Group 4 Post-metallocene Complexes Incorporating Tridentate Silyl-Substituted Bis(naphthoxy)pyridine and Bis(naphthoxy)thiophene Ligands: Probing Systems for "Oscillating" Olefin Polymerization Catalysis

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New bulky silyl *ortho*-substituted tridentate 2,6-bis(naphthol)pyridine ({ ONO^{SiR3} }H₂, SiR₃ = SiPh₃, SiMe₂*t*Bu) and 2,5-bis(naphthol)thiophene ({ OSO^{SiPh3} }H₂) pro-ligands were synthesized via a fourstep approach. The solid-state structures of pro-ligands { ONO^{SiPh3} }H₂ (**3a**) and { OSO^{SiPh3} }H₂ (**3b**) were established by X-ray diffraction analysis. Both types of ligands were introduced onto group 4 metal centers (M = Ti, Zr, Hf) using straightforward one-step alkane, amine, or alcohol elimination protocols. Dibenzyl { ONO^{SiPh3} }M(CH₂Ph)₂ (M = Ti, **4a**; Zr, **5a**; Hf, **6a**) and { ONO^{SiPh3} }M(CH₂Ph)₂ (M = Ti, **4b**; Zr, **5b**), diamido { ONO^{SiPh3} }Hf(NMe₂)₂ (**7a** and **7a** (**NHMe**₂)), and di(isopropoxy) { ONO^{SiPh3} }Ti(*OiP*r)₂ (**8a**) complexes were authenticated using NMR spectroscopy and X-ray crystal-lography methods for some of them. In the solid state, complexes **4a**, **4b**, and **6a** feature *rac*-like binding of the ligand, while ligands in complexes **5b** and **7a** (**NHMe**₂) are *meso*-like coordinated. The solution structures of **4b** and **5b** were investigated by VT NMR spectroscopy, which revealed that both complexes exist as *rac* and *meso* stereoisomers, which interconvert (activation parameters: **4b**, $\Delta H^{\ddagger} = 12.9(7)$ kcal·mol⁻¹ and $\Delta S^{\ddagger} = -3(1)$ cal·mol⁻¹·K⁻¹; **5b**, $\Delta H^{\ddagger} = 13.4(8)$ kcal·mol⁻¹ and $\Delta S^{\ddagger} = -7(1)$ cal·mol⁻¹·K⁻¹). A mechanism for this interconversion process, implying straightforward racemization, was proposed on the basis of DFT computations at the B3LYP (BP86) level, with computed activation barriers for Ti, Zr, and Hf complexes of 11.4 (10.1), 12.5 (11.2), and 12.2 (11.1) kcal·mol⁻¹, respectively. The catalytic activity of dibenzyl and diamido precursors in homopolymerization of propylene and ethylene, upon activation with MAO, "dried-MAO", and [Ph₃C](B(C₆F₅)₄]/Al(*i*Bu)₃, has been explored as well.

Introduction

The production of thermoplastic elastomeric materials composed of polyolefins stereoblocks has constituted a challenge of both fundamental and industrial relevance over the past decades.¹ Successful manufacturing of such valuable materials requires the development of nonconventional catalytic processes and/or advanced catalyst systems.² If traditional Ziegler–Natta polymerization catalysis (including its single-site developments), with its Cossee–Arlman coordinative/insertive mechanism, is reasonably considered for this application, its main drawback lies in the fact that the geometry of an active site normally remains unchanged and, as a consequence, the growing polymer chain features a constant distribution of imposed stereosequences. Such a

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problem can be tackled by engineering of a single-site catalyst component that would alternate geometry of its active site through a reversible interconversion between several stable stereodictating forms. A conceptual advance along this line came from Waymouth³ and others,⁴ who proposed that the atropisomeric metallocenium cation [(2-phenylindenyl)₂ZrMe]⁺ may exist under two conformational states, namely *rac* and *meso*, in "quasi-controlled" equilibrium (Scheme 1); this would provide enchainment of propylene in a given growing polymer chain, under different

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rac-like conformations (isospecific)

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stereoenvironments, giving rise to multiblock isotactic– atactic polypropylene. Yet, as argued by Busico et al.,⁵ the reality of this effective process appeared even more sophisticated, incorporation of propylene proceeding into conformationally "locked" *rac*-like species with restricted ring mobility and probable important contribution of the counteranion.

In a general fashion, viability of the production of stereoblock polyolefin chains via "oscillating" polymerization catalysis is ensured by the following main requirements: (i) activation of a given catalyst precursor must give rise to the formation of a catalytically active species that undergoes a reasonably easy dynamic interconversion between geometrically stable isomers, e.g., rac (stereospecific) and meso (nonstereospecific); that is, in terms of thermodynamics, these species must be ground states with close energies and connected through an attainable transition state. (ii) The "oscillation"/interconversion rate must be somewhat lower than the propagation rates. (iii) The latter propagation rates for isomers of the active species must be significantly higher than rates of termination/transfer processes, to allow building up/ chain growth of blocks. It must be noted that the system may be sensitive to the polymerization conditions and to the nature of the activator as well. Indeed, activators possessing an appropriate hydrodynamic volume and/or coordinating propensity can interact not necessarily with the metal center, but rather with the ligand backbone of a catalytic species,^{5d,6} thus interfering in the interconversion process.

In a recent contribution, Bercaw et al. investigated for the first time the concept of "oscillation" in post-metallocene

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polymerization catalysis.⁷ Group 4 metal complexes supported by tridentate bis(phenolate) ligand systems bridged by a fused ring L-type donor (pyridine, thiophene, furan) were shown to adopt either C_2 (in Ti complexes) or C_1/C_s (in Zr complexes) symmetry in the solid state (Scheme 2).^{7,8} However, the sole species observed in solution by NMR over a broad range of temperatures featured an average symmetric binding of the tridentate ligands. This result was accounted for by a fast exchange between species of different symmetry. As a consequence, propylene polymerization reactions mediated by these complexes yielded atactic polymers.⁷

Also encouraged by the outstanding catalytic performances of phenoxy-based catalysts,⁹⁻¹² we independently investigated systems that incorporate sterically demanding ligands related to those of Bercaw (Scheme 3).¹³ The anticipated key feature of these ligands is the possibility for firm stereoselective coordination to the metal center provided by the non-coplanar orientation of the bridging heterocyclic

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and adjacent naphthoxy groups, due to steric repulsion between protons at *meta* and 8-positions¹⁴ of these moieties, respectively.

In this contribution we report the synthesis of tridentate pyridine- and thiophene-bridged bis(naphthoxy) pro-ligands having bulky silyl *ortho*-substituents and group 4 metal complexes derived thereof. The solid-state and solution structures, as well as the interconversion/racemization process taking place in those species, have been investigated by experimental (X-ray crystallography, NMR spectroscopy) and theoretical (DFT) methods. The performance of those catalyst precursors in propylene and ethylene polymerization reactions is reported.

Results and Discussion

Synthesis of Pro-ligands. Preparation of the diprotio proligand { ONO^{SiPh3} }H₂ was initially attempted starting from commercially available and inexpensive 2-methoxynaphthalene (Scheme 4, protecting group, Pg = Me). The four-step procedure, followed by Negishi cross-coupling reaction using extended S-Phos Buchwald's phosphine ligand,¹⁵ ended up with the formation of Ph₃Si-substituted 2,6-bis-(methoxynaphthyl)pyridine, **1a-Me**, in good yield. However, further deprotection of the methoxy groups in **1a-Me** to

(14) The following atom numbering of the naphtholate unit is used:







XXX

ÝΧ

Since the above approach turned out to be problematic, an alternative pathway was investigated. The preparation of 2,6-bis(naphthol)pyridine pro-ligands **3a** and **3b** was successfully achieved starting from methoxymethyl-protected β -napthol (Pg = MOM), following a similar three-step synthetic protocol as depicted in Scheme 3.¹⁹ The same synthetic strategy was applied to the preparation of a congener thiophene-bridged pro-ligand ({OSO^{SiPh3}}H₂, **3c**), although it resulted in somehow lower isolated yield (see the Experimental Section). Despite the fact that 2,6-dichloropyridine is quite active toward cross-coupling under the conditions used, we observed that no reaction took place when 1,4-dichlorophthalazine was used (Scheme 4). Presumably, the latter observation may stem from a larger steric hindrance imposed by the adjacent phenyl ring of the phthalazine fragment.

Pro-ligands $3\mathbf{a}-\mathbf{c}$ are stable compounds at room temperature and are all readily soluble in aromatic hydrocarbons and other common solvents (CHCl₃, CH₂Cl₂, THF). These compounds were fully characterized in solution by ¹H and ¹³C NMR spectroscopy and by elemental analysis. The NMR spectra at 25 °C (in CDCl₃ or CD₂Cl₂) show a single

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^{(19) (}a) Interestingly, the cross-coupling reaction using the S-Phos ligand did not proceed in more than 50% yield (in the best case, with 2,6-dibromopyridine), regardless of the reaction time and temperature. The main byproduct isolated after workup turned out to be [3-(methoxymethoxy)-2-naphthyl](R-)silane. The yield in the desired cross-coupling product could be fairly increased when the bulkier X-Phos phosphine ligand was used. (b) Formation of unidentified heavy aromatic side products that contain no SiMe₂/Bu groups was also detected when synthesizing **1b-MOM** by cross-coupling reaction.



set of resonances, consistent with a single, time-averaged species and low rotation barriers of the substituted naphthol fragments with respect to the central heterocycle plane.²⁰ In addition, the solid-state structures of **3a** and **3b** were determined by X-ray diffraction studies (*vide infra*).

Synthesis of Group 4 Metal Complexes $\{OZO^{SiR3}\}MX_2$. σ -Bond metathesis reactions between group 4 metal precursors MX_4 (X = CH₂Ph, NMe₂, O*i*Pr; M = Ti, Zr, and Hf) and pro-ligands $\{OZO^{SiR3}\}H_2(Z = N, S)$ were investigated. For instance, the reaction between $Ti(CH_2Ph)_4$ or $Hf(NMe_2)_4$ and 1 equiv of $\{ONO^{SiPh3}\}H_2$ in benzene- d_6 or toluene- d_8 solution was monitored by ¹H NMR spectroscopy and found to proceed readily at room temperature within a few minutes to yield quantitatively the desired dibenzyl or diamido complexes, with concomitant release of 2 equiv of alkane or amine, respectively. The target compounds were readily resynthesized on a preparative scale using this procedure (Scheme 5). Freshly prepared hafnium amido complex $7a \cdot (NHMe_2)$ appeared to be rather unstable, as it readily loses the coordinated NHMe2 molecule upon standard workup (recrystallization, drying under vacuum), to afford base-free complex 7a. Alternatively, the latter compound 7a can be prepared in a more straightforward manner, by performing the amine elimination reaction in diethyl ether. Note, however, that similar alkane elimination reactions between pro-ligand **3a** and $M(CH_2Ph)_4$ (M = Zr and Hf) and between 3c and $Ti(CH_2Ph)_4$ appeared to be less facile when conducted in diethyl ether (in contrast to those performed in toluene), giving rise to unidentified byproducts, which were only difficultly removed by recrystallization. The preparative-scale reaction of 3a and Ti(OiPr)4 in benzene enabled the synthesis of diisopropoxide complex 8a in good yield.

