82.9 Hz, *C*H(CH$_3$)$_2$), 15.9 (s, CH(*C*H$_3$)), 15.7 (s, CH(*C*H$_3$)). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ ppm: 52.9 (s). *m*/*z* (FAB$^+$): 325 [M + H]$^+$. IR (nujol mull, NaCl) ν cm^{-1}: 3172 (m, N−H), 1209 (w), 1168 (m, *P* = O), 1151 (m, *P* = O), 1117 (m, *P* = O), 1078 (w), 887 (m).

3. Recrystallized from ethyl acetate to give colorless crystals (1.80 g, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 3.26 (m, 2 H, N*H*), 2.87 (br s, 2 H, NC*H*), 2.15 (m, 4 H, CH_2), 2.00 (d sept, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 2.8 Hz, 4 H, CH(CH$_3$)$_2$), 1.66 (m, 2 H, CH_2), 1.25 (m, 4 H, CH_2), 1.21 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 14.4 Hz, 12 H, CH(CH_3)$_2$), 1.17 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 14.4 Hz, 12 H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ ppm: 56.0 (s, N*C*H), 36.3 (s, *C*H$_2$) 27.0 (d, $^1J_{PC}$ = 85.5 Hz, *C*H(CH$_3$)$_2$), 25.9 (d, $^1J_{PC}$ = 79.9, *C*H(CH$_3$)$_2$), 25.1 (s, *C*H$_2$), 16.5 (s, CH(*C*H$_3$)), 16.4 (s, CH(*C*H$_3$)), 16.3 (s, CH(*C*H$_3$)), 16.2 (s, CH(*C*H$_3$)). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ ppm: 52.4. *m*/*z* (FAB$^+$): 379 [M + H]$^+$. IR (nujol mull, NaCl) ν cm^{-1}: 3501 (m, N−H), 3456 (m, N−H), 1270 (s), 1171 (s, *P* = O), 1152 (s, *P* = O), 1101 (s), 1074 (s), 901 (s), 884 (s). Anal. Calcd for $C_{18}H_{40}N_2O_2P_2$: C, 57.12; H, 10.65; N, 7.40%. Found: C, 57.01, H, 10.60, N, 7.31%.

4. Recrystallized from ethyl acetate to give colorless crystals (1.51 g, 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 3.26 (m, 2 H, N*H*), 2.87 (br s, 2 H, NC*H*), 2.15 (m, 4 H, CH_2), 2.00 (d sept, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 2.8 Hz, 4 H, CH(CH$_3$)$_2$), 1.66 (m, 2 H, CH_2), 1.25 (m, 4 H, CH_2), 1.21 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 14.4 Hz, 12 H, CH(CH_3)$_2$), 1.17 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 14.4 Hz, 12 H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ ppm: 56.0 (s, N*C*H), 36.3 (s, *C*H$_2$), 27.0 (d, $^1J_{PC}$ = 85.5 Hz, *C*H(CH$_3$)$_2$), 25.9 (d, $^1J_{P-C}$ = 79.9 Hz, *C*H(CH$_3$)$_2$), 25.1 (s, *C*H$_2$), 16.5 (s, CH(*C*H$_3$)), 16.4 (s, CH(*C*H$_3$)), 16.3 (s, CH(*C*H$_3$)), 16.2 (s, CH(*C*H$_3$)). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ ppm: 52.4 (s). *m*/*z* (FAB$^+$): 379 [M + H]$^+$. IR (nujol mull, NaCl) ν cm^{-1}: 3195 (m, N−H), 1269 (m), 1170 (m), 1156 (s, *P* = O), 1156 (s, *P* = O), 1068 (m), 887 (m). Anal. Calcd for $C_{18}H_{40}N_2O_2P_2$: C, 57.12; H, 10.65; N, 7.40%. Found: C, 56.97, H, 10.68, N, 7.32%.

5. Recrystallized from ethyl acetate to give colorless crystals (1.49 g, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.34−7.31 (m, 2 H, Ar*H*), 6.85−6.82 (m, 2 H, Ar*H*), 6.45 (d, 2 H, $^2J_{PH}$ = 11.6 Hz, N*H*), 2.13 (d sept, 4 H, $^2J_{PH}$ = 11.6 Hz, $^3J_{HH}$ = 7.2 Hz, CH(CH$_3$)$_2$), 1.22 (dd, 12 H, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 23.4 Hz CH(CH_3)$_2$), 1.14 (dd, 12 H, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 23.4 Hz CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ ppm: 134.0 (s, Ar*C*), 124.0 (s, Ar*C*), 123.4 (s, Ar*C*), 26.1 (d, $^1J_{PC}$ = 101.4 Hz, *C*H), 15.9 (d, $^2J_{PC}$ = 28.8 Hz, *C*H$_3$). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ ppm: 52.5 (s). *m*/*z* (FAB$^+$): 379 [M + H]$^+$. IR (nujol mull, NaCl) ν cm^{-1}: 3377 (m, N−H), 1667 (w), 1594 (m, Ar C=C stretch), 1296 (s), 1208 (s, *P* = O), 1157 (s, *P* = O), 1027 (s), 951 (m), 887 (m). Anal. Calcd for $C_{18}H_{34}N_2O_2P_2$: C, 58.05; H, 9.20; N, 7.52%. Found: C, 57.90; H, 9.31; N, 7.62%.

General Procedure for 6−9.[38] Diphenyl phosphinic chloride (3.05 mL, 16 mmol) was added dropwise, via a syringe, to a stirred solution of the appropriate diamine (8 mmol) and triethylamine (6.97 mL, 40 mmol) in CH_2Cl_2 (40 mL) at 0 °C. The reaction mixture was brought to room temperature and stirred for 2 h, after which time the reaction mixture was washed with saturated $NaHCO_3$ solution (20 mL). The aqueous and organic layers were separated, and the aqueous layer extracted with dichloromethane (3 × 20 mL). The combined organic extracts were dried ($MgSO_4$), and the solvents removed under reduced pressure to give a colorless residue. The product was precipitated by addition of ethyl acetate and filtered.

6.[37] Colorless solid (2.33 g, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.82 (m, 8 H, Ar*H*), 7.49−7.37 (m, 12 H, Ar*H*), 4.08 (br s, 2 H, N*H*), 2.83 (dd, $^2J_{HH}$ = 7.0 Hz, $^2J_{HP}$ = 9.5 Hz, 4 H, CH_2), 0.86 (s, 6 H, CH_3). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ ppm: 25.9 (s). Anal. Calcd for $C_{29}H_{32}N_2O_2P_2$: C, 69.31; H, 6.42; N, 5.57%. Found: C, 69.40; H, 6.38; N, 5.49%.

7.[41,42] Colorless solid (3.17 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.75−7.71 (m, 8 H, Ar*H*), 7.38−7.27 (m, 12 H, Ar*H*), 4.24, (br s, 2 H, N*H*), 2.98 (m, 4 H, CH_2). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ ppm: 25.0 (s). Anal. Calcd for $C_{26}H_{26}N_2O_2P_2$: C, 67.82; H, 5.69; N, 6.08%. Found: C, 67.81; H, 5.80; N, 6.01%.

8. Colorless solid (3.67 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.85 (m, 4 H, Ar*H*), 7.65 (m, 4 H, Ar*H*), 7.31 (m, 8 H, Ar*H*), 7.18 (m, 4 H, Ar*H*), 4.16 (m, 2 H, N*H*), 2.82 (m, 2 H, NC*H*), 1.87 (m, 2 H, CH_2), 1.38 (m, 2 H, CH_2), 1.15 (m, 2 H, CH_2), 0.92 (m, 2 H, CH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ ppm: 133.7 (Ar*C*), 133.6 (Ar*C*), 132.5 (Ar*C*), 132.4 (Ar*C*), 131.5 (Ar*C*), 131.4 (Ar*C*), 131.3 (Ar*C*), 128.3 (Ar*C*), 128.1 (Ar*C*), 55.7 (*C*N), 45.5 (*C*N), 35.8 (*C*H$_2$), 35.7 (*C*H$_2$), 24.9 (*C*H$_2$), 8.4 (*C*H$_2$). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ ppm: 25.3 (s). IR (nujol mull, NaCl) ν cm^{-1}: 3183 (s, N−H), 1309 (w), 1283 (w), 1237 (w), 1189 (s, *P* = O), 1122 (s), 1110 (s), 1068 (m), 976 (m), 904 (m). Anal. Calcd for $C_{30}H_{32}N_2O_2P_2$: C, 70.03; H, 6.27; N, 5.44%. Found: C, 69.92; H, 6.38; N, 5.34%.

