2892 *Organometallics* **2010,** *29,* 2892–2900
DOI: 10.1021/om1001233

ORGANOMETALLICS
Article

Iminophosphorane Neodymium(III) Complexes As Efficient Initiators for Lactide Polymerization

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Received February 15, 2010

Bis(iminophosphoranyl)methanide ($\{CH(PPh_2NR)\}^-$, R = *i*Pr or Ph) neodymium(III) complexes were prepared from $NdI_3(THF)_{3.5}$. The steric bulk of the ligand controlled the stoichiometry of the resulting complexes. Thus, three new complexes, bearing one or two ancillary ligands, were prepared and characterized using various spectroscopic techniques and by single-crystal X-ray diffraction. Reaction of the heteroleptic neodymium iodide complexes with amido groups yielded viable initiators for the ring-opening polymerization of lactide. The polymerizations were conducted using either the heteroleptic neodymium amido complexes or the *in situ* generated alkoxide complexes. Using such conditions, the neodymium complexes showed very fast and well-controlled polymerizations, with complete conversion being obtained in only a few minutes and yielding polylactide with controlled molecular weight and narrow polydispersity index. An initiating system comprising a rare neodymium-alkyl-carbene complex $[Nd\{C(PPh_2N\mathit{i}Pr)_2\}\{CH(PPh_2N\mathit{i}Pr)_2\}]$ and externally added *i*PrOH was also an unexpected catalyst for the ROP of lactide.

Introduction

With current concerns about the environmental impact of the plastics industry, in terms of both resource utilization and plastics' disposal, bioderived polyesters are a promising alternative to petrochemicals.[1] Among these, polylactide (PLA) is particularly interesting because it is made from lactic acid (produced by fermentation of corn or sugar beet), it has suitable thermal and mechanical properties to displace polyolefins, and it can be degraded to lactic acid by hydrolysis.[2] PLA is currently manufactured on a large scale in the United States and by smaller companies in the EU and Japan[3] and has been used in both degradable packaging and fiber applications. Furthermore, thanks to its biocompatibility and its ability to degrade *in vivo*, PLA can be applied in medicine for the fabrication of degradable sutures, bone screws and pins, as a vector for long-term drug delivery and, more recently, as a matrix material for tissue engineering.[4]

The most widely used synthesis of PLA is the ring-opening polymerization (ROP) of lactide.[5] The ring-opening polymerization is thermodynamically favorable (ΔH = 22.1 kJ mol^{-1} for 1 M solutions of (*S*,*S*)-lactide at room temperature), due to the relief of the lactone ring strain.[6] When using metal initiators having a nucleophilic co-ligand (e.g., an amido or alkoxide group), a coordination insertion mechanism is proposed (Scheme 1). According to such a mechanism, the Lewis acidic metal center coordinates and activates a lactide molecule, enabling it to be attacked by the metal-bound alkoxide/amide group. The putative tetrahedral intermediate undergoes ring-opening to generate a ring-opened lactide molecule with an ester/amide chain end and a new metal alkoxide bond. The metal alkoxide subsequently goes on to bind, activate, and attack another lactide molecule; this cycle repeats itself until the equilibrium conversion is reached and polymer is formed. The selection of the initiator is of the utmost importance, as it governs the polymerization rate, control, and any stereoselectivity; therefore it profoundly influences the physical and chemical properties of the polymeric material. Homoleptic metal amide/alkoxide complexes are effective initiators, but they are frequently rather difficult to characterize, poorly soluble, in some cases show complex kinetics, and lack any stereocontrol.[7] To overcome these limitations, researchers have investigated

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(1) (a) Ragauskas, A. J.; Williams, C. K.; Davison, B. H.; Britovsek, G.; Cairney, J.; Eckert, C. A.; Fredrick, W. J., Jr.; Hallett, J. P.; Leak, D. J.; Liotta, C. L.; Mielenz, J. R.; Murphy, R.; Templer, R.; Tschaplinski, T. *Science* **2006**, *311*, 484–489. (b) Mecking, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1078–1085.

(2) Drumright, R. E.; Gruber, P. R.; Henton, D. E. *Adv. Mater.* **2000**, *12*, 1841–1846.

(3) http://www.cargilldow.com; http://www.mitsui.com; http://www.hycail.com.

(4) (a) Ha, C.-S.; Gardella, J. A. *Chem. Rev.* **2005**, *105*, 4205–4232. (b) Middlenton, J. C.; Tipton, A. J. *Biomaterials* **2000**, *21*, 2335–2346. (c) Jain, R. A. *Biomaterials* **2000**, *21*, 2475–2490. (d) Place, E. S.; George, J. H.; Williams, C. K.; Stevens, M. M. *Chem. Soc. Rev.* **2009**, *38*, 1139–1151.

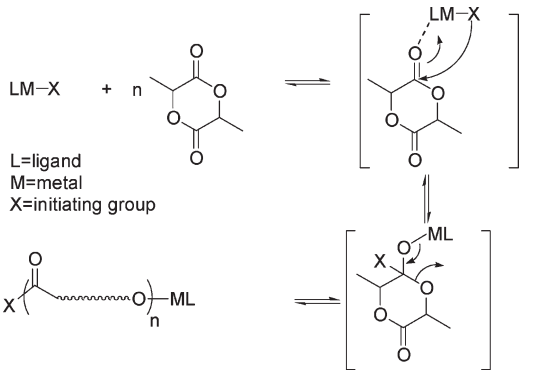
(5) (a) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147–6176. (b) Platel, R. H.; Hodgson, L. M.; Williams, C. K. *Polym. Rev.* **2008**, *48*, 11–63.

(6) Duda, A.; Penczek, S. Thermodynamics, kinetics and mechanisms of cyclic esters polymerisation. In *Polymers from Renewable Resources: Biopolyesters and Biocatalysis*; Scholz, C.; Gross, R. A., Eds.; ACS Symposium Series; Oxford University Press: Washington, DC, 1996,; Vol. *5*, pp 317−343.

(7) In the case of yttrium, see for example: Stevels, W. M.; Ankone, M. J. K.; Dijkstra, P. J.; Feijen, J. *Macromolecules* **1996**, *29*, 6132–6138.

 Published on Web 06/15/2010

Scheme 1. Coordination−Insertion Mechanism for the ROP of Lactide



heteroleptic complexes of the form [L_nMX], where L is an ancillary ligand and X is the initiating group.[8−11] Heteroleptic group 3 and lanthanide complexes have shown particular promise, as they generally exhibit very favorable rates and some of them are able to exert good polymerization and tacticity control.[9b,h,t,y,12,14b]

During the last few decades, neutral and monoanionic ancillary ligands with sp^2-hybridized nitrogen atoms have become a well-established motif in coordination chemistry, and their complexes have been extensively explored in catalysis.[13] The phosphorus analogues, i.e., ligands with the iminosphosphorane (RP═NR′) moiety, have attracted far less attention, despite their unusual electronic properties.[14] In direct contrast to imines, iminophosphoranes do not exhibit any π-accepting capacity; the electron density on the nitrogen is instead stabilized by negative hyperconjugation into the phosphorus σ^* orbitals. Thus iminophosphoranes essentially behave as strong π and σ donor ligands due to the presence of two lone pairs on the nitrogen atom. One example of this ligand class is bis(iminophosphoranyl)methanides, which are

(8) Other reviews on lactide ROP promoted by heteroleptic metallic complexes: (a) O'Keefe, B. J.; Hillmyer, M. A.; Tolman, W. B. *J. Chem. Soc., Dalton Trans.* **2001**, 2215–2224. (b) Wu, J.; Yu, T.-L.; Chen, C.-T.; Lin, C.-C. *Coord. Chem. Rev.* **2006**, *250*, 602–626. (c) Amgoune, A.; Thomas, C. M.; Carpentier, J.-F. *Pure Appl. Chem.* **2007**, *79*, 2013–2030.