The isolated complexes are air-sensitive, colored materials $({ONO^{SiPh3}}Ti(CH_2Ph)_2$ (4a), ${ONO^{SiMe2rBu}}Ti(CH_2Ph)_2$ (4b), and ${OSO^{SiPh3}}Ti(CH_2Ph)_2$ (4c): brownish-red; ${ON-O^{SiPh3}}Zr(CH_2Ph)_2$ (5a), ${ONO^{SiMe2rBu}}Zr(CH_2Ph)_2$ (5b),





 $\begin{array}{l} \textbf{3a: } \{ONO^{SIPh3}\}H_2, \ \text{Het} = pyridine \\ \textbf{3b: } \{ONO^{SiMe2tBu}\}H_2, \ \text{Het} = pyridine \\ \textbf{3c: } \{OSO^{SIPh3}\}H_2, \ \text{Het} = thiophene \\ \end{array}$







4a: {ONO^{SIPh3}}Ti(CH₂Ph)₂ 5a: {ONO^{SIPh3}}Zr(CH₂Ph)₂ 6a: {ONO^{SIPh3}}Hf(CH₂Ph)₂ 7a: {ONO^{SIPh3}}Hf(NMe₂)₂ 8a: {ONO^{SIPh3}}Ti(OiPr)₂

 $\begin{array}{l} \textbf{4b: } \{ONO^{SiMe2tBu}\}Ti(CH_2Ph)_2\\ \textbf{5b: } \{ONO^{SiMe2tBu}\}Zr(CH_2Ph)_2 \end{array}$

4c: {OSO^{SiPh3}}Ti(CH₂Ph)₂

{ONO^{SiPh3}}Hf(CH₂Ph)₂ (**6a**), and {ONO^{SiPh3}}Hf(NMe₂)₂ (**7a** and **7a** · (NHMe₂)): bright yellow; {ONO^{SiPh3}}Ti(O*i*Pr)₂ (**8a**): pale yellow). These compounds are moderately (SiPh₃substitued) to readily (SiMe₂*t*Bu-substituted) soluble in aromatic hydrocarbons (benzene, toluene) and in methylene chloride as well. Dibenzyl complexes **4a,b,c**, **5a**, **6a**, and **8a** were found to be thermally robust and do not undergo decomposition in solution (benzene, toluene) up to 100 °C (hours, ¹H NMR monitoring). Also, no significant decay was observed upon aging toluene solutions of these complexes at room temperature over 3 months. On the other hand, dibenzyl zirconium complex **5b**, which is stable in the solid state, slowly ($\tau_{1/2} \approx 40$ h) decomposes in solution (benzene, toluene) at room temperature, giving mixtures of vet unidentified products.

Solid-State Structures of Pro-ligands 3a and 3c and Complexes 4a,b, 5b, 6a, and $7a \cdot (NHMe_2)$. Single crystals suitable for X-ray diffraction studies were successfully prepared by recrystallization for the following compounds: 2 and 3c from chloroform, 4a from toluene, 3a and $7a \cdot (NHMe_2)$ from benzene, 4b from hexane, 5b from hexane/toluene, and 6a from benzene/toluene.

The molecule of pro-ligand **3a** adopts in the solid state an approximate (noncrystallographic) C_2 symmetry, in which

⁽²⁰⁾ The racemization barrier for 1,1'-binaphthalene-2,2'-diol ("Binol") was measured to be $\Delta G^{\ddagger}_{493 \text{ K}} = 37.7 \text{ kcal} \cdot \text{mol}^{-1}$: Meca, L.; Reha, D.; Havlas, Z. J. Org. Chem. **2003**, 68, 5677.

the naphthol groups are twisted from the pyridine plane in the opposite directions (Figure 1). The resulting *rac*-conformation features large torsion angles of 44.57° and 47.79° between the planes of the pyridine unit and the naphthol fragments. The relatively short distance of 4.224 Å between the oxygen atoms in **3a** apparently results from intramolecular hydrogen bonding²¹ between the nitrogen atom N(1) and the HO(1) and HO(2) groups (N···H distances of 1.885 and 1.980 Å, respectively). In the C₂-symmetric molecule of **3c** (Figure 2), the nearly coplanar naphthol fragments (torsion angle of 4.49°) are bent off the thiophene plane by 68.45° and 68.13°. No short intramolecular hydrogen bonding between the sulfur atom and hydroxy groups is observed.

The borate ester **2** features in the solid state a monomeric structure with a tetrahedral geometry typical of boron compounds bearing tridentate {ONO}-type ligands (Figure 3).²² The B(1)–N(1) and B(1)–O(1,2) bond lengths, as well as the N(1)–B(1)–O angles (105.68(2)°, 106.65(2)°, and 107.33(3)°) in **2** compare well with those observed in related boron compounds of bis(phenolate)pyridine ligands (104.9(2)–109.1(2)°).²² Both naphthoxy moieties take position on the same side of the pyridine unit. An interesting feature of **2** lies in the intramolecular hydrogen bonding involving the HO(3) group and one of phenyl rings of the Ph₃Si(2) group (shortest distance of 2.935 Å between hydrogen and *ortho* carbon atoms). A similar type of OH··· π interaction was previously observed in [(2,6-*t*Bu₂PhO)-(Ph)B(OH)]₂ dimer.²³

The solid-state structures of base-free complexes $\{OZO^{SiR3}\}MX_2$ **4a,b**, **5b**, and **6a** reveal five-coordinate mononuclear species (Figures 4–7). The metal centers (Ti, Zr, and Hf, respectively) are in a distorted trigonalbipyramidal geometry, similar to that observed recently for related CR₃ (R = Me, Et) *ortho*-substituted pyridine-bis-(phenolate) group 4 metal complexes.⁷ Complexes of titanium **4a,b** and hafnium **6a** revealed one common feature in the solid state, that is, *rac*-coordination of the $\{ONO^{SiR3}\}$ ligand, leading to an approximate (noncrystallographic) C_2 symmetry in these molecules (Figures 4, 5, and 7).^{24,25} The twist angles between the naphthoxy and pyridine fragment planes in **4a,b** are, on average, ca. $3-8^{\circ}$ larger than the

(23) Galbraith, E.; Fyles, T. M.; Marken, F.; Davidson, M. G.; James, T. D. *Inorg. Chem.* **2008**, *47*, 6236.

(24) The molecular structure of complex **4b** possesses a crystallographic C_2 axis.

(25) Titanium bis(isopropoxy) complex **8a** also displays *rac* coordination of the { ONO^{SiPh3} }²⁻ ligand in the solid state; however, due to the poor final *R* value (ca. 20%), the structural parameters are not reported.

(26) η^2 -Binding of benzyl groups onto zirconium is documented in the literature by short $Zr-C_{ipso}$ distances (typically, 2.57–2.65 Å) and acute $Zr-C-C_{ipso}$ angles (typically, 82.7–84.9°): (a) Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P.; Huffman, J. C. *Organometallics* 1985, 4, 902. (b) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. J. Am. Chem. Soc. 1987, 109, 4111. (c) Jordan, R. F.; LaPointe, R. E.; Baenziger, N.; Hinch, G. D. Organometallics 1990, 9, 1539. (d) Growther, D. J.; Borkowsky, S. L.; Swenson, D.; Meyer, T. Y.; Jordan, R. F. Organometallics 1993, 12, 2897. (e) Pellecchia, C.; Grassi, A.; Immirzi, A. J. Am. Chem. Soc. 1983, 115, 1160. (f) Cloke, F. G. N.; Geldbach, T. J.; Hitchcock, P. B.; Love, J. B. J. Organomet. Chem. 1996, 506, 343. (g) Bochmann, M.; Lancaster, S. J.; Hursthouse, M. B.; Abdul Malik, K. M. Organometallics 2000, 19, 2944. (i) Kirillov, E.; Lavanant, L.; Thomas, C. M.; Roisnel, T.; Chi, Y.; Carpentier, J.-F. Chem–Eur. J. 2007, 13, 923.



Figure 1. Molecular structure of pro-ligand $\{ONO^{SiPh3}\}H_2(3a)$ (all hydrogen atoms, except of hydroxyl groups, are omitted for clarity; thermal ellipsoids drawn at 50% probability). Selected bond distances (Å) and angles (deg): H(O(1))-N(1), 1.885; H(O(2))-N(1), 1.980; $\angle Py-Np(1)$, 44.57; $\angle Py-Np(2)$, 47.79.



Figure 2. Molecular structure of pro-ligand $\{OSO^{SiPh3}\}H_2$ (**3c**·2CHCl₃) (disordered atoms of the thiophene, solvent molecules, and all hydrogen atoms, except of hydroxyl groups, are omitted for clarity; thermal ellipsoids drawn at 50% probability). Selected bond distances (Å) and angles (deg): H(O(1))-S(1), 2.800; H(O(2))-S(1), 3.514; \angle Thioph-Np(1), 68.45; \angle Thioph-Np(2), 68.13.

corresponding angles in the C_2 -symmetric dibenzyltitanium pyridine-bis(phenolate) complexes described by Bercaw et al.⁷ (Table 1). This slight but noticeable difference apparently stems from a larger constraint imposed by bulkier SiR₃ groups, as compared to CR₃ groups. At the same time, however, the distances between the phenolate oxygens (d_{OO}) in **4a**,**b** are identical (3.79 Å) and only slightly larger than that observed in {ONO^{CMe3}}Ti(CH₂Ph)₂ (3.70 Å).⁷ Interestingly, in C_2 -symmetric complexes **4a**,**b** and **6a**, the two benzyl groups are clearly η^1 -bound to the metal center, as revealed by long $M \cdots C_{ipso}$ contacts (>2.97 Å) and obtuse $M-C-C_{ipso}$ angles (>108°).^{26,27} This leads to formally

⁽²¹⁾ Steiner, T. Angew. Chem., Int. Ed. 2002, 41, 48.

 ^{(22) (}a) Zhang, H.; Huo, C.; Zhang, J.; Zhang, P.; Tian, W.; Wang, Y.
 Chem. Commun. 2006, 281. (b) Zhang, H.; Huo, C.; Ye, K.; Zhang, P.; Tian,
 W.; Wang, Y. *Inorg. Chem.* 2006, 45, 2788.

⁽²⁷⁾ Due to the large number of aromatic carbons in those complexes, the ¹³C NMR resonances for the C_{ipso} atoms of benzylic groups in **4a,b** and **6a** could not be unambiguously assigned and could not therefore be used to probe the coordination mode of benzyl groups in solution. Usually, low-field chemical shifts (δ ca. 144–146 ppm) indicate that benzyl groups are η^1 -coordinated onto the metal center, while η^2 -coordinated benzyl groups appear at high-field (δ ca. 140–141 ppm); see ref 26.



Figure 3. Molecular structure of $\{ONO^{SiPh3}\}B(OH)$ (2·2CH-Cl₃) (all solvent molecules and hydrogen atoms, except that of the hydroxyl group, are omitted for clarity; in the bottom view, the SiPh₃ phenyl rings are also omitted; thermal ellipsoids drawn at 50% probability). Selected bond distances (Å) and angles (deg): B(1)-O(1), 1.475(3); B(1)-O(2), 1.469(3); B(1)-O(3), 1.414(3); B(1)-N(1), 1.604(3); N(1)-B(1)-O(1), 105.68(2), N(1)-B(1)-O(2), 106.65(2); N(1)-B(1)-O(3), 107.33(3); O(1)-B(1)-O(3), 114.74(3).

14-electron species, counting the phenoxides as four-electron (σ, π) donors.²⁸

On the other hand, in the five-coordinate base-free complex 5b and six-coordinate octahedral NHMe₂ adduct 7a. (NHMe₂), the pyridine-bis(naphthoxy) ligands are coordinated in a C_s -symmetric fashion. In both molecules, the pyridine planes are deviated from the M-N vector in the same direction, as observed also for pyridine-bis(phenolate) complexes of group 4 and 5 metals.⁷ The twist angles between the pyridine unit and naphthoxy planes in 5b and 7a. (NHMe₂) are, at least, 5° more tilted than those in C_2 symmetric analogues. Also, in striking contrast to C_2 -symmetric dibenzyl complexes 4a,b and 6a, zirconium complex **5b** features noticeable η^2 binding of both benzyl groups with the metal center. This is evidenced by short M-Cipso distances (2.632 and 2.716 Å) and relatively acute $M-C-C_{ipso}$ angles (89.55° and 85.59°).^{26,27} This situation can result from two either independent or synergetic effects: (i) following the hypothesis proposed by Bercaw et al.,⁷ the less donating character of the tilted pyridine moiety (vide supra), as compared to that of the "in-line" (vs the M-N vector) pyridine moiety in C_2 -symmetric compounds, generates a more electrophilic metal center in C_s-symmetric compounds (e.g., **5b**); (ii) C_s coordination of the pyridine-bis(phenolate) or pyridine-bis(naphthoxy) ligands provokes steric unloading of the metal center. The different coordination mode of



Figure 4. Molecular structure of $\{ONO^{SiPh3}\}Ti(CH_2Ph)_2$ (**4a** · 2C₇H₈) (all solvent molecules and hydrogen atoms are omitted for clarity; in the bottom view, the SiPh₃ phenyl rings are also omitted; thermal ellipsoids drawn at 50% probability). Selected bond distances (Å) and angles (deg): Ti-O(1), 1.905(1); Ti-O(2), 1.918(1); Ti-N(1), 2.174(2); Ti-C(1), 2.099(2); Ti-C(2), 2.094(2); N(1)-Ti-O(1), 82.25(9); C(1)-Ti-C(2), 107.78(9); O(1)-Ti-O(2), 164.62(6).

 $\{ONO^{SiR3}\}^{2-}$ ligands in complexes **5b** (C_s) and **6a** (C_2) [at least in the solid state] is somewhat surprising considering the close similarity of ionic radii of Zr and Hf;^{29,7} however, too few data are available to establish what parameter(s) actually dictate(s) the coordination mode in this series of complexes.