9.[38] Colorless solid (3.15 g, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.85 (m, 4 H, Ar*H*), 7.65 (m, 4 H, Ar*H*), 7.31 (m, 8 H, Ar*H*), 7.18 (m, 4 H, Ar*H*), 4.16 (m, 2 H, N*H*), 2.82 (m, 2 H, NC*H*), 1.87 (m, 2 H, CH_2), 1.38 (m, 2 H, CH_2), 1.15 (m, 2 H, CH_2), 0.92 (m, 2 H, CH_2). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ ppm: 25.3 (s). Anal. Calcd for $C_{30}H_{32}N_2O_2P_2$: C, 70.03; H, 6.27; N, 5.44%. Found: C, 69.97; H, 6.35; N, 5.38%.

10.[27] To a solution of [Y{N(SiHMe$_2$)$_2$}$_3$(THF)$_2$] (0.13 g, 0.20 mmol) in toluene (2 mL) was added **1** (0.07 g, 0.20 mmol) in toluene (3 mL). The solution was stirred for 20 h, before removing the solvents in vacuo to leave a white solid (0.09 g, 74%). ^{1}H NMR (400 MHz, C_6D_6) δ ppm: 5.19 (m, 2H, Si*H*), 3.42 (dd, $^2J_{HH}$ = 11.8 Hz, $^3J_{HP}$ = 4.0 Hz, 1H, CH_2), 3.31 (dd, $^2J_{HH}$ = 12.0 Hz, $^3J_{HP}$ = 4.0 Hz, 1H, CH_2), 2.94 (m, 3H, CH_2 and CH(CH$_3$)$_2$), 2.32 (sept, $^3J_{HH}$ = 7.2 Hz, 1H, CH(CH$_3$)$_2$), 2.24 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH(CH$_3$)$_2$), 1.78 (sept, $^3J_{HH}$ = 6.4 Hz, 1H, CH(CH$_3$)$_2$), 1.50 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 15.2 Hz, 3H, CHCH_3), 1.41 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 15.8 Hz, 3H, CHCH_3), 1.23 (m, 9H, CH_3), 1.16 (s, 3H, CH_3), 1.05 (m, 9H, CHCH_3), 0.92 (s, 3H, CH_3), 0.49 (d, $^3J_{HH}$ = 2.8 Hz, 6H, SiHCH_3), 0.47 (d, $^3J_{HH}$ = 2.8 Hz, 6H, SiHCH_3). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ ppm: 57.0 (s, *C*H$_2$), 56.4 (s, *C*H$_2$), 37.5 (s, *C*(CH$_3$)$_2$), 31.5 (d, $^1J_{CP}$ = 69.0 Hz, *C*H(CH$_3$)$_2$), 29.7 (d, $^1J_{CP}$ = 33.6 Hz, *C*H(CH$_3$)$_2$), 29.0 (d, $^1J_{CP}$ = 37.2 Hz, *C*H(CH$_3$)$_2$), 27.1 (s, C*C*H$_3$), 26.6 (d, $^1J_{CP}$ = 66.5 Hz, *C*H(CH$_3$)$_2$), 25.4 (s, C*C*H$_3$), 18.6 (s, CH*C*H$_3$), 17.7 (s, CH*C*H$_3$), 17.4 (s, CH*C*H$_3$), 17.2 (s, CH*C*H$_3$), 17.0 (s, CH*C*H$_3$), 16.4 (s, CH*C*H$_3$), 4.8 (s, Si*C*H$_3$), 4.4 (s, Si*C*H$_3$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ ppm: 69.0 (m, 1P), 67.1 (ddd, $^2J_{PY}$ = 5.10, 3.97 Hz; $^4J_{PP}$ = 1.78 Hz, 13P), 56.9 (d, J_{PY} = 4 Hz, 1H,), 55.1 (dd, $^2J_{PY}$ = 4.65 Hz; $^4J_{PP}$ = 1.76 Hz, 13P). IR (nujol mull, NaCl) ν cm^{-1}: 2089 (s, Si−H), 2044 (m, Si−H), 1599 (w), 1288 (m, Si-CH$_3$ deformation), 1263 (m, Si-CH$_3$ deformation),

(41) Gümgüm, B.; Akba, O.; Durap, F.; Yildirim, L. T.; Ülkü, D.; Özkar, S. *Polyhedron* **2006**, *25*, 3133.

(42) Dolinsky, M. C. B.; Lin, W. O.; Dias, M. L. *J. Mol. Catal. A: Chem.* **2006**, *258*, 267.

1240 (s, *P* = O), 1223 (s, *P* = O), 1184 (m), 1165 (m), 1061 (s), 1012 (s). Anal. Calcd for $C_{18}H_{46}N_3O_2P_2Si_2Y$: C, 39.77; H, 8.53; N, 7.73%. Found: C, 39.82; H, 8.45; N, 7.88%.

11. To a solution of $[Y\{N(SiHMe_2)_2\}_3(THF)_2]$ (0.220 g, 0.349 mmol) in toluene (3 mL), was added **2** (0.113 g, 0.349 mmol) in toluene (3 mL). The solution was stirred for 24 h, before removing the solvents in vacuo to leave a white residue. This was dissolved in pentane, and the solvents removed in vacuo to give a white solid. This was recrystallized from hexane to give the title compound as a white, crystalline solid (0.130 g, 69%). ^{1}H NMR (400 MHz, C_6D_6) δ ppm: 5.28 (m, 2H, Si*H*), 3.72 (m, 1H, CH_2), 3.40 (m, 1H, CH_2), 3.27 (m, 1H, CH_2), 3.11 (m, 1H, CH_2), 2.30 (m, 2H, CH(CH_3)$_2$), 1.95 (m, 1H, CH(CH_3)$_2$), 1.78 (m, 2H, CH(CH_3)$_2$), 1.42−1.03 (m, 24H, CH_3), 0.52 (m, 12H, Si(CH_3)$_2$);^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ ppm: 48.8 (s, *C*H$_2$), 48.7 (s, *C*H$_2$), 28.6 (d, $^1J_{P-C}$ = 76.8 Hz, *C*H(CH$_3$)$_2$), 27.0 (d, $^1J_{PC}$ = 107 Hz, *C*H(CH$_3$)$_2$), 24.9 (d, $^1J_{P-C}$ = 163 Hz, *C*H(CH$_3$)$_2$), 22.9 (d, $^1J_{PC}$ = 76.8 Hz, *C*H(CH$_3$)$_2$), 16.6 (s, *C*H$_3$), 16.4 (s, *C*H$_3$), 16.3 (s, *C*H$_3$), 16.0 (s, *C*H$_3$), 15.7 (s, *C*H$_3$), 4.3 (s, Si*C*H$_3$), 3.9 (s, Si*C*H$_3$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ ppm: 61.0 (1P, d, $^2J_{PY}$ = 3.79 Hz,), 53.2 (1P, d, $^2J_{PY}$ = 9.12 Hz). IR (nujol mull, NaCl) ν cm^{-1}: 2101 (m, Si−H), 2057 (m, Si−H), 1340 (m), 1272 (s), 1240 (s, *P* = O), 1123 (m, *P* = O), 1084 (m), 1052 (m), 1052 (m), 1022 (m). Anal: Calcd for $C_{21}H_{52}N_3O_2P_2Si_2Y$: C, 43.07; H, 8.95; N, 7.17%; Found: C, 43.09; H, 9.05; N, 7.08%.

