Inorganic Chemistry

ARTICLE

pubs.acs.org/IC

Group 4 Complexes of a *tert*-Butylphosphine-Bridged Biphenolate Ligand

Lan-Chang Liang,* Yu-Lin Hsu, and Sheng-Ta Lin

Department of Chemistry and Center for Nanoscience & Nanotechnology, National Sun Yat-sen University, Kaohsiung 80424, Taiwan

Supporting Information

ABSTRACT: The coordination chemistry of group 4 complexes supported by the tridentate, dianionic biphenolate phosphine ligand that carries a phosphorus-bound *tert*-butyl group, 2,2′-*tert*-butylphosphino-bis(4,6-di-*tert*-butylphenolate) ([^{t}Bu-OPO]$^{2-}$), is described. Metathetical reactions of {[^{t}Bu-OPO]Li$_2$(DME)}$_2$ with 2 or 1 equiv of TiCl$_4$(THF)$_2$ selectively produce [^{t}Bu-OPO]TiCl$_2$(THF) (**1a**) and Ti[^{t}Bu-OPO]$_2$ (**2a**), respectively. Protonolysis of Ti(O^{i}Pr)$_4$ with 2 or 1 equiv of H$_2$[^{t}Bu-OPO] cleanly generates **2a** and [^{t}Bu-OPO]Ti(O^{i}Pr)$_2$ (**3a**), respectively. Complex **1a** can alternatively be prepared from comproportionation of **2a** with 1 equiv of TiCl$_4$(THF)$_2$. Treatment of **1a** with 2 equiv of NaO^{t}Bu affords [^{t}Bu-OPO]Ti(O^{t}Bu)$_2$ (**4a**). In contrast, reactions of {[^{t}Bu-OPO]Li$_2$(DME)}$_2$ with ZrCl$_4$(THF)$_2$ or HfCl$_4$(THF)$_2$, regardless of stoichiometry of the starting materials employed, selectively give bis-ligated M[^{t}Bu-OPO]$_2$ [M = Zr (**2b**), Hf (**2c**)]. Comproportionation of **2b,c** with MCl$_4$(THF)$_2$ (M = Zr, Hf) leads to the formation of [^{t}Bu-OPO]MCl$_2$(THF) [M = Zr (**1b**), Hf (**1c**)], which, upon being treated with 2 equiv of NaO^{t}Bu, generates [^{t}Bu-OPO]M(O^{t}Bu)$_2$(THF) (**4b,c**). These synthetic results are markedly different from those obtained from analogous reactions employing a biphenolate phosphine ligand bearing a phosphorus-bound phenyl group ([Ph-OPO]$^{2-}$), highlighting a profound phosphorus substituent effect on complex conformation. The alkoxide complexes **3a** and **4a**−**c** are all active initiators for catalytic ring-opening polymerization of ε-caprolactone. To assess the potential phosphorus substituent effect on catalysis, [Ph-OPO]Ti(O^{i}Pr)$_2$ (**5a**) was prepared, and its reactivity was examined. Interestingly, polymers prepared from **3a** are characterized by low polydispersities with molecular weights that are linearly dependent on the monomer-to-initiator ratio, thus featuring a living system. The polydispersitiy indexes of polymers prepared from **5a**, however, are relatively larger, indicative of the significance of the phosphorus-bound *tert*-butyl group in **3a** in view of discouraging the undesirable transesterification.

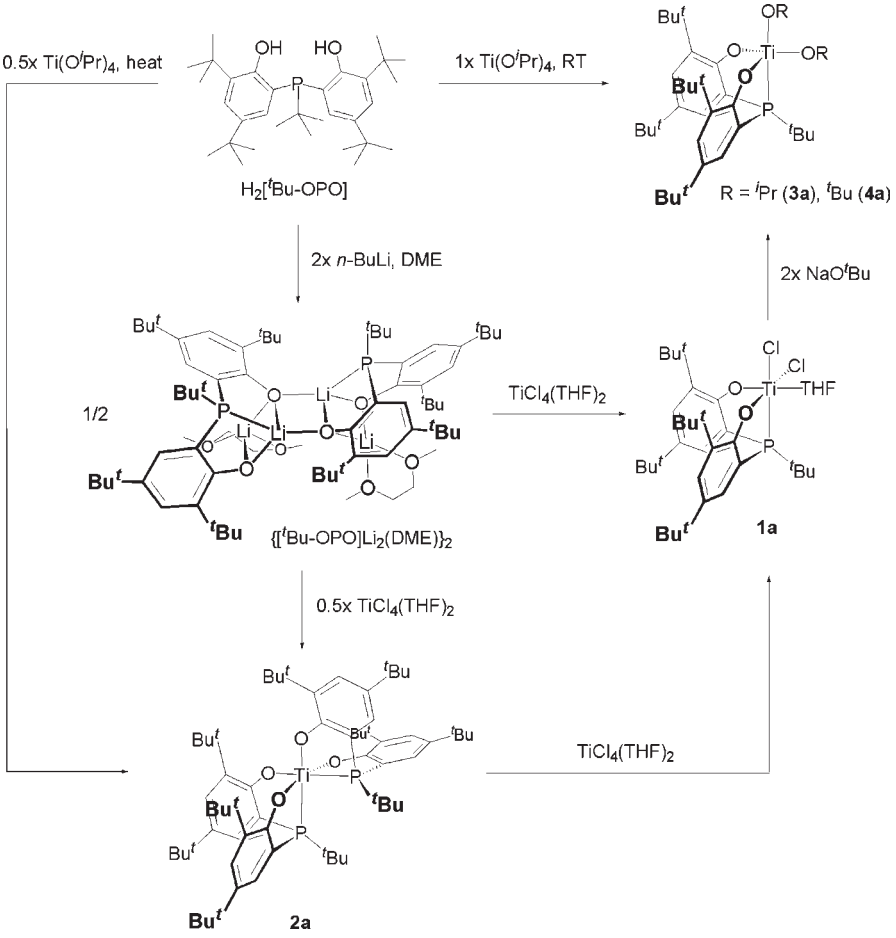
INTRODUCTION

Group 4 complexes containing chelating biphenolate ligands continue to constitute an active area of exploratory research. Much recent attention has focused on the development of homogeneous catalysts for the polymerization of α-olefins and the ring-opening polymerization (ROP) of heterocyclic molecules.[1−14] Chelating biphenolate ligands are versatile in view of the wide range of distinct aryl substituents potentially available for electronic and steric tuning. Additionally, the two phenolate rings can be either directly connected to each other in the ortho position[15−17] or bridged by a donor atom[6,17−31] or a hydrocarbon linkage.[17,23,25,32−35] As a result, a rich structural variety of biphenolato group 4 complexes has evolved. It has been shown that the reactivity of these compounds depends largely on the identity of the biphenolate linkage. For instance, the titanium complexes of the sulfide-bridged 2,2′-thiobis(6-*tert*-butyl-4-methylphenolate) ligand ([OSO]$^{2-}$) are active catalyst precursors for α-olefin polymerization,[17,24,36−38] the catalytic activity of which has been found to be higher than that of the methylene-bridged 2,2′-methylenebis(6-*tert*-butyl-4-methylphenolate) analogues.[33−35] The increased reactivity of the former has been ascribed to sulfur coordination to the electrophilic titanium center in the catalytically active species, though likely in a hemilabile fashion, thus leading to a lower activation barrier for olefin insertion than that for the latter.[24,39,40]

We are currently investigating reaction chemistry involving metal complexes of hybrid chelating ligands.[41−50] In particular, a series of groups 1, 4, 5, and 14 derivatives of the biphenolate phosphine ligand 2,2′-phenylphosphino-bis(4,6-di-*tert*-butylphenolate) ([Ph-OPO]$^{2-}$) have been prepared.[51−54] It has been demonstrated that [Ph-OPO]$^{2-}$ appears to have a strong tendency to form bis-ligated complexes with metals from groups 4 and 5.[51,52] We envisioned that such a propensity could perhaps be inhibited, at least to some degree, by replacing the phosphorus-bound phenyl group with a *tert*-butyl group; the monoligated complexes derived from the resulting complex should be more sterically demanding and less electronically deficient, thereby discouraging undesirable reactions with a second biphenolate phosphine ligand. Having this in mind, we have set out to explore the coordination chemistry of group 4 complexes involving 2,2′-*tert*-butylphosphino-bis(4,6-di-*tert*-butylphenolate) ([^{t}Bu-OPO]$^{2-}$), aiming to demonstrate that the identity of the phosphorus substituent in these biphenolate phosphine ligands plays an important role in complex conformation. The catalytic activities of these group 4 derivatives with

Received: November 1, 2010
Published: March 23, 2011

Scheme 1. Synthesis of Titanium Complexes



respect to the ROP of ε-caprolactone (ε-CL) were also investigated.

RESULTS AND DISCUSSION

Synthesis and Characterization of Titanium Complexes. It has been shown that reactions of either H_2[Ph-OPO] with $Ti(O^iPr)_4$ or Li_2[Ph-OPO] with $TiCl_4(THF)_2$ (THF = tetrahydrofuran) in a variety of solvents produce the bis-ligated Ti[Ph-OPO]$_2$ regardless of stoichiometry of the starting materials employed.[52] The intermediate [Ph-OPO]TiX_2 (X = O^{i}Pr, Cl) is presumably too electrophilic to be isolable. Interestingly, treating $TiCl_4(THF)_2$ with 0.5 equiv of $\{[^t$Bu-OPO$]Li_2$-$(DME)\}_2$[55] (DME = dimethoxyethane) in toluene at room temperature cleanly generated the monoligated [^{t}Bu-OPO]$TiCl_2$(THF) (**1a**, Scheme 1). Protonolysis of $Ti(O^iPr)_4$ with 1 equiv of $H_2[^t$Bu-OPO][55] in toluene at room temperature led exclusively to the formation of [^{t}Bu-OPO]$Ti(O^iPr)_2$ (**3a**). No bis-ligated Ti[^{t}Bu-OPO]$_2$ (**2a**, vide infra) was found in these reactions as evidenced by $^{31}P\{^1H\}$ nuclear magnetic resonance (NMR) spectra. These results clearly indicate a profound phosphorus substituent effect in these biphenolate phosphine ligands on titanium complex conformation and corroborate the postulate that the more electron-releasing and sterically demanding *tert*-butyl group in $[^t$Bu-OPO$]^{2-}$ effectively stabilizes the monoligated compounds **1a** and **3a**. Both **1a** and **3a** are stable for days in solutions, even at elevated temperatures (e.g., 100 °C); no sign of either decomposition or **2a** formation was found, as indicated by $^{31}P\{^1H\}$ NMR spectroscopy.