Actually, the same factors may govern the formation of $7a \cdot (NHMe_2)$ (Figure 8). The coordination of the pyridine moiety in this compound is rather weak, as revealed by the relatively long Hf-N(1) distance of 2.480(2) Å.³⁰ Coordination of an additional molecule of the relatively weak donor NHMe₂ to the hafnium center obviously compensates its electronic demand. Such coordination is also not strong, as judged from the relatively long Hf-N(2) distance (2.461(2) Å).³¹ This is consistent with the observation that $7a \cdot (NHMe_2)$ rapidly loses the coordinated NHMe₂ molecule under vacuum to eventually yield 7a (*vide supra*). Attempts to grow

^{(28) (}a) Tsukahara, T.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 3303. (b) Lavanant, L.; Chou, T.-Y.; Chi, Y.; Lehmann, C. W.; Toupet, L.; Carpentier, J.-F. *Organometallics* **2004**, *23*, 5450.

⁽²⁹⁾ Effective ionic radii for six-coordinate metal centers: Ti⁴⁺, 0.605 Å; Zr⁴⁺, 0.72 Å; Hf⁴⁺, 0.71 Å. Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751–767.

⁽³⁰⁾ Hf-N(pyridine) distances are typically in the range 2.292–2.472 Å: (a) Boussie, T. R.; Diamond, G. M.; Goh, C.; Hall, K. A.; LaPointe, A. M.; Leclerc, M. C.; Murphy, V.; Shoemaker, J. A. W.; Turner, H.; Rosen, R. K.; Stevens, J. C.; Alfano, F.; Busico, V.; Cipullo, R. *Angew. Chem., Int. Ed.* **2006**, *45*, 3278. (b) Domski, G. J.; Edson, J. B.; Keresztes, I.; Lobkovsky, E. B.; Coates, G. W. *Chem. Commun.* **2008**, 6137.

⁽³¹⁾ Hf-NHR₂ distances are typically in the range 2.458–2.462 Å:
(a) Gao, M.; Tang, Y.; Xie, M.; Qian, C.; Xie, Z. *Organometallics* 2006, 25, 2578. (b) Roberts, J. L.; Marshall, P. A.; Jones, A. C.; Chalker, P. A.; Bickley, J. F.; Williams, P. A.; Taylor, S.; Smith, L. M.; Critchlow, G. W.; Schumacher, M.; Lindner, J. J. Mater. Chem. 2004, 14, 391.



Figure 5. Molecular structure of $\{ONO^{SirBuMe2}\}$ Ti $(CH_2Ph)_2$ (**4b**) (all hydrogen atoms are omitted for clarity; thermal ellipsoids drawn at 50% probability). Selected bond distances (Å) and angles (deg): Ti-O(1), Ti(1)-O(2), 1.9234(12); Ti-N(1), 2.155(2); Ti-C(1), Ti-C(2), 2.110(2); N(1)-Ti-O(1), 80.91(4); C(1)-Ti-C(2), 102.82(17); O(1)-Ti-O(2), 161.82(7).



Figure 6. Molecular structure of $\{ONO^{SirBuMe2}\}Zr(CH_2Ph)_2$ (**5b**) (all hydrogen atoms are omitted for clarity; thermal ellipsoids drawn at 50% probability). Selected bond distances (Å) and angles (deg): Zr(1)–O(1), 1.999(5), Zr(1)–O(2), 2.018(5); Zr(1)–N(1), 2.449(6); Zr(1)–C(1), 2.282(6); Zr(1)–C(2), 2.277(6); Zr(1)–C(1)–G_{ipso}(1), 2.716(6); Zr(1)–C_{ipso}(2), 2.632(6); N(1)–Zr(1)–O(1), 80.25(2); C(1)–Zr(1)–C(2), 97.18(2); O(1)–Zr(1)–O(2), 158.45(19).

crystals of the latter compound suitable for X-ray diffraction study failed so far.

Dynamic Properties of Dibenzyl Complexes in Solution. All the compounds within the series of dibenzyl complexes of $\{ONO^{SiR3}\}^{2-}$ ligands (i.e., 4a-c, 5a,b, and 6a) feature fluxional dynamics in toluene or dichloromethane solution, as revealed by VT NMR studies. The room-temperature ¹H NMR spectra of these compounds display broadened resonances (Figures S4–S6; see the Supporting Information). Upon raising the temperature to 80 °C (70 °C for 4a and 60 °C for 4b), the resonances collapse to a set of sharp signals, affording a pattern consistent with a single average C_2 - or C_s symmetric structure on the NMR time scale. Key resonances include (a) one sharp singlet for H⁴ hydrogens of the naphthoxy groups, 14 (b) one sharp triplet for H_{para} of the pyridine group, (c) one (still broadened) singlet resonance for the CH_2 benzyl groups, (d) optionally, for 4b and 5b, singlet resonances for both SiMe₂ and *t*Bu groups.

Complexes incorporating o-SiPh₃ groups (4a-6a) are poorly soluble and precipitated out from toluene- d_8 or



Figure 7. Molecular structure of complex { ONO^{SiPh3} }Hf-(CH₂Ph)₂ (**6a**) (thermal ellipsoids drawn at 50% probability). Selected bond distances (Å) and angles (deg): Hf-O(1), 2.017(3); Hf-O(2), 2.017(3); Hf-N(1), 2.280(4); Hf-C(1), 2.207(5); Hf-C(2), 2.211(5); Hf-C_{ipso}(1), 2.971(5); Hf-C_{ipso}(2), 3.068(5); N(1)-Hf-O(1), 79.05(13); C(1)-Hf-C(2), 110.8(3); O(1)-Hf-O(2), 158.00(13).

CD₂Cl₂ solutions upon lowering the temperature. Therefore, detailed low-temperature NMR studies were performed only for {ONO^{SiMe2/Bu}}Ti(CH₂Ph)₂ (4b) and {ONO^{SiMe2/Bu}}- $Zr(CH_2Ph)_2$ (5b). Upon cooling a toluene solution of 4b, the signals in the ¹H NMR spectrum decoalesced ($T_{coal} = ca$. 10 °C for TiCH₂Ph at 500 MHz) and, finally, split and sharpened at -50 °C. At this temperature, the ¹H NMR spectrum of 4b contains two sets of signals attributed to two species found in a 5:1 molar ratio (Figure 9). The major compound is represented by a singlet at δ 8.23 ppm for the naphthoxy H⁴ hydrogens, two doublets at δ 3.98 and 3.69 ppm (${}^{2}J_{H-H} = 8.1$ Hz) characteristic of an AB system for diastereotopic TiCHHPh hydrogens, a singlet resonance at δ 1.26 ppm for the tBu groups, and two singlets at δ 1.16 and 0.70 ppm for nonequivalent SiMeMe groups. Some of the resonances of the minor compound overlap with those of the major compound; however, some key resonances were identified and typically found shifted downfield from those of the major compound: the resonance for the naphthoxy H⁴ hydrogens is found at δ 8.35 ppm, two singlets of equal intensity for the Ti(CH₂Ph)₂ groups appear at δ 4.43 and 4.02 ppm, while resonances for the tBu and nonequivalent Si*MeMe* groups are found at δ 1.34 and δ 1.30 and 0.86 ppm, respectively. These observations are consistent with 4b existing as a mixture of two isomers of different symmetry, namely, C_2 or *rac*-4b (major; as observed in the solid state) and C_s or meso-4b (minor), which dynamically interconvert via an equilibrium, fast on the NMR time scale. At -50 °C, when the interconversion is frozen, the molar ratio between these species³² allowed calculating the energy difference (0.71 kcal·mol⁻¹) between the ground states using Maxwell-Boltzmann statistics.33

⁽³²⁾ The fact that the ratio between the two isomers is thermodynamically controlled was confirmed by the following experiment: an NMR tube with the desired sample was reheated at 90 °C over 3 h, and ¹H NMR spectroscopy was recorded again at low temperature (-50 °C for **4b**,-40 °C for **5b**). The same ratio between the two isomers was observed, whatever was the cooling rate.

⁽³³⁾ The Maxwell–Boltzmann statistical equation was used: $N_1/N_2 = (g_1/g_2)e^{-\Delta E/RT}$, where N_1/N_2 is the molar isomeric ratio, $g_1 = g_2 =$ degeneracy. (a) Goodman, J. M.; Kirby, P. D.; Hausted, L. O. *Tetrahedron Lett.* **2000**, 41, 9879. (b) McQuarrie, D. A.; Simon, J. D. *Molecular Thermodynamics*; University Science Books: Sausalito, CA, 1999.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complexes 4a,b, 5b, 6a, and 7a (NHMe₂)

complex	twist angle (deg)	$d_{\rm OO}({\rm \AA})$	М-С (Å)	M-C _{ipso} (Å)	M-C-C _{ipso} (deg)
{ONO ^{SiPh3} }Ti(CH ₂ Ph) ₂ (4a)	38.7	3.79	2.094(2)	2.924(2)	108.59(9)
	40.8		2.099(2)	2.998(2)	112.70(9)
$\{ONO^{SitBuMe2}\}Ti(CH_2Ph)_2$ (4b)	44.3	3.79	2.110(2)	3.120(2)	119.34(7)
$ONO^{SitBuMe2}$ $Zr(CH_2Ph)_2$ (5b)	50.96	3.95	2.282(6)	2.716(6)	89.55(2)
	62.68		2.277(6)	2.632(6)	85.59(2)
$\{ONO^{SiPh3}\}Hf(CH_2Ph)_2$ (6a)	40.5	3.96	2.207(5)	2.971(5)	110.87(15)
	40.5		2.211(5)	3.068(5)	105.79(17)
$\{ONO^{SiPh3}\}$ Hf $(NMe_2)_2 \cdot (NHMe_2)$ (7a)	45.9	3.96			
	64.4				
{ONO ^{CMe3} }Ti(CH ₂ Ph) ₂ (from ref 7)	27.6	3.70	2.1207(17)	2.74	96.92(10)
	28.2		2.1222(17)	2.73	97.43(10)
$\{ONO^{CEt3}\}$ Ti $(CH_2Ph)_2$ (from ref 7)	35.3	3.74	2.1022(10)	3.03	114.04(7)
	36.1		2.1167(10)	2.93	107.67(7)



Figure 8. Molecular structure of $\{ONO^{SiPh3}\}Hf(NMe_2)_2 \cdot (NHMe_2)$ (**7a** · (**NHMe_2**) · 4(C₆H₆)) (all solvent molecules and hydrogen atoms are omitted for clarity; thermal ellipsoids drawn at 50% probability). Selected bond distances (Å) and angles (deg): Hf–O(1), 2.040(2); Hf–O(2), 2.068(2); Hf–N(1), 2.480(2); Hf–N(2), 2.461(2); Hf–N(3), 2.054(2); Hf–N(4), 2.043(2); N(1)–Hf–N(4), 173.72(8); N(2)–Hf–N(3), 175.22-(9); O(1)–Hf–O(2), 148.95(7).