12. To a solution of $[Y\{N(SiHMe_2)_2\}_3(THF)_2]$ (0.126 g, 0.200 mmol) in toluene (3 mL) was added **4** (0.076 g, 0.200 mmol) in toluene (3 mL). The solution was stirred at 70 °C for 48 h, before removing the solvents in vacuo to leave a white residue. Pentane was added, and the solvents removed in vacuo to give the title compound as an off-white solid (0.065 g, 54%). ^{1}H NMR (400 MHz, C_6D_6) δ ppm: 5.32 (m, 1H, Si*H*(CH$_3$)$_2$), 5.28 (m, 1H, Si*H*(CH$_3$)$_2$), 3.61 (m, 1H, C*H*N), 3.06 (m, 1H, C*H*N), 2.88 (m, 2 H, CH_2), 2.16 (m, 2H, CH(CH$_3$)$_2$), 1.95 (m, 1H, CH(CH$_3$)$_2$), 1.83 (m, 1H, CH(CH$_3$)$_2$), 1.75 (m, 2H, CH_2), 1.61 (m, 4H, CH_2), 1.52−1.05 (m, 24H, CH(CH_3)$_2$), 0.54 (d, $^3J_{HH}$ = 2.8 Hz, 3H, SiH(CH_3)$_2$), 0.50 (d, $^3J_{HH}$ = 2.8 Hz, 6H, SiH(CH_3)$_2$), 0.49 (d, $^3J_{HH}$ = 2.8 Hz, 3H, SiH(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ ppm: 66.1 (d, $^2J_{CP}$ = 9.6 Hz, *C*HN), 65.2 (d, $^2J_{CP}$ = 9.2 Hz, *C*HN), 63.7 (d, $^2J_{CP}$ = 16.3 Hz, *C*HN), 63.1 (d, $^2J_{CP}$ = 16.7 Hz, *C*HN), 39.1 (s, *C*H$_2$), 38.6 (s, *C*H$_2$), 37.6 (s, *C*H$_2$), 37.2 (s, *C*H$_2$), 30.7 (d, $^1J_{CP}$ = 37.2 Hz, CH_2), 29.9 (d, $^1J_{CP}$ = 71.8 Hz, CH_2), 29.7 (s, *C*H$_2$), 29.8 (d, $^1J_{CP}$ = 70.2 Hz, CH_2), 28.8 (d, $^1J_{CP}$ = 12.7 Hz, CH_2), 27.9 (d, $^1J_{CP}$ = 59.7 Hz, CH_2), 26.1 (s, *C*H$_2$), 26.0 (s, *C*H$_2$), 25.8 (s, *C*H$_2$), 25.4 (d, $^1J_{CP}$ = 31.7 Hz, CH_2), 18.3 (s, CH(*C*H$_3$)$_2$), 17.9 (s, CH(*C*H$_3$)$_2$), 17.6 (s, CH(*C*H$_3$)$_2$), 17.5 (s, CH(*C*H$_3$)$_2$), 17.3 (s, CH(*C*H$_3$)$_2$), 17.2 (s, CH(*C*H$_3$)$_2$), 17.0 (s, CH(*C*H$_3$)$_2$), 16.9 (s, CH(*C*H$_3$)$_2$), 16.5 (s, CH(*C*H$_3$)$_2$), 16.3 (s, CH(*C*H$_3$)$_2$), 15.8 (s, CH(*C*H$_3$)$_2$), 4.7 (s, SiH(*C*H$_3$)$_2$), 4.6 (s, SiH(*C*H$_3$)$_2$), 4.5 (s, SiH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ ppm: 66.7 (dd, unresolved, 1H), 62.1 ppm (dd, $^2J_{PY}$ = 3.23, 4.55 Hz, 1H), 54.0 ppm (br s, 1H), 49.2 ppm (d, $^2J_{PY}$ = 4.65 Hz, 1H). IR (nujol mull, NaCl) ν cm^{-1}: 2123 (m, Si−H), 2048 (m, Si−H), 1239 (w), 1240 (s, *P* = O), 1231 (s, *P* = O), 1195 (w), 1120 (w), 1041 (s), 1025 (s). Anal. Calcd. for $C_{22}H_{52}N_3O_2P_2Si_2Y$: C, 44.21; H, 8.77; N, 7.03%. Found: C, 44.25; H, 8.91; N, 6.91%.

13. To a mixture of **5** (0.186 g, 0.500 mmol) and $[Y\{N(SiHMe_2)_2\}_3(THF)_2]$(0.315 g, 0.500 mmol) was added toluene (5 mL). The resulting colorless solution was heated to 70 °C, with stirring for 24 h. The solvents were removed in vacuo to leave a pale brown residue. To this was added hexane (7 mL). The resulting white precipitate was filtered, washed with cold hexane (5 mL) and dried in vacuo to give a white powder (0.130 g, 42%). ^{1}H NMR (400 MHz, C_6D_6) δ ppm: 6.88 (m, 1H, Ar*H*), 6.80 (m, 1H, Ar*H*), 6.70 (d, 1H, $^3J_{HH}$ = 6.8 Hz, Ar*H*), 6.63 (d, 1H, $^3J_{HH}$ = 6.8 Hz, Ar*H*), 5.18 (m, 2H, Si*H*), 2.99 (sept, 1H, $^3J_{HH}$ = 7.2 Hz, C*H*(CH$_3$)$_2$), 2.53 (sept, 1H, $^3J_{HH}$ = 7.2 Hz, C*H*(CH$_3$)$_2$), 2.18 (sept, 1H, $^3J_{HH}$ = 7.2 Hz, C*H*(CH$_3$)$_2$), 1.89 (sept, 1H, $^3J_{HH}$ = 7.2 Hz, C*H*(CH$_3$)$_2$), 1.55 (dd, 3H, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 16.2 Hz, CHC*H*$_3$), 1.51 (dd, 3H, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 15.8 Hz, CHC*H*$_3$), 1.30 (dd, 3H, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 15.8 Hz, CHC*H*$_3$), 1.24 (dd, 3H, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 16.4 Hz, CHC*H*$_3$), 1.13 (dd, 3H, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 16.8 Hz, CHC*H*$_3$), 1.04 (dd, 3H, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 15.0 Hz, CHC*H*$_3$), 0.91 (dd, 3H, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 14.6 Hz, CHC*H*$_3$), 0.82 (dd, 3H, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 15.2 Hz, CHC*H*$_3$), 0.42 (d, 6H, $^3J_{HH}$ = 3.2 Hz, SiH(C*H*$_3$)$_2$), 0.40 (d, 6H, $^3J_{HH}$ = 2.8 Hz, SiH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ ppm: 143.3 (d, $^2J_{CP}$ = 15 Hz, Ar*C*N), 142.1 (d, $^2J_{CP}$ = 13 Hz, Ar*C*N), 120.2 (s, Ar*C*), 119.3 (s, Ar*C*), 118.7 (s, Ar*C*), 118.1 (s, Ar*C*), 30.3 (d, $^1J_{CP}$ = 44.6 Hz, *C*H(CH$_3$)$_2$), 29.4 (d, $^1J_{CP}$ = 44.6 Hz, *C*H(CH$_3$)$_2$), 26.5 (d, $^1J_{CP}$ = 44.6 Hz, *C*H(CH$_3$)$_2$), 25.5 (d, $^1J_{CP}$ = 44.6 Hz, *C*H(CH$_3$)$_2$), 17.6 (s, CH*C*H$_3$), 17.4 (s, CH*C*H$_3$), 17.2 (s, CH*C*H$_3$), 16.7 (s, CH*C*H$_3$), 16.3 (s, CH*C*H$_3$), 16.2 (s, CH*C*H$_3$), 16.1 (s, CH*C*H$_3$), 16.0 (s, CH*C*H$_3$), 15.9 (s, CH*C*H$_3$), 15.8 (s, CH*C*H$_3$), 4.1 (s, SiH(*C*H$_3$)$_2$) ppm. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ ppm: 67.0 (dd, $^2J_{PY}$ = 5.15, 3.24 Hz, 1 P), 54.5 (d, $^2J_{PY}$ = 4.24 Hz, 1 P). IR (nujol mull, NaCl) ν cm^{-1}: 2360 (m), 2341 (m), 2040 (w, Si−H stretch), 1311 (m), 1274 (m), 1154 (m), 1116 (w), 1060 (m). Anal. Calcd. for $C_{22}H_{46}N_3O_2P_2Si_2Y$: C, 44.66; H, 7.84; N, 7.10%. Found: C, 44.55; H, 6.80; N, 7.00%.

14. To a mixture of **6** (0.251 g, 0.500 mmol) and $[Y\{N(SiHMe_2)_2\}_3(THF)_2]$ (0.315 g, 0.500 mmol) was added toluene (5 mL). The resulting colorless solution was heated to 70 °C, with stirring for 24 h. The pale yellow residue was washed with hexane (7 mL) and recrystallized from the minimum volume of toluene to give the title compound as a white, crystalline solid (0.108 g, 30%). ^{1}H NMR (400 MHz, C_7D_8) δ ppm: 8.30 (br s, 4H, Ar*H*), 7.61 (br s, 4H, Ar*H*), 7.37−7.30 (m, 6H, Ar*H*), 7.13−7.05 (m, 6H, Ar*H*), 5.32 (m, 2H, Si*H*), 2.99 (dd, 2H, $^2J_{HH}$ = 12 Hz, $^3J_{HP}$ = 20 Hz, CH_2), 1.53 (dd, 2H, $^2J_{HH}$ = 12 Hz, $^3J_{HP}$ = 20 Hz, CH_2), 0.86 (s, 3H, CH_3), 0.66 (s, 3H, CH_3), 0.31 (d, 12H, $^3J_{HH}$ = 2.8 Hz, Si(CH_3)$_2$) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_7D_8) δ ppm: 135.0 (d, $^1J_{CP}$ = 106 Hz, Ar*C*), 133.1 (s, Ar*C*), 132.9 (s, Ar*C*), 131.4 (s, Ar*C*), 131.1 (s, Ar*C*), 131.0 (s, Ar*C*), 56.2 (s, *C*H$_2$), 37.0 (s, *C*(CH$_3$)$_2$), 26.7 (s, *C*H$_3$), 22.8 (s, *C*H$_3$), 3.6 (s, Si*C*H$_3$).^{31}P{^{1}H} NMR (162 MHz, C_7D_8) δ ppm: 293 K, 38.8 (br s), 383 K, 38.3 (s). IR (nujol mull, NaCl) ν cm^{-1}: 2187 (m, Si−H), 2044 (m, Si−H), 1305 (w), 1240 (m), 1221 (m), 1175 (m), 1123 (m), 1056 (w). Anal. Calcd for $C_{33}H_{44}N_3O_2P_2Si_2Y$: C, 54.92; H, 6.14; N, 5.82%. Found: C, 55.00; H, 6.03; N, 5.71%.