(9) For recent examples of lactide polymerization: (a) Binda, P. I.; Delbridge, E. E.; Abrahamson, H. B.; Skelton, B. W. *Dalton Trans.* **2009**, 2777–2787. (b) Otero, A.; Fernández-Baeza, J.; Lara-Sánchez, A.; Alonso-Moreno, C.; Márquez-Segovia, I.; Sánchez-Barba, L. F.; Rodríguez, A. M. *Angew. Chem., Int. Ed.* **2009**, *48*, 2176–2179. (c) Mahrova, T. V.; Fukin, G. K.; Cherkasov, A. V.; Trifonov, A. A.; Ajellal, N.; Carpentier, J.-F. *Inorg. Chem.* **2009**, *48*, 4258–4266. (d) Wheaton, C. A.; Ireland, B. J.; Hayes, P. G. *Organometallics* **2009**, *28*, 1282–1285. (e) Labourdette, G.; Lee, D. J.; Patrick, B. O.; Ezhova, M. B.; Mehrkhodavandi, P. *Organometallics* **2009**, *28*, 1309–1319. (f) Alaaeddine, A.; Thomas, C. M.; Roisnel, T.; Carpentier, J.-F. *Organometallics* **2009**, *28*, 1469–1475. (g) Wang, J.; Yao, Y.; Zhang, Y.; Shen, Q. *Inorg. Chem.* **2009**, *48*, 744–751. (h) Ajellal, N.; Lyubov, D. M.; Sinenkov, M. A.; Fukin, G. K.; Cherkasov, A. V.; Thomas, C. M.; Carpentier, J.-F.; Trifonov, A. A. *Chem.—Eur. J.* **2008**, *14*, 5440–5448. (i) Knight, P. D.; White, A. J. P.; Williams, C. K. *Inorg. Chem.* **2008**, *47*, 11711–11719. (j) Florczak, M.; Duda, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 9088–9091. (k) Douglas, A. F.; Patrick, B. O.; Mehrkodavandi, P. *Angew. Chem., Int. Ed.* **2008**, *47*, 2290–2293. (l) Pang, X.; Du, H. H.; Chen, X.; Wang, X. M.; Jing, X. *Chem.—Eur. J.* **2008**, *14*, 3126–3136. (m) Hodgson, L. M.; Platel, R. H.; White, A. J. P.; Williams, C. K. *Macromolecules* **2008**, *41*, 8603–8607. (n) Platel, R. H.; White, A. J. P.; Williams, C. K. *Inorg. Chem.* **2008**, *48*, 6840–6849. (o) Guofu, Z.; Qiuwen, W.; Li, X.; Haibin, S. *Dalton Trans.* **2008**, 5930–5944. (p) Chmura, A. J.; Chuck, C. J.; Davidson, M. G.; Jones, M. D.; Lunn, M. D.; Bull, S. D.; Mahon, M. F. *Angew. Chem., Int. Ed.* **2007**, *46*, 2280–2283. (q) Platel, R. H.; Hodgson, L. M.; White, A. J. P.; Williams, C. K. *Organometallics* **2007**, *26*, 4955–4963. (r) Heck, R.; Schulz, E.; Collin, J.; Carpentier, J.-F. *J. Mol. Catal. A* **2007**, *268*, 163–168. (s) Nomura, N.; Ishii, R.; Yamamoto, Y.; Kondo, T. *Chem.—Eur. J.* **2007**, *13*, 4433–4451. (t) Du, H.; Pang, X.; Yu, H.; Zhuang, X.; Chen, X.; Cui, D.; Wang, X.; Jing, X. *Macromolecules* **2007**, *40*, 1904–1913. (u) Liu, B.; Cui, D.; Ma, J.; Chen, X.; Jing, X. *Chem.—Eur. J.* **2007**, *13*, 834–845. (v) Pietrangelo, A.; Hillmyer, M. A.; Tolman, W. B. *Chem. Commun.* **2009**, 2736–2737. (w) Chmura, A. J.; Davidson, M. G.; Frankis, C. J.; Jones, M. D.; Lunn, M. D. *Chem. Commun.* **2008**, 1293–1295. (x) Platel, R. H.; White, A. J. P.; Williams, C. K. *Chem. Commun.* **2009**, 4115–4117. (y) Arnold, P. L.; Buffet, J.-C.; Blaudeck, R.; Sujecki, S.; Wilson, C. *Chem.—Eur. J.* **2009**, *15*, 8241–8250. (z) Chmura, A. J.; Cousins, D. M.; Davidson, M. G.; Jones, M. D.; Lunn, M. D.; Mahon, M. F. *Dalton Trans.* **2008**, 1437–1443. (aa) Jones, M. D.; Davidson, M. G.; Keir, C. G.; Hughes, L. M.; Mahon, M. F.; Apperley, D. C. *Eur. J. Inorg. Chem.* **2009**, 435–642. (bb) Johnson, A. L.; Davidson, M. G.; Pérez, Y.; Jones, M. D.; Merle, N.; Raithby, P. R.; Richards, S. P. *Dalton Trans.* **2009**, 5551–5558. (cc) Peckermann, I.; Kapelski, A.; Spaniol, T. P.; Okuda, J. *Inorg. Chem.* **2009**, *28*, 5526–5534. (dd) Buffet, J.-C.; Okuda, J.; Arnold, P. L. *Inorg. Chem.* **2010**, *49*, 419–426. (ee) Chen, H.-Y.; Lin, M.-Y.; Sutar, A. K.; Lin, C.-C. *Inorg. Chem.* **2010**, *49*, 665–674. (ff) Bouyahyi, M.; Roisnel, T.; Carpentier, J.-F. *Organometallics* **2010**, *29*, 491–500.

(10) About the influence of the initiating group, see for example: (a) Chisholm, M. H.; Delbridge, E. E. *New J. Chem.* **2003**, *27*, 1177–1183. (b) Ma, H.; Okuda, J. *Macromolecules* **2005**, *38*, 2665–2673.

(11) Concerning the influence of the ancillary ligand architecture, see for example: (a) Chamberlain, B. M.; Cheng, M.; Moore, D. R.; Lobkovsky, E. B.; Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 3229–3238. (b) Amgoune, A.; Thomas, C. M.; Roisnel, T.; Carpentier, J.-F. *Chem.—Eur. J.* **2006**, *12*, 169–179.

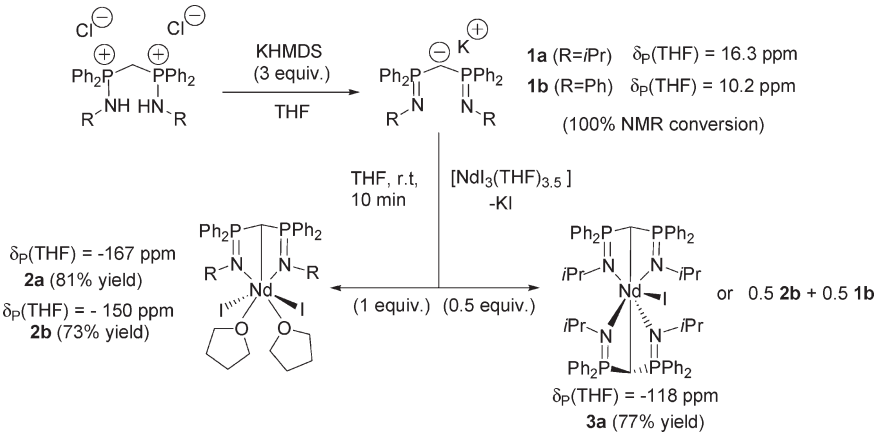
(12) (a) Chamberlain, B. M.; Sun, Y.; Hagadorn, J. R.; Hemmesch, E. W.; Young, V. G., Jr.; Pink, M.; Hillmyer, M. A.; Tolman, W. B. *Macromolecules* **1999**, *32*, 2400–2402. (b) Chamberlain, B. M.; Jazdzewski, B. A.; Pink, M.; Hillmyer, M. A.; Tolman, W. B. *Macromolecules* **2000**, *33*, 3970–3977. (c) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 4072–4073. (d) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 1316–1326. (e) Ma, H.; Spaniol, T. P.; Okuda, J. *Dalton Trans.* **2003**, 4770–4780. (f) Ma, H.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7818–7821. (g) Cai, C. X.; Amgoune, A.; Lehmann, C. W.; Carpentier, J.-F. *Chem. Commun.* **2004**, 330–331. (h) Hodgson, L. M.; White, A. J. P.; Williams, C. K. *J. Polym. Sci., Polym. Chem.* **2006**, *44*, 6646–6651. (i) Westmoreland, I.; Arnold, J. *Dalton Trans.* **2006**, 4155–4163. (j) Alaaeddine, A.; Amgoune, A.; Thomas, C. M.; Dagorne, S.; Bellemin-Laponnaz, S. *Eur. J. Inorg. Chem.* **2006**, 3652–3658. (k) Arnold, P. L.; Buffet, J.-C.; Blaudeck, R.; Sujecki, S.; Blake, A. J.; Wilson, C. *Angew. Chem., Int. Ed.* **2008**, *47*, 6033–603. (l) Ma, H.; Spaniol, T. P.; Okuda, J. *Inorg. Chem.* **2008**, *47*, 3328–3339. (m) Konkol, M.; Spaniol, T. P.; Kondracka, M.; Okuda, J. *Dalton Trans.* **2007**, 4095–4103.

(13) (a) Mindiola, D. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 6198–6200. (b) Bourget-Merle, L.; Lappert, M. F.; Severn, J. S. *Chem. Rev.* **2002**, *102*, 3031–3066. (c) Holland, P. L. *Acc. Chem. Res.* **2008**, *41*, 905–914. (d) Gibson, V. C.; Redshaw, C.; Solan, G. A. *Chem. Rev.* **2007**, *107*, 1745–1776.