Similar low-temperature NMR investigations were performed for **5b**. The decoalescence of the $ZrCH_2Ph$ benzylic signals was observed at higher temperature ($T_{coal} = ca. 40 \,^{\circ}C$ at 500 MHz), as compared to that determined for its Ti analogue 4b, and the exchange was entirely frozen at -40 °C (Figure 10). Similarly to **4b**, the low-temperature (-40 °C)¹H NMR spectrum of **5b** displays two sets of resonances that are consistent with coexistence of two isomers in a 10:1 ratio. The major isomer of **5b** features a C_s -symmetric structure in solution, in agreement with the solid-state structure (Figure 6). The most characteristic NMR feature, diagnostic of the meso-like coordination of the ligand, is the pattern of two singlets of equal intensity at δ 3.76 and 3.39 ppm for two nonequivalent $Zr(CH_2Ph)_2$ groups. This assignment was confirmed in the ¹³C NMR spectrum (-40 °C, 125 MHz), where the $ZrCH_2Ph$ benzylic carbons appear as two resonances at δ 64.7 and 63.9 ppm.²⁷ The minor isomer of **5b** is evidently C_2 -symmetric and, accordingly, shows the same pattern of ¹H NMR resonances as established for rac-4b, in particular a diagnostic AB system for the ZrCHHPh groups with two doublets (${}^{2}J_{H-H} = 10.1$ Hz) at δ 2.68 and 2.49 ppm. Also, the ¹³C NMR spectrum of *rac*-**5b** at $-40 \,^{\circ}$ C contains only one resonance for the benzyl groups at δ 69.4 ppm (as established from 2D ¹H-¹³C HMBC and HMQC experiments). An energy preference of 1.01 kcal·mol⁻¹ for *meso*-**5b** over *rac*-**5b** was calculated on the basis of NMR data at -40 °C.³³

The kinetics of *rac/meso* interconversion/racemization for 4b and 5b were probed by line-shape analysis of the benzyl region of the ¹H NMR spectra (-50 to 60 °C for 4b, Figure 11; -40 to 80 °C for 5b; Figure S13, see the Supporting Information). In each case, the spectra were simulated for a two-site system with the populations corresponding to the isomeric ratio found experimentally, i.e., 5:1 for 4b and 10:1 for **5b**. The activation parameters for the interconversion/ racemization process were extracted by a standard Eyring analysis (Figure S14, Supporting Information): **4b**, $\Delta H^{\dagger} =$ 12.9(7) kcal·mol⁻¹ and $\Delta S^{\dagger} = -3(1)$ cal·mol⁻¹·K⁻¹; **5b**, $\Delta H^{\dagger} = 13.4(8)$ kcal·mol⁻¹ and $\Delta S^{\dagger} = -7(1)$ cal·mol⁻¹·K⁻¹. The interconversion/racemization thus appeared to be somewhat more facile for 4b, as evaluated from the rate constant ratios k^{4b}/k^{5b} of 7.8 at 313 K and the difference between the experimentally determined free energies for these complexes, $\Delta G^{\dagger}_{313}(\mathbf{4b}) = 13.8(7) \text{ kcal} \cdot \text{mol}^{-1}$ and $\Delta G^{\dagger}_{313}(\mathbf{5b}) =$ 15.6(8) kcal·mol⁻¹, respectively.

In sharp contrast with the aforementioned pyridine-bis-(naphthoxy) complexes, compound **4c**, bearing thiophenebased ligand { OSO^{SiPh3} }²⁻, showed no fluxional dynamics phenomena (i.e., no broadening) in toluene- d_8 in the temperature range 0 to 80 °C.³⁴ The room-temperature ¹H NMR spectrum of **4c** showed a series of sharp signals consistent with the presence of only one species. Key resonances include (a) a singlet for naphthoxy H⁴ hydrogens at δ 8.37 ppm, (b) a singlet for the thiophene hydrogens at δ 6.45 ppm, and (c) two singlets for the nonequivalent Ti(CH₂Ph)₂ groups at δ 2.51 and 2.15 ppm. In the ¹³C NMR spectrum (25 °C, 125 MHz), benzylic carbons appear as two resonances at δ 94.7 and 93.7 ppm. These data indicate that **4c** features an average C_s symmetry in toluene.³⁵

Theoretical Investigation on the Interconversion Mechanism. To get a better insight in the mechanism of interconversion that operates in these neutral group 4 metal pyridinebis(naphthoxy) systems, DFT calculations were carried out at both B3LYP and BP86 levels (see the Experimental Section, Computational Details). In order to evaluate the "net" impact of the coordination mode of the pyridine-bis(naphthoxy) ligand backbone on the thermodynamic distribution of isomers and nature of the transition state, a few simplifications were imposed on the model system: the bulky SiR₃ groups and benzyl groups at the metal center were replaced by hydrogen and methyl groups, respectively. The main relevant computed data are summarized in Table 2.

⁽³⁴⁾ Below 0 $^{\circ}$ C, significant precipitation is observed due to the poor solubility of this complex.

⁽³⁵⁾ If any putative C_1 stereoisomer would be considered, this would indicate very low interconversion barrier.



Figure 9. ¹H NMR (500 MHz, toluene- d_8 , 223 K) spectrum of {ONO^{Si/BuMe2}}Ti(CH₂Ph)₂ (**4b**); $\blacksquare = rac-4b$, $\blacktriangle = meso-4b$ (* stands for residual solvent resonances).



Figure 10. ¹H NMR (500 MHz, toluene- d_8 , 233 K) spectrum of {ONO^{Si/BuMe2}}Zr(CH₂Ph)₂ (**5b**); $\blacksquare = rac$ -**5b** (* stands for residual solvent resonances).

First, the structures of the two stationary points (i.e., C_2 and C_s isomers) for each of the Ti, Z,r and Hf {ONO^H}-MMe₂ complexes were optimized to assess the degree of agreement between the experimental and calculated geometrical parameters on both levels of theory. Regardless the nature (or ionic radius) of the metal center or DFT functional used, the meso-like conformation was found to be systematically favored over the rac-like conformation. This is in agreement only for Zr complex 5b, as solid-state and solution structures of 4a,b, 6a, and 8a²⁵ indicate that the *rac* conformation is more stable. However, it must be noted that the energy differences between the computed meso and rac conformations were quite low $(0.5-1.8 \text{ kcal} \cdot \text{mol}^{-1} \text{ at the BP86 level};$ 2.1-3.6 kcal·mol⁻¹ at the B3LYP level), which remain within the uncertainty of these DFT calculations.³⁶ Apart from the two ground states (C_2 and C_s isomers), no other stable stationary points (species featuring geometries other than those of the C_2 and C_s isomers) or intermediates (for example, species with unbound pyridine group) were located.³⁷

In every case, the transition state connecting directly the two minima of the C_2 and C_s isomers was located. The nature of the TS was probed by a full vibrational analysis, which resulted in a single imaginary frequency. The transition-state geometries found for the three metal systems (Ti, Zr, and Hf) are very similar. The general optimized structure (Figure 12) clearly features an asymmetric coordination of the {ONO} ligand, which is intermediary between those represented in C_2 and C_s isomers; that is, one naphthoxy moiety becomes substantially twisted with respect to the bridging pyridine unit (\angle (pyridine– naphthoxy)[1] = 52.25–55.21° and d_{HH} [1] = 2.454–2.521 Å), while the second naphthoxy moiety approaches the plane of the pyridine unit with its proximal edge (\angle (pyridine–naphthoxy)[2] = 35.34–40.37° and d_{HH} [2] = 1.563–1.591 Å).

The activation barriers calculated for this process (Ti, 11.4(10.1) kcal·mol⁻¹; Zr, 12.5(11.2) kcal·mol⁻¹; Hf, 12.2(11.1) kcal·mol⁻¹) turned out to be very close to those determined experimentally for Ti (**4b**) and Zr (**5b**) complexes (12.9(7) and 13.4(8) kcal·mol⁻¹, respectively).

Studies on the Polymerization Activity. The catalytic potential of the prepared compounds was preliminarily investigated in the polymerization of propylene using different conditions (Table 3). The results obtained appeared to be somewhat disappointing and not easy to rationalize. Surprisingly enough, no activity was observed with all

⁽³⁶⁾ It must be emphasized that a simplified model was used for calculations, with the assumption that the contribution of benzyl groups at the metal and SiR_3 groups at the *ortho* positions of the naphthoxy moieties to the final geometry of the ligand framework is insignificant.

⁽³⁷⁾ Attempts to optimize each of these geometries as starting points led to the ground states of either C_2 or C_s isomers.

Table 2. Main Computed Data for C_2/C_s Interconversion Process in {ONO}MMe₂ Complexes^{*a*}

	Ti				Zr		Hf		
	<i>C</i> ₂	C_s	TS	<i>C</i> ₂	C_s	TS	C_2	C_s	TS
relative energy (kcal·mol ⁻¹)	2.13	0	11.41	3.53	0	12.48	3.56	0	12.19
	(0.48)	(0)	(10.06)	(5.84)	(0)	(11.16)	(1.76)	(0)	(11.08)
M-O	1.878, 1.878	1.827, 1.827	1.831, 1.850	2.034, 2.035	1.985, 1.985	1.982, 1.999	2.001, 2.001	1.955, 1.955	1.952, 1.967
	(1.889, 1.889)	(1.844, 1.844)	(1.845, 1.865)	(2.044, 2.044)	(1.995, 1.996)	(1.994, 2.012)	(2.010, 2.010)	(1.964, 1.964)	(1.962, 1.978)
	[1.905, 1.918]				[1.999, 2.018]		[2.016, 2.017]		· · · · · ·
M-N(1)	2.201	2.512	2.339	2.358	2.590	2.491	2.338	2.566	2.472
	(2.178) [2.174]	(2.379)	(2.269)	(2.335)	(2.516) [2.449]	(2.437)	(2.312) [2.279]	(2.496)	(2.419)
M-C	2.063, 2.064	2.062, 2.068	2.061, 2.075	2.227, 2.228	2.230, 2.231	2.229, 2.234	2.203, 2.203	2.203, 2.206	2.203, 2.210
	(2.074, 2.074)	(2.074, 2.084)	(2.072, 2.090)	(2.227, 2.227)	(2.231, 2.235)	(2.229, 2.238)	(2.201, 2.201)	(2.203, 2.207)	(2.201, 2.211)
	[2.100, 2.094]	(,)	(,		[2.277, 2.282]		[2.207. 2.211]	(, ,	(, ,
doo	3 711	3 566	3 605	3,969	3 845	3.838	3 910	3,788	3 374
00	(3,739)	(3.634)	(3.650)	(3.997)	(3.892)	(3.884)	(3,939)	(3.832)	(3.819)
	[3,788]	(51051)	(51050)	(515577)	[3.947]	(51001)	[3,959]	(0.002)	(5.015)
duu	2 241 2 242	2 353 2 355	1 574 2 454	2 293 2 293	2 405 2 406	1 587 2 517	2 281 2 281	2 386 2 387	1 591 2 488
whn	(2, 259, 2, 259)	(2 333 2 334)	(1.563 2.455)	$(2\ 309\ 2\ 310)$	(2 391 2 391)	(1.584, 2.521)	(2 297 2 297)	$(2 \ 374 \ 2 \ 377)$	(1581 2492)
	(2.23), 2.23)	(2.333, 2.334)	(1.505, 2.455)	(2.50), 2.510)	[2.371, 2.371]	(1.504, 2.521)	(2.297, 2.297) [2.243, 2.279]	(2.574, 2.577)	(1.501, 2.4)2)
N(1) - M - O(1)	81.09	77.81	76.86	77 25	75 91	72.90	77 76	76.12	73 41
	(81.75)	(80.63)	82 39	(77.89)	(77, 59)	79.40	(78 44)	(77.80)	79.50
	[82 25]	(00.05)	(78 30 83 66)	(//.05)	[79 01 80 25]	(74 17 80 70)	[78 98 79 05]	(77.00)	(74 65 80 74)
C(1) - M - C(2)	110.96	104 22	107.16	110.94	106 50	108.06	109 19	104 94	105 78
C(1) M $C(2)$	(112.19)	(107.94)	(109.89)	(111.60)	(107.88)	(109.37)	(109.56)	(105.55)	(106.74)
	[107 78]	(107.54)	(10).0))	(111.00)	[97 18]	(10).57)	[110 32]	(105.55)	(100.74)
O(1) - M - O(2)	162.18	154.85	156 75	154 53	151 17	149 11	155 53	151 37	148 73
O(1) IVI $O(2)$	(163.50)	(160.45)	(150.50)	(155,77)	(154, 30)	(151.60)	(156.87)	(154.60)	(151, 50)
	[164.62]	(100.45)	(159.50)	(155.77)	[159.42]	(151.09)	[158.02]	(134.09)	(151.59)
twist angle	29 52 29 54	17 61 17 62	25 24 52 25	40 44 40 45	10.82 10.05	28 12 51 65	20.82 20.84	19 95 19 02	27 02 52 16
twist aligie	(20.16, 20.10)	(45.70, 47.02)	(26 24 52.25)	40.44, 40.43	+7.03, 47.73 (10 15 10 17)	(40.27 55.21)	(10 17 10 10)	40.03, 40.93	(20, 52, 53.10)
	(39.10, 39.19)	(43.70, 43.71)	(30.24, 32.83)	(40.99, 40.99)	(40.43, 40.47)	(40.57, 55.21)	(40.47, 40.48)	(47.31, 47.09)	(39.32, 33.80)
	[38.67, 40.79]				[30.96, 49.33]		[40.47, 40.50]		

^{*a*} The first values correspond to the B3LYP level, the values in parentheses correspond to the BP86 level; in the square brackets are the average experimental values for complexes 4a (Ti), 5b (Zr), and 6a (Hf).