15. To a solution of $[Y\{N(SiHMe_2)_2\}_3(THF)_2]$ (0.315 g, 0.500 mmol) in toluene (3 mL), was added **7** (0.243 g, 0.500 mmol) in toluene (3 mL). The solution was stirred for 24 h, before removing the solvents in vacuo to leave a white residue. This was recrystallized from toluene at −35 °C to give the title compound as a white, crystalline solid (0.226 g, 67%). ^{1}H NMR (500 MHz, THF-d_8) δ ppm: 8.50−6.49 (m, 20H, *Ar*H), 5.05 (m, 2H, Si*H*), 3.75−1.73 (m, 4H, CH_2), 0.31 (m, 12H, SiH(CH_3)$_2$. ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2) δ ppm: 132.7 (br m, Ar*C*), 128.7 (br m, Ar*C*), 3.66 (SiH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (162 MHz, THF-d_8) δ ppm: 33.8 (m). IR (nujol mull, NaCl) ν cm^{-1}: 2039 (m, Si−H), 1591 (w), 1305 (m), 1242 (m), 1122 (s, *P* = O), 1067 (s), 1028 (m). Anal. Calcd. for $C_{30}H_{38}N_3O_2P_2Si_2Y$: C, 53.01; H, 5.64; N, 6.18%. Found: C, 53.09; H, 5.72; N, 6.23%.

16. To a mixture of **8** (0.257 g, 0.500 mmol) and $[Y\{N(SiHMe_2)_2\}_3(THF)_2]$ (0.315 g, 0.500 mmol) was added toluene (20 mL). The resulting colorless solution was stirred at room temper-

ature for 20 h. The solvents were removed in vacuo to leave a white residue. To this was added pentane (20 mL), which was then removed in vacuo to leave the title product (0.148 g, 40%) as a fine white powder. ^{1}H NMR (500 MHz, C_7D_8) δ ppm: 8.10−8.02 (m, 4H, Ar*H*), 7.53−7.47 (m, 4H, Ar*H*), 7.21−7.16 (m, 4H, Ar*H*), 7.13−7.09 (m, 4H, Ar*H*), 6.98−6.96 (m, 4H, Ar*H*), 6.86−6.82 (m, 4H, Ar*H*), 5.45 (m, 0.5H, Si*H*(CH_3)$_2$), 4.92 (m, 1.5H, Si*H*(CH_3)$_2$), 3.69 (m, 1H, NC*H*), 2.53 (m, 1H, NC*H*), 1.84 (m, 1H CH_2), 1.74 (m, 1H CH_2), 1.65 (m, 1H CH_2), 1.31 (m, 2H CH_2), 1.10 (m, 1H CH_2), 0.96 (m, 1H CH_2), 0.70 (m, 1H CH_2), 0.60 (d, 3H, SiH(CH_3), 0.20 (d, 6H, SiH(CH_3), 0.12 (d, 3H, SiH(CH_3). ^{13}C{^{1}H} NMR (125 MHz, C_7D_8) δ ppm: 138.2 (Ar*C*), 136.9 (Ar*C*), 135.9 (Ar*C*), 135.5 (Ar*C*), 134.5 (Ar*C*), 134.1 (Ar*C*), 133.1 (Ar*C*), 131.9 (Ar*C*), 131.3 (Ar*C*), 130.7 (Ar*C*), 65.9 (*C*HN), 64.4 (*C*HN), 38.2 (*C*H_2), 35.7 (*C*H_2), 26.1 (*C*H_2), 25.6 (*C*H_2), 4.2 (SiH(*C*H_3)), 3.6 (SiH(*C*H_3)), 3.3 (SiH(*C*H_3)).^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ ppm: 293 K, 34.1 (br s, 1H), 27.9 (br s, 1H). IR (nujol mull, NaCl) ν cm^{-1}: 2047 (s, Si−H), 1591 (m), 1331 (w), 1236 (s), 1182 (m), 1122 (s), 1045 (s). Anal. Calcd. for $C_{34}H_{44}N_3O_2P_2Si_2Y$: C, 55.65; H, 6.04; N, 5.73%. Found: C, 55.71; H, 5.99; N, 5.82%.

17. To a mixture of **9** (0.257 g, 0.500 mmol) and [Y{N(SiHMe$_2$)$_2$}$_3$(THF)$_2$] (0.315 g, 0.500 mmol) was added toluene (5 mL). The resulting colorless solution was stirred at room temperature for 20 h. The solvents were removed in vacuo to leave a white residue. To this was added pentane (20 mL), which was then removed in vacuo to leave the title product (0.132 g, 34%) as a fine white powder. ^{1}H NMR (500 MHz, C_7D_8) δ ppm: 8.10−8.02 (m, 4H, Ar*H*), 7.53−7.47 (m, 4H, Ar*H*), 7.21−7.16 (m, 4H, Ar*H*), 7.13−7.09 (m, 4H, Ar*H*), 6.98−6.96 (m, 4H, Ar*H*), 6.86−6.82 (m, 4H, Ar*H*), 5.45 (m, 0.5H, Si*H*(CH_3)$_2$), 4.92 (m, 1.5H, Si*H*(CH_3)$_2$), 3.69 (m, 1H, NC*H*), 2.53 (m, 1H, NC*H*), 1.84 (m, 1H CH_2), 1.74 (m, 1H CH_2), 1.65 (m, 1H CH_2), 1.31 (m, 2H CH_2), 1.10 (m, 1H CH_2), 0.96 (m, 1H CH_2), 0.70 (m, 1H CH_2), 0.60 (d, 3H, SiH(CH_3), 0.20 (d, 6H, SiH(CH_3), 0.12 (d, 3H, SiH(CH_3). ^{13}C{^{1}H} NMR (125 MHz, C_7D_8) δ ppm: 138.2 (Ar*C*), 136.9 (Ar*C*), 135.9 (Ar*C*), 135.5 (Ar*C*), 134.5 (Ar*C*), 134.1 (Ar*C*), 133.1 (Ar*C*), 131.9 (Ar*C*), 131.3 (Ar*C*), 130.7 (Ar*C*), 65.9 (*C*HN), 64.4 (*C*HN), 38.2 (*C*H_2), 35.7 (*C*H_2), 26.1 (*C*H_2), 25.6 (*C*H_2), 4.2 (SiH(*C*H_3)), 3.6 (SiH(*C*H_3)), 3.3 (SiH(*C*H_3)). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ ppm: 293 K, 34.1 (br s, 1P), 27.9 (br s, 1P). IR (nujol mull, NaCl) ν cm^{-1}: 2049 (Si−H stretch), 1237, 1122. Anal. Calcd for $C_{34}H_{44}N_3O_2P_2Si_2Y$: C, 55.65; H, 6.04; N, 5.73%. Found: C, 55.55; H, 5.91; N, 5.96%.

***In Situ* Generation of Isopropoxide Complex.** To a solution of **13** (0.059 g, 0.1 mmol) in C_6D_6 (0.25 mL) in a Young's tap NMR tube was added isopropanol (7.7 μL, 0.2 mmol) via a microsyringe. The mixture was shaken vigorously. After 10 min, NMR spectra confirmed the reaction was complete. ^{1}H NMR (500 MHz, C_6D_6) δ ppm: 6.85 (m, 2H, Ar*H*), 6.65 (m, 2H, Ar*H*), 4.39 (sept. 1H, $^3J_{HH}$ = 6.6 Hz, OC*H*(CH_3)$_2$), 2.19−2.03 (m, 4H, C*H*(CH_3)$_2$), 1.30−1.17 (m, 24H, CH(CH_3)$_2$), 1.09 (d, 3H, $^3J_{HH}$ = 6.6 Hz, OCH(CH_3)$_2$), 1.05 (d, 3H, $^3J_{HH}$ = 6.6 Hz, OCH(CH_3)$_2$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ ppm: 58.8 ppm.