Attempts to prepare organotitanium complexes of $[^t$Bu-OPO$]^{2-}$ by alkylation of **1a** with either alkyl lithium or Grignard reagents were not successful. Although $^{31}P\{^1H\}$ NMR spectra of these reaction aliquots suggested clean conversion for all alkylations attempted, the products were rather intractable, and thus, no well-defined mono- or dialkyl complexes could be isolated. In contrast, addition of 2 equiv of NaO^{t}Bu to a diethyl ether solution of **1a** produced [^{t}Bu-OPO]$Ti(O^tBu)_2$ (**4a**) in 65% isolated yield. Similar reactions employinzg the phosphorus-bound phenyl-derived [Ph-OPO]$TiCl_2$(THF)[52] and NaO^{i}Pr generated [Ph-OPO]Ti-$(O^iPr)_2$ (**5a**) in 73% yield, but attempts to prepare [Ph-OPO]$Ti(O^tBu)_2$ (**6a**) led unfortunately to intractable materials. Although isolable, the *tert*-butoxide **4a** gradually disproportionated upon mild heating in solutions over a few hours to give **2a** and $Ti(O^tBu)_4$ and ultimately reached an equilibrium (eq 1) as indicated by ^1H and $^{31}P\{^1H\}$ NMR studies. The equilibrium was investigated over a temperature range of 60−100 °C, leading to a van't Hoff plot (Figure S1, see Supporting Information) and a value for the standard enthalpy of reaction ($\Delta H°$) of −1.31(4) kcal/mol. The isopropoxide **5a**, on the other hand, was found to be thermally robust (100 °C). These results are surprising, as the *tert*-butoxide complexes **4a**

dx.doi.org/10.1021/ic102194z |*Inorg. Chem.* 2011, 50, 3363–3372

and **6a** are close higher homologues of their isopropoxide counterparts **3a** and **5a**, respectively.

$$2(\mathbf{4a}) \rightleftharpoons \mathbf{2a} + \mathrm{Ti}(\mathrm{O}^t\mathrm{Bu})_4 \qquad (1)$$

The homoleptic **2a** could be prepared cleanly by treating toluene solutions of either $\{[^t\text{Bu-OPO}]\mathrm{Li}_2(\mathrm{DME})\}_2$[55] with 1 equiv of $\mathrm{TiCl}_4(\mathrm{THF})_2$ or $\mathrm{H}_2[^t\text{Bu-OPO}]$[55] with 0.5 equiv of $\mathrm{Ti}(\mathrm{O}^i\mathrm{Pr})_4$. Note that heating is necessary for the latter strategy, or the reaction at room temperature would give equimolar **3a** and $\mathrm{H}_2[^t\text{Bu-OPO}]$ even after several days (^{31}P NMR evidence). Interestingly, comproportionation of **2a** with 1 equiv of $\mathrm{TiCl}_4(\mathrm{THF})_2$ cleanly afforded **1a** at room temperature in 1 h, whereas no reaction was found for **2a** with $\mathrm{Ti}(\mathrm{O}^i\mathrm{Pr})_4$, even at elevated temperatures (100 °C, 12 h).

Attempts to prepare well-defined trivalent titanium complexes of $[^t\text{Bu-OPO}]^{2-}$ were not successful. Reduction of **1a** with sodium amalgam gave intractable materials. Treating toluene solutions of $\{[^t\text{Bu-OPO}]\mathrm{Li}_2(\mathrm{DME})\}_2$[55] with either 1 or 2 equiv of TiCl_3 led immediately to the formation of an orange solution, the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum of which indicated the presence of **2a**. Some redox processes apparently occur rapidly in these reactions. After standard workup, orange prisms of **2a** suitable for X-ray diffraction analysis were grown from a concentrated DME solution at −35 °C. Figure 1 illustrates the molecular structure. Selected bond distances and angles are summarized in Table 1. As anticipated in view of the inherent pyramidal geometry for a phosphorus donor, the $[^t\text{Bu-OPO}]^{2-}$ ligands adopt a facial coordination mode. The structure is C_2-symmetric, with the two phosphorus donors being approximately cis to each other in a distorted octahedral core structure. The C_2 axis lies approximately on the mean P1−O2A−O2−P1A plane and bisects the P−Ti−P angle. The trans-disposed O−Ti−P orientation is in line with the anticipated trans influence trend of these donor atoms. These phenomena are reminiscent of what was found for $\mathrm{Ti}[\text{Ph-OPO}]_2$.[52] In accordance with the steric sizes of the mutually cis-disposed phosphorus substituents involved, the P−Ti−P angle of 107.67(6)° in **2a** is much wider than that in $\mathrm{Ti}[\text{Ph-OPO}]_2$ [89.93(4)°].[52] The Ti−P lengths of 2.670(1) Å in **2a** are also significantly longer than those in $\mathrm{Ti}[\text{Ph-OPO}]_2$ [2.5422(13) and 2.5599(13) Å].[52] Nevertheless, the Ti−P lengths of **2a** are notably shorter than the Ti−S distances of $\mathrm{Ti}[\mathrm{OSO}]_2$ (2.765 Å average),[24] a result that is somewhat surprising in view of the relatively larger atomic size and lower hardness of the phosphorus donor than sulfur, but likely indicative of a stronger chemical bonding for the former to bind hard titanium(IV) than the latter. Such enhanced interaction between titanium and the phosphorus donor, as compared to the sulfur in the biphenolate complexes, is beneficial in view of the decreased insertion barrier for catalytic α-olefin polymerization, as suggested by computational studies.[39,40] The Ti−O distances of **2a** are well within the expected values for six-coordinate titanium phenolate complexes and comparable to those of $\mathrm{Ti}[\text{Ph-OPO}]_2$ (1.896 Å average),[52] $\mathrm{TiCl}_2(\text{2-OC}_6\mathrm{H}_4\mathrm{PPh}_2)_2$ (1.854 Å average),[56] $\mathrm{Ti(OPr)}_2[(\text{2-O-3,5-Cl}_2\mathrm{C}_6\mathrm{H}_2)\mathrm{CH}_2\mathrm{N(Me)CH}_2\mathrm{CH}_2\mathrm{N(Me)CH}_2\text{-(2-O-3,5-Cl}_2\mathrm{C}_6\mathrm{H}_2)]$ (1.911 Å average),[21] and $\{(^i\mathrm{PrO})_2\mathrm{Ti}(\mu^3\text{-O})\mathrm{TiCl}(^i\mathrm{PrO})[(\text{2-OC}_6\mathrm{H}_4)_2\mathrm{PPh}]\}_2$ (2.044 Å average).[57]

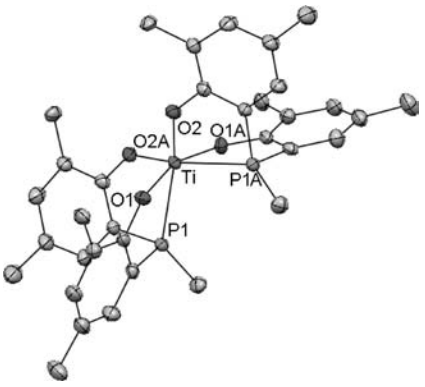


Figure 1. Molecular structure of **2a** with thermal ellipsoids drawn at the 35% probability level. All methyl groups in *tert*-butyl are omitted for clarity.

The solution structures of these derived titanium complexes were all characterized by multinuclear NMR spectroscopy. Consistent with its X-ray structure, the homoleptic **2a** is C_2-symmetric in solution at room temperature on the NMR time scale. The ^{1}H NMR spectrum revealed four well-resolved singlet resonances for the aryl *tert*-butyl groups and one doublet for the *tert*-butylphosphine bridge. A variable-temperature ^{1}H NMR study (in toluene-d_8) indicated that the four singlet resonances do not tend to coalesce upon heating to 90 °C, suggesting that both soft phosphorus donors in **2a** likely remain bound to the hard, six-coordinate, tetravalent titanium center even at elevated temperatures. The two phosphorus donors are cis-disposed to each other, as evidenced by the doublet of doublets, rather than virtual triplet, resonances observed for some aromatic carbons in the $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectra. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum exhibits a singlet resonance at 19 ppm, a value that is shifted relatively upfield as compared to that of $\mathrm{Ti}[\text{Ph-OPO}]_2$ (20 ppm).

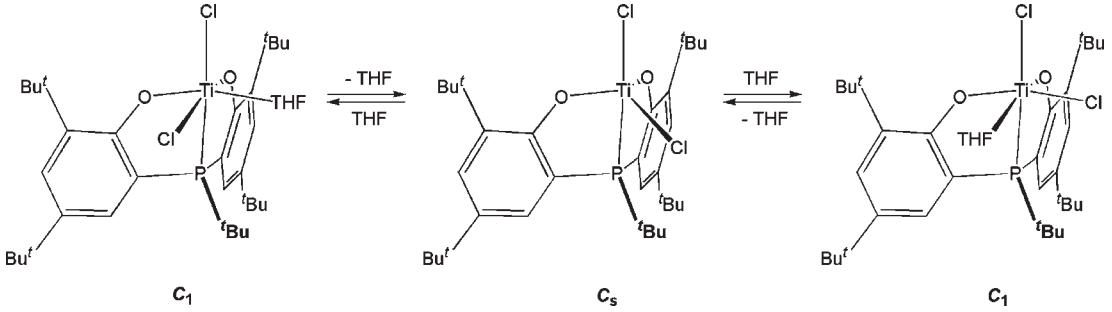
The solution NMR data of **1a** at room temperature are all consistent with time-averaged C_s symmetry. The ^{1}H NMR spectrum exhibited 1 equiv of coordinated THF per $[^t\text{Bu-OPO}]^{2-}$ ligand. The α- and β-CH_2 moieties of the titanium-bound THF were observed as two broad resonances in C_6D_6 at 4.01 and 1.30 ppm, respectively. In the presence of an excess amount (e.g., 6 equiv) of THF, solutions of **1a** exhibited only one set of resonances for the THF protons, a result that is ascribed to a facile exchange process between the coordinated and free THF molecules. The coordinated THF in **1a** is thus presumably labile and tends to dissociate from the titanium center. Interestingly, a variable-temperature ^{1}H NMR study (toluene-d_8) revealed two poorly resolved resonances with equal intensity at 4.2 and 4.1 ppm for the α-CH_2 groups of the coordinated THF at −70 °C, reflecting the diastereotopic nature of the α-CH_AH_B moieties at low temperatures. The four aryl *tert*-butyl groups in **1a** were observed as four well-resolved singlet resonances at −70 °C but two sharp singlet resonances at temperatures higher than −20 °C, consistent with a fluxional exchange between

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for 2a

O(1)−Ti	1.896(3)	O(2)−Ti	1.857(3)	P(1)−Ti	2.670(1)
O(2)−Ti−O(2A)	106.5(2)	O(1)−Ti−O(1A)	158.8(2)	O(2)−Ti−P(1)	164.88(9)
O(2)−Ti−O(1)	92.8(1)	O(1)−Ti−P(1)	72.20(8)	O(2A)−Ti−P(1)	74.98(9)
O(2A)−Ti−O(1)	99.8(1)	O(1)−Ti−P(1A)	95.09(9)	P(1A)−Ti−P(1)	107.67(6)

dx.doi.org/10.1021/ic102194z |*Inorg. Chem.* 2011, 50, 3363–3372

Scheme 2. Proposed Fluxional Exchange Mechanism



molecules that are C_1- and C_s-symmetric. These results suggest that the coordinated THF in the static structure of **1a** cannot be trans to the phosphorus donor, assuming that the core geometry of **1a** is octahedral. Scheme 2 illustrates a plausible mechanism for this fluxional process on the basis of the labile nature of the coordinated THF, in which the THF likely dissociates from the six-coordinate titanium center, thereby generating a five-coordinate, trigonal-bipyramidal [^{t}Bu-OPO]TiCl$_2$, followed by recoordination of the freed THF molecule. A similar phenomenon was also found for [Ph-OPO]TiCl$_2$(THF),[52] although at a lower exchange rate, consistent with the less electron-deficient nature of the titanium center in **1a**. The phosphorus donor of [^{t}Bu-OPO]$^{2-}$ in **1a** was observed as a singlet resonance at 27 ppm in the ^{31}P{^{1}H} NMR spectrum.