(14) (a) Cavell, R. G.; Aparna, K.; Babu, R. P. K.; Wang, Q. Y. *J. Mol. Catal. A* **2002**, *189*, 137–143. (b) Gamer, M. T.; Rastätter, M.; Roesky, P. W.; Steffens, A.; Glanz, M. *Chem.—Eur. J.* **2005**, *11*, 3165–3172. (c) Gamer, M. T.; Roesky, P. W.; Palard, I.; Le Hellaye, M.; Guillaume, S. M. *Organometallics* **2007**, *26*, 651–657. (d) Wiecko, M.; Roesky, P. W.; Burlakov, V. V.; Spannen, A. *Eur. J. Inorg. Chem.* **2007**, 876–881. (e) Panda, T. K.; Zulys, A.; Gamer, M. T.; Roesky, P. W. *Organometallics* **2005**, *24*, 2197–2202. (f) Rastätter, M.; Zulys, A.; Roesky, P. W. *Chem. Commun.* **2006**, 874–876. (g) Rastätter, M.; Zulys, A.; Roesky, P. W. *Chem.—Eur. J.* **2007**, *13*, 3606–3616. (h) Buchard, A.; Auffrant, A.; Klemps, C.; Vu-Do, L.; Boubekeur, L.; Le Goff, X. F.; Le Floch, P. *Chem. Commun.* **2007**, 1502–1504. (i) Buchard, A.; Komly, B.; Auffrant, A.; Le Goff, X. F.; Le Floch, P. *Organometallics* **2008**, *27*, 4380–4385. (j) Buchard, A.; Heuclin, H.; Auffrant, A.; Le Goff, X. F.; Le Floch, P. *Dalton Trans.* **2009**, 1659–1667. (k) Picot, A.; Dyer, H.; Buchard, A.; Auffrant, A.; Vendier, L.; Le Floch, P.; Sabo-Etienne, S. *Inorg. Chem.* **2010**, *49*, DOI: 10.1021/ic902339j.

(15) (a) Babu, R. P. K.; Aparna, K.; McDonald, R.; Cavell, R. G. *Inorg. Chem.* **2000**, *39*, 4981–4984. (b) Al-Benna, S.; Sarsfield, M. J.; Thornton-Pett, M.; Ormsby, D. L.; Maddox, P. J.; Brès, P.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **2000**, 4247–4257. (c) Babu, R. P. K.; Aparna, K.; McDonald, R.; Cavell, R. G. *Organometallics* **2001**, *20*, 1451–1455. (d) Wei, P. R.; Stephan, D. W. *Organometallics* **2002**, *21*, 1308–1310. (e) Evans, D. J.; Hill, M. S.; Hitchcock, P. B. *Dalton Trans.* **2003**, 570–574. (f) Hill, M. S.; Hitchcock, P. B. *Dalton Trans.* **2003**, 4570–4571. (g) Hill, M. S.; Hitchcock, P. B. *Chem. Commun.* **2003**, 1758–1759. (h) Sarsfield, M. J.; Steele, H.; Helliwell, M.; Teat, S. J. *Dalton Trans* **2003**, 3443–3449. (i) Wei, P. R.; Stephan, D. W. *Organometallics* **2003**, *22*, 601–604. (j) Hill, M. S.; Hitchcock, P. B. *J. Organomet. Chem.* **2004**, *689*, 3163–3167. (k) Bibal, C.; Pink, M.; Smurnyy, Y. D.; Tomaszewski, J.; Caulton, K. G. *J. Am. Chem. Soc.* **2004**, *126*, 2312–2313. (l) Panda, T. K.; Benndorf, P.; Roesky, P. W. *Z. Anorg. Allg. Chem.* **2005**, *631*, 81–84. (m) Ahmed, S. A.; Hill, M. S.; Hitchcock, P. B. *Organometallics* **2006**, *25*, 394–402. (n) Gamer, M. T.; Dehnen, S.; Roesky, P. W. *Organometallics* **2001**, *20*, 4230–4236.

Scheme 2. Synthesis of Complexes 2a, 2b, and 3a



able to donate six electrons to the metal center and are well adapted to stabilize electron-poor metal centers, including lanthanides.[15] Hill and co-workers have already reported bis(iminophosphoranyl)methanide zinc alkoxide complexes for the ROP of lactide, nicely illustrating the potential for such ligand systems.[16] Yet, despite the good precedence for the use of neodymium complexes in a range of catalytic reactions, including for the ROP of lactide,[9b,11b] iminophosphorane-based neodymium complexes are still under-exploited.[14b] Herein, we wish to report the coordination of anionic bis(iminophosphoranyl)methanide ligands to various neodymium precursors and the use of the resulting complexes as initiators for lactide ROP.

Results and Discussion

The ligand syntheses were carried out following the Kirsanov route,[17] which enables the nitrogen substituent to be easily altered. The two bis(iminophosphoranyl)methanide anions **1a** and **1b**, bearing isopropyl and phenyl nitrogen substituents, respectively, were obtained by *in situ* deprotonation of the bis(aminophosphonium) salt, using 3 equiv of potassium hexamethyldisilazane in THF.[18] Subsequent coordination of the ligands to $[NdI_3(THF)_{3.5}]$, in ratios of 1:1 and 2:1 **1a/1b**:Nd, yielded the corresponding neodymium iodide complexes (Scheme 2). This synthetic approach was devised so that complexes with either one or two initiating groups could be obtained by metathesis reactions with the halide precursors.

As described in a preliminary report from our group,[19] using ligand **1a** resulted in neodymium complexes with one (**3a**) or two (**2a**) iodide ligands. Complexes $[Nd\{CH(PPh_2N\textit{i}Pr)_2\}(THF)_2I_2]$ (**2a**) and $[Nd\{CH(PPh_2N\textit{i}Pr)_2\}_2I]$ (**3a**) were isolated as pale blue-green, air- and moisture-sensitive solids. They were unequivocally characterized, despite their paramagnetism, by multinuclear ($^{31}P\{^1H\}$ and ^1H) NMR spectroscopy and by X-ray crystallography (see Supporting Information Figure S1(i), and ref 19). A representation of the molecular structure of **3a**, obtained by X-ray crystallography, is presented in Figure 1. Most of the relevant structural parameters are listed in the corresponding caption.

In complex **3a**, the Nd atom is coordinated by two tridentate bis(iminophosphoranyl)methanide ligands, each in a twisted boat conformation, and an iodide ligand. The geometry at the metal center is distorted pentagonal bipyramidal with a N1−Nd1−I1 angle of 172.20(8)°. The steric congestion around the metal center precludes any solvent coordination. This suggests that the steric hindrance of the ligand, in particular the size of the nitrogen substituents, is key to controlling the formation of this complex. In contrast, the analogous reaction between the phenyl-substituted ligand **1b** and 0.5 equiv of $[NdI_3(THF)_{3.5}]$ at room temperature resulted, as shown by $^{31}P\{^1H\}$ NMR spectroscopy, in a mixture of complex **2b** (broad singlet at −150 ppm) and the residual ligand. The formation of $[NdI\{CH(PPh_2NPh)_2\}_2]$ was not observed, presumably due to the increased steric hindrance of the ligand. On the other hand, the reaction of **1b** with 1 equiv of $[NdI_3(THF)_{3.5}]$ successfully led to **2b**, which was isolated as a pale blue-green solid in good yield (Scheme 2). It was fully characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography (see Experimental Section and Supporting Information, Figure S1(ii)).

As iodide ligands would not be sufficiently nucleophilic to initiate lactide ROP, σ-metathesis reactions were performed in order to replace them with better initiating groups. Initial attempts using potassium alkoxides (KOEt, KO*t*Bu) led to only redistribution products. However, the substitution of the iodide groups with amido ligands could be achieved by reaction of THF solutions of complexes **2a**/**2b** with potassium hexamethyldisilazide (Scheme 3). The resulting complexes **4a** and **4b** were characterized by broad singlets in the $^{31}P\{^1H\}$ NMR spectra (in THF) at −140 and −118 ppm, respectively. Moreover, ^1H NMR spectroscopy confirmed the presence of the $N(SiMe_3)_2$ groups. The molecular structures of both **4a** and **4b** were confirmed by X-ray crystallographic analyses of single crystals grown either by slow evaporation of a pentane solution (**4a**) or by diffusion of petroleum ether into a THF solution (**4b**).

Figure 2 presents the molecular structures of complexes **4a** and **4b**, along with significant bond distances and angles in the corresponding caption.

The coordination polyhedra of **4a** and **4b** are, as predicted, made up of two bis(trimethylsilyl)amido co-ligands and a tridentate bis(iminophosphoranyl)methanide ligand. There is not any THF coordination in either complex, probably as a

(16) Hill, M. S.; Hitchcock, P. B. *J. Chem. Soc., Dalton Trans.* **2002**, 4694–4702.
(17) Demange, M.; Boubekeur, L.; Auffrant, A.; Mézailles, N.; Ricard, L.; Le Goff, X.; Le Floch, P. *New J. Chem.* **2006**, *30*, 1745–1754.
(18) Klemps, C.; Buchard, A.; Houdard, R.; Auffrant, A.; Mézailles, N.; Le Goff, X.-F.; Ricard, L.; Saussine, L.; Magna, L.; Le Floch, P. *New J. Chem.* **2009**, 1748–1752.
(19) Buchard, A.; Auffrant, A.; Ricard, L.; Le Goff, X.-F.; Platel, R. H.; Williams, C. K.; Le Floch, P. *Dalton Trans.* **2009**, 10219–10222.