Typical Polymerization Procedure. To a rapidly stirred solution of *rac*-lactide (0.216 g, 1.5 mmol) in dichloromethane (1.12 mL), in a vial in the glovebox, was added the appropriate initiator, **10**−**17** (0.38 mL of a 0.02 M solution in dichloromethane) via a syringe. Aliquots of the reaction mixture were taken at various times and quenched in hexanes. Solvents were removed in vacuo to leave the samples of lactide/polylactide as colorless residues.

X-ray Crystallography. Data were collected using Oxford Diffraction Xcalibur 3 (**13** and **16**) and Xcalibur PX Ultra (**14**) diffractometers. CCDC 676795 to 676797 respectively (Table 1).

Table 1. Crystallographic Data for Compounds **13**, **14**, and **16**

data	**13**	**14**	**16**
chemical	$C_{44}H_{92}N_6O_4P_4Si_4Y_2$	$C_{66}H_{88}N_6O_4P_4Si_4Y_2$	$C_{68}H_{88}N_6O_4P_4Si_4Y_2$
solvent	$0.5C_7H_8$	$2C_7H_8$	
fw	1229.36	1627.75	1467.50
T (°C)	−100	−100	−100
space group	$I4_1/a$ (No. 88)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a (Å)	17.77032(11)	14.23934(5)	12.5447(3)
b (Å)		18.35109(5)	13.3084(4)
c (Å)	40.3177(4)	16.82037(6)	13.3297(4)
α (deg)			110.425(3)
β (deg)		109.9403(4)	94.826(2)
γ (deg)			117.684(3)
V (Å^3)	12731.67(16)	4131.78(3)	1763.55(9)
Z	8[a]	2[b]	1[b]
ρ_{calcd} (g cm^{-3})	1.283	1.308	1.382
λ (Å)	0.71073	1.54184	0.71073
μ (mm^{-1})	2.032	3.558	1.847
R_1[c]	0.035	0.024	0.040
wR_2[d]	0.08	0.066	0.096

[a] The molecule has crystallographic C_2 symmetry. [b] The molecule has crystallographic C_i symmetry. [c] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

Results and Discussion

Synthesis. Previously, we reported the preparation of three (*bis*(di-isopropyl-phosphinic)-2,2-dimethylpropyldiamido)(amido) yttrium complexes where the amido group was trimethylsilyl, dimethylsilyl (**10**) and di-isopropyl.[27] The complexes were very rapid initiators for lactide ring-opening polymerization. The goal of the current study is to establish the influence, if any, of the ancillary ligand. A series of proligands were prepared, with two substitution sites being varied: the substituents on the phosphorus atom were isopropyl or phenyl and the linkage between the diamido groups were 2,2-dimethyl-1,3-propylene, 1,2-ethylene, *rac-trans*-cyclohexylene, *RR-trans*-cyclohexylene, and 1,2-phenylene (Table 2). They were synthesized by literature methods (**1**, **6**, **7**, **9**)[27,37,38,41,42] or by an adaptation of the literature methods[27] and were isolated in good yields (41−89%). The yttrium initiators were prepared by an extended silylamide route,[43] where the diamine proligands were reacted with [Y{N(SiHMe$_2$)$_2$}$_3$(THF)$_2$], in toluene for 20 h (Scheme 2, Table 2). The complexation occurred at room temperature using ligands **1** and **2**, but required elevated temperature for ligands **4**−**9**, presumably because of the steric protection afforded by phenyl substituents and/or cyclic diamine groups.

The reactions were monitored by ^{31}P{^{1}H} NMR spectroscopy which showed the disappearance of the singlet due to the diamine ligand (**1**-**9**) and the growth of multiplets due to the coordination complex (**10**-**17**). The complexes were isolated in reasonable yields (30−60%) and their purity was established by elemental analysis.

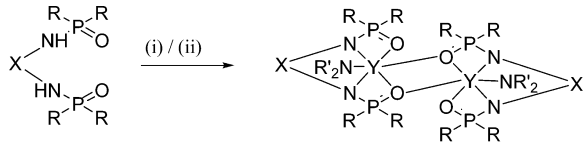
X-ray Crystal Structures. Crystals suitable for X-ray diffraction were grown from solutions of **13**, **14**, and **16** (Table 1) and their molecular structures are represented in Figures 1–3 (Tables 3–6).

(43) Runte, O.; Priermeier, T.; Anwander, R. *Chem. Commun.* **1996**, 1385.

Table 2. Key Showing the Compound Numbering and Substituents at Positions X and R

Ligand #	X	R	Complex #
1	$CH_2C(CH_3)_2CH_2$	^{i}Pr	**10**
2	CH_2CH_2	^{i}Pr	**11**
3	 *rac-*	^{i}Pr	
4	 *R,R*	^{i}Pr	**12**
5	C_6H_4	^{i}Pr	**13**
6	$CH_2C(CH_3)_2CH_2$	Ph	**14**
7	CH_2CH_2	Ph	**15**
8	 *rac-*	Ph	**16**
9	 *R,R*	Ph	**17**

Scheme 2. Synthesis of Complexes **10**−**17**[a]



1-9 **10-17**

[a] X and R were systematically varied (see Table 2 for the key) and R′ = $SiMe_2H$. Reagents and conditions: (i) $[Y\{N(SiHMe_2)_2\}_3(THF)_2]$, toluene, 20 h, 298 K (**10, 11**); (ii) $[Y\{N(SiHMe_2)_2\}_3(THF)_2]$, toluene, 20 h, 373 K (**12**−**17**).

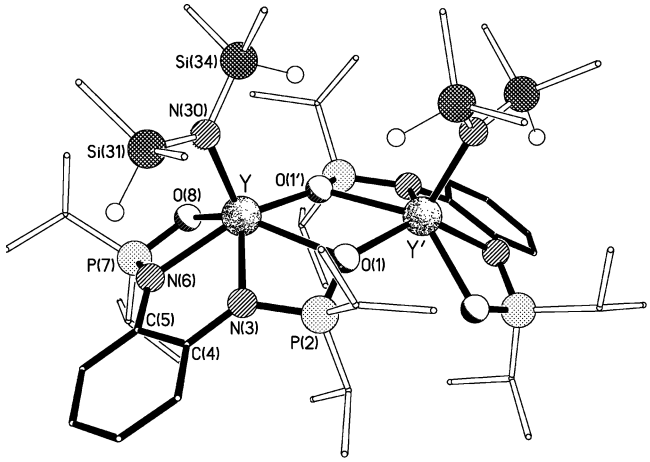


Figure 1. Molecular structure of the C_2 symmetric complex **13**.

All three complexes are dimeric in the solid state, with the each ligand having one phosphinic group bridging between two yttrium centers and the other coordinating a single yttrium center. Such a coordination mode has previously been observed in the X-ray crystal structure of **10**.[27]

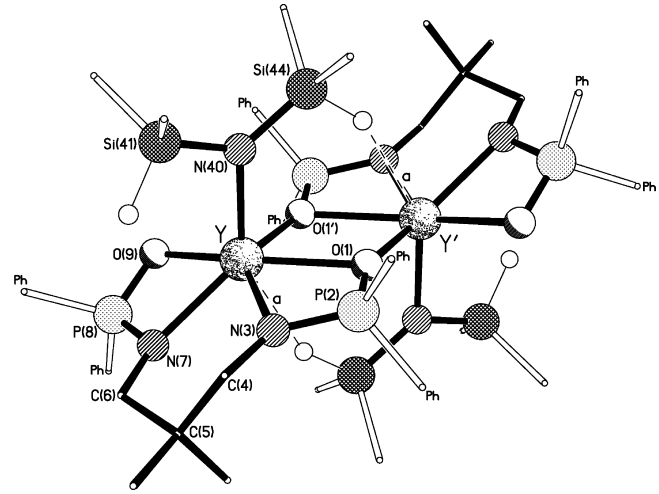


Figure 2. Molecular structure of the C_i symmetric complex **14** (phenyl rings replaced with Ph for clarity). The H···Y contact (**a**) has H···Y 2.58 Å and Si−H···Y 154° (Si−H distance fixed at 1.45 Å), and the H···Y−N(40) angle is about 151°.