The solution structures of five-coordinate **3a**, **4a**, and **5a** were all found to be C_s symmetric on the NMR time scale. In these cases, the aryl *tert*-butyl groups were observed as two distinct singlet resonances in the ^{1}H NMR spectra. In contrast to the dichloride **1a** and [Ph-OPO]TiCl$_2$(THF),[52] these alkoxide complexes do not coordinate THF. The ^{1}H NMR spectra of **3a**−**5a** exhibited two sets of well-resolved resonances for the alkoxide ligands, consistent with a trigonal-bipyramidal geometry for these molecules where [^{t}Bu-OPO]$^{2-}$ adopts a facial coordination mode. Variable-temperature ^{1}H NMR studies of **3a** and **5a** (in toluene-d_8) revealed that resonances for isopropoxide ligands do not tend to coalesce even at 80 °C. Interestingly, the quaternary carbon in axial *tert*-butoxide ligand of **4a** displayed a doublet resonance at 83.1 ppm with $^3J_{CP}$ = 4.7 Hz in the ^{13}C{^{1}H} NMR spectrum, thus confirming the coordination of the trans-disposed phosphorus donor. The phosphorus donors in **3a** and **4a** resonated at ca. 6 and 7 ppm, respectively, whereas that of **5a** resonated at −2 ppm.

Attempts to grow X-ray-quality crystals of these dialkoxide complexes were not successful. To better probe the coordination parameters of these compounds, we performed DFT computations on **3a** and **5a**. Consistent with the NMR studies, DFT geometry optimization revealed a trigonal-bipyramidal structure[58] for these species with the biphenolate phosphine ligands being in a facial coordination mode. Although all bond lengths and angles are well within the expected values (see Supporting Information), the Ti−P distance in **3a** (2.64 Å) is significantly shorter than that in **5a** (2.87 Å), consistent with the anticipated electron-releasing property for a *tert*-butyl group in the former.

Synthesis and Characterization of Zirconium and Hafnium Complexes. In contrast to what was found for titanium, reactions of {[^{t}Bu-OPO]Li$_2$(DME)}$_2$[55] with ZrCl$_4$(THF)$_2$ or HfCl$_4$(THF)$_2$, irrespective of the molar ratio, generated bis-ligated M[^{t}Bu-OPO]$_2$ [M = Zr (**2b**), Hf (**2c**)] selectively (Scheme 3); no desired monoligated complexes were detected by ^{31}P{^{1}H} NMR spectroscopy of the reaction aliquots. The discrepancy in titanium chemistry and its heavier congeners is ascribed to the larger atomic sizes for the latter. Nevertheless, these results are interesting in comparison with those involving [Ph-OPO]$^{2-}$ that led instead to intractable products under similar conditions.[52] The bis-ligated M[Ph-OPO]$_2$ (M = Zr, Hf), prepared by treating H$_2$[Ph-OPO] with [(Me$_3$Si)$_2$N]$_2$MCl$_2$, could be isolated only as an aqua adduct in which both zirconium and hafnium are seven-coordinate.[52] With the coordination of the more electron-releasing and sterically larger *tert*-butyl-substituted phosphorus donors, neither **2b** nor **2c** was found to be associative with strong coordinating solvents such as Et$_2$O, THF, or DME on the basis of NMR studies. Reminiscent of those of **2a**, solution NMR data of **2b** and **2c** at room temperature are all consistent with C_2 symmetry, with the aryl *tert*-butyl groups appearing as four distinct singlet resonances and the *tert*-butylphosphine bridge as one doublet in the ^{1}H NMR spectrum. In six-coordinate **2b,c**, the two phosphorus donors are also cis-disposed, as evidenced by doublet of doublets resonances observed for some aromatic carbons in the ^{13}C{^{1}H} NMR spectra. The phosphorus donors resonated at −7 ppm for **2b** and −3 ppm for **2c**, both being relatively upfield shifted as compared to **2a**.

Comproportionation of **2b,c** with MCl$_4$(THF)$_2$ (M = Zr and Hf) proved to be an effective strategy for preparing [^{t}Bu-OPO]MCl$_2$(THF) [M = Zr (**1b**), Hf (**1c**)]. In contrast to the behavior of **1a**, heating appeared necessary to expedite the formation of both **1b** and **1c**; no reaction proceeded at all at room temperature in 12 h as evidenced by ^{31}P{^{1}H} NMR spectroscopy, reflecting the stronger metal−ligands bond strengths in **2** for M = Zr and Hf than for M = Ti. Subsequent metathetical reactions of **1b,c** with 2 equiv of NaO^{t}Bu generated [^{t}Bu-OPO]M(O^{t}Bu)$_2$(THF) [M = Zr (**4b**), Hf (**4c**)]. In accordance with the relatively larger atomic sizes of these heavier metals, both **4b** and **4c** adopt one more coordinated THF molecule than **4a**. Unlike **4a**, both **4b** and **4c** are thermally stable in toluene solutions at 100 °C for days, likely as a consequence of the lower steric congestion for the latter than the former. On the basis of variable-temperature ^{1}H NMR studies, the solution structure and fluxionality of **1b,c** and **4b,c** are proposed to be similar to that of **1a** (Scheme 2).

Catalysis. Alkoxide complexes of group 4 metals are known to be active initiators for catalytic the ROP of heterocyclic molecules.[4,6,7,10,59−63] The catalytic activities of **3a**, **4a**−**c**, and **5a** with ε-CL were examined in this regard. In general, these alkoxides are all active, producing poly(ε-caprolactone) (PCL) effectively under the conditions employed. Gel permeation chromatography

dx.doi.org/10.1021/ic102194z |*Inorg. Chem.* 2011, 50, 3363–3372

Scheme 3. Synthesis of Zirconium and Hafnium Complexes

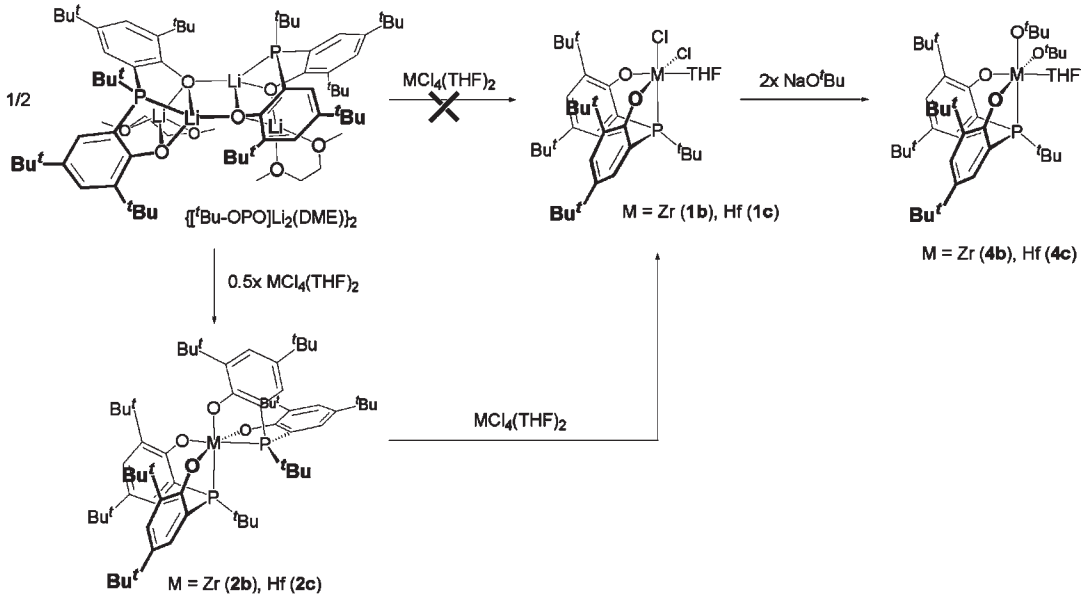


Table 2. Polymerization of ε-CL[a]

entry	$[\varepsilon\text{-CL}]_0/[I]_0$	I	conv[b] (%)	M_n (kg mol^{-1}) calcd[c]	exp[d]	corrected exp[e]	PDI[d]
1	50	**3a**	100	5.7	8.9	5.0	1.14
2	100	**3a**	100	11.4	12.0	6.7	1.17
3	150	**3a**	100	17.1	16.8	9.4	1.21
4	200	**3a**	100	22.8	21.9	12.3	1.12
5	250	**3a**	100	28.5	25.4	14.2	1.18
6	300	**3a**	100	34.2	29.3	16.4	1.08
7	100	**4a**	81	9.2	31.7	17.8	1.16
8	100	**4b**	100	11.4	46.7	26.2	1.67
9	100	**4c**	100	11.4	26.1	14.6	1.56
10	100	**5a**	100	11.4	7.6	4.3	1.45
11	200	**5a**	100	22.8	23.6	13.2	1.51
12	100	**2a**	4	0.5			
13	100	$Ti(O^tBu)_4$	27	3.1	7.5	4.2	1.92

[a] Conditions: $[I]_0$ = 1.5 mM, toluene, 80 °C, 3 h; these parameters were not optimized except for entry 6.[64] [b] Determined by ^{1}H NMR analysis. [c] Calculated from fw of ε-CL x ($[\varepsilon\text{-CL}]_0/[I]_0$) × conversion, assuming one propagation chain per group 4 atom. [d] Measured by GPC in THF, calibrated with polystyrene standards. [e] Multiplied by a factor of 0.56.[65,66]

(GPC) analyses revealed a monomodal trace for each polymeric product. Table 2 summarizes the polymerization results and characterization data.