Figure 11. Experimental (left) and simulated (right) ¹H NMR spectra (region of benzylic protons) of $\{ONO^{Si/BuMe2}\}$ -Ti(CH₂Ph)₂ (**4b**). Best fit first-order rate constants are given above the spectra.

dibenzyl complexes when $[Ph_3C][B(C_6F_5)_4]$ was used as the activator (entries 1, 3, 5, 10). 38 In the series of benzyl complexes, only zirconium precursor 5b was found to be active when activated with MAO (1000 equiv vs Zr). However, the activity of the 5b/MAO system (320-490 kg. $mol^{-1} \cdot h^{-1}$) was at least 1 order of magnitude inferior to that of related systems based on pyridine-bis(phenoxy) zirconium dibenzyl complexes.⁷ The polymers recovered were oily products and readily soluble in toluene and hardly precipitated by addition of methanol. These products were analyzed by GPC and ¹H and ¹³C NMR spectroscopy. In line with the observations made by Bercaw et al. on similar catalytic systems,⁷ the polypropylenes obtained with **5b**/ MAO featured bimodal distributions, that is, a minor high $(M_{\rm n} = 120\,000 - 140\,000 \text{ g} \cdot \text{mol}^{-1}, \text{PDI} = 1.25 - 1.37)$ and a major low $(M_n = 720 - 800 \text{ g} \cdot \text{mol}^{-1}, \text{ PDI} = 1.24 - 1.53)$ molecular weight fraction (Figure 13b) (entries 6-8). The observation of two relatively narrow distributions could be explained by the presence of two types of "singlesite" catalysts, possibly resulting from different activation pathways of the neutral precursor with commercial MAO.⁷ The latter reagent is actually well known to contain significant amounts of AlMe₃ (TMA). To assess this hypothesis, an experiment with activation of 5b by a TMA-free, so-called "dried" MAO ("DMAO") was attempted (entry 9). In this case, the catalytic system produced selectively the lower molecular weight fraction (Figure 13a).

⁽³⁸⁾ All attempts to isolate the cationic species resulting from neutral benzyl complexes failed. This hampered us also from investigating interconversion processes in these species, which are more relevant to polymerization than their neutral precursors.





Figure 12. DFT-optimized structure of the transition state for the C_2/C_s interconversion process in {ONO}MMe₂ complexes.



Figure 13. GPC traces for propylene oligo/polymers obtained with **5b**: (a) activated with "DMAO" (entry 9, Table 3), (b) activated with MAO (entry 7, Table 3).

entry	cat. (µmol)	cocat. (equiv vs M)	T_{polym} (°C)	time (min)	m (g)	activity, $(kg \cdot mol^{-1} \cdot h^{-1})$	$M_{\rm n} ({\rm g} \cdot {\rm mol}^{-1})$	$M_{ m w}/M_{ m n}$
1	4a (9.0)	Trityl/TIBAL (3:200)	50	30	0	0		
2	4b (9.0)	"DMAO" (1000)	25	15	0	0		
3	4b (9.0)	Trityl/TIBAL (3:200)	50	30	0	0		
4	5a (9.0)	"DMAO" (1000)	25	15	0	0		
5	5a (9.0)	Trityl/TIBAL (3:200)	50	30	0	0		
6	5b (25.0)	MAO (1000)	25	15	3.00	480	120 100	1.3
							800	1.5
7	5b (9.0)	MAO (1000)	25	15	1.11	490	116300	1.4
	. /						760	1.5
8	5b (9.0)	MAO (1000)	50	15	0.71	320	140 800	1.2
		~ /					720	1.2
9	5b (9.0)	"DMAO" (1000)	25	15	0.93	413	1100	1.4
10	5b (9.0)	Trityl/ TIBAL (3:200)	50	15	0	0		

 Table 3. Propylene Polymerization Data^a

^{*a*} General conditions, unless otherwise stated: toluene (80 mL), P = 5 bar.

The ${}^{13}C{}^{1}H$ NMR spectra of the oligo/polypropylenes obtained with 5b/MAO and 5b/"DMAO" were overall very similar to those recorded for materials obtained with pyridine-bis(phenolate) systems.⁷ As evidenced by the complex pattern of signals in the CH region at δ 27.0–27.8 ppm, these materials feature an irregular microstructure (Figure 14).³⁹ Although the overall pattern of resonances is similar when "DMAO" was used instead of MAO, the intensity ratio of some signals was affected. For instance, the intensities of the resonances for isobutyl end-groups at δ 22–24 ppm were substantially decreased when "DMAO" was used.40 With both MAO and "DMAO", the presence of intense olefinic resonances was observed in the downfield region of both the ^1H and ^{13}C NMR spectra at δ 4.73 and 4.66 (δ 144.9 and 111.5) $(CH_2 = CH(CH_3) -)$, 5.48 and 5.40 (δ 139.5 and 120.4) (CH₃CH=CH-), and 5.81, 5.00, and 4.93 (& 145.0 and 114.2) (CH₂=CHCH(CH₃)-) ppm.⁴¹ These observations indicate that enchainment of propylene is not regioselective and proceeds both in 1,2- and 2,1-fashions and that chain termination proceeds via β -H and β -Me elimination.

(40) This fact is in agreement with one of the hypotheses by Bercaw et al. (ref 7) that isobutyl groups are formed not only by primary insertion of a propylene molecule in the [Zr-Me] bond but also by chain transfer to Al of TMA followed by hydrolysis upon quenching.

The performance of Ti (4a,b,c), Zr (5a), and Hf (7a) precursors was also briefly assessed in ethylene polymerization (Table 4). When activated with MAO (1000 equiv vs metal), M{ONO^{SiR3}}-type complexes 4a and 7a showed a low catalytic activity (entries 1 and 7, respectively) and vielded polyethylenes with bimodal distributions, as observed with 5b/MAO in propylene polymerization (vide supra). When activated with [Ph₃C](B(C₆F₅)₄]/Al(*i*Bu)₃ (3:200),⁴² dibenzyl complexes **4a**,**b** and **5a** provided higher activities (2090-3010 kg·mol⁻¹·h⁻¹ at 50 °C, 5 atm), which are comparable to those of Chan's pyridine-bis(phenolate) systems.⁸ The isolated polymers all featured monomodal distributions, even when $[Ph_3C](B(C_6F_5)_4]/Al(iBu)_3$ was used, which calls for the absence of any chain transfer to Al. The melting temperatures were in the range 134–140 °C, indicative of the linear microstructure of these polyethylenes. Surprisingly enough, dibenzyl-titanium complex 4c derived from the sulfur-based $\{OSO^{SiPh3}\}^{2-}$ ligand was found completely inactive (entries 4, 5). This observation highlights the key influence of the bridging heteroatom. We have previously reported that some Ti-{OSO} complexes based on thio-bridged dialkoxide ligands are poorly active for ethylene polymerization when activated with MAO, while analogous Zr-{OSO}/MAO systems are quite active but

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⁽⁴³⁾ Lavanant, L.; Silvestru, A.; Faucheux, A.; Toupet, L.; Jordan, R. F.; Carpentier, J.-F. *Organometallics* **2005**, *24*, 5604.



Figure 14. Selected region of ¹³C NMR spectra of propylene oligo/polymers obtained with **5b**: (up) activated with "DMAO" (entry 9, Table 3), (bottom) activated with MAO (entry 7, Table 3).

Table 4. Ethylene Polymerization Data^a

entry	cat. (µmol)	cocat. (equiv vs M)	$T_{\rm polym}$ (°C)	time (min)	<i>m</i> (g)	activity, $(kg \cdot mol^{-1} \cdot h^{-1})$	$M_{\rm n} ({\rm g} \cdot {\rm mol}^{-1})$	$M_{\rm w}/M_{\rm n}$	$T_{\rm m}$ (°C)
1	4a (4.5)	MAO (1000)	50	30	0.55	244	7 200 752 000	2.8 2.0	136
2	4a (9.0)	Trityl/TIBAL (3:200)	50	10	3.14	2090	15700	4.2	134
3	4b (9.0)	Trityl/TIBAL (3:200)	50	5	1.97	2360	12230	2.5	132
4	4c (9.0)	MAO (1000)	50	10	0	0			
5	4c (9.0)	Trityl/TIBAL (3:200)	50	10	0	0			
6	5a (9.0)	Trityl/TIBAL (3:200)	50 (~60)	5	2.26	3010	135 500	4.1	140
7	7a (9.0)	MAO (1000)	50	15	0.11	48	7 920	58	131
8	7a (9.0)	Trityl/TIBAL (3:200)	50	15	0	0			

^{*a*} General conditions, unless otherwise stated: 300 mL glass reactor, toluene (80 mL), P = 5 bar.

deactivate extremely rapidly (within seconds).⁴³ The polymerization performance and overall behavior of this family of catalysts was also quite different from those of related catalysts based on amino-dialkoxide ligands.⁴⁴

Conclusions and Perspectives

We have elaborated a simple and effective synthetic strategy toward a new type of silyl-substituted bis(naphthoxy)based ligand system incorporating both pyridine and thiophene donors. A variety of pro-ligands have been synthesized and used in the preparation of discrete mononuclear group 4 metal complexes. As anticipated, the {ONO^{SiR3}}²⁻ ligands provide two different coordination modes, giving rise to two stable stereoisomers in neutral compounds, namely, C_2 (*rac*-like)- and C_s (*meso*-like)-symmetric forms; on the other hand, the {OSO^{SiPh3}}²⁻ ligand apparently leads only to C_s -symmetric compounds. No notable effect of the metal ionic radius on the coordination mode was revealed. In titanium and hafnium neutral complexes, the {ONO^{SiR3}}²⁻ framework chelates in a *rac*-like fashion, while with zirconium the ligand coordination is *meso*-like. Possible interconversion between these two stereoisomeric neutral compounds has been demonstrated using both experimental and computational methods.³⁸

Among the different complexes prepared, only zirconium complex **5b** supported by a $\{ONO^{SiMe2tBu}\}^{2-}$ ligand, upon activation with MAO, was found to oligomerize propylene. The surprising inactivity of dibenzyl precursors **4a**, **b** and **5a** may stem from significant sterical hindrance imposed by SiR₃ groups. Further modification of these systems by tuning of ligand platforms to enhance their catalytic performance is underway and will be reported in due course.

Experimental Section

General Considerations. All manipulations were performed under a purified argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents were distilled from Na/ benzophenone (THF, Et₂O) and Na/K alloy (toluene, pentane) under nitrogen, degassed thoroughly, and stored under nitrogen prior to use. Deuterated solvents (benzene- d_6 , toluene- d_8 , THF- d_8 ; >99.5% D, Eurisotop) were vacuum-transferred from Na/K alloy into storage tubes. Tetrabenzyl M(CH₂Ph)₄

⁽⁴⁴⁾ Lavanant, L.; Toupet, L.; Lehmann, C. W.; Carpentier, J.-F. Organometallics 2005, 24, 5620, and references therein.

(M = Ti, Zr, Hf), Hf(NMe₂)₄ precursors, S-Phos (dicyclohexyl-(2',6'-dimethoxy-1,1'-biphenyl-2-yl)phosphine), and RuPhos (dicyclohexyl(2',6'-diisopropoxy-1,1'-biphenyl-2-yl)phosphine) were prepared using reported procedures.¹⁵ Other starting materials were purchased from Acros, Strem, and Aldrich and used as received. NMR spectra of complexes were recorded on Bruker AC-200, AC-300, and AM-500 spectrometers in Teflon-valved NMR tubes at 25 °C unless otherwise indicated. ¹H and ¹³C chemical shifts are reported in ppm vs SiMe₄ and were determined by reference to the residual solvent peaks. Assignment of resonances for organometallic complexes was made from 2D ¹H⁻¹³C HMQC and HMBC NMR experiments. Coupling constants are given in hertz. Elemental analyses (C, H, N) were performed using a Flash EA1112 CHNS Thermo Electron apparatus and are the average of two independent determinations.