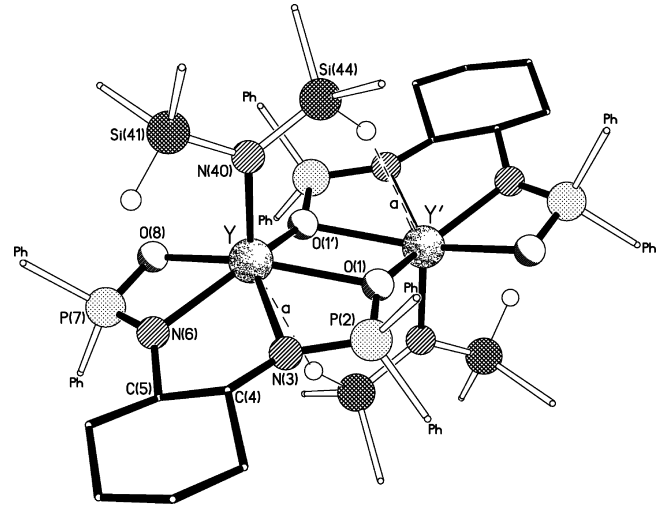


Figure 3. Molecular structure of the C_i symmetric complex **16** (phenyl rings replaced with Ph for clarity). The H···Y contact (**a**) has H···Y 3.01 Å and Si−H···Y 154° (Si−H distance fixed at 1.45 Å), and the H···Y−N(40) angle is about 156°.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **13**

Y−O(1)	2.4720(13)	Y−N(3)	2.3560(17)
Y−N(6)	2.3348(17)	Y−O(8)	2.3409(15)
Y−N(30)	2.2406(17)	Y−O(1′)	2.3121(13)
Y···Y	3.9234(4)		
O(1)−Y−N(3)	60.52(5)	O(1)−Y−N(6)	122.42(6)
O(1)−Y−O(8)	136.23(5)	O(1)−Y−N(30)	111.26(6)
O(1)−Y−O(1′)	69.25(6)	N(3)−Y−N(6)	67.15(6)
N(3)−Y−O(8)	123.98(6)	N(3)−Y−N(30)	100.61(6)
N(3)−Y−O(1′)	126.50(5)	N(6)−Y−O(8)	62.27(6)
N(6)−Y−N(30)	99.96(7)	N(6)−Y−O(1′)	137.13(5)
O(8)−Y−N(30)	110.08(6)	O(8)−Y−O(1′)	81.38(5)
N(30)−Y−O(1′)	114.07(6)	Y−O(1)−Y′	110.14(5)

The geometries at the yttrium centers are best described as pentagonal pyramidal with the $N(SiMe_2H)_2$ groups occupying the apical position. The bond lengths for the Y−O and Y−N ligand substituents for all three complexes are similar, and also compare closely with those previously reported for **10**.[27] There is a correlation between the phosphorus substituents and the *syn* or *anti* disposition of the $N(SiMe_2H)_2$ ligands. Thus, **10**[27] and **13** (with iso-propyl substituents) have C_2

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **14**

Y−O(1)	2.4621(10)	Y−N(3)	2.3542(12)
Y−N(7)	2.3681(12)	Y−O(9)	2.3548(10)
Y−N(40)	2.2848(13)	Y−O(1′)	2.3085(10)
Y···Y	3.7938(2)		
O(1)−Y−N(3)	61.34(4)	O(1)−Y−N(7)	129.52(4)
O(1)−Y−O(9)	154.12(4)	O(1)−Y−N(40)	86.30(4)
O(1)−Y−O(1′)	74.69(4)	N(3)−Y−N(7)	75.04(4)
N(3)−Y−O(9)	137.67(4)	N(3)−Y−N(40)	98.37(4)
N(3)−Y−O(1′)	134.54(4)	N(7)−Y−O(9)	62.72(4)
N(7)−Y−N(40)	126.02(5)	N(7)−Y−O(1′)	133.52(4)
O(9)−Y−N(40)	103.96(4)	O(9)−Y−O(1′)	81.65(4)
N(40)−Y−O(1′)	89.32(4)	Y−O(1)−Y′	105.31(4)

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **16**

Y−O(1)	2.4444(16)	Y−N(3)	2.395(2)
Y−N(6)	2.336(2)	Y−O(8)	2.3336(17)
Y−N(40)	2.236(2)	Y−O(1′)	2.2942(16)
Y···Y′	3.7669(5)		
O(1)−Y−N(3)	61.46(6)	O(1)−Y−N(6)	127.29(7)
O(1)−Y−O(8)	152.06(6)	O(1)−Y−N(40)	96.01(7)
O(1)−Y−O(1′)	74.74(6)	N(3)−Y−N(6)	67.53(7)
N(3)−Y−O(8)	128.34(7)	N(3)−Y−N(40)	104.15(8)
N(3)−Y−O(1′)	131.26(7)	N(6)−Y−O(8)	63.06(6)
N(6)−Y−N(40)	108.62(8)	N(6)−Y−O(1′)	139.70(7)
O(8)−Y−N(40)	104.82(7)	O(8)−Y−O(1′)	83.20(6)
N(40)−Y−O(1′)	100.48(7)	Y−O(1)−Y′	105.26(6)

Table 6. Comparative Selected Bond Lengths (Å) and Angles (deg) for **10**,[27] **13**, **14**, and **16**

	syn		*anti*	
	10[27]	**13**	**14**	**16**
Y···Y	4.0472(17)	3.9235(4)	3.7938(2)	3.7669(5)
O···O	2.691(6)	2.722(3)	2.8964(19)	2.879(3)
O−Y−O	67.46(15)	69.25(6)	74.69(4)	74.74(6)
	66.48(15)			
Y−O−Y	113.74(18)	110.14(5)	105.31(4)	105.26(6)
	111.36(17)			
Y−N($SiMe_2H$)$_2$	2.216(6)	2.2406(17)	2.2848(13)	2.236(2)
	2.253(7)			

symmetry, and a *syn* arrangement for the two N($SiMe_2H$)$_2$ ligands, while **14** and **16** (with phenyl substituents) have C_i symmetry and an *anti* arrangement for the two N($SiMe_2H$)$_2$ ligands. The orientation of each N($SiMe_2H$)$_2$ ligand with respect to the Y···Y vector also correlates with the phosphorus substituents. In **14** and **16** the N−Si vectors are almost perfectly aligned with the Y···Y vector [the Y′···Y−N(40)−Si(44) dihedral angles are about 2° in each case] while in **10** and **13** the N−Si vectors are significantly skewed with respect to the Y···Y vector [the equivalent dihedral angles being about 43° in **13**, and about 64 and 77° in **10**]. The reason for both these differences is the presence in both **14** and **16** of four C−H···π interactions between the methyl groups of one $SiMe_2H$ unit [based on Si(44)] and their proximal phenyl rings on P(2) and its symmetry related counterpart (see interactions b and c in Supporting Information, Figures S3 and S5). These interactions also bring the Si−H proton on Si(44) close to the other yttrium center (interaction a in Figures 2 and 3), approaching the pentagonal plane approximately opposite to the apical ligand [the H···Y−N(40) angles are ca. 151 and 156° in **14** and **16** respectively].

All four complexes have the same Y−N bond lengths to the apical N($SiMe_2H$)$_2$ ligands. The length of the Y−N($SiMe_2H$)$_2$ bond is significant because it must be broken/inserted into during the initiation step in the polymerization mechanism. The similarity of the bond lengths suggests that this bond strength does not vary greatly and is minimally influenced by the ancillary ligand environment. Some caution should be applied to such analysis as the bond length/strength could vary on monomer coordination, but the differences in rate observed with the different initiators (see *polymerization kinetics*) are tentatively assigned to variations in monomer binding and/or steric hindrance of the active site.

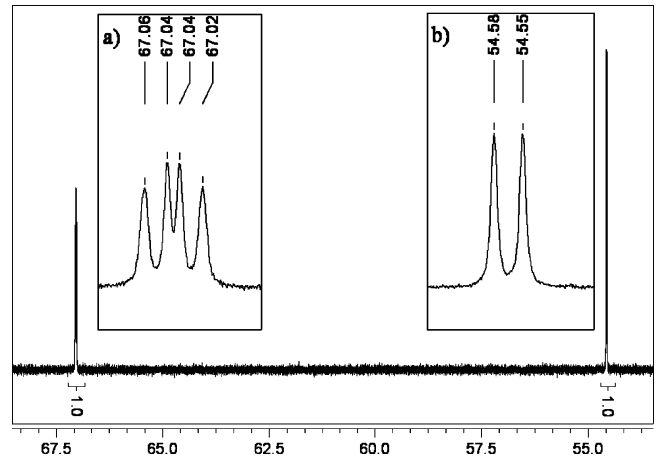


Figure 4. $^{31}P\{^1H\}$ NMR spectrum of complex **13** in benzene-d_6. Main spectrum: the whole spectrum containing two peaks (67.0 and 54.5 ppm) in a 1:1 ratio. Inset a: The peak at 67.0 ppm (dd, $^2J_{PY}$ = 5.15, 3.24 Hz). Inset b: The peak at 54.5 ppm (d, $^2J_{PY}$ = 4.24 Hz).