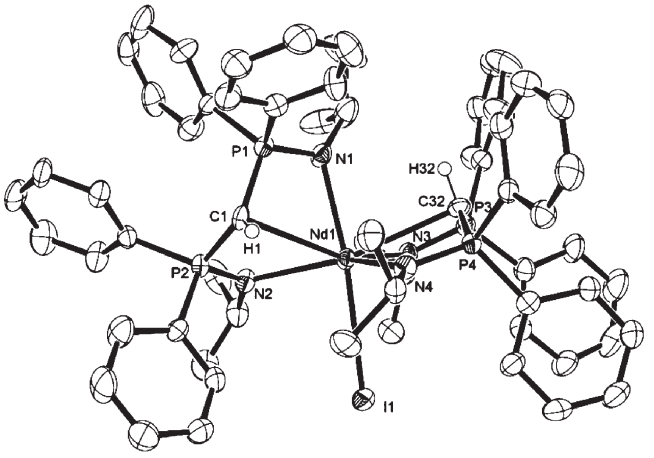
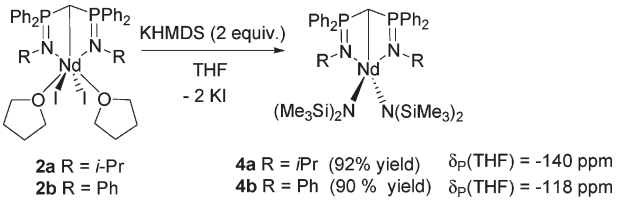


Figure 1. ORTEP view of complex **3a**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected distances (Å) and angles (deg): Nd1−I1 = 3.270(4), Nd1−N1 = 2.454(4), Nd1−N2 = 2.512(3), Nd1−N3 = 2.525(3), Nd1−N4 = 2.456(3), Nd1−C1 = 2.898(3), Nd1−C32 = 2.837(3), N1−P1 = 1.609(3), N2−P2 = 1.594(3), N3−P3 = 1.611(3), N4−P4 = 1.607(3), C1−P1 = 1.731(4), C1−P2 = 1.739(4), C32−P3 = 1.716(4), C2−P1 = 1.836(4), N1−Nd1−I1 = 172.20(8), N2−Nd1−I1 = 83.67(8), N3−Nd1−I1 = 85.07(7), N4−Nd1−I1 = 85.70(8), C1−Nd1−I1 = 116.86(7), C32−Nd1−I1 = 107.50(8), P1−C1−P2 = 115.9(2), P4−C32−P3 = 136.2(2), N1−Nd1−N2 = 88.8(1), N4−Nd1−N3 = 112.0(1), Nd1−P1−P2−C1 = 80.29(15), P1−N1−N2−Nd1 = 55.08(15), Nd1−N1−N2−C1 = 80.34(12), Nd1−P4−P3−C32 = 81.65(19), P4−N4−N3−Nd1 = 20.25(20), Nd1−N3−N4−C32 = 46.71(17), N1−P1−P2−C1 = 72.96(21), N3−P3−P4−C32 = 81.04(1), N1−P1−P2−N2 = 8.87(20), N4−P4−P3−N3 = 11.29(24), N1−Nd1−C1−P2 = 57.74(21), N2−Nd1−C1−P1 = 66.06(18), N3−Nd1−C32−P4 = 42.20(20), N4−Nd1−C32−P3 = 34.23(17).

result of the steric hindrance of the trimethylsilyl groups. Like in **2a**, in **2b**, and in other reported bis(iminophosphoranyl)methanide neodymium(III) complexes,[14b] a metallacycle (N1−P1−C1−P2−N2−Nd1) was formed upon chelation of the iminophosphorane moieties to the metal. In this boat-shaped conformation, the central carbon atom and the neodymium atom are displaced from the almost planar (dihedral angle N1−P1−P2−N2 = 5.08(5)° and 6.24(22)° in **4a** and **4b**, respectively) N_2P_2 base (N1−Nd1−C1−P2 = 44.92(8)° and 52.33(11)°, N2−Nd1−C1−P1 = −49.42(8)° and 47.51(10)° in **4a** and **4b**, respectively). The steric hindrance around the Nd center also influences the bonding of the (N,C,N) fragments in both complexes. Indeed, the Nd−$C_{central}$ bonds are rather longer in both **4a**,**b** compared to those measured in **2a**,**b** (2.886(2) and 2.857(3) Å in **4a** and **4b**, respectively, vs 2.807(4) and 2.801(4) Å in **2a** and **2b**, respectively). Likewise, the Nd−N bonds are elongated in complexes **4a**,**b** compared to those in complexes **2a**,**b**. Yet interestingly in **4b** they are both equal to 2.478(3) Å (vs Nd−N = 2.413 Å on average in **2b**), revealing a symmetrical binding of the {$CH(PPh_2NPh)_2$} ligand. On the contrary, in **4a**, the Nd−N bond lengths differ, showing an unsymmetrical bonding of the two ligands in the complex (Nd1−N1 and Nd1−N2 being 2.490(2) and 2.471(2) Å, respectively, vs 2.403(1) and 2.418(4) in **2a**). Lastly, the two amido groups are not equivalent but are orthogonal to one another; this arrangement may account for the steric crowding. Furthermore, no γ-CH agostic interaction could be observed between the methyl group on the silicon atom and the metal.

Scheme 3. Synthesis of complexes 4a and 4b



In the case of complex **3a**, as we have already reported,[19] the substitution reaction of the iodide ligand using 1 equiv of KHMDS did not occur. Instead, a deprotonation reaction occurred, yielding an unexpected mixed alkyl-carbene neodymium complex, **5a** (Scheme 4).

Given the ability of lanthanide initiators in the ROP of lactide,[9b,h,t,y,12,14b] it was of interest to determine the activity of complexes **4a** and **4b**. Although lacking an initiating group, complex **5a** was also tested. The polymerization reactions were carried out using 1 M concentrations of *rac*-lactide and 0.005 M concentrations of complexes **4a**/**4b** in THF (i.e., at a ratio of 200:1, LA:**4a**/**4b**). Under these conditions, the solutions became very viscous after only a few seconds of reaction, indicating rapid polymerization was occurring. The crude products were analyzed by ^{1}H NMR spectroscopy (by integration of the methine resonances due to lactide and polylactide; see the Experimental Section); this showed that complete conversion (> 95%) was achieved within 5 min using both initiators. The GPC analyses showed a linear increase in the M_n of the PLA produced with the percentage conversion of lactide (e.g., using **4b**, see Figure S2a of the Supporting Information), and the PLA had relatively narrow PDI values (around 1.3), as expected for a controlled polymerization. In addition, MALDI-ToF mass spectrometry confirmed that the polymer chains were systematically end-capped with a bis(trimethylsilyl)amido group and a hydroxy group, with no cyclic oligomer being observed (for the spectrum obtained using **4a**; see Figure S3 of the Supporting Information). The MALDI-ToF spectrum also showed evidence for transesterification reactions (series separated by 72 atomic mass units). However, the M_n values for the PLA were approximately 10 times those calculated ($M_{n,calc}$ = % conversion × $M_{lactide}$ × 200/number of initiating groups), throughout the polymerization run (Figure S2a). This anomalously high M_n suggested that only one-tenth of the initiators were active. For **4b**, the polymerization kinetics were first-order[20] with respect to the *rac*-LA concentration (k_{app} = 0.013 s^{-1}; see Figure S2b), and no significant initiation period was observed, discounting slow initiation as the cause of the unexpectedly high molecular number. The polymerization was also analyzed *in situ* by $^{31}P\{^1H\}$ NMR spectroscopy at complete monomer conversion, and this showed significant quantities of unreacted catalyst **4b** (δ = −118 ppm). Comparable results were also obtained using solutions of **4b** in toluene, precluding the coordination of THF to the Nd as an explanation for the reduced control (further reinforced by findings that **4b** is not solvated by THF molecules in the solid state). Finally, it has already been established that bis(trimethylsilyl)amido groups are relatively poor initiating groups, due to their steric

(20) A slow-down of the reaction rate from 90% conversion was observed.