Remarkably, compound **3a** was found to be quite reactive, converting 300 equiv of ε-CL quantitatively to give PCL with a polydispersity index (PDI) of 1.08. The low PDI value implies that the identity of the catalytically active species in this system is likely uniform. Interestingly, the measured M_n values were approximately proportional to the monomer-to-initiator ratios (Figure 2), indicating that the propagating chains grew at a

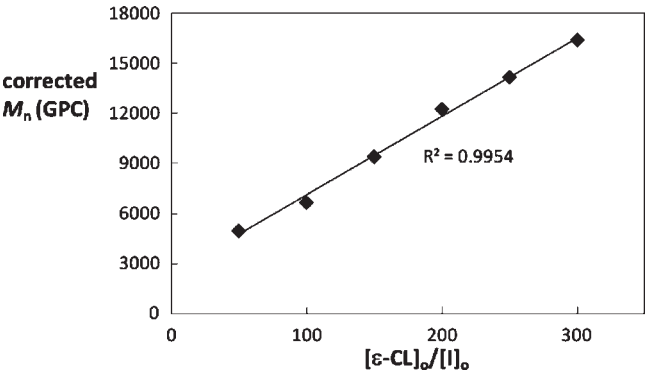


Figure 2. Plot of M_n (corrected) versus monomer-to-initiator ratio (entries 1−6 in Table 2).

nearly constant rate. Collectively, this polymerization system is thus living. End-group analyses of the isolated PCLs by ^{1}H NMR spectroscopy (Figure 3) revealed the presence of one isopropyl ester group (δ 5.00 for methine and δ 1.23 for methyl) per PCL chain, as evidenced by the relative integral ratio to the hydroxyl methylene end group (3.65 ppm), irrespective of the number of intervening repeat units. These results suggest that the initiation step occurs with insertion of the coordinated monomer into the Ti−O^{i}Pr bond. Subsequent cleavage of the acyl-oxygen bond then ring-opens the monomer and regenerates a new, reactive titanium alkoxide intermediate for chain propagation. A coordination−insertion mechanism is thus operating in this system. A ^{1}H NMR NOE difference experiment for the first ring-opening product [^{t}Bu-OPO]Ti(O^{i}Pr)-(O(CH$_2$)$_5$C(O)O^{i}Pr) (Figure 4) revealed NOE contacts between the phosphorus-bound *tert*-butyl group and the methylene groups α and β to the alkoxide oxygen. In contrast, no enhancement was found for the axial isopropoxide resonances in the same NOE experiment, suggesting that the equatorial O^{i}Pr in **3a** is exclusively involved in the initiation step. Upon acidic workup, the

dx.doi.org/10.1021/ic102194z |*Inorg. Chem.* 2011, 50, 3363–3372

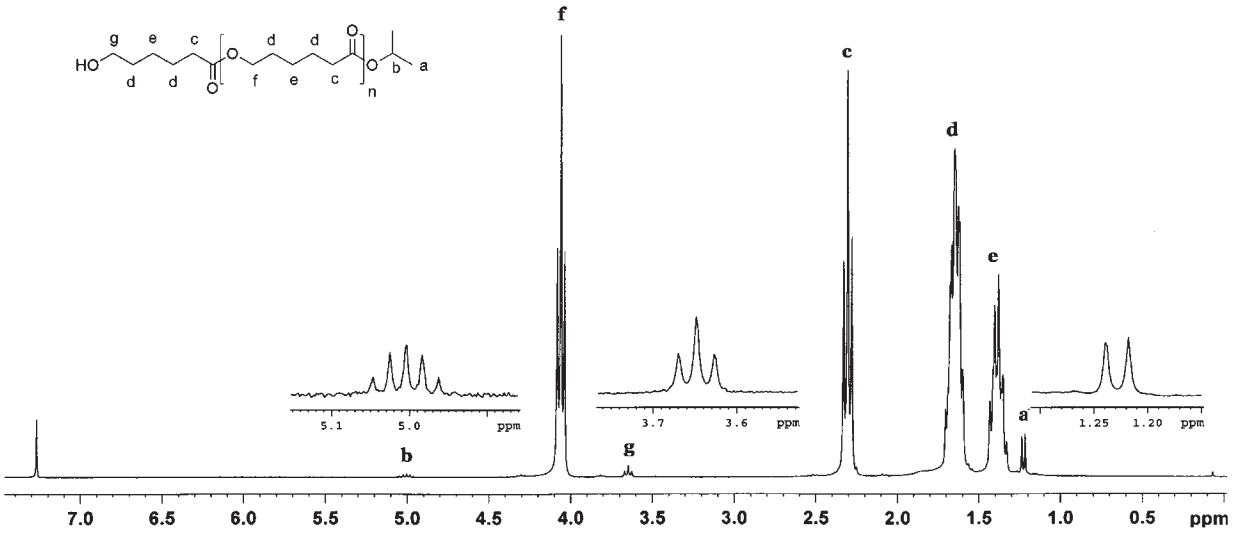


Figure 3. ^{1}H NMR spectrum of PCL (in $CDCl_3$, 300 MHz) prepared by catalytic **3a**.

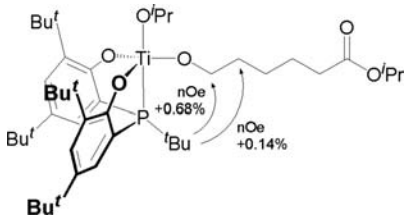


Figure 4. Selected NOE enhancement results.

titanium alkoxide chain end is protonated to give the hydroxyl end group.

In comparison, the monomer conversion by catalytic **4a** was lower (81%, entry 7), and the measured M_n value was much larger than expected, implying that only a portion of the **4a** was involved in ROP of ε-CL. Coincidentally, the monomer conversion found was consistent with the percentage of **4a** remaining (80.5%) in solution upon thermolysis at 80 °C (eq 1). To corroborate the ROP efficiency of **4a**, the activities of **2a** and $Ti(O^tBu)_4$ were also examined (entries 12 and 13). Apparently, both **2a** and $Ti(O^tBu)_4$ react with ε-CL at much lower rates than **4a**. The much lower monomer conversions and higher PDI values found for reactions employing **2a** and $Ti(O^tBu)_4$ also imply that the effects of these compounds, although present as minor components at equilibrium, on the ROP activity of **4a** cannot be significant. The fact that the reaction rate of **4a** is much lower than that of **3a** is ascribed to the larger steric size of the *tert*-butoxide ligands in the former that retards the initiation rate. Nevertheless, the PDI value of PCL obtained from **4a** remained lower than 1.2. When the zirconium- and hafnium-derived complexes **4b** and **4c** were used, the monomer conversions were quantitative at the expense of comparatively larger PDIs of ca. 1.6, indicating that transesterification takes place more frequently at these larger, heavier group 4 metals.

It is interesting to compare polymerization results derived from catalytic **3a** and **5a**. Although quantitative monomer conversions were found for **5a** (entries 10 and 11), the relatively larger PDIs of ca. 1.5 suggest the occurrence of transesterification. The identity of phosphorus substituents thus apparently has a significant effect on the propensity of this undesirable side reaction. The relatively shorter Ti—P distance of **3a** that contains a bulky *tert*-butyl group appears beneficial to sterically diminish the probability of transesterification. The electron-releasing property of the *tert*-butyl group in **3a**, on the other hand, might also electronically decrease the activation barrier for ε-CL insertion. With the longer Ti—P distance and the less electron-releasing phenyl substituent, **5a** is thus comparatively prone to transesterification.

CONCLUSIONS

We have prepared and characterized a series of group 4 complexes supported by the tridentate biphenolate phosphine ligand $[^t$Bu-OPO$]^{2-}$ that carries a *tert*-butyl group at the phosphorus donor. The synthetic chemistry described herein is markedly different from that derived from the analogous ligand bearing a phenylphosphine bridge. This discrepancy clearly underlines a profound phosphorus substituent effect on complex conformation. In particular, the preparation of mono-[R-OPO]$^{2-}$-ligated complexes is efficiently facilitated with R = ^{t}Bu because of its more sterically demanding and electronically releasing nature. Despite the incorporation of a sterically demanding *tert*-butyl substituent, the Ti—P distances in **2a** are shorter than the Ti—S distances in $Ti[OSO]_2$, suggesting somewhat stronger chemical bonding for the soft phosphorus donor in the former to bind the hard tetravalent titanium than for sulfur in the latter.[24,59] A number of alkoxide complexes, namely, **3a**, **4a**—**c**, and **5a**, were prepared. These compounds are active initiators for the catalytic ROP of ε-CL. Remarkably, the catalytic ROP initiated by **3a** is living, producing PCLs with anticipated molecular weights and narrow molecular weight distributions. In contrast, polymers prepared using **4b**,**c** and **5a** are characterized by wider molecular weight distributions, indicating the occurrence of undesirable transesterification. The identity of the phosphorus substituents (**3a** versus **5a**) thus also plays an important role in ROP catalysis.

EXPERIMENTAL SECTION

General Procedures. Unless otherwise specified, all experiments were performed under nitrogen using standard Schlenk or glovebox

techniques. All solvents were reagent grade or better and were purified by standard methods. The NMR spectra were recorded on a Varian Unity or Bruker AV instrument. Chemical shifts (δ) are listed as parts per million downfield from tetramethylsilane, and coupling constants (J) and peak widths at half-height ($\Delta\nu_{1/2}$) are in hertz. ^{1}H NMR spectra are referenced using the residual solvent peak at δ 7.16 for C_6D_6. ^{13}C NMR spectra are referenced using the internal solvent peak at δ 128.39 for C_6D_6. The assignment of the carbon atoms is based on the DEPT ^{13}C NMR spectroscopy. ^{31}P NMR spectra are referenced externally using 85% H_3PO_4 at δ 0. Routine coupling constants are not listed. All NMR spectra were recorded at room temperature in specified solvents unless otherwise noted. Elemental analysis was performed on a Heraeus CHN-O rapid analyzer. With multiple attempts, we were not able to obtain satisfactory analysis for some complexes reported herein, likely because of incomplete combustion of the samples examined.

GPC analyses were carried out at 45 °C on a JASCO instrument equipped with two Waters Styragel HR columns in series and a JASCO RI-2031 refractive index detector. HPLC-grade THF was supplied at a constant flow rate of 1.0 mL/min with a JASCO PU-2080 isocratic HPLC Pump. Molecular weights (M_n and M_w) were determined by interpolation from calibration plots established with polystyrene standards.