Solution Structures. As the polymerization is conducted in solution, it is useful to establish the solution structures of the novel yttrium complexes. The ^1H NMR spectra show the disappearance of the NH resonances, the splitting into doublets of the resonances due to the methylene protons (**10**−**12**, **14**−**17**) and the shifting to lower field of the Si−H groups. The IR spectra show the appearance of weak Si−H absorptions at about 2040 cm^{-1}. These changes are all consistent with complexation, but it is the $^{31}P\{^1H\}$ NMR spectra which are the most useful for elucidating the solution structures. The $^{31}P\{^1H\}$NMR spectra for the isopropyl substituted complexes (**10**, **11**, **13**) show two multiplets, consistent with the dimeric structure being maintained in solution. The spectrum of **13** (Figure 4) shows a doublet of doublets at 67.0 ppm, assigned to the bridging phosphinic group, and a doublet at 54.5 ppm, assigned to the terminally bound phosphinic group. The bridging group is asymmetrically placed between the two yttrium centers in the solid state (for **13**: Y−O(1A) = 2.31, Y−O(1) = 2.47 Å). This asymmetry is maintained in solution as the magnitude of the coupling constants differs, indicating that the phosphorus is closer to one yttrium center than the other (for **13**: the doublet of doublets at 67.0 has $^2J_{PY}$ = 5.15, 3.24 Hz).

Complex **12** has an *R,R*-cyclohexylene backbone group and therefore all the phosphorus atoms are inequivalent. The $^{31}P\{^1H\}$ NMR spectrum shows four multiplets; two doublets of doublets, due to the bridging groups, and upfield two doublets, due to the terminally bound groups. The isopropyl substituted complexes show NMR spectra which do not change on heating to 363 K, consistent with the dimeric structures being maintained over the temperature range. The

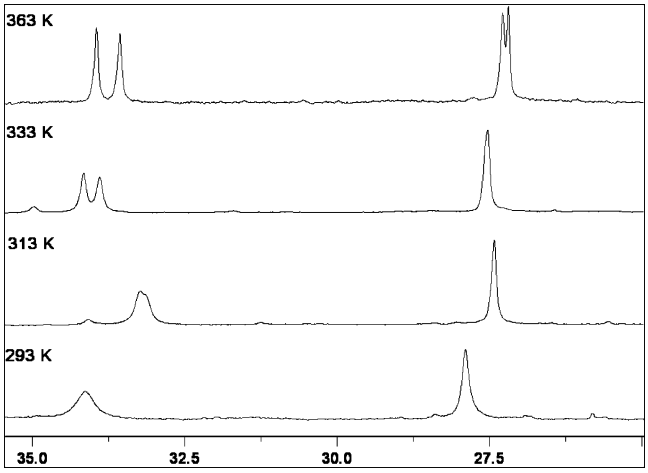


Figure 5. $^{31}P\{^{1}H\}$ NMR spectra of **16** from 293−363 K.

phenyl substituted complexes (**14**−**17**) have broadened spectra, at room temperature, indicating fluxionality. Complex **14** shows an averaged broad signal at room temperature which sharpens on heating to 383 K. However, complex **15** shows a very broad resonance which does not sharpen on heating. As expected, complexes **16** and **17** show identical spectra (Figure 5). At 293 K, two broadened resonances are observed which resolve to four resonances, on heating to 363 K. These four resonances are assigned to a dimeric solution structure where all the phosphorus atoms are inequivalent because of the chirality of the diamine backbone. At intermediate temperatures (313 and 333 K), there are minor peaks integrating to <10% of the total, which are attributed to other conformations.

Finally, all attempts to disrupt the dimeric solution structures by the addition of coordinating solvents (e.g., THF), did not change the NMR spectra.

Lactide Ring-Opening Polymerization. Lactide ring-opening polymerization was undertaken using initiators **10**−**17** (Table 7) under mild conditions (CH_2Cl_2, 298 K). All the polymerizations occurred rapidly. The conversion was monitored by ^{1}H NMR and the M_n was determined by SEC (with light scattering detection). The time required for complete conversion of 200 equiv of lactide for all the initiators, except **13** and **15**, was less than 10 min. These times compare with the fastest yttrium initiators.[7,10,14,18,19,22,24] However, caution should be applied on analyzing such rapid polymerizations using single point kinetic data as the precise end-point is difficult to determine.

Polymerization kinetics. The pseudo first order rate constants, k_1 and k_2, were determined from the plots of ln $\{[LA]_0/[LA]_t\}$ versus time (Figure 6 shows the plot for **13**). These plots showed two stages to the polymerizations: an initial region with slow polymerization occurring (k_1), but where the total conversion remains low (>15%), and then a second stage in which very rapid polymerization occurs (k_2) and the conversion reaches completion (>99%).

It was proposed that k_1 represents an initiation process(es), while k_2, which is significantly (∼8 ×) larger, represents propagation. To investigate any changes in coordination chemistry of the yttrium intermediate, the slowest polymerization (using initiator **13**) was monitored by spectroscopy. The $^{31}P\{^{1}H\}$ NMR spectra were measured in both the initiation and propagation regimes (Figure 7).

The dimeric structure was clearly maintained both during the initiation and propagation phases, so cleavage of the dimer was not occurring during the initiation period. Instead, it is proposed that the hindered *bis*(dimethylsilyl)amido group initiates the lactide binding/ring-opening relatively slowly (this is responsible for k_1 in Figure 6). Once the insertion has occurred, then the putative yttrium-alkoxide propagating species is less hindered and therefore polymerizes lactide more rapidly (responsible for k_2 in Figure 6). Initiators **11** and **15** (both have ethylene backbones) do not show the initiation period, that is, they show initiation rates which exceed the propagation rate. The behavior of these ethylene bridged complexes is under further study. Therefore, the different initiators are best compared using k_2 values (Table 7). The k_2 values compare with the most active initiators for this polymerization.[5] In the series of complexes, the rates depend on the diamine backbone substituents rather than on the phosphorus substituents. In general, the rates decrease in the order 2,2-dimethyl-1,3-propylene > *trans*-1,2-cyclohexylene > 1,2-ethylene ≫ 1,2-phenylene. It is proposed that the C-2 backbones provide a more sterically congested active site and thus slow the binding and/or ring-opening of the lactide and decrease the rate. The large difference in rate between complex **13** and the other complexes indicates that the electronic nature of the ligand also affects the rate.

Other groups increased the polymerization rate and improved the control by addition of alcohol to yttrium amido initiators.[19,34,35] Therefore, complex **13**, which showed the least control, was reacted with 2 equiv of iso-propanol and cleanly formed an alkoxide complex, *in situ*. The ^{1}H NMR spectrum showed the liberation of two equivalents of *bis*(dimethylsilyl)amine and new peaks at 4.39, 1.09, and 1.05 ppm due to the isopropoxide groups. The $^{31}P\{^{1}H\}$ NMR spectrum showed a single resonance at 58.8 ppm. The alkoxide was a controlled initiator; the ln $\{[LA]_0/[LA]_t\}$ versus time plot was linear (Supporting Information, Figure S7), showed no initiation period, and a high k_2 value (17.3×10^{-3} s^{-1}). The k_2 value far exceeds that for complex **13**. This indicates that although propagation reactions dominate the k_2 regime there can still be some initiation occurring and this decreases the overall rate.

Polymerization Control. Although there was a linear increase in M_n with % conversion for all the initiators (illustrated in Figure 8 for **17**), the M_n obtained exceed those predicted on the basis of initiator concentration (M_n predicted = 28000). In fact, the M_n obtained for most initiators were approximately double the predicted values (Figure 8, Table 7). The polymerizations were all conducted in an anaerobic environment (glovebox) and the monomer purity was established by elemental analysis. The initiator purity was established by elemental analysis and by *in situ* $^{31}P\{^{1}H\}$

(44) Kowalski, A.; Duda, A.; Penczek, S. *Macromolecules* **1998**, *31*, 2114.
(45) At t_0 there should be no LA conversion, the appearance of a positive *y*-intercept is due to the low conversions from 0−500s (4−6%) and the low signal-to-noise ratio of NMR; thus there are significant errors associated with these initial conversions.

Table 7. Polymerization Data for Initiators **10**−**17**[a]

complex #	% conversion[b]	time/s	$k_1 \times 10^{-3}/s^{-1}$ [c]	$k_2 \times 10^{-3}/s^{-1}$ [c]	M_n[d]	PDI[d]
10	99	221	3.69	24.8	66409[e]	1.66
11	97	540	n/a	13.8 ± 4.1	48500	1.29
12	99	400	2.12	15.5	41120	1.71
13	99	8515	0.0365 ± 0.0004	0.252 ± 0.05	147900	1.66
13[f]	98	390	n/a	17.3	29060	1.15
14	99	360	1.03 ± 0.2	32.0 ± 4.7	56900	1.39
15	80	1200	n/a	7.60	47500	1.80
16	97	360	3.46 ± 0.82	14.2 ± 0.2	46900	1.47
17	98	320	1.41	14.3	41200	1.28

[a] Reaction conditions: $[LA]_0 = 1.0$ M in CH_2Cl_2, $[LA]_0/[N(SiHMe_2)_2] = 200$. [b] Determined from the ^1H NMR spectra, by integration of the methyne resonances for lactide and polylactide. [c] Determined from the gradients of the ln $\{[LA]_t/[LA]_0\}$ versus time plots. [d] Determined by SEC, in THF, using multiangle laser light scattering (GPC-MALLS) to obtain the absolute M_n. [e] Determined by SEC, in THF, using polystyrene standards and a correction factor of 0.58.[44] [f] $[LA]_0 = 0.5$ M. $[LA]_0/[^iPrOH]/[N(SiHMe_2)_2] = 200:1:1$.