(3-Methoxy-2-naphthyl)(triphenyl)silane. A solution of sec-BuLi (15.3 mL of a 1.3 M solution in hexane/cyclohexane, 19.9 mmol) was added dropwise to a stirred solution of 2-methoxynaphthalene (3.00 g, 19.0 mmol) in THF (70 mL) at -30 °C over 15 min. After stirring overnight at room temperature, a dark solution was obtained, to which was added a solution of Ph₃SiCl (5.87 g; 19.9 mmol) and HMPA (3.46 mL, 19.9 mmol) in THF (50 mL). The reaction mixture was refluxed for 20 h, cooled, and diluted with water (500 mL). The organic part was extracted with Et₂O (3×50 mL). The combined organic extracts were dried over MgSO4 and evaporated. The crude residue was recrystallized from heptane and dried under vacuum to give (3-methoxy-2-naphthyl)(triphenyl)silane (7.11 g, 17.1 mmol, 90%). ¹H NMR (200 MHz, CDCl₃, 25 °C): δ 7.80 (m, 2H), 7.67 (m, 7H), 7.55-7.23 (m, 12 H), 3.69 (s, 3H, OCH₃). Anal. Calcd for C₂₉H₂₄OSi: C, 83.61; H, 5.81. Found: C, 83.5; H, 5.73

(4-Bromo-3-methoxy-2-naphthyl)(triphenyl)silane. A 150 mL Schlenk flask was charged with (3-methoxy-2-naphthyl)-(triphenyl)silane (4.68 g, 11.23 mmol) and NBS (2.20 g, 12.36 mmol) under argon, followed by addition of DMF (10 mL). The resultant mixture was stirred overnight at room temperature, then diluted with water (500 mL) and extracted with CH₂Cl₂ (3×50 mL). The combined organic extracts were washed with water (200 mL) and brine and dried over Na₂SO₄. The product was purified by passing through a short silica column using heptane/EtOAc (15:1) as eluent, to afford the product as an off-white solid (5.28 g, 10.66; 96%). ¹H NMR (200 MHz, CDCl₃, 25 °C): δ 8.29 (d, J = 8.4 Hz, 1H), 7.80 (s, 1H), 7.66 (m, 8H), 7.52–7.27 (m, 10H), 3.18 (s, 3H, OCH₃). Anal. Calcd for C₂₉H₂₃BrOSi: C, 70.30; H, 4.68. Found: C, 70.0; H, 4.56. **One-Pot Synthesis of {ONO**^{SIPh3}}B(OH) (2). (i) To a solution

of (4-bromo-3-methoxy-2-naphthyl)(triphenyl)silane (1.44 g, 2.91 mmol) in THF (20 mL) was added iPrMgCl·LiCl (3.7 mL of a 0.82 M solution in THF, 3.06 mmol). The reaction mixture was stirred at 60 °C for 2 h; then volatiles were removed under vacuum. (ii) Anhydrous ZnCl₂ (0.41 g, 3.01 mmol) was charged in a Schlenk flask, THF (30 mL) was vacuum transferred, and the resultant solution was stirred for 30 min at room temperature. (iii) The previous solution was transferred to a Teflon-valved Schlenk followed by addition of Pd₂(dba)₃ (0.053 g, 57.9 µmol), S-Phos (0.095 g, 231 µmol), and 2,6-dibromopyridine (0.34 g, 1.45 mmol). The reaction mixture was stirred for 30 h at 105 °C, cooled to room temperature, diluted with water (200 mL), and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were dried over MgSO4 and evaporated to dryness. The crude material was composed of ca. 80% of desired product, 2,6-bis[2-methoxy-3-(triphenylsilyl)-1-naphthyl]pyridine, as judged by ¹H NMR spectroscopy. (iv) The crude material was redissolved in dry CH₂Cl₂ (40 mL) under argon and treated with BBr₃ (4.36 mL of a 1.0 M solution in CH₂Cl₂, 4.36 mmol) at -30 °C. The resultant solution was stirred overnight at room temperature, cooled to 0 °C, and then quenched with water (50 mL). The organic layer was separated and dried

over Na₂SO₄. Solvent was removed under vacuum, and the residue was purified by column chromatography (silica, heptane/CH₂Cl₂, 1:1, $R_f = 0.12$) to give **2** as a pale yellow microcrystalline material (0.57 g, 0.63 mmol, 43%). ¹H NMR (500 MHz, CD₂Cl₂, 25 °C): δ (resonance for OH was not observed) 8.29 (d, J = 8.5 Hz, 2H), 8.10 (d, J = 7.9 Hz, 2H), 8.02 (t, J =7.9 Hz, 1H), 7.78 (s, 2H), 7.60 (d, J = 7.9 Hz, 2H), 7.54 (t, J =8.0 Hz, 2H), 7.48 (d, J = 7.2 Hz, 12H), 7.32 (t, J = 7.9 Hz, 2H), 7.27 (t, J = 7.2 Hz, 6H), 7.14 (t, J = 7.2 Hz, 12H). ¹³C{¹H} NMR (125 MHz, CD₂Cl₂, 25 °C): δ 139.3, 136.7, 136.5, 136.3, 134.6, 132.1, 129.7, 129.3, 129.1, 129.1, 128.3, 127.6, 126.7, 123.6, 122.9, 122.4, 111.9. MS-FAB (m/z): 905.3 (M⁺). Anal. Calcd for C₆₁H₄₄BNO₃Si₂: C, 80.87; H, 4.90. Found: C, 80.7; H, 4.34.

2-(Methoxymethoxy)naphthalene. To a suspension of NaH (5.00 g, 208 mmol) in DMF (150 mL), under argon flow, was added solid 2-hydroxynaphthalene (20.0 g, 138.7 mmol) at 0 °C by small portions. After stirring for 4 h at room temperature, methoxymethyl chloride (17.8 g, 221 mmol) was added slowly, and the reaction mixture was stirred for 10 h. The reaction mixture was carefully diluted with water (ca. 1 L), and organic materials were extracted with CH₂Cl₂ (3 × 50 mL). The combined organic extracts were washed with water (2 × 500 mL) and brine and dried over MgSO₄. The solution was evaporated to dryness at 80 °C to give a colorless oily product (25.1 g, 133.3 mmol), which was used without further purification. ¹H NMR (200 MHz, CDCl₃, 25 °C): δ 7.80 (m, 3H), 7.55–7.37 (m, 3H), 7.26 (m, 1H), 5.34 (s, 2H, OCH₂O), 3.57 (s, 3H, OCH₃). Anal. Calcd for C₁₂H₁₂O₂: C, 76.57; H, 6.43. Found: C, 76.59; H, 6.55.

[3-(Methoxymethoxy)-2-naphthyl](triphenyl)silane. A solution of sec-BuLi (19.0 mL of a 1.3 M solution in hexane/ cyclohexane, 24.7 mmol) was added dropwise to a stirred solution of 2-(methoxymethoxy)naphthalene (4.64 g, 24.7 mmol) in THF (150 mL) at -78 °C over 15 min. After stirring overnight at room temperature, a dark solution was obtained, to which was added a solution of Ph₃SiCl (7.27 g, 24.7 mmol) and HMPA (4.3 mL, 24.7 mmol) in THF (100 mL). The reaction mixture was refluxed for 40 h, cooled to room temperature, and diluted with water (1 L). The organic materials were extracted with $Et_2O(3 \times 100 \text{ mL})$, and the combined organic extracts were dried over MgSO₄ and evaporated to dryness. The crude residue was recrystallized from heptane and dried under vacuum to give [3-(methoxymethoxy)-2-naphthyl](triphenyl)silane (8.25 g, 18.5 mmol, 75%). ¹H NMR (200 MHz, CDCl₃, 25 °C): δ 7.83–7.75 (m, 2H), 7.72-7.58 (m, 7H), 7.55-7.25 (m, 12 H), 4.96 (s, 2H, OCH_2O , 3.00 (s, 3H, OCH_3). Anal. Calcd for $C_{30}H_{26}O_2Si$: C, 80.68; H, 5.87. Found: C, 80.4; H, 5.41.

[3-(Methoxymethoxy)-2-naphthyl](tert-butyldimethyl)silane. A solution of sec-BuLi (25.3 mL of a1.3 M solution in hexane/ cyclohexane; 32.9 mmol) was added dropwise to a stirred solution of 2-(methoxymethoxy)naphthalene (6.20 g, 32.9 mmol) in THF (180 mL) at -78 °C over 15 min. After stirring overnight at room temperature, a dark solution was obtained, to which was added a solution of tBuMe₂SiCl (5.00 g, 33.2 mmol) and HMPA (5.7 mL, 32.8 mmol) in THF (50 mL). The reaction mixture was refluxed for 40 h, cooled at room temperature, and diluted with water (1 L). The organic materials were extracted with $Et_2O(3 \times 100 \text{ mL})$, and the combined organic extracts were dried over MgSO4 and evaporated to dryness. The residue was redissolved in heptane (100 mL), passed through a short pad of silica, and evaporated. The resultant pale yellow oil was dried under vacuum to give [3-(methoxymethoxy)-2-naphthyl](tert-butyldimethyl)silane (8.97 g, 29.7 mmol, 90%). ¹H NMR (200 MHz, CDCl₃, 25 °C): δ 7.91 (s, 1H), 7.78 (m, 2H), 7.41 (m, 3H), 5.31 (s, 2H, OCH₂O), 3.54 (s, 3H, OCH₃), 0.97 (s, 9H, tBu), 0.41 (s, 6H, Me). Anal. Calcd for C₁₈H₂₆O₂Si: C, 71.47; H, 8.66. Found: C, 71.1; H, 8.76.

One-Pot Synthesis of \{ONO^{SiPh3}\}H_2(3a). (i) To a solution of [3-(methoxymethoxy)-2-naphthyl](triphenyl)silane (2.30 g, 5.15 mmol) in THF (40 mL) was added TMEDA (0.78 mL, 5.16 mmol) followed by addition of *sec*-BuLi (4.2 mL of a 1.3 M

solution in hexane/cyclohexane, 5.46 mmol) at -78 °C. The reaction mixture was stirred at room temperature overnight; afterward volatiles were evaporated and the residue was dried for 1 h under vacuum. (ii) Anhydrous ZnCl₂ (0.70 g, 5.15 mmol) was charged in a Schlenk flask, THF (30 mL) was vacuum transferred in, and the resultant solution was stirred for 30 min at room temperature. (iii) The previous solution was transferred to a Teflon-valved Schlenk followed by addition of Pd₂(dba)₃ (0.094 g, 103 $\mu mol),$ S-Phos (0.168 g, 409 $\mu mol),$ and 2,6-dibromopyridine (0.61 g, 2.57 mmol). The reaction mixture was stirred for 40 h at 105 °C, cooled to room temperature, diluted with water (200 mL), and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were dried over MgSO₄ and evaporated to dryness. The crude material contained ca. 50% of desired product, 2,6-bis[2-(methoxymethoxy)-3-(triphenylsilyl)-1-naphthyl]pyridine, as judged by ¹H NMR spectroscopy. This crude material was purified by column chromatography (silica, heptane/EtOAc (15:1), $R_f = 0.12$). (iv) The resultant solid was dissolved in a mixture of concentrated HCl (20 mL), CHCl₃ (30 mL), and EtOH (40 mL), and the solution was refluxed for 24 h. The reaction mixture was cooled to 0 °C and then carefully diluted with a concentrated solution of NaOH (50 mL). Then, a concentrated solution of NH₄Cl was added to adjust the pH value to 7-8. The product was extracted with CH_2Cl_2 (3 × 20 mL), and the combined organic extracts were dried over MgSO4 and evaporated to afford 3a as an offwhite solid (1.11 g, 1.26 mmol, 98%). ¹H NMR (500 MHz, CD_2Cl_2 , 25 °C): δ 9.88 (br s, 2H, OH), 8.12 (t, J = 7.9 Hz, 1H), 8.06 (m, 2H), 7.83 (m, 4H), 7.71-7.63 (m, 14H), 7.52-7.43 (m, 9H), 7.38-7.33 (m, 13H). ${}^{13}C{}^{1}H{}$ NMR (125 MHz, CD₂Cl₂, 25 °C): δ 157.5 (C-O), 155.8, 142.6, 138.3, 136.3, 134.4, 133.3, 129.5, 129.0, 128.9, 127.9, 127.8, 125.4, 124.1, 123.7, 123.4, 115.7. MS-FAB (m/z): 880.3 (M⁺). Anal. Calcd

for $C_{61}H_{44}NO_2Si_2$: C, 83.24; H, 5.15. Found: C, 82.8; H, 5.01. One-Pot Synthesis of {ONO^{SiMe2/Bu}}H₂ (3b). Using a similar synthetic approach to that described above for $\{ONO^{SiPh3}\}H_2$, pro-ligand $\{ONO^{SiMe2tBu}\}H_2$ was prepared from [3-(methoxymethoxy)-2-naphthyl](tert-butyldimethyl)silane (2.75 g, 9.09 mmol), TMEDA (1.40 mL, 9.09 mmol), sec-BuLi (7.3 mL of a 1.3 M solution in hexane/cyclohexane, 9.10 mmol), ZnCl₂ (1.24 g, 9.09 mmol), Pd₂(dba)₃ (0.083 g, 90.0 µmol), S-Phos (0.147 g, 358 µmol), and 2,6-dibromopyridine (1.08 g, 4.56 mmol). The reaction mixture was stirred for 40 h at 105 °C, cooled to room temperature, diluted with water (200 mL), and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were dried over MgSO₄ and evaporated to dryness. The crude material contained ca. 20% of desired product, 2,6-bis[3-[tert-butyl-(dimethyl)silyl]-2-(methoxymethoxy)-1-naphthyl]pyridine, as judged by ¹H NMR spectroscopy. This crude material was passed through a silica column (heptane/EtOAc (15:1), $R_f =$ 0.42) and used further without complete characterization. After the deprotection step and purification by column chromatography (silica, heptane/CH₂Cl₂ (3:1), $R_f = 0.38$), pure **3b** was recovered as an off-white powder (0.53 g, 0.89 mmol). ¹H NMR (500 MHz, CDCl₃, 25 °C): δ 10.39 (s, 2H, OH), 8.11 (m, 3H), 8.00 (s, 2H), 7.85 (m, 4H), 7.50 (m, 2H), 7.39 (m, 2H), 0.95 (s, 18H, tBu), 0.40 (s, 12H, Me). ¹³C{¹H} NMR (125 MHz, CDCl₃, 25 °C): δ 158.4 (C-O), 156.0, 140.1, 138.4, 138.2, 132.4, 129.1, 128.4, 127.4, 124.8, 123.3, 114.5, 72.3, 27.3 (CCH₃), 17.7 (CCH₃), -4.6 (SiMe₂). Anal. Calcd for $C_{37}H_{45}NO_2Si_2$: C, 75.08; H, 7.66. Found: C, 74.7; H, 7.59. One-Pot Synthesis of {OSO^{SiPh3}}H₂ (3c). Using a similar