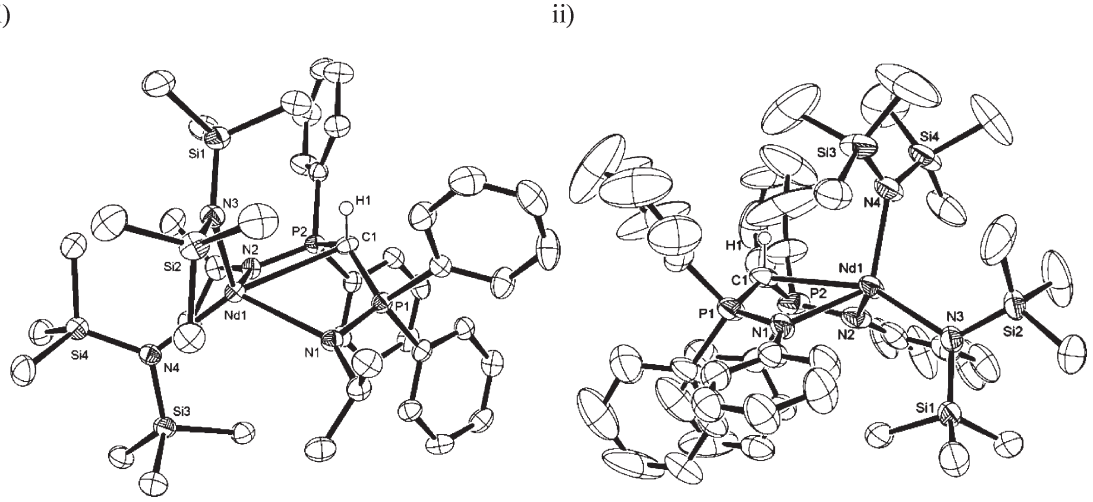
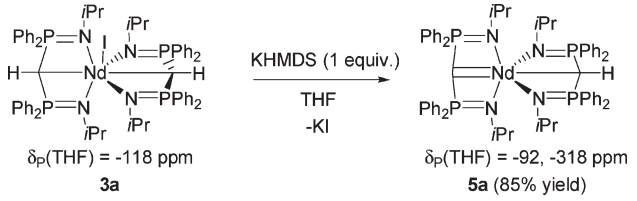
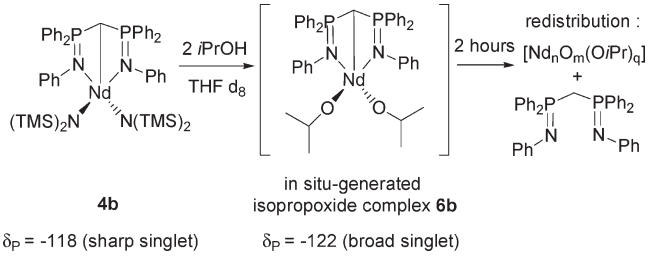


Figure 2. ORTEP views of complex **4a** (i) and **4b** (ii). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected distances (Å) and angles (deg): **4a**: Nd1−N3 = 2.345(2), Nd1−N4 = 2.384(2), Nd1−N1 = 2.490(2), Nd1−N2 = 2.471(2), Nd1−C1 = 2.886(2), N1−P1 = 1.622(2), N2−P2 = 1.618(2), C1−P1 = 1.728(2), C1−P2 = 1.820(2), N3−Nd1−N4 = 110.60(7), N3−Nd1−N1 = 103.8(8), N3−Nd1−N2 = 123.3(7), N4−Nd1−N1 = 118.26(7), N4−Nd1−N2 = 95.70(7), N3−Nd1−C1 = 97.85(6), N4−Nd1−C1 = 150.10(6), P2−C1−P1 = 131.1(1), N2−Nd−N1 = 106.02(7), Nd1−N1−N2−C1 = 60.93(7), Nd1−P1−P2−C1 = 82.92(9), P1−N1−N2−Nd1 = 36.65(10), N1−P1−P2−C1 = 80.84(13), N1−P1−P2−N2 = 5.08(15)(1), N1−Nd1−C1−P2 = 44.92(8), N2−Nd1−C1−P1 = 49.42(8); **4b**: Nd1−N3 = 2.325(3), Nd1−N4 = 2.384(2), Nd1−N1 = 2.478(3), Nd1−N2 = 2.478(3), Nd1−C1 = 2.857(3), N1−P1 = 1.626(3), N2−P2 = 1.620(3), C1−P1 = 1.720(3), C1−P2 = 1.736(3), N3−Nd1−N4 = 110.2(1), N3−Nd1−N1 = 110.6(1), N3−Nd1−N2 = 118.14(8), N4−Nd1−N1 = 109.33(8), N4−Nd1−N2 = 105.27(8), N3−Nd1−C1 = 94.7(1), N4−Nd1−C1 = 155.0(1), P1−C1−P2 = 131.1(2), N2−Nd−N1 = 102.7 (1), Nd1−N1−N2−C1 = 66.46(12), Nd1−P1−P2−C1 = 79.83(22), P1−N1−N2−Nd1 = 46.92(10), N1−P1−P2−C1 = 75.15(20), N1−P1−P2−N2 = 6.24(22), N1−Nd1−C1−P2 = 52.33(11), N2−Nd1−C1−P1 = 47.51(10).

Scheme 4. Synthesis of complexes 4a and 4b



Scheme 5. *In Situ* Formation of Complex 6b



bulk and reduced nucleophilicity, and this is the probable explanation for the behavior observed here.[9p,11b]

Complexes with alkoxide initiating groups, which mimic the putative propagating actives species, are known to be superior initiators.[9f,g,11b,21] However, isolated examples of such heteroleptic lanthanide alkoxide complexes are not very common.[9c,h,22] Previously, metal alkoxide complexes have been generated *in situ* by addition of alcohols to metal amido complexes and then used directly in the ROP.[9h,q,n,11,16] For lanthanide complexes, these alkoxides can be observed by NMR spectroscopy but are difficult to isolate, as they are believed to aggregate.[10,23] Nevertheless, the isolation of a bis(alkoxide) Nd complex, [Nd{CH(PPh$_2$NPh)$_2$}(OR)$_2$], was attempted. The addition of sodium isopropoxide or potassium *tert*-butoxide to the iodide complex **2b** did not yield the expected alkoxide complexes but rather led to ligand displacement. However, the addition of 2 equiv of *i*PrOH to complex **4b** led to the formation of a new alkoxide complex. Indeed, *in situ* $^{31}P\{^1H\}$ NMR spectroscopy showed a broad signal at −122 ppm, consistent with the formation of a heteroleptic alkoxide complex. ^1H NMR spectroscopy was not conclusive due to the complex paramagnetism, but the release of bis(trimethylsilyl)amine was apparent.

The heteroleptic complex is unstable, and after two hours, only free ligand is observed (see Scheme 5). Although complex **6b** could not be isolated, its lifetime was sufficient to enable its use *in situ* in polymerization runs (Table 1). Thus, addition of 2 equiv of *i*PrOH to a 0.005 M solution of **4b**, in THF, and subsequent addition of the mixture to a 1 M solution of LA (THF) led to highly efficient ROP. The polymerizations were even faster than using solutions of **4b**, with 90% conversion being reached in only 90 s and complete conversion within 6 min (the reaction rate decreasing at the end of the reaction; see Figure S5 of the Supporting

(21) (a) Williams, C. K.; Brooks, N. R.; Hillmyer, M. A.; Tolman, W. B. *Chem. Commun.* **2002**, 2132–2133. (b) Cheng, M.; Moore, D. R.; Reczek, J. J.; Chamberlain, B. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 8738–8749. (c) Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 8738–8749. (d) Simic, V.; Spassky, N.; Hubert-Pfalzgraf, L. G. *Macromolecules* **1997**, *30*, 7338–7340. (e) Stevels, W. M.; Ankoné, M. J. K.; Dijkstra, P. J.; Feijen, J. *Macromolecules* **1996**, *29*, 6132–6138.

(22) Izod, K.; Liddle, S. T.; McFarlane, W.; Clegg, W. *Organometallics* **2004**, *23*, 2734–2743.

(23) (a) Barnhart, D. M.; Clark, D. L.; Huffman, J. C.; Vincent, R. L.; Watkin, J. G. *Inorg. Chem.* **1993**, *32*, 4077–4083. (b) Gromada, J.; Mortreux, A.; Chenal, T.; Ziller, J. W.; Leising, F.; Carpentier, J.-F. *Chem.—Eur. J.* **2002**, *8*, 3773–3778.