Materials. Compounds $MCl_4(THF)_2$[67] (M = Ti, Zr, Hf), $H_2[^t$Bu-OPO], [55] $\{[^t$Bu-OPO]$Li_2(DME)\}_2$, [55] and [Ph-OPO]$TiCl_2(THF)$ [52] were prepared according to the literature procedures. NaO^{i}Pr was prepared by deprotonation of HO^{i}Pr with an excess amount of NaH in THF, followed by filtration. ε-CL was dried over CaH_2 (1 wt %) at 80 °C for 0.5 h and distilled under reduced pressure. All other chemicals were obtained from commercial vendors and used as received.

DFT Computations. The Gaussian 03 suite of programs was employed in this study.[68] The three-parameter hybrid of exact exchange and Becke's exchange energy functional[69] and Lee−Yang−Parr's gradient-corrected correlation energy functional[70] (B3LYP) were used. All optimized structures were verified to be genuine minima on the potential energy surface through vibrational frequency analysis. The 6-31G(d) basis sets were used for all atoms.

Synthesis of 1a. Method 1: To a toluene suspension (1 mL) of $TiCl_4(THF)_2$ (111 mg, 0.333 mmol) at room temperature was added a toluene solution (4 mL) of $\{[^t$Bu-OPO]$Li_2(DME)\}_2$ (200 mg, 0.167 mmol). The reaction solution was stirred at room temperature for 1 h and filtered through a pad of Celite. All volatiles were revmoved in vacuo. The solid residue was dissovled in DME (1 mL). Cooling the DME solution to −35 °C afforded the product as a brownish red solid; yield 204 mg (89%). **Method 2:** To a toluene suspension (0.5 mL) of $TiCl_4(THF)_2$ (4.8 mg, 0.014 mmol) at room temperature was added a toluene solution (0.5 mL) of **2a** (15 mg, 0.014 mmol). The reaction progress was monitored by ^{31}P{^{1}H} NMR spectroscopy, which showed quantitative formation of **1a** in 1 h at room temperature. The reacction solution was filtered through a pad of Celite and evaported to dryness under reduced pressure to give the product as a brownish red solid; yield 7.7 mg (80%). ^{1}H NMR (C_6D_6, 500 MHz) δ 7.61 (dd, 2, $^3J_{HP}$ = 6.0, $^4J_{HH}$ = 2.0, ArH), 7.45 (d, 2, $^4J_{HH}$ = 2.0, ArH), 4.01 (br s, 4, OCH_2CH$_2$), 1.52 (s, 18, ArCMe_3), 1.47 (d, 9, $^3J_{HP}$ = 16.0, PCMe_3), 1.30 (br m, 4, OCH$_2$CH_2), 1.19 (s, 18, ArCMe_3). ^{13}C{^{1}H} NMR (C_6D_6, 125.7 MHz) δ 168.95 (s, C), 168.74 (s, C), 145.87 (d, J_{CP} = 4.53, C), 137.11 (d, J_{CP} = 4.65 C), 128.30 (s, CH), 127.47 (d, J_{CP} = 1.89, CH), 73.01 (br s, OCH$_2$CH$_2$), 35.95 (s, ArCMe$_3$), 35.00 (s, ArCMe$_3$), 34.68 (d, J_{CP} = 12.82, PCMe$_3$), 31.87 (s, ArCMe_3), 30.18 (s, ArCMe_3), 28.76 (d, J_{CP} = 5.53, PCMe_3), 25.63 (s, OCH$_2$CH$_2$). ^{31}P NMR (C_6D_6, 202.3 MHz) δ 27.49 ($\Delta\nu_{1/2}$ = 81). Anal. Calcd for $C_{36}H_{57}Cl_2O_3PTi$: C, 62.87; H, 8.36. Found: C, 63.00; H, 8.25.

Synthesis of 1b. To a toluene suspension (3 mL) of $ZrCl_4(THF)_2$ (42 mg, 0.11 mmol) at room temperature was added a toluene solution (3 mL) of **2b** (120 mg, 0.11 mmol). The reaction mixture was heated to 80 °C in an oil bath for 4 h. After the mixture had been cooled to room temperature, all insoluble materials were removed by filtration through a pad of Celite. Evaporation of the filtrate under reduced pressure to dryness gave an off-white residue, which was washed with pentane (0.5 mL × 3) and dried in vacuo to give the product as an off-white solid; yield 112 mg (70%). ^{1}H NMR (C_6D_6, 500 MHz) δ 7.69 (dd, 2, $^3J_{HP}$ = 6.0, $^4J_{HH}$ = 2.0, ArH), 7.45 (d, 2, $^4J_{HH}$ = 2.0, ArH), 4.04 (br s, 4, OCH_2CH$_2$), 1.54 (d, 9, $^3J_{HP}$ = 15.5, PCMe_3), 1.53 (s, 18, ArCMe_3), 1.24 (s, 18, ArCMe_3), 1.14 (br s, 4, OCH$_2$CH_2). ^{13}C{^{1}H} NMR (C_6D_6, 125.7 MHz) δ 165.21 (d, J_{CP} = 24.26, C), 143.63 (d, J_{CP} = 4.53, C), 137.98 (d, J_{CP} = 5.03, C), 128.06 (s, C), 127.52 (s, CH), 126.99 (d, J_{CP} = 1.89, CH), 74.36 (br s, OCH$_2$CH$_2$), 35.92 (d, J_{CP} = 1.38, ArCMe$_3$), 34.92 (s, ArCMe$_3$), 32.70 (d, J_{CP} = 13.70, PCMe$_3$), 32.03 (s, ArCMe_3), 30.18 (s, ArCMe_3), 29.66 (d, J_{CP} = 8.30, PCMe_3), 25.34 (s, OCH$_2$CH$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.3 MHz) δ 3.39.

Synthesis of 1c. To a toluene suspension (3 mL) of $HfCl_4(THF)_2$ (52 mg, 0.11 mmol) at room temperature was added a toluene solution (3 mL) of **2c** (130 mg, 0.11 mmol). The reaction mixture was heated to 80 °C in an oil bath for 4 h. After the mixture had been cooled to room temperature, all insoluble materials were removed by filtration through a pad of Celite. Evaporation of the filtrate under reduced pressure to dryness gave an off-white residue, which was washed with pentane (0.5 mL × 3) and dried in vacuo to give the product as an off-white solid; yield 116 mg (64%). ^{1}H NMR (C_6D_6, 500 MHz) δ 7.70 (dd, 2, $^3J_{HP}$ = 6.0, $^4J_{HH}$ = 2.5, ArH), 7.48 (d, 2, $^4J_{HH}$ = 2.0, ArH), 4.03 (br s, 4, OCH_2CH$_2$), 1.54 (s, 18, ArCMe_3), 1.54 (d, 9, $^3J_{HP}$ = 16.0, PCMe_3), 1.25 (s, 18, ArCMe_3), 1.12 (br s, 4, OCH$_2$CH_2). ^{13}C{^{1}H} NMR (C_6D_6, 125.7 MHz) δ 165.34 (d, J_{CP} = 22.37, C), 143.22 (d, J_{CP} = 4.65, C), 138.90 (d, J_{CP} = 4.65, C), 127.61 (d, J_{CP} = 0.88, CH), 127.31 (d, J_{CP} = 32.56, C), 127.01 (d, J_{CP} = 1.38, CH), 75.12 (br s, OCH$_2$CH$_2$), 35.87 (d, J_{CP} = 1.89, ArCMe$_3$), 34.87 (s, ArCMe$_3$), 32.81 (d, J_{CP} = 15.46, PCMe$_3$), 32.07 (s, ArCMe_3), 30.19 (s, ArCMe_3), 29.68 (d, J_{CP} = 7.79, PCMe_3), 25.39 (s, OCH$_2$CH$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.3 MHz) δ 4.50.

Synthesis of 2a. Method 1: To a toluene solution (1 mL) of $TiCl_4(THF)_2$ (40.0 mg, 0.12 mmol) at room temperature was added a toluene solution (4 mL) of $\{[^t$Bu-OPO]$Li_2(DME)\}_2$ (150 mg, 0.12 mmol). The reaction solution was stirred at room temperature for 1 h and filtered through a pad of Celite. All volatiles were removed in vacuo. DME (1 mL) was added. The DME solution was cooled to −35 °C to give the product as an orange solid; yield 94 mg (75%). **Method 2:** A toluene solution containing Ti(O^{i}Pr)$_4$ (4 mg, 0.015 mmol) and $H_2[^t$Bu-OPO] (15 mg, 0.03 mmol) was loaded into a Teflon-sealed J. Young NMR tube. The reaction solution was heated to 80 °C in an oil bath and the reaction progress was monitored by ^{31}P{^{1}H} NMR spectroscopy, which showed slow but clean formation of **2a** (70% yield, 60 h). **Method 3:** To a toluene solution (1 mL) of $TiCl_3$ (19 mg, 0.12 mmol) at room temperature was added a toluene solution (4 mL) of $\{[^t$Bu-OPO]Li_2-$(DME)\}_2$ (150 mg, 0.12 mmol). The reaction solution was stirred at room temperature for 1 h and filtered through a pad of Celite. All volatiles were removed in vacuo. DME (1 mL) was added. The DME solution was cooled to −35 °C to give the product as orange prisms suitable for X-ray diffraction analysis; yield 90 mg (72%). **Method 4:** Procedures were similar to those described for method 2 except that 0.5 equiv of $\{[^t$Bu-OPO]$Li_2(DME)\}_2$ was used, leading to orange prisms of **2a** (NMR evidence) in 30% yield. ^{1}H NMR (C_6D_6, 500 MHz) δ 7.65 (dd, 2, $^3J_{HP}$ = 5.5, $^4J_{HH}$ = 2.0, ArH), 7.44 (s, 3, ArH), 7.42 (m, 3, ArH), 1.68 (s, 18, ArCMe_3), 1.47 (s, 18, ArCMe_3), 1.43 (d, 18, $^3J_{HP}$ = 15.0, PCMe_3), 1.29 (s, 18, ArCMe_3), 1.20 (s, 18, ArCMe_3). ^{13}C{^{1}H} NMR (C_6D_6, 125.7 MHz) δ 167.90 (d, J_{CP} = 23.38, C), 166.91 (dd, J_{CP} = 17.47, J_{CP} = 4.15, C), 143.18 (d, J_{CP} = 4.02, C), 141.97 (d, J_{CP} = 4.53, C), 136.36 (d, J_{CP} = 3.77, C), 136.30 (d, J_{CP} = 6.41, C), 131.81 (dd, J_{CP} = 26.15, J_{CP} = 2.26, C), 128.09 (s, CH), 126.92 (d, J_{CP} = 31.68, C), 126.67 (s, CH), 126.51 (s, CH), 125.48 (s, CH), 36.02 (br s, ArCMe$_3$), 34.89 (s, ArCMe$_3$), 34.88 (s, ArCMe$_3$), 32.78 (d, J_{CP} = 9.55, PCMe$_3$), 32.17

dx.doi.org/10.1021/ic102194z |*Inorg. Chem.* 2011, 50, 3363–3372

(s, ArCMe_3), 32.00 (s, ArCMe_3), 30.59 (s, PCMe_3), 30.50 (s, ArCMe_3), 30.40 (s, ArCMe_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.3 MHz) δ 18.55.