One-Pot Synthesis of {**OSO**^{SIPh3}}**H**₂ (3c). Using a similar synthetic approach to that described above for {**ONO**^{SIPh3}}**H**₂, pro-ligand {**OSO**^{SIPh3}}**H**₂ was prepared from [3-(methoxy-methoxy)-2-naphthyl](triphenyl)silane (3.48 g, 7.79 mmol), TMEDA (1.18 mL, 7.82 mmol), *sec*-BuLi (6.3 mL of a 1.3 M solution in hexane/cyclohexane, 8.18 mmol), ZnCl₂ (1.06 g, 7.78 mmol), Pd₂(dba)₃ (0.142 g, 155 μ mol), S-Phos (0.255 g, 621 μ mol), and 2,5-dibromothiophene (0.94 g, 3.89 mmol). The yield of (3-(methoxymethoxy)-4-{5-[2-(methoxymethoxy)-3-(triph-

enylsilyl)-1-naphthyl]thien-2-yl}-2-naphthyl)(triphenyl)silane after Pd-catalyzed coupling reached ca. 30% over 100 h. After the deprotection step and further workup, crude **3c** was recovered as a deep blue powder, which was purified by passing through a short silica pad (heptane/CH₂Cl₂, 1:1) to afford **3c** as a colorless solid (1.01 g, 1.14 mmol, 98%). ¹H NMR (500 MHz, CDCl₃, 25 °C): δ 7.89 (s, 2H), 7.76 (d, J = 8.6 Hz, 2H), 7.73–7.69 (m, 14H), 7.54– 7.46 (m, 8H), 7.46–7.41 (m, 12H), 7.38–7.33 (m, 4H), 5.85 (s, 2H, OH). ¹³C{¹H} NMR (125 MHz, CDCl₃, 25 °C): δ 155.7 (C–O), 141.9, 137.6, 136.4, 135.4, 134.3, 130.9, 129.6, 128.7, 128.6, 128.0, 127.9, 124.2, 123.6, 122.9, 112.1. Anal. Calcd for C₆₀H₄₄O₂SSi₂: C, 81.41; H, 5.01. Found: C, 80.9; H, 4.87.

C, 81.41; H, 5.01. Found: C, 80.9; H, 4.87. $\{ONO^{SiPh3}\}Ti(CH_2Ph)_2$ (4a). A Schlenk flask was charged with $\{ONO^{SiPh3}\}H_2$ (0.20 g, 0.23 mmol) and $Ti(CH_2Ph)_4$ (0.094 g, 0.23 mmol), and toluene (5 mL) was vacuum transferred in. The reaction mixture was stirred overnight at room temperature, filtered, evaporated, and dried in vacuo to give 4a as a brownish-red microcrystalline material (0.24 g, 0.22 mmol, 95%). ¹H NMR (500 MHz, toluene- d_8 , 70 °C): δ 8.29 (s, 2H), 8.02 (m, 12 H), 7.48 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H),7.32 (d, J = 8.2 Hz, 2H), 7.23 (m, 12H), 7.13 (t, J = 6.8 Hz, 2H),7.06 (m, 2H), 6.99 (m, 6H), 6.81 (t, J = 8.2 Hz, 1H), 6.05 (t, J = 7.5 Hz, 2H, CH_2Ph), 5.94 (t, J = 7.5 Hz, 4H, CH_2Ph), 5.75 (d, $J = 7.5 \text{ Hz}, 4\text{H}, \text{CH}_2Ph), 2.36 (\text{br s}, 4\text{H}, \text{CH}_2\text{Ph}).$ ¹³C{¹H} NMR (125 MHz, benzene- d_6 , 70 °C) (three signals from quaternary aromatic carbons and one from CH₂ of the benzylic groups were not observed): δ 161.3 (C-O), 151.0, 144.1, 142.3, 137.1, 137.0, 134.6, 133.1, 129.6, 128.3, 128.1, 125.7, 125.2, 123.0, 122.9, 122.0, 121.9, 116.9. Anal. Calcd for C₇₅H₅₇NO₂Si₂Ti: C, 81.28; H, 5.18. Found: C, 80.9; H, 4.97.

 $\{ONO^{SiPh3}\}Zr(CH_2Ph)_2$ (5a). In a similar manner to that described above for 4a, complex 5a was prepared from $\{ONO^{SiPh3}\}H_2$ (0.350 g; 0.397 mmol) and $Zr(CH_2Ph)_4$ (0.181 g; 0.397 mmol) and isolated as a yellow solid (0.412 g, 90%). ¹H NMR (500 MHz, C₆D₆, 80 °C): δ 8.29 (s, 2H), 8.05 (m, 12 H), 7.56 (d, ³J = 7.9 Hz, 2H), 7.49 (d, ³J = 8.6 Hz, 2H), 7.40-7.15 (m, 24H), 6.99 (t, ³J = 7.9 Hz, 1H), 6.40 (t, ³J = 7.3 Hz, 2H, CH₂Ph), 6.30 (t, ³J = 7.3 Hz, 4H, CH₂Ph), 6.25 (d, ³J = 7.3 Hz, 4H, CH₂Ph), 6.25 (d, ³J = 7.3 Hz, 2H, CH₂Ph), 1.66 (m, 4H, CH₂Ph). ¹³C{¹H} NMR (125 MHz, benzene-d₆, 80 °C) (several signals overlapped): δ 160.3 (C-O), 157.3, 143.9, 138.8, 136.9, 135.4, 129.5, 128.8, 128.2, 127.2, 125.5, 123.8, 123.7, 122.7, 121.6, 118.7, 65.7 (CH₂Ph). Anal. Calcd for C₇₅H₅₇NO₂Si₂Zr: C, 78.22; H, 4.99. Found: C, 78.0; H, 4.59.

(ONO^{SiPh3}**)Hf**(CH₂Ph)₂ (6a). Complex 6a was prepared in a similar manner to that described above for 4a, starting from $\{ONO^{SiPh3}\}$ H₂ (0.350 g, 0.398 mmol) and Hf(CH₂Ph)₄ (0.216 g, 0.398 mmol). 6a was recovered as a bright yellow crystalline solid (0.424 g, 86%). Crystals suitable for X-ray diffraction analysis were obtained from this batch. ¹H NMR (500 MHz, C₆D₆, 80 °C): δ 8.43 (s, 2H), 8.11 (m, 12 H), 7.58 (d, ³J = 8.4 Hz, 2H), 7.46 (d, ³J = 8.0 Hz, 2H), 7.40-6.95 (m, 24H), 6.83 (t, ³J = 8.0 Hz, 2H), 6.38-6.05 (m, 10H, CH₂Ph), 1.49 (m, 4H, CH₂Ph). ¹³C{¹H} NMR (75 MHz, benzene-d₆, 80 °C) (two signals from quaternary aromatic carbons and one from CH₂ of the benzylic groups were not observed): δ 160.6 (C–O), 153.7, 144.3, 144.1, 140.0, 138.0, 136.7, 135.0, 133.6, 131.7, 130.2, 128.8, 129.6, 128.1, 128.0, 124.5, 122.8, 121.5, 117.4. Anal. Calcd for C₇₅H₅₇NO₂Si₂Hf: C, 72.71; H, 4.64. Found: C, 72.4; H, 4.07.

 $C_{75}H_{57}NO_2Si_2Hf: C, 72.71; H, 4.64.$ Found: C, 72.4; H, 4.07. {ONO^{SiPh3}}Hf(NMe₂)₂(NHMe₂) (7a·(NHMe₂)). (A) A Schlenk flask was charged with {ONO^{SiPh3}}H₂ (0.11 g, 0.12 mmol) and Hf(NMe₂)₄ (0.044 g, 0.12 mmol), and benzene (5 mL) was vacuum transferred in. The reaction mixture was stirred overnight at room temperature. Yellow crystals of {ONO^{SiPh3}}Hf(NMe₂)₂(NHMe₂) suitable for X-ray analysis were obtained from this solution at room temperature. The solution was evaporated and dried *in vacuo* to give 7a as a yellow microcrystalline material (0.12 g, 0.10 mmol, 84%). (B) Alternatively, complex 7a was prepared from {ONO^{SiPh3}}H₂(0.255 g, 0.290 mmol) and Hf(NMe₂)₄ (0.103 g, 0.290 mmol) in Et₂O (8 mL) at room temperature and then recrystallized from a hexane/toluene (1:5) mixture to yield **7a** as a yellow microcrystalline material (0.295 g, 89%). ¹ H NMR (500 MHz, toluene- d_8 , 80 °C): δ 8.10 (s, 2H), 7.83 (m, 12 H), 7.68 (br m, 6H), 7.42 (m, 4H), 7.35–6.95 (18H overlapped with solvent signals), 6.87 (br s, 1H), 2.48 (s, 6H, NMe₂). ¹³C{¹H} NMR (75 MHz, toluene- d_8 , 80 °C): 165.6 (C–O), 156.5, 144.2, 143.9, 142.9, 136.1, 135.8, 135.1, 129.9, 128.8, 128.4, 128.2, 127.3, 126.4, 123.2, 119.5, 38.2 (NMe₂). Anal. Calcd for C₆₅H₅₅HfN₃O₂Si₂: C, 68.19; H, 4.84. Found: C, 67 9; H, 4.64.