Table 1. Ring-Opening Polymerization of *rac*-Lactide in THF by *in Situ* Generated 6a and 6b[a]

entry	initiator [I]	$[LA]_0/[I]_0$	time [s]	conversion [%]	$M_{n,exp}$[b]	$M_{n,calc}$[c]	PDI[b,d]	P_r[e]
1	**6b**	200	360	95	12 600	13 700	1.05	0.58
2	**6b**	400	360	95	25 100	27 400	1.04	0.60
3	**6b**	1000	600	94	109 000	67 700	1.21	0.57
4[f]	**6b**	200	300	96	12 700	13 800	1.07	
5	**6a**	200	300	96	14 600	13 800	1.07	0.57
6	$[Nd(OiPr)_3]$	200	300	95	17 500	9100	1.17	0.51
7	$[Nd(OiPr)_3]$	400	300	96	29 000	18 400	1.18	0.52

[a] All reactions were performed with $[rac\text{-LA}]_0 = 1$ M at 298 K, in THF, under inert atmosphere. **6a** and **6b** are generated *in situ* by adding 2 equiv of dry 2-propanol to solutions of **4a** and **4b**, respectively, in THF. Conversions were determined by integration of the methine resonances of LA (^{1}H NMR δ = 4.92 ppm in $CDCl_3$) and PLA (^{1}H NMR δ = 5.00−5.30 ppm in $CDCl_3$). [b] Experimental M_n and M_w were determined by GPC in THF, using multiangle laser light scattering (GPC-MALLS). [c] $M_{n,calc} = 144 \times 200 \times$ % conversion LA $\times$ 0.5. [d] PDI = M_w/M_n. [e] P_r is the probability of racemic linkages between monomer units and is determined from the homonuclear decoupled ^{1}H NMR spectrum: $^1H\{^1H\}$ NMR δ 5.14 and 5.22 ppm in $CDCl_3$ for heterotactic PLA.[24] [f] (*S,S*)-LA was used instead of *rac*-LA in order to detect epimerization.

Information). Moreover, the molecular number of the polymer showed an excellent correlation with the calculated values. The polydispersity index was narrow (1.05), indicating a high level of polymerization control. End-group analysis by MALDI-ToF mass spectrometry showed that the polymer chains were systematically end-capped with an isopropyl ester and a hydroxy group; no cyclic oligomer was detected (see Figure S6), although, once again, there was evidence for transesterification (series separated by 72 atomic mass units). The use of lower initiator loadings was also possible (up to 1000:1), with complete conversion being achieved within 15 min (Table 1, entries 2 and 3). Some molecular weight control is, however, lost for high monomer: initiator ratios, as already observed.[25] The controlled nature of the polymerization was also confirmed by a sequential monomer addition experiment. The experiment involved addition of a further 100 equiv of lactide to a typical polymerization run (100:1, LA:**6b**, M_n = 6800, PDI = 1.05) after 5 min (93% conversion); these further equivalents were polymerized to yield PLA of increased molecular number (M_n = 14 200, PDI = 1.14, 95% conversion overall). As **6b** was known to slowly degrade in THF (or toluene), further investigation was required to rule out the involvement of any homoleptic tris-alkoxide neodymium complexes. Thus, Nd alkoxide species were formed *in situ* (by reaction of 3 equiv of isopropanol with $[Nd(N(SiMe_3)_2)_3]$)[26] and were then used to initiate a LA ROP (entries 6 and 7 in Table 1). Previously, *in situ* generated rare-earth homoleptic tris-isopropoxide species (e.g., Y or La) were reported to be very fast initiators for the LA ROP, with excellent control over molecular number on the basis of three polymer chains growing per metal center (i.e., all three alkoxide groups initiate).[27] In our case, the homoleptic neodymium species was poorly soluble in THF, which makes any discussion of its control of the molecular weight more difficult, although there was not a good agreement between the experimental values for M_n and those calculated assuming initiation from three sites. On the exclusive basis of the excellent correlation between experimental and calculated M_n using **6a**,**b**, it was not possible to unambiguously rule out the presence of significant quantities of homoleptic Nd alkoxide complex. However, the *in situ* generated heteroleptic complexes **6a**,**b** were soluble in THF and, more importantly, on the time scale of the polymerization runs, exhibited a single signal in the $^{31}P\{^1H\}$ NMR spectra, without any traces of free ligand, which would be expected to result from the formation of homoleptic species. For these reasons, when using **4b** and 2-propanol for polymerizations, we do not expect there to be significant quantities of homoleptic alkoxides contaminating.

No stereocontrol was observed using **4b**/*i*PrOH (P_r = 0.58, probability of racemic linkage between the LA units). Furthermore, a controlled polymerization of (*S,S*)-lactide by the **4b**/*i*PrOH system (entry 4 in Table 1) resulted in only isotactic PLA, evidenced by the single sharp resonance in the methine region in the homonuclear decoupled ^{1}H NMR spectrum (^{1}H NMR δ 5.16 ppm in $CDCl_3$).[23] Some polymerization reactions were also conducted in THF by addition of 2 equiv of *i*PrOH to a solution of **4a** (Table 1, entry 5) to generate *in situ* the bis-alkoxide complex **6a**. This **4a**/*i*PrOH system also led to highly efficient ROP. With a monomer: initiator ratio of 200:1, polymerization was even faster than when using *in situ* generated **6b**, with 91% conversion being reached in only 30 s and 96% conversion being achieved within 5 min. GPC analysis revealed good control of the PLA molecular number and a narrow polydispersity index. The influence of the steric hindrance at the nitrogen atom of the iminophosphorane groups on the rates was, however, unremarkable.

Polymerization experiments conducted using complex **5a** were unsuccessful, as expected from the lack of an initiating group. Addition of a single equivalent of alcohol led to protonation of the methanide or methanediide moieties, and the iminophosphorane ligand displacement occurred immediately. Moreover, polymerizations initiated using a solution of **5a** and 2-propanol indicated that the active species was a homoleptic Nd alkoxide species (as evidenced by very fast conversion and poor control of M_n). However completely different behavior was observed if the monomer and then the alcohol were added to a solution of **5a**. In this case, the polymerization occurred relatively quickly (complete conversion within 90 min) and showed good control of the molecular number and a narrow PDI (< 1.1) over the entire run (Table 2, entries 1−3). MALDI-ToF analysis, at low conversion, revealed PLA end-capped with isopropoxy ester groups. The high degree of polymerization control was confirmed by a sequential monomer addition experiment. By adding 100 extra equivalents of monomer after 60 min of a typical run (LA:**6b**:*i*PrOH = 100:1:1, M_n = 11 000, PDI = 1.1 at 88%), complete consumption of the lactide and an

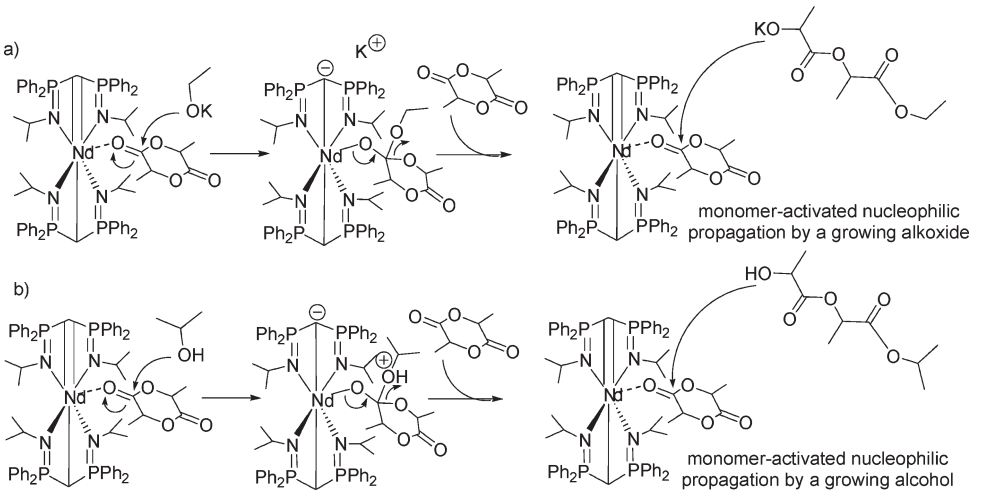
(24) Coudane, J.; Ustariz-Peyret, C.; Schwach, G.; Vert, M. *J. Polym. Sci., Polym. Chem.* **1997**, *35*, 1651–1658.
(25) Williams, C. K.; Breyfogle, L. E.; Choi, S. K.; Nam, W. W.; Young, V. G., Jr.; Hillmyer, M. A.; Tolman, W. B. *J. Am. Chem. Soc.* **2003**, *123*, 11350–11359.
(26) Kritikos, M.; Moustiakimov, M.; Wijk, M.; Westin, G. *J. Chem. Soc., Dalton Trans.*, **2001**, 1931−1938, and references therein.
(27) (a) Stevels, W. M.; Ankoné, M. J. K.; Dijkstra, P. J.; Feijen, J. *Macromolecules* **1996**, *29*, 3332–3333. (b) Vesna Simic, V.; Spassky, N.; Hubert-Pfalzgraf, L. G. *Macromolecules* **1997**, *30*, 7338–7340.