Synthesis of 2b. Method 1: To a toluene suspension (2 mL) of $ZrCl_4(THF)_2$ (31 mg, 0.083 mmol) at room temperature was added a toluene solution (4 mL) of $\{[^t$Bu-OPO$]Li_2(DME)\}_2$ (100 mg, 0.083 mmol). The reaction solution was stirred at room temperature for 1 h and evaported to dryness under reduced pressure. Diethyl ether (4 mL) was added. The ether solution was filtered through a pad of Celite and evaported to dryness under reduced pressure to give the product as an off-white solid; yield 81 mg (90%). **Method 2:** Procedures were similar to those described for method 1 except that 0.5 equiv of $\{[^t$Bu-OPO$]Li_2(DME)\}_2$ was used, leading to exclusive formation of **2b** as indicated by $^{31}P\{^1H\}$ NMR spectroscopy. ^1H NMR (C_6D_6, 500 MHz) δ 7.79 (dd, 2, $^3J_{HP}$ = 5.5, $^4J_{HH}$ = 2.0, Ar*H*), 7.71 (dd, 2, $^3J_{HP}$ = 5.5, $^4J_{HH}$ = 2.5, Ar*H*), 7.49 (d, 2, $^4J_{HH}$ = 2.0, Ar*H*), 7.46 (d, 2, $^4J_{HH}$ = 2.0, Ar*H*), 1.60 (d, 18, $^3J_{HP}$ = 15.0, PCMe_3), 1.51 (s, 18, ArCMe_3), 1.48 (s, 18, ArCMe_3), 1.35 (s, 18, ArCMe_3), 1.20 (s, 18, ArCMe_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.7 MHz) δ 165.91 (d, J_{CP} = 24.26, *C*), 165.09 (dd, J_{CP} = 24.26 and 1.89, *C*), 142.67 (d, J_{CP} = 3.65, *C*), 142.04 (d, J_{CP} = 3.65, *C*), 137.82 (d, J_{CP} = 5.03, *C*), 137.53 (d, J_{CP} = 4.53, *C*), 128.99 (s, *C*H), 127.82 (s, *C*H), 126.89 (s, *C*H), 126.81 (s, *C*H), 124.09 (s, *C*), 123.87 (s, *C*) 36.06 (d, J_{CP} = 1.38, ArCMe$_3$), 36.00 (d, J_{CP} = 1.89, ArCMe$_3$), 34.89 (s, ArCMe$_3$), 34.72 (s, ArCMe$_3$), 32.22 (s, ArCMe_3), 31.97 (d, J_{CP} = 11.94, PCMe$_3$), 31.95 (s, ArCMe_3), 30.93 (s, ArCMe_3), 30.42 (s, ArCMe_3), 30.16 (d, J_{CP} = 10.18, PCMe_3). ^{31}P NMR (C_6D_6, 202.3 MHz) δ −7.26. Anal. Calcd for $(C_{64}H_{98}O_4P_2Zr)(OEt_2)_2$: C, 70.13; H, 9.65. Found: C, 69.98; H, 9.28.

Synthesis of 2c. Method 1: To a diethyl ether suspension (4 mL) of $HfCl_4(THF)_2$ (39 mg, 0.083 mmol) at room temperature was added a diethyl ether solution (4 mL) of $\{[^t$Bu-OPO$]Li_2(DME)\}_2$ (100 mg, 0.083 mmol). The reaction solution was stirred at room temperature for 1 h, filtered through a pad of Celite, and evaported to dryness under reduced pressure to give the product as an off-white solid; yield 85 mg (87%). **Method 2:** Procedures were similar to those described for method 1 except that 0.5 equiv of $\{[^t$Bu-OPO$]Li_2(DME)\}_2$ was used, leading to exclusive formation of **2c** as indicated by $^{31}P\{^1H\}$ NMR spectroscopy. ^1H NMR (C_6D_6, 500 MHz) δ 7.78 (dd, 2, $^3J_{HP}$ = 6.0, $^4J_{HH}$ = 2.5, Ar*H*), 7.70 (dd, 2, $^3J_{HP}$ = 5.5, $^4J_{HH}$ = 2.5, Ar*H*), 7.52 (d, $^4J_{HH}$ = 2.5, Ar*H*), 7.48 (d, $^4J_{HH}$ = 2.5, Ar*H*), 1.60 (d, 18, $^3J_{HP}$ = 15.5, PCMe_3), 1.51 (s, 18, ArCMe_3), 1.50 (s, 18, ArCMe_3), 1.35 (s, 18, ArCMe_3), 1.19 (s, 18, ArCMe_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.7 MHz) δ 166.09 (dd, J_{CP} = 23.38, J_{CP} = 1.38, *C*), 165.25 (dd, J_{CP} = 22.37, J_{CP} = 1.76, *C*), 142.50 (d, J_{CP} = 4.15, *C*), 141.88 (d, J_{CP} = 2.77, *C*), 138.75 (d, J_{CP} = 2.77, *C*), 138.46 (d, J_{CP} = 1.76, *C*), 129.08 (s, *C*H), 128.68 (s, *C*H), 127.99 (s, *C*H), 127.39 (d, J_{CP} = 30.80, *C*), 126.95 (d, J_{CP} = 2.77, *C*H), 123.56 (d, J_{CP} = 30.29, *C*), 36.05 (s, ArCMe$_3$), 35.96 (s, ArCMe$_3$), 34.85 (s, ArCMe$_3$), 34.68 (s, ArCMe$_3$), 32.44 (d, J_{CP} = 14.20, PCMe$_3$), 32.22 (s, ArCMe_3), 31.95 (s, ArCMe_3), 31.00 (s, ArCMe_3), 30.46 (s, ArCMe_3), 30.18 (d, J_{CP} = 9.68, PCMe_3). ^{31}P NMR (C_6D_6, 202.3 MHz) δ −3.33. Anal. Calcd for $C_{64}H_{98}HfO_4P_2$: C, 65.57; H, 8.43. Found: C, 65.31; H, 8.71.

Synthesis of 3a. To a toluene solution (2 mL) of $Ti(O^iPr)_4$ (114 mg, 0.401 mmol) was added a toluene solution (4 mL) of $H_2[^t$Bu-OPO] (0.20 g, 0.401 mmol) at room temperature. The solution was stirred at room temperature for 1 h and evaporated to dryness under reduced pressure. Diethyl ether (8 mL) was added. The ether solution was filtered through a pad of Celite and evaporated to dryness under reduced pressure to give the product as a yellow solid; yield 250 mg (95%). ^1H NMR (C_6D_6, 500 MHz) δ 7.74 (dd, 2, $^3J_{HP}$ = 6.0, $^4J_{HH}$ = 2.0, Ar*H*), 7.54 (d, 2, $^4J_{HH}$ = 2.0, Ar*H*), 5.02 (br s, 1, OC*H*Me$_2$), 4.95 (br s, 1, OC*H*Me$_2$), 1.56 (s, 18, ArCMe_3), 1.43 (br s, 6, OCHMe_2), 1.41 (d, 9, $^3J_{HP}$ = 15.5, PCMe_3), 1.38 (br s, 6, OCHMe_2), 1.31 (s, 18, ArCMe_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.7 MHz) δ 170.25 (d, J_{CP} = 30.17, *C*), 142.59 (d, J_{CP} = 4.65, *C*), 137.28 (d, J_{CP} = 5.40, *C*), 128.09 (s, *C*H), 127.61 (d, J_{CP} = 2.64, *C*H), 120.77 (d, J_{CP} = 33.94, *C*), 80.48 (br s, O*C*HMe$_2$), 77.74 (br s, OCHMe$_2$), 35.96 (d, J_{CP} = 1.76, ArCMe$_3$), 34.78 (s, ArCMe$_3$), 33.09 (d, J_{CP} = 14.58, PCMe$_3$), 32.14 (s, ArCMe_3), 30.20 (s, ArCMe_3), 28.13 (d, J_{CP} = 8.30, PCMe_3), 27.30 (s, OCHMe_2), 26.91 (s, OCHMe_2). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.3 MHz) δ 5.50. Anal. Calcd for $(C_{38}H_{63}O_4PTi)(OEt_2)$: C, 68.44; H, 9.99. Found: C, 68.30; H, 9.61.

Synthesis of 4a. To a diethyl ether solution (6 mL) of **1a** (0.15 g, 0.22 mmol) was added a diethyl ether solution (4 mL) of NaO^{t}Bu (42 mg, 0.44 mmol) at room temperature. The solution was stirred at room temperature for 1 h, filtered through a pad of Celite, and evaporated to dryness under reduced pressure. Pentane (2 mL) was added. The pentane solution was filtered through a pad of Celite and cooled to −35 °C to give the product as a colorless crystalline solid; yield 98 mg (65%). ^1H NMR (C_6D_6, 500 MHz) δ 7.73 (dd, 2, $^3J_{HP}$ = 5.5, $^4J_{HH}$ = 2.0, Ar*H*), 7.54 (d, 2, $^4J_{HH}$ = 2.0, Ar*H*), 1.59(s, 18, ArCMe_3), 1.52 (s, 9, OCMe_3), 1.41 (d, 9, $^3J_{HP}$ = 15.5, PCMe_3), 1.38 (s, 9, OCMe_3), 1.32 (s, 18, ArCMe_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.7 MHz) δ 170.88 (d, J_{CP} = 31.17, *C*), 142.19 (d, J_{CP} = 4.53, *C*), 137.14 (d, J_{CP} = 6.03, *C*), 127.99 (s, *C*H), 127.56 (d, J_{CP} = 2.39, *C*H), 120.36 (d, J_{CP} = 33.43, *C*), 84.41 (s, OCMe$_3$), 83.10 (d, $^3J_{CP}$ = 4.65, OCMe$_3$), 35.98 (d, J_{CP} = 1.89, ArCMe$_3$), 34.76 (s, ArCMe_3), 33.19 (d, J_{CP} = 13.70, PCMe$_3$), 32.94 (s, PCMe_3), 32.16 (s, ArCMe_3), 30.39 (s, ArCMe_3), 28.09 (s, OCMe_3), 28.02 (s, OCMe_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.3 MHz) δ 6.77.