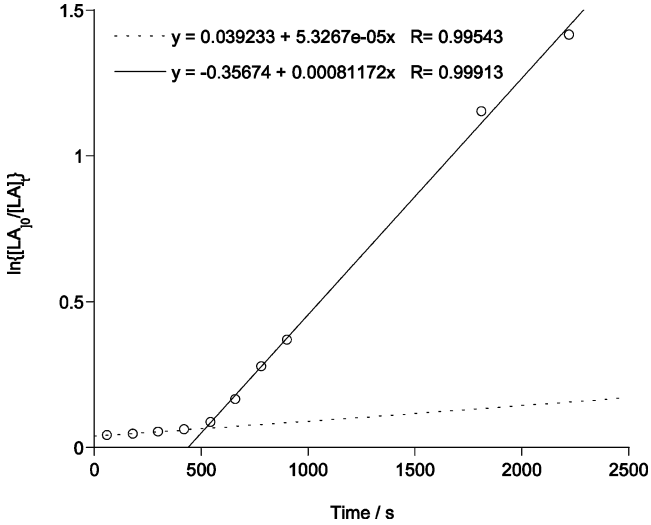


Figure 6. Plot showing ln $\{[LA]_0/[LA]_t\}$ versus time (s) for initiator **13**.[45] The polymerization conditions: $[LA]_0 = 1$ M, $[N(SiHMe_2)_2]_0 = 0.01$ M, CH_2Cl_2, 289 K.

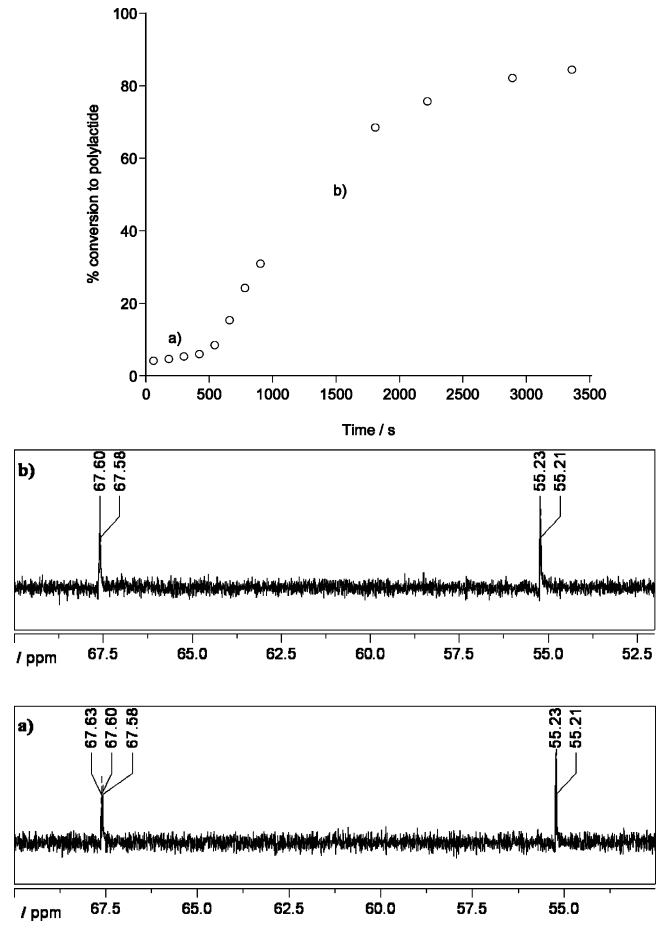


Figure 7. Conversion versus time plot for initiator **13**.[45] (a) $^{31}P\{^1H\}$ NMR spectrum of the species during the initiation region. (b) $^{31}P\{^1H\}$ NMR spectrum of the species during the propagation region.

NMR monitoring (Figure 7). So, the deactivation of approximately half the initiator (e.g., by reaction with water) can be ruled out as an explanation for the high M_n. Instead, we propose that the anomalous M_n data likely arise due to only a fraction (in most cases, one-half) of the amido groups initiating the polymerization. This is also consistent with the slow initiation periods observed in the reaction kinetics and the solution studies which indicate that the initiators remain as dimers throughout the polymerization. In contrast, the *in situ* generated alkoxide complex showed much better control with a M_n of 29000 and a polydispersity index (PDI) of 1.15.

The PDIs are broad throughout the polymerization (Table 7), rationalized by both the slow initiation and transesterification side reactions occurring. This is supported by MALDI-TOF spectra (Supporting Information, Figure S8), at low conversions, showing a series of peaks, capped by $-N(SiHMe_2)_2$ groups, separated by 72 amu.

Complex **10** gave slightly heterotactic PLA ($P_r = 0.62$) as discussed previously;[27] changes in ligand structure did not affect the stereochemistry.

Conclusions

A series of novel *bis*(phosphinic)diamido yttrium complexes have been synthesized, using a straightforward extended silylamide method. The new complexes were fully characterized, including by X-ray crystallography. In the solid state, the complexes have dimeric structures where one phosphinic group bridged two yttrium centers and the other bonds to only one yttrium center. These dimeric structures were maintained in solution, as shown by $^{31}P\{^1H\}$ NMR spectroscopy where multiplets consistent with bridging and terminally bound phosphinic groups are observed. All the new complexes were tested as initiators for lactide ring-opening polymerization. They showed very high activity and had rates comparable with the best literature initiators. Most of the initiators displayed kinetic plots showing two distinct regions: an initiation period and a propagation period. The polymerization was monitored by $^{31}P\{^1H\}$ NMR spectros-

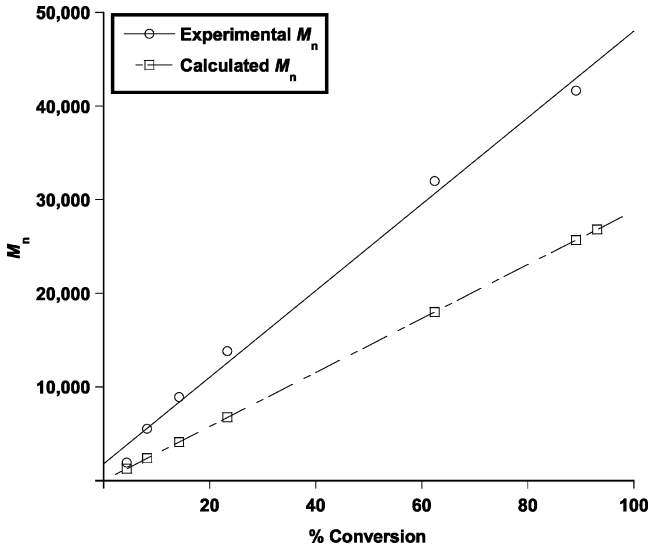


Figure 8. Plot showing M_n vs % conversion for **17**. Polymerization conditions: $[LA]_0 = 1.0$ M, $[N(SiHMe_2)_2]_0 = 5$ mM in CH_2Cl_2 at 298 K. M_n calculated $= (144 \times [LA]_0/[N(SiHMe_2)_2]_0 \times$ % conversion/100).

copy which showed that the dimeric structure was maintained throughout the polymerization. The bulky amido groups are responsible for the slow initiation from these complexes. The propagation rate constants were compared; the backbone diamine linker groups exerted the most influence, with the order of decreasing rate being 2,2-dimethyl-1,3-propylene > *trans*-1,2-cyclohexylene > 1,2-ethylene ≫ 1,2-phenylene. The initiators all gave rise to linear increases in M_n with percentage conversion; however, the values of M_n obtained were approximately double the value expected, on the basis of the initiator stoichiometry, because of only a fraction of the amide groups initiating the polymerization reaction.

In conclusion, we report the synthesis, characterization, and polymerization studies of a series of new yttrium complexes. These are highly active species for lactide ring-opening polymerization. This study has uncovered the influence of ligand substitution on rate. In the future, it will be possible to further modify the ligand structure leading to improvements in both the polymerization rate and control.

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

Supporting Information Available: X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC800419T