Table 2. Ring-Opening Polymerization of *rac*-Lactide in THF Using 5a[a]

entry	$[LA]_0$:$[5a]_0$:[*i*PrOH]	*t* [min]	conversion [%]	$M_{n,exp}$[b]	$M_{n,calc}$[c]	PDI[b,d]	P_r[e]
1	200:1:1	5	57	16 000	16 400	1.05	
2	200:1:1	30	80	24 200	23 000	1.08	
3	200:1:1	90	100	31 000	28 800	1.11	0.60
4[f]	200:1:1	60	81	21 100	23 300	1.04	
5	200:0:0 ($[KOEt]_0$ = 0.01)[g]	5	93	19 200	13 400[g]	1.66	
6[f]	200:0:0 ($[KOEt]_0/[5a]_0$ = 1)[h]	60	85	20 200	24 400	1.05	

[a] All reactions were performed with $[LA]_0$ = 1 M and $[LA]_0$:$[I]_0$:[*i*PrOH] = 200:1:1 at 298 K, in THF, under inert atmosphere. Conversions were determined by integration of the methine resonances of LA (^{1}H NMR δ = 4.92 ppm in $CDCl_3$) and PLA (^{1}H NMR δ = 5.00−5.30 ppm in $CDCl_3$). [b] Experimental M_n and M_w were determined by GPC, in THF, using multiangle laser light scattering (GPC-MALLS). [c] $M_{n,calc}$ = 144 × ($[LA]_0/[I]_0$) × conversion LA. [d] PDI = M_w/M_n. [e] P_r is the probability of racemic linkages between monomer units and is determined from the homonuclear decoupled ^{1}H NMR spectrum: δ 5.14 and 5.22 ppm in $CDCl_3$ for heterotactic PLA.[24f] (*S,S*)-LA was used instead of *rac*-LA to detect epimerization. [g] KOEt was used as the only initiator for the polymerization, $M_{n,calc}$ = 144 × 100 × % conversion LA. [h] KOEt was added to the reaction mixture instead of 2-propanol.

Scheme 6. Activated Monomer Mechanism Proposed to Rationalize the Controlled Activity of 5a/KOEt (a) and 5a/*i*PrOH (b) in the ROP of Lactide



increase in the M_n of all the polymer chains were observed (M_n = 21 700, PDI = 1.18, overall conversion of 96% after 2 extra hours). Finally, using this protocol, no epimerization of (*S,S*)-lactide was detected (only isotactic PLA was obtained).

$^{31}P\{^1H\}$ NMR spectroscopy was used to analyze the mixture; no **5a**−monomer adduct was detected, and *in situ* $^{31}P\{^1H\}$ NMR analysis of polymerization runs revealed only the unchanged signal of complex **5a**. Furthermore, by using *in situ* ATR FTIR spectroscopy, no stretching of the carbonyl bond of the lactide monomer could be evidenced in the presence of **5a**. Crystallization attempts to isolate a **5a**−monomer adduct[28] were also unsuccessful. However, after several hours and the completion of the reaction, the decomposition of the complex and the release of the protonated ligands were observed. Successful polymerization was also possible using KOEt as the additive instead of 2-propanol (Table 2, entries 5 and 6). While KOEt proved to be a very active but chaotic initiator for the polymerization when used alone (Table 2, entry 5), control of the molecular weight and narrow polydispersity index was obtained when it was combined with **5a** (Table 2 entry 6).

An activated-monomer mechanism is proposed to explain the activity of complex **5a** (see Scheme 6) in the presence of either externally added alcohol or alkoxide groups.[29] According to such a mechanism, the Nd complex activates the monomer, which is subsequently attacked by the externally added nucleophiles (either alcohol or alkoxide). If an alkoxide is added, the tetrahedral intermediate undergoes ring-opening and proton exchange to liberate complex **5a** and a new alkoxide (a ring-opened species with potassium α-ester-ω-alkoxide end groups). The cycle of reactions (i.e., activation, nucleophilic attack, and release of an alkoxide) repeats until all the monomer is consumed and a polymer is formed (see Scheme 6a). When adding alcohol, the tetrahedral intermediate undergoes ring-opening and proton exchange to liberate complex **5a** and a new alcohol (a ring-opened species with α-ester-ω-alcohol end groups). The activation, nucleophilic attack, and release of an alcohol series of reactions repeat until all the monomer is consumed and a polymer is formed (see Scheme 6b). Once all the monomer is consumed, the polymeric alcohol is free to attack **5a** and decomposition occurs (presumably generating a polymeric alkoxide, which is protonated during the aqueous workup). The use of excess alcohol was not feasible, as it led only to the decomposition of **5a** to the protonated ligand.

In summary, we have developed a series of new neodymium complexes, bearing either one or two iminophosphorane ligands and either iodide or amido co-ligands, with the complex stoichiometry depending on the nitrogen substituent (either phenyl or isopropyl). All the Nd complexes were fully characterized, including in all cases by single-crystal X-ray diffraction. The amido complexes (**4a/b**) were rapid

(28) Koeller, S.; Joji Kadota, J.; Alain Deffieux, A.; Peruch, F.; Massip, S.; Léger, J.-M.; Desvergne, J.-P.; Bibal, B. *J. Am. Chem. Soc.* **2009**, *131*, 15088–15089.
(29) Nomura, N.; Taika, A.; Tomioka, T.; Okada, M. *Macromolecules* **2000**, *33*, 1497–1499.

initiators for the ring-opening polymerization of *rac*-lactide but showed reduced polymerization control. However, *in situ* addition of alcohol to complexes **4a** and **4b**, generated isopropoxide complexes, which were even faster initiators and still showed excellent polymerization control. An initiating system comprising a rare neodymium-alkyl-carbene complex [Nd{C(PPh$_2$N*i*Pr)$_2$}{CH(PPh$_2$N*i*Pr)$_2$}] (**5a**) and externally added *i*PrOH was also an unexpected catalyst for the ROP of lactide. This may be due to an activated-monomer mechanism, in contrast to the traditional coordination−insertion mechanism invoked for initiator **4a** or **4b**.

Experimental Section

General Conditions. All experiments were performed under an atmosphere of dry nitrogen or argon using standard Schlenk and glovebox techniques. Solvents were freshly distilled under nitrogen from Na/benzophenone (THF, diethyl ether, petroleum ether), from P_2O_5 (dichloromethane), or from CaH_2 (2-propanol). Unless stated, reagents were purchased from commercial sources and used without further purification. [Nd(BH$_4$)$_3$(THF)$_3$], [Nd(N(SiMe$_3$)$_2$)$_3$], [NdI$_3$THF$_{3.5}$],[30] isopropyl-substituted bis(aminophosphonium)methane salts, and complexes **2a**, **3a**, **4a**, and **5a** were prepared according to literature procedures.[19] *rac*-Lactide was generously donated by Purac Plc. and was recrystallized from anhydrous toluene and sublimed three times under vacuum prior to use.

Instruments and Measurements. Nuclear magnetic resonance spectra were recorded on a Bruker Avance 300 spectrometer operating at 300 MHz for ^{1}H, 75.5 MHz for ^{13}C, and 121.5 MHz for ^{31}P. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to Me$_4$Si as external standard. ^{31}P are relative to a 85% H_3PO_4 external reference. Coupling constants are expressed in hertz. The following abbreviations are used: b, broad; s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet; v, virtual. Elemental analyses were performed by the "Service d'Analyse de l'Université de Dijon", at Dijon, France. MALDI-TOF mass spectra were determined at the EPSRC NMSSC, Swansea, UK. Mass spectra were performed on a Micromass Autospec Premier machine, using LSIMS (FAB) ion sources. The MALDI-TOF conditions were using a dithranol matrix in THF at a loading of 1:5 with sodium trifluoroacetate as the cationizing agent. The polymer's molecular number 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}.[31]

Synthesis of Bis(iminophosphoranyl)methanide, 1b. KHMDS (38 mg, 0.19 mmol) was added to a suspension of 0.063 mmol of the corresponding bis(aminophosphonium) chloride **1** in THF (5 mL). The reaction mixture immediately became clear, taking a pale yellow color. The potassium chloride precipitate was removed by centrifugation and the supernatant solution dried *in vacuo* to yield a pale yellow powder. **1b**: yield 38 mg (0.062 mmol, 99%). ^{31}P{^{1}H} NMR (121.5 MHz, [D$_8$]-THF, 20 °C): δ 10.2 (s, P) ppm. ^{1}H NMR (300 MHz, [D$_8$]-THF, 20 °C): δ 1.65 (t, $^2J_{HP}$ = 3.5 Hz, 1H, PC*H*P), 6.33 (t, $^3J_{HH}$ = 7.0 Hz, 2H, *p*-C*H* (NPh)), 6.53 (m, $^3J_{HH}$ = 8.0 Hz, 4H, *m*-C*H* (NPh)), 6.75 (t, $^3J_{HH}$ = 7.0 Hz, 4H, *m*-C*H* (NPh)), 7.20 (m, $^3J_{HH}$ = 7.5 Hz, 12H, *m*,*p*-C*H* (PPh$_2$)), 7.86 (m, 8H, *o*-C*H* (PPh$_2$)) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, [D$_8$]-THF, 20 °C): δ 14.3 (t, $^1J_{CP}$ = 131.0 Hz, P*C*HP), 113.0 (s, *p*-*C*H (NPh)), 121.2 (t, $^3J_{CP}$ = 9.5 Hz, *o*-*C*H (NPh)), 126.0 (t, $^2J_{CP}$ = 5.0 Hz, *m*-*C*H (PPh$_2$)), 126.8 (s, *m*-*C*H (NPh)), 127.4 (s, *p*-*C*H (PPh$_2$)), 130.8 (t, $^3J_{CP}$ = 4.5 Hz, *o*-C*H* (PPh$_2$)), 138.7 (d, $^1J_{CP}$ = 98.5 Hz, *ipso*-*C* (PPh$_2$)), 153.5 (s, *ipso*-*C* (NPh)) ppm.