Synthesis of 4b. To a diethyl ether solution (4 mL) of **1b** (0.10 g, 0.137 mmol) was added a diethyl ether solution (4 mL) of NaO^{t}Bu (26 mg, 0.274 mmol) at room temperature. The solution was stirred at room temperature for 1 h, filtered through a pad of Celite, and evaporated to dryness under reduced pressure. Pentane (2 mL) was added. The pentane solution was filtered through a pad of Celite and cooled to −35 °C to give the product as a colorless crystalline solid; yield 71 mg (64%). ^1H NMR (C_6D_6, 500 MHz) δ 7.74 (dd, 2, $^3J_{HP}$ = 5.5, $^4J_{HH}$ = 2.0, Ar*H*), 7.47 (d, 2, $^4J_{HH}$ = 2.0, Ar*H*), 3.80 (br s, 4, OCH_2CH$_2$), 1.62 (s, 18, ArCMe_3), 1.59 (d, 9, $^3J_{HP}$ = 14.5, PCMe_3), 1.48 (s, 9, OCMe_3), 1.44 (s, 9, OCMe_3), 1.31 (s, 18, ArCMe_3), 1.23 (br s, 4, OCH$_2$CH_2). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.7 MHz) δ 166.83 (d, J_{CP} = 24.64, *C*), 140.00 (s, *C*), 137.09 (d, J_{CP} = 3.65, *C*), 127.20 (s, *C*H), 126.50 (s, CH), 125.59 (d, J_{CP} = 26.52, *C*), 76.49 (br s, OCMe$_3$), 74.79 (br s, OCMe$_3$), 72.00 (s, OCH$_2$CH$_2$), 36.05 (s, ArCMe$_3$), 34.77 (s, ArCMe$_3$), 33.61 (br s, OCMe_3), 32.29 (s, ArCMe_3), 31.66 (d, J_{CP} = 10.18, PCMe$_3$), 30.40 (s, ArCMe_3), 30.35 (br s, OCMe_3), 30.27 (s, PCMe_3), 25.48 (s, OCH$_2$CH$_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.3 MHz) δ −10.05.

Synthesis of 4c. To a diethyl ether solution (4 mL) of **1c** (0.10 g, 0.122 mmol) was added a diethyl ether solution (4 mL) of NaO^{t}Bu (24 mg, 0.244 mmol) at room temperature. The solution was stirred at room temperature for 1 h, filtered through a pad of Celite, and evaporated to dryness under reduced pressure. Pentane (2 mL) was added. The pentane solution was filtered through a pad of Celite and cooled to −35 °C to give the product as a colorless crystalline solid; yield 74 mg (68%). ^1H NMR (C_6D_6, 500 MHz) δ 7.74 (dd, 2, $^3J_{HP}$ = 5.0, $^4J_{HH}$ = 2.0, Ar*H*), 7.48 (d, 2, $^4J_{HH}$ = 2.0, Ar*H*), 3.88 (t, 4, OCH_2CH$_2$), 1.62 (s, 18, ArCMe_3), 1.61 (d, 9, $^3J_{HP}$ = 14.5, PCMe_3), 1.56 (br s, 9, OCMe_3), 1.40 (br s, 9, OCMe_3), 1.31 (s, 18, ArCMe_3), 1.21 (br s, 4, OCH$_2$CH_2). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.7 MHz) δ 167.19 (d, J_{CP} = 23.38, *C*), 139.80 (d, J_{CP} = 3.77, *C*), 137.84 (d, J_{CP} = 4.15, *C*), 127.22 (d, J_{CP} = 1.38, *C*H), 126.56 (s, *C*H), 125.62 (d, J_{CP} = 28.41, *C*), 76.34 (br s, OCMe$_3$), 74.86 (br s, OCMe$_3$), 72.81 (s, OCH$_2$CH$_2$), 36.05 (s, ArCMe$_3$), 34.74 (s, ArCMe$_3$), 33.95 (br s, OCMe_3), 32.30 (s, ArCMe_3), 31.99 (d, J_{CP} = 11.82, PCMe$_3$), 30.44 (s, ArCMe_3), 30.36 (s, PCMe_3), 25.43 (s, OCH$_2$CH$_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.3 MHz) δ −5.56.

Synthesis of 5a. To a diethyl ether solution (4 mL) of [Ph-OPO]$TiCl_2(THF)$ (0.10 g, 0.14 mmol) was added a diethyl ether solution (2 mL) of NaO^{i}Pr (43 mg, 0.28 mmol) at room temperature. The solution was stirred at room temperature for 1 h, filtered through a pad of Celite, and evaporated to dryness under reduced pressure to give the product as a yellow solid; yield 83 mg (73%). ^1H NMR (C_6D_6, 500

dx.doi.org/10.1021/ic102194z |*Inorg. Chem.* 2011, 50, 3363–3372

MHz) δ 8.01 (br s, 2, Ar*H*), 7.51 (br s, 3, Ar*H*), 7.26 (t, 2, Ar*H*), 7.09 (t, 2, Ar*H*), 4.96 (br m, 1, OC*H*Me$_2$), 4.80 (br m, 1, OC*H*Me$_2$), 1.69 (s, 18, ArC*Me*$_3$), 1.46 (br s, 6, OCH*Me*$_2$), 1.25 (s, 18, ArC*Me*$_3$), 1.16 (br s, 6, OCH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 125.7 MHz) δ 168.83 (br d, J_{CP} = 22.88, *C*), 139.90 (br s, *C*), 135.61 (s, *C*), 133.76 (s, *C*H), 129.29 (s, *C*H), 128.90 (s, *C*H), 127.03 (s, *C*H), 126.60 (s, *C*H), 126.04 (s, *C*), 124.29 (s, *C*), 74.26 (br s, OCHMe$_2$), 72.80 (br s, OCHMe$_2$), 35.99 (s, ArCMe$_3$), 34.90 (s, ArCMe$_3$), 32.24 (s, ArC*Me*$_3$), 30.78 (s, ArC*Me*$_3$), 28.12 (br s, OCH*Me*$_2$), 27.31 (br s, OCH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.3 MHz) δ −2.03.

Reaction of 3a with 1 equiv of ε-CL. To a C_6D_6 solution (0.5 mL) of **3a** (15.0 mg, 0.023 mmol) was added a C_6D_6 solution (0.5 mL) of ε-CL (2.6 mg, 0.023 mmol) at room temperature. The solution was transferred to a Teflon-sealed J. Young NMR tube, and the reaction was monitored by ^{1}H NMR spectroscopy, which showed complete conversion of ε-CL in 1 h at room temperature. ^{1}H NMR (C_6D_6, 500 MHz) δ 7.74 (dd, 2, $^3J_{HP}$ = 5.7, $^4J_{HH}$ = 2.4, Ar*H*), 7.54 (d, 2, $^4J_{HH}$ = 3.5, Ar*H*), 5.03 (m, 1, OC*H*Me$_2$), 4.61 (br s, 1, OC*H*Me$_2$), 3.97 (m, 2, OCH_2), 2.19 (m, 2, CH_2), 2.08 (m, 2, CH_2), 1.72 (m, 4, CH_2), 1.56 (s, 18, ArC*Me*$_3$), 1.41 (d, 15, OCH*Me*$_2$ mixed with PC*Me*$_3$), 1.31 (s, 18, ArC*Me*$_3$), 1.06 (d, 6, $^3J_{HH}$ = 5.7, OCH*Me*$_2$).

Catalytic ROP of ε-CL. A toluene solution (1 mL) of initiators (1.5 mM) was added to a toluene solution (1 mL) of ε-CL (with prescribed concentration based on the $[\varepsilon\text{-CL}]_0/[\text{I}]_0$ ratios listed in Table 2). The solution was transferred to a Teflon-sealed reaction vessel and heated to 80 °C for 3 h. After the solution had been cooled to room temperature, the reaction was quenched with a methanol solution of HCl (1 M, 2 mL). The solid thus precipitated was collected, washed with hexane, and dried under reduced pressure until constant weight was achieved.

X-ray Crystallography and Data Collection for 2a. Orange crystals of **2a** were grown from a concentrated DME solution at −35 °C. The crystals were quickly moved from a scintillation vial to a microscope slide covered with Paratone N. Under the microscope, an orange prism of approximate dimensions 0.36 × 0.15 × 0.06 mm was picked and mounted on a glass fiber with silicone grease and placed in a cold dinitrogen stream in a Bruker-Nonius Kappa CCD diffractometer. Data were collected with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å) at 200(2) K. A total of 43494 reflections were collected ($-14 \le h \le 14$, $-27 \le k \le 36$, $-22 \le l \le 14$) in the θ range of 1.28−25.03° of which 6230 were unique (R_{int} = 0.1071). The structure was solved by direct methods and refined by full matrix least-squares procedures against F^2 using SHELXL-97.[71] All full-weight non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. The largest peak and hole in the difference map were 1.412 and −0.637 e/Å^3, respectively. The structure contained disordered solvent molecules. Attempts to obtain a suitable disorder model failed. The SQUEEZE procedure of Platon program[72] was used to obtain a new set of F^2 (*hkl*) values without the contribution of solvent molecules, leading to the presence of significant voids in the structure. The refinement reduced the R1 value to 0.0790. Two *tert*-butyl groups are disordered with the methyl substituents being in the ratio of either ca. 70:30 or 78:22 over two conformations. Crystal data for $C_{64}H_{98}O_4P_2Ti$: M = 1041.26, orthorhombic, space group *Pnna*, Z = 4, a = 12.3848(7) Å, b = 30.7971(18) Å, c = 18.5819(11) Å, V = 7087.4(7) Å^3, D_{calc} = 0.976 g/cm^3, μ(Mo−Kα) = 0.204 mm^{-1}, final R1 [$I > 2\sigma(I)$] = 0.0790, wR2 [$I > 2\sigma(I)$] = 0.2176, R1 (all data) = 0.1363, wR2 (all data) = 0.2405, GOF (on F^2) = 1.062. CCDC reference number 796843.

■ ASSOCIATED CONTENT

Supporting Information. X-ray crystallographic data in CIF format for **2a**; van't Hoff plot for eq 1; DFT-optimized structures and selected bond distances and angles for **3a** and **5a**; and NMR spectra of **2a**, **4a**, **4b**, **4c**, and **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: lcliang@mail.nsysu.edu.tw.