Found: C, 67.9; H, 4.64. {**ONO**^{SiPh3}}**Ti(O***i***Pr**)₂ (**8a**). Similarly, complex **8a** was prepared from {ONO^{SiPh3}}**H**₂ (0.100 g; 0.11 mmol) and Ti(O*iP***r**)₄ (0.032 g; 0.11 mmol) in toluene (10 mL). The reaction mixture was evaporated under vacuum, and the residue was recrystallized from hexane to give pale yellow crystals (0.085 g, 0.08 mmol, 72%). ¹H NMR (500 MHz, C₆D₆, 25 °C): δ 8.30 (s, 2H), 8.08 (m, 12H), 7.78 (d, ³*J* = 8.3 Hz, 2H), 7.49 (d, ³*J* = 7.9 Hz, 2H), 7.46 (d, ³*J* = 8.3 Hz, 2H), 7.32 (m, 20H), 7.14 (m, 2H), 6.92 (t, ³*J* = 7.9 Hz, 1H), 4.24 (m, ³*J* = 5.8 Hz, 2H, C*H*(CH₃)₂), 0.51 (d, ³*J* = 5.8 Hz, 12H, CH(CH₃)₂). ¹³C{¹H} NMR (125 MHz, C₆D₆, 25 °C): δ 165.0 (C–O), 144.6, 136.9, 135.7, 133.9, 129.4, 129.2, 129.1, 128.9, 127.7, 127.6, 127.3, 125.9, 124.4, 123.7, 122.7, 116.3, 80.9 (CH(CH₃)₂), 25.0 (CH(CH₃)₂). Anal. Calcd for C₆₇H₅₂NO₄Si₂Ti: C, 77.06; H, 5.50. Found: C, 76.7; H, 5.34.

for $C_{67}H_{57}NO_4Si_2Ti$: C, 77.06; H, 5.50. Found: C, 76.7; H, 5.34. {**ONO**^{SiMe2/Bu}}**Ti**(CH₂Ph)₂ (4b). Similarly, complex 4b was prepared from {ONO^{SiMe2/Bu}}H₂ (0.080 g, 0.14 mmol) and Ti(CH₂Ph)₄ (0.056 g, 0.14 mmol) and recrystallized from hexane to give brownish-red crystals (0.098 g, 0.12 mmol, 88%). ¹H NMR (500 MHz, toluene-d₈, 60 °C): δ 8.20 (s, 2H), 7.79 (m, 2H), 7.41 (m, 2H), 7.24 (d, ${}^{3}J = 7.7$ Hz, 2H), 7.18 (m, 4H), 6.83 (t, ${}^{3}J = 8.1$ Hz, 1H), 6.47 (d, ${}^{3}J = 7.7$ Hz, 4H, CH₂Ph), 6.23 (t, ${}^{3}J =$ 7.7 Hz, 4H, CH_2Ph), 6.11 (t, ${}^{3}J = 7.7$ Hz, 2H, CH_2Ph), 3.74 (br s, 4H, CH_2Ph), 1.22 (s, 18H, tBu), 0.95 (br s, 6H, Me). ¹³C{¹H} NMR (125 MHz, toluene-d₈, 60 °C): δ 161.5 (C-O), 141.2, 137.1, 136.8, 135.5, 133.8, 129.4, 128.7, 127.8, 127.0, 126.5, 125.2, 125.0, 124.9, 124.5, 122.7, 122.5, 27.2 (CCH₃), 17.7 (CCH₃), -3.4 (SiMe₂) (the signal from the methylene unit of the benzyl group was not observed, due to long relaxation times). ¹H NMR (500 MHz, toluene- d_8 , -50 °C) (only resonances for the major species are reported): δ 8.23 (s, 2H), 7.67 (d, ${}^{3}J = 7.7$ Hz, 2H), 7.37 (d, ${}^{3}J = 8.3$ Hz, 2H), 7.23 (m, 5H), 7.13 (m, 2H), 6.55 (d, ${}^{3}J = 7.5$ Hz, 4H, CH₂*Ph*), 6.38 (t, ${}^{3}J = 7.5$ Hz, 7.5 Hz, 4H, CH₂*Ph*), 6.23 (t, ${}^{3}J = 7.5$ Hz, 2H, CH₂*Ph*), 3.98 (d, ${}^{2}J = 8.1$ Hz, 2H, C*H*HPh), 3.69 (d, ${}^{2}J = 8.1$ Hz, 2H, CH*H*Ph), 1.26 (s, 18H, tBu), 1.16 (s, 6H, Me), 0.70 (3, 6H, Me). Anal. Calcd for $\begin{array}{l} C_{51}H_{57}NO_{2}Si_{2}Ti: C, 74.70; H, 7.01. \ Found: C, 74.3; H, 6.91. \\ \{ONO^{SiMe2rBu}\}Zr(CH_{2}Ph)_{2} \ (5b). \ Similarly, \ complex \ 5b \ was \end{array}$

prepared from $\{ONO^{SiMe2rBu}\}H_2$ (0.342 g, 0.578 mmol) and Zr(CH₂Ph)₄ (0.263 g, 0.578 mmol) and recrystallized from a hexane/toluene (1:1) mixture to give a bright yellow microcrystalline powder (0.300 g, 60%). ¹H NMR (500 MHz, toluene- d_8 , -40 °C) (only resonances for the major species are reported): δ 8.21 (s, 2H), 7.67 (m, 2H), 7.27 (m, 2H), 7.23-7.15 (m, 6H), 6.67 $(m, 4H, Ar(1H) + CH_2Ph^1(3H)), 6.55 (m, 3H, CH_2Ph^1(1H) +$ $CH_2Ph^2(2H)$), 6.43 (t, ${}^{3}J = 7.3$ Hz, $CH_2Ph^1(1H)$)), 5.76 (t, ${}^{3}J =$ 7.4 Hz, $CH_2Ph^2(1H)$), 5.69 (t, ${}^{3}J = 7.4$ Hz, $CH_2Ph^1(2H)$), 3.76 (s, 2H, CHHPh), 3.39 (s, 2H, CHHPh), 1.25 (s, 18H, tBu), 1.16 (s, 6H, Me), 0.65 (3, 6H, Me). ${}^{13}C{}^{1}H{}$ NMR (125 MHz, toluene-d₈, -40 °C): δ 159.3 (C-O), 158.1, 140.4, 137.3, 134.6, 133.9, 132.4, 130.3, 129.5, 129.2, 129.1, 128.6, 128.5, 128.0, 127.4, 125.3, 123.2, 122.7, 122.5, 121.6, 119.4, 64.6 (CH₂Ph), 63.9 (CH₂Ph), 27.3 (CCH₃), 17.9 (CCH₃), -1.9 (SiMeMe), -4.1 (SiMeMe). Anal. Calcd for C₅₁H₅₇NO₂Si₂Zr: C, 70.95; H, 6.65. Found: C, 70.4; H, 6.45.

{ OSO^{SiPh3} }Ti(CH_2Ph_2 (4c). A Schlenk flask was charged with { OSO^{SiPh3} }H₂(0.100 g, 0.11 mmol) and Ti(CH_2Ph)₄(0.050 g, 0.12 mmol), and benzene (5 mL) was vacuum transferred in. The reaction mixture was stirred overnight at room temperature and evaporated to dryness. The brownish residue was twice recrystallized from benzene and dried *in vacuo* to give 4c as a brown-red microcrystalline powder (0.080 g, 0.073 mmol, 65%). ¹H NMR (500 MHz, toluene- d_8 , 25 °C): δ 8.37 (s, 2H), 8.14 (d, ³J = 8.3 Hz, 2H), 8.06 (m, 12H), 7.42 (d, ³J = 7.9 Hz, 2H), 7.33 (m, 2H), 7.28–7.20 (m, 18H), 7.11 (m, 2H), 6.49–6.36 (m, 8H, CH₂*Ph* (6H) + thiophene (C*H*=, 2H)), 6.28–6.22 (m, 4H, CH₂*Ph*), 2.51 (s, 2H, CH₂Ph), 2.15 (s, 2H, CH₂Ph). ¹³C{¹H} NMR (125 MHz, toluene- d_8 , 25 °C): δ 165.9 (C–O), 142.4, 138.1, 137.1, 136.9, 136.8, 135.7, 134.9, 133.7, 130.7, 130.4, 129.6, 129.2, 128.9, 128.8, 128.0, 127.9, 125.2, 125.0, 124.4, 124.1, 123.5, 121.9, 118.9, 94.7 (CH₂Ph), 93.7 (CH₂Ph). Anal. Calcd for C₇₄H₅₆O₂S-Si₂Ti: C, 79.83; H, 5.07. Found: C, 79.4; H, 4.87.

Crystal Structure Determination of 3a, 3c, 4a, 4b, 5b, 6a, and 7a · (NHMe₂). Crystals of 3a, 3c, 4a, 4b, 5b, 6a, and 7a · (NHMe₂) suitable for X-ray diffraction analysis were obtained by recrystallization of purified products (see Experimental Section). Diffraction data were collected at 100 K using a Bruker APEX CCD diffractometer with graphite-monochromatized Mo Ka radiation ($\lambda = 0.71073$ Å). A combination of ω and ϕ scans was carried out to obtain at least a unique data set. The crystal structures were solved by direct methods, and remaining atoms were located from difference Fourier synthesis followed by fullmatrix least-squares refinement based on F^2 (programs SIR97 and SHELXL-97).45 Many hydrogen atoms could be found from the Fourier difference analysis. Carbon- and nitrogenbound hydrogen atoms were placed at calculated positions and forced to ride on the attached atom. The hydrogen atom contributions were calculated but not refined. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystals of 4a and 6a were found to contain lattice disordered solvent molecules, which could not be sufficiently modeled in the refinement cycles. These molecules were removed using the SQUEEZE procedure⁴⁶ implemented in the PLATON package.⁴⁷ The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities were of no chemical significance. Crystal data and details of data collection and structure refinement for the different compounds are given in the Supporting Information. Main crystallographic data (excluding structure factors) are available as Supporting Information, as cif files.

Variable-Temperature ¹H NMR Study. ¹H NMR spectra were recorded on a Bruker AM-500 spectrometer using the following parameters: relaxation delay D1, 1.5 s; number of scans, 24. Simulation of ¹H NMR spectra was carried out using the gNMR Simulation Package of Budzelaar.⁴⁸ First, the chemical shifts observed for benzylic protons in the slow exchange limit at $-50 \ ^{\circ}C$ (for 4b) and at $-40 \ ^{\circ}C$ (for 5b) were used to set up the exchange system. The relative populations were fixed at molar fraction ratios of 1:0.2 for 4b and 1:0.1 for 5b. The natural line width in the absence of exchange (3.0 Hz) was measured at given temperatures and confirmed by observation of the same line width at -60 °C for both species. A linear extrapolation was used to estimate the chemical shifts of benzylic protons in the explored temperature range. For the two species in equilibrium, 1 and 2, incorporating nuclei 1-1, 1-2 and 2-1, 2-2, respectively, the exchange matrix was set as follows:

	k'	$k^{\prime\prime}$
1-1	1-2	2-1
1-2	1 - 1	2-2
2-1	2 - 2	1-1
2-2	2 - 1	1-2

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where the exchange rate was set k = k' = k''. For 10 temperatures in the range 50 to 60 °C for **4b** and 12 temperatures in the range 40 to 80 °C for **5b**, the exchange rate k was varied to get the best fit between experimental and simulated data. The activation parameters for the isomerization process were obtained from a standard least-squares Eyring analysis according to the equation

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta E}{RT} + \frac{\Delta S}{R} + \ln\frac{k_{\rm B}}{h}$$

where k is the first-order rate constant and $k_{\rm B}$ is the Boltzmann constant. The standard deviations from the leastsquares fit were used to estimate the uncertainties in ΔE^{\ddagger} and $\Delta S^{\ddagger, 49}$

Computational Details. DFT calculations were carried out using the Gaussian 03 package,⁵⁰ employing B3LYP⁵¹ and BP86⁵² functionals, and using a standard double- ξ polarized basis set, namely, the LANL2DZ set, augmented with a single polarization *f* function on titanium, zirconium, and hafnium (1.506, 0.875, and 0.784, respectively). All stationary points were fully characterized via analytical frequency calculations as either true minima (all positive eigenvalues) or transition states (one imaginary eigenvalue). The IRC procedure was used to confirm the nature of each transition state connecting

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two minima.⁵³ Zero-point vibrational energy corrections (ZPVE) were estimated by a frequency calculation at the same level of theory, to be considered for the calculation of the total energy values. Pictures of the optimized structures were generated using the program MOLEKEL 5.3.0.⁵⁴

Typical Procedure for (Co)polymerization. A 300 mL highpressure glass reactor was charged with 80 mL of freshly distilled toluene under argon flash. Mechanical stirring (Pelton turbine, 1000 rpm) was started. The reactor was then purged with the appropriate gas (ethylene or propylene), loaded with a solution of MAO, "DMAO", or TIBAL at atmospheric pressure, and then kept at the desired temperature by circulating water in the double wall. A solution of $[Ph_3C][B(C_6F_5)_4]$ (when used) in 2 mL of toluene was injected in by syringe, followed by injection of a solution of the precatalyst in 2 mL of toluene. The gas pressure in the reactor was maintained immediately and kept constant with a back regulator throughout the experiment. The ethylene consumption was monitored via an Aalborg flow meter. After a given time period, the reactor was depressurized and the reaction was quenched by adding ca. 5 mL of a 10% solution of HCl in methanol. The polymer was further precipitated by adding 500 mL of methanol, washed, and dried in vacuo overnight at room temperature.

When oligomers of propylene were formed, the toluene solution was washed twice with a water/HCl solution and, then, with water. An aliquot of the toluene solution (1 mL) was then analyzed by GLC to probe the presence of light oligomers. The rest was evaporated and dried under vacuum to afford oily materials.

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Supporting Information Available: Crystallographic data for 3a, 3c, 4a, 4b, 5b, 6a, and 7a · (NHMe₂) as CIF files and a table summarizing crystal and refinement data; NMR spectra of ligands 3a-3c and complexes 4a-4c, 5a, 5b, 7a, and 8a. This material is available free of charge via the Internet at http:// pubs.acs.org.

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