Synthesis of [Nd{CH(PPh$_2$NPh)$_2$}I$_2$(THF)$_2$], 2b. In THF (5 mL), [NdI$_3$THF$_{3.5}$] (49 mg, 0.063 mmol) was added to a solution of bis(iminophosphoranyl)methanide (**1b**) (39 mg, 0.063 mmol), resulting in an immediate color change of the reaction mixture. After 2 h of stirring, the reaction mixture was centrifuged and the supernatant solution was dried *in vacuo*. The light green solid residue was finally washed with petroleum ether (2 × 5 mL). Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexanes into a solution of **2b** in THF at room temperature (298 K). **2b**: yield 51 mg (0.046 mmol, 73%). ^{31}P{^{1}H} NMR (121.5 MHz, [D$_8$]-THF, 20 °C): δ −150 (bs, P) ppm. ^{1}H NMR (300 MHz, [D$_8$]-THF, 20 °C): δ −50.7 (bs, 2H, *p*-C*H* NPh), −25.0 (bs, 1H, PC*H*P), −14.9 (bs, 4H, C*H* NPh), −10.5 (bs, 4H, C*H* NPh), 4.5 (bs, 8H, OCH$_2$C*H*$_2$ THF), 6.5 (bs, 8H, OC*H*$_2$CH$_2$ THF) 12.1 (bs, 4H, *p*-C*H* (PPh$_2$)), 14.5 (bs, 8H, C*H* (PPh$_2$)), 19.8 (bs, 8H, C*H* (PPh$_2$)) ppm. Anal. Calcd (%) for C$_{45}$H$_{47}$N$_2$O$_2$P$_2$NdI$_2$: C 48.79, H 4.28 N 2.53. found: C 49.17, H 4.37 N 2.45.

Synthesis of [Nd{CH(PPh$_2$NPh)$_2$}(N(SiMe$_3$)$_2$)$_2$], 4b. In THF (5 mL), KHMDS (36 mg, 0.180 mmol) was added to a solution of complex **2b** (100 mg, 0.090 mmol), resulting in an immediate precipitation of KI. After 2 h of stirring, the reaction mixture was centrifuged and the supernatant solution was dried *in vacuo*. The light green solid residue was finally washed with petroleum ether (2 × 5 mL). Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexanes into a solution of **4b** in THF at room temperature (298 K). **4b**: yield 83 mg (0.081 mmol, 90%). ^{31}P{^{1}H} NMR (121.5 MHz, [D$_8$]-THF, 20 °C): δ −118 (s, P) ppm. ^{1}H NMR (300 MHz, [D$_8$]-THF, 20 °C): δ −14.7 (bs, 8H, C*H* (PPh$_2$)), −10.3 (bs, 36H, Si(CH$_3$)$_3$), 8.3−10.5 (m, 10H, C*H* NPh), 15.2 (bs, 8H, C*H* (PPh$_2$)), 53.7 (bs, 4H, C*H* (PPh$_2$)) ppm. Anal. Calcd (%) for C$_{49}$H$_{67}$N$_2$P$_2$Si$_4$Nd: C 57.10, H 6.55 N 5.44. Found: C 57.35, H 6.61 N 5.41.

***In Situ* Generation of Bis(iminophosphoranyl)methanide Alkoxide Neodymium Complex 6a or 6b.** In the glovebox, 0.5 mL of a 0.08 M solution of 2-propanol in THF was added at room temperature in a vial to a stirred solution of **4a** (19.2 mg, 0.02 mmol) or **4b** (20.6 mg, 0.02 mmol) in THF (0.5 mL). This 0.02 M solution of putative **6a** or **6b** was used immediately in a polymerization experiment.

Polymerization of *rac*-Lactide Using 4a, 4b, 6b, or 6a. In a typical experiment, in the glovebox, a freshly prepared solution of **4a** (9.6 mg, 0.01 mmol), **4b** (10.3 mg, 0.01 mmol), **6a**, or **6b** in THF (0.5 mL) was added via a syringe to a rapidly stirred solution of *rac*-lactide (0.288 g, 2 mmol) in THF (1.5 mL) in a vial, so as to make up a solution of overall concentration in LA of 1 M. Aliquots of the reaction mixture were taken at various times and precipitated in hexanes. Solvents were removed under vacuum to leave the samples of lactide/polylactide as colorless residues. Conversions were determined by the compared integration of the methine resonances of lactide (quintuplet δ = 4.92 ppm) and polylactide (multiplet δ = 5.00−5.30 ppm) in the ^{1}H NMR spectrum in CDCl$_3$.

Polymerization of *rac*-Lactide Using 5a. In a typical experiment (Table 2, entry 1), in the glovebox, a freshly prepared solution of **5a** (11.3 mg, 0.01 mmol) in THF (0.5 mL) was added via a syringe to a rapidly stirred solution of *rac*-lactide (0.288 g, 2 mmol) in THF (1.25 mL), in a vial. After 5 min, 0.25 mL of a 0.08 M solution of 2-propanol in THF was added. The reaction mixture was stirred vigorously. Aliquots of the reaction mixture

(30) (a) Cendrowski-Guillaume, S. M.; Le Gland, G.; Nierlich, M.; Ephritikhine, M. *Organometallics* **2000**, *19*, 5654–5660. (b) Zhou, S.-L.; Wang, S.-W.; Yang, G.-S.; Liu, X.-Y.; Sheng, E.-H.; Zhang, K.-H.; Cheng, L.; Huang, Z.-X. *Polyhedron* **2003**, 1019–1024. (c) Izod, K.; Liddle, S. T.; Clegg, W. *Inorg. Chem.* **2004**, *43*, 214–218.

(31) 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*, 3100–3111.

were taken at various times and precipitated in hexanes. Solvents were removed under vacuum to leave the samples of lactide/polylactide as colorless residues. Conversions were determined by the compared integration of the methine resonances of lactide and polylactide in the ^{1}H NMR spectrum in $CDCl_3$ (see above).

X-ray Crystallography. Data were collected on a Nonius Kappa CCD diffractometer using a Mo Kα (λ = 0.71073 Å) X-ray source and a graphite monochromator. Experimental details are described in Tables S1 and S2. CCDC-751373 (**2a**), CCDC-751374 (**2b**), CCDC-751375 (**3a**), CCDC-751376 (**4a**), and CCDC-751377 (**4b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk]. The crystal structures were solved using SIR 97[32] and Shelxl-97.[33] Molecular views of X-ray structures were made using ORTEP-3[34] for Windows.

(32) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115–119.

(33) Sheldrick, G. M. *SHELXS-96*, Program for the Solution of Crystal Structures; University of Göttingen: Göttingen (Germany), 1996.

(34) Farrugia, L. J. ORTEP-3. *J. Appl. Crystallogr.* **1997**, *32*, 565.

Acknowledgment. We thank the EPSRC (EP/C544846/1 and EP/C544838/1), the CNRS, and the Ecole Polytechnique, for financial support. *rac*-Lactide was donated by Purac Plc. The EPSRC National Mass Spectrometry Service Centre, Swansea, is thanked for collecting the MALDI-ToF spectra. Dr. Florian Jaroschick is thanked for his help with neodymium precursors and helpful discussions.

Supporting Information Available: Crystallographic data for **2a**, **2b**, **3a**, **4a**, and **4b** as CIF files; tables giving crystallographic data for **2a**, **2b**, **3a**, **4a**, and **4b** (including refinement details for the X-ray structure determination); ORTEP plots (50% thermal ellipsoids) of the molecular structures of complexes **2a** and **2b** with relevant bond distances and angles; plot of PLA M_n vs % *rac*-LA conversion for **4b**; semilogarithmic plot of relative *rac*-LA concentration vs time for **4b**; MALDI-TOF mass spectrometry spectrum of PLA synthesized by ROP using **4a**; plot of M_n vs % *rac*-LA conversion for **4b**/*i*PrOH system; plot of *rac*-LA conversion vs % time for **4b**/*i*PrOH system; semilogarithmic plot of relative *rac*-LA concentration vs time for **4b**/iPrOH system; MALDI-TOF mass spectrometry spectra of PLA synthesized by ROP using the **4b**/*i*PrOH system. This material is available free of charge via the Internet at http://pubs.acs.org.