■ ACKNOWLEDGMENT

We thank the National Science Council of Taiwan for financial support (NSC 99-2113-M-110-003-MY3 and 99-2119-M-110-002); Mr. Ting-Shen Kuo (NTNU) for assistance with X-ray crystallography; Ms. Ching-Wei Lu (NTU), Ms. I-Chuan Chen (NCHU), and Ms. Chia-Chen Tsai (NCKU) for elemental analysis; Ms. Chao-Lien Ho (NSYSU), Ms. Mei-Yueh Chien (NCHU), and Ms. Ru-Rong Wu (NCKU) for assistance with NMR spectroscopy; the National Center for High-Performance Computing (NCHC) for computer time and facilities; and Professor Jyh-Tsung Lee for the access to a GPC instrument.

■ REFERENCES

(1) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 429–447.
(2) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147–6176.
(3) Yeori, A.; Goldberg, I.; Shuster, M.; Kol, M. *J. Am. Chem. Soc.* **2006**, *128*, 13062–13063.
(4) Gendler, S.; Segal, S.; Goldberg, I.; Goldschmidt, Z.; Kol, M. *Inorg. Chem.* **2006**, *45*, 4783–4790.
(5) Tshuva, E. Y.; Goldberg, I.; Kol, M. *J. Am. Chem. Soc.* **2000**, *122*, 10706–10707.
(6) Kim, Y.; Jnaneshwara, G. K.; Verkade, J. G. *Inorg. Chem.* **2003**, *42*, 1437–1447.
(7) Zelikoff, A. L.; Kopilov, J.; Goldberg, I.; Coates, G. W.; Kol, M. *Chem. Commun.* **2009**, 6804–6806.
(8) Coates, G. W.; Hustad, P. D.; Reinartz, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2236–2257.
(9) Chisholm, M. H.; Lin, C. C.; Gallucci, J. C.; Ko, B. T. *Dalton Trans.* **2003**, 406–412.
(10) Romain, C.; Brelot, L.; Bellemin-Laponnaz, S.; Dagorne, S. *Organometallics* **2010**, *29*, 1191–1198.
(11) Boyd, C. L.; Toupance, T.; Tyrrell, B. R.; Ward, B. D.; Wilson, C. R.; Cowley, A. R.; Mountford, P. *Organometallics* **2005**, *24*, 309–330.
(12) Meppelder, G. J. M.; Fan, H. T.; Spaniol, T. P.; Okuda, J. *Inorg. Chem.* **2009**, *48*, 7378–7388.
(13) Meppelder, G. J. M.; Fan, H. T.; Spaniol, T. P.; Okuda, J. *Organometallics* **2009**, *28*, 5159–5165.
(14) Chen, H.-Y.; Liu, M.-Y.; Sutar, A. K.; Lin, C.-C. *Inorg. Chem.* **2010**, *49*, 665–674.
(15) Alexander, J. B.; La, D. S.; Cefalo, D. R.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1998**, *120*, 4041–4042.
(16) Zhu, S. S.; Cefalo, D. R.; La, D. S.; Jamieson, J. Y.; Davis, W. M.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 8251–8259.
(17) van der Linden, A.; Schaverien, C. J.; Meijboom, N.; Ganter, C.; Orpen, A. G. *J. Am. Chem. Soc.* **1995**, *117*, 3008–3021.
(18) Carmichael, C. D.; Fryzuk, M. D. *Dalton Trans.* **2008**, 800–806.
(19) Takashima, Y.; Nakayama, Y.; Watanabe, K.; Itono, T.; Yeyama, N.; Nakamura, A.; Yasuda, H.; Harada, A. *Macromolecules* **2002**, *35*, 7538–7544.
(20) Groysman, S.; Goldberg, I.; Goldschmidt, Z.; Kol, M. *Inorg. Chem.* **2005**, *44*, 5073–5080.
(21) Segal, S.; Goldberg, I.; Kol, M. *Organometallics* **2005**, *24*, 200–202.
(22) Capacchione, C.; Proto, A.; Ebeling, H.; Mulhaupt, R.; Moller, K.; Spaniol, T. P.; Okuda, J. *J. Am. Chem. Soc.* **2003**, *125*, 4964–4965.

(23) Sernetz, F. G.; Mulhaupt, R.; Fokken, S.; Okuda, J. *Macromolecules* **1997**, *30*, 1562–1569.
(24) Fokken, S.; Spaniol, T. P.; Kang, H. C.; Massa, W.; Okuda, J. *Organometallics* **1996**, *15*, 5069–5072.
(25) Takashima, Y.; Nakayama, Y.; Hirao, T.; Yasuda, H.; Harada, A. *J. Organomet. Chem.* **2004**, *689*, 612–619.
(26) Darensbourg, D. J.; Moncada, A. I.; Choi, W.; Reibenspies, J. H. *J. Am. Chem. Soc.* **2008**, *130*, 6523–6533.
(27) Sergeeva, E.; Kopilov, J.; Goldberg, I.; Kol, M. *Inorg. Chem.* **2010**, *49*, 3977–3979.
(28) Gendler, S.; Zelikoff, A. L.; Kopilov, J.; Goldberg, I.; Kol, M. *J. Am. Chem. Soc.* **2008**, *130*, 2144–2145.
(29) Sanz, M.; Cuenca, T.; Galakhov, M.; Grassi, A.; Bott, R. K. J.; Hughes, D. L.; Lancaster, S. J.; Bochmann, M. *Organometallics* **2004**, *23*, 5324–5331.
(30) Hormnirun, P.; Marshall, E. L.; Gibson, V. C.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **2004**, *126*, 2688–2689.
(31) Silvernail, C. M.; Yao, L. J.; Hill, L. M. R.; Hillmyer, M. A.; Tolman, W. B. *Inorg. Chem.* **2007**, *46*, 6565–6574.
(32) Takeuchi, D.; Nakamura, T.; Aida, T. *Macromolecules* **2000**, *33*, 725–729.
(33) Floriani, C.; Corazza, F.; Lesueur, W.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem., Int. Ed.* **1989**, *28*, 66–67.
(34) Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1991**, *30*, 145–148.
(35) Okuda, J.; Fokken, S.; Kang, H. C.; Massa, W. *Chem. Ber.* **1995**, *128*, 221–227.
(36) Kakugo, M.; Miyatake, T.; Mizunuma, K. *Chem. Express* **1987**, *2*, 445–448.
(37) Miyatake, T.; Mizunuma, K.; Seki, Y.; Kakugo, M. *Makromol. Chem., Rapid Commun.* **1989**, *10*, 349–352.
(38) Schaverien, C. J.; van der Linden, A. J.; Orpen, A. G. *Polym. Prepr. (Am. Chem. Soc., Polym. Div.)* **1994**, *35*, 672–673.
(39) Froese, R. D. J.; Musaev, D. G.; Matsubara, T.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 7190–7196.
(40) Froese, R. D. J.; Musaev, D. G.; Morokuma, K. *Organometallics* **1999**, *18*, 373–379.
(41) Liang, L.-C. *Coord. Chem. Rev.* **2006**, *250*, 1152–1177.
(42) Liang, L.-C.; Chien, P.-S.; Huang, Y.-L. *J. Am. Chem. Soc.* **2006**, *128*, 15562–15563.
(43) Liang, L.-C.; Lin, J.-M.; Lee, W.-Y. *Chem. Commun.* **2005**, 2462–2464.
(44) Liang, L.-C.; Lin, J.-M.; Hung, C.-H. *Organometallics* **2003**, *22*, 3007–3009.
(45) Liang, L.-C.; Chien, P.-S.; Lee, P.-Y. *Organometallics* **2008**, *27*, 3082–3093.
(46) Lee, P.-Y.; Liang, L.-C. *Inorg. Chem.* **2009**, *48*, 5480–5487.
(47) Liang, L.-C.; Chien, P.-S.; Lin, J.-M.; Huang, M.-H.; Huang, Y.-L.; Liao, J.-H. *Organometallics* **2006**, *25*, 1399–1411.
(48) Liang, L.-C.; Chien, P.-S.; Huang, M.-H. *Organometallics* **2005**, *24*, 353–357.
(49) Huang, M.-H.; Liang, L.-C. *Organometallics* **2004**, *23*, 2813–2816.
(50) Liang, L.-C.; Lee, W.-Y.; Hung, C.-H. *Inorg. Chem.* **2003**, *42*, 5471–5473.
(51) Liang, L.-C.; Cheng, L.-C.; Tsai, T.-L.; Hu, C.-H.; Guo, W.-H. *Inorg. Chem.* **2009**, *48*, 5697–5703.
(52) Liang, L.-C.; Chang, Y.-N.; Lee, H. M. *Inorg. Chem.* **2007**, *46*, 2666–2673.
(53) Liang, L.-C.; Chang, Y.-N.; Chen, H.-S.; Lee, H. M. *Inorg. Chem.* **2007**, *46*, 7587–7593.
(54) Chang, Y.-N.; Liang, L.-C. *Inorg. Chim. Acta* **2007**, 136–142.
(55) Hsu, Y.-L.; Liang, L.-C. *Organometallics* **2010**, *29*, 6201–6208.
(56) Long, R. J.; Gibson, V. C.; White, A. J. P.; Williams, D. J. *Inorg. Chem.* **2006**, *45*, 511–513.
(57) Priya, S.; Balakrishna, M. S.; Mague, J. T. *Chem. Lett.* **2004**, *33*, 308–309.
(58) The possibility of an isopropoxide-bridged dimer cannot be ruled out; for example, see ref 24.
(59) Nakayama, Y.; Watanabe, K.; Ueyama, N.; Nakamura, A.; Harada, A.; Okuda, J. *Organometallics* **2000**, *19*, 2498–2503.
(60) Cayuela, J.; Bounor-Legare, V.; Cassagnau, P.; Michel, A. *Macromolecules* **2006**, *39*, 1338–1346.
(61) Chuck, C. J.; Davidson, M. G.; Jones, M. D.; Kociok-Kohn, G.; Lunn, M. D.; Wu, S. *Inorg. Chem.* **2006**, *45*, 6595–6597.
(62) Davidson, M. G.; Jones, M. D.; Lunn, M. D.; Mahon, M. F. *Inorg. Chem.* **2006**, *45*, 2282–2287.
(63) Gornshtein, F.; Kapon, M.; Botoshansky, M.; Eisen, M. S. *Organometallics* **2007**, *26*, 497–507.
(64) Conversion of ca. 90% in 2.5 h.
(65) Save, M.; Schappacher, M.; Soum, A. *Macromol. Chem. Phys.* **2002**, *203*, 889–899.
(66) Haddad, M.; Laghzaoui, M.; Welter, R.; Dagorne, S. *Organometallics* **2009**, *28*, 4584–4592.
(67) Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135–140.
(68) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.05; Gaussian, Inc.: Pittsburgh, PA, 2003.
(69) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
(70) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.
(71) Sheldrick, G. M. *SHELXTL*, version 5.1; Bruker AXA Inc.: Madison, WI, 1998.
(72) Spek, A. L. *PLATON: A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2003.