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Polymerization of α-Olefins and Butadiene and Catalytic Cyclotrimerization of 1-Alkynes by a New Class of Group IV Catalysts. Control of Molecular Weight and Polymer Microstructure via Ligand Tuning in Sterically Hindered Chelating Phenoxide Titanium and Zirconium Species

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Abstract: A new class of homogeneous catalysts for olefin oligo-polymerization is reported. These titanium or zirconium sterically hindered chelating alkoxide complexes were prepared by reaction of $M(CH_2Ph)_4$ (M = Ti, Zr) or $Zr(CH_2Ph)_2Cl_2(OEt_2)_2$ with the appropriate biphenol or binaphthol, or by reaction of $TiCl_4$ with the diol. Using these methodologies, a range of binaphthoxide and biphenoxide catalysts with varying steric hindrance have been prepared: {1,1′-(2,2′,3,3′-$OC_{10}H_5SiR_3$)}$_2ZrCl_2$ {R_3 = Me_3 (**1**); R_3 = $MePh_2$ (**2**); R_3 = Ph_3 (**3**)}, {1,1′-(2,2′,3,3′-$OC_{10}H_5SiMe_3$)}$_2Ti(CH_2Ph)_2$ (**4**), {1,1′-(2,2′,3,3′-$OC_{10}H_5SiMePh_2$)}$_2Zr(CH_2Ph)_2$ (**5**), (1,1′-(2,2′,3,3′-$OC_{10}H_5SiPh_3$)}$_2M(CH_2Ph)_2$ {M = Ti (**7**), M = Zr (**8**)}, 2,2′-S(4-Me,6-$^tBuC_6H_2O)_2MX_2$ {MX_2 = $TiCl_2$ (**10**); MX_2 = $ZrCl_2$ (**11**); MX_2 = $Ti(CH_2Ph)_2$ (**12**)}, {2,2′-S(4-Me,6-$^tBuC_6H_2O)_2$}$_2Ti$ (**13**), 2,2′-(4,6-$^tBu_2C_6H_2O)_2MX_2$ {MX_2 = $Ti(CH_2Ph)_2$ (**14**); MX_2 = $ZrCl_2(THF)_2$ (**15**)}, {2,2′-(4-OMe,6-$^tBuC_6H_2O)_2$}$_2Ti$ (**16**), 2,2′-(4-OMe,6-$^tBuC_6H_2O)_2Ti(CH_2Ph)_2$ (**17**)}, 2,2′-CH_2(4-Et,6-$^tBuC_6H_2O)_2TiX_2$ {X = CH_2Ph (**18**), X = Cl (**19**), and {2,2′-CH_2(4-Et,6-$^tBuC_6H_2O)_2$}$_2Ti$ (**20**). This class of L_2MCl_2 systems can be regarded as being analogous to the well-documented range of Group IV metallocenes. Alkylation of (O−O)$ZrCl_2$ ((O−O = chelating phenoxide) allowed access to other alkyl species. Therefore, reaction of **3** with MeLi or Me_3SiCH_2Li afforded {1,1′-{2,2′,3,3′-$OC_{10}H_5SiPh_3$}$_2ZrX_2$ {X = Me (**6**); X = CH_2SiMe_3 (**9**)}, respectively. The X-ray crystal structure of **17** is reported. At 213 K, **17**$\cdot{}^1/_2OEt_2$ has space group $P\bar{1}$ and unit cell dimensions a = 8.737(9) Å, b = 11.840(10) Å, c = 17.135(17) Å, α = 98.28(7)°, β = 90.53(8)°, γ = 101.38(7)°, μ(Mo Kα) = 2.88 cm^{-1}. Attempts to prepare analogous sterically hindered binaph*thiolates* were thwarted by the absence of known sterically hindered chelating *binaphthiols*. Synthetic routes to such ligands were attempted albeit without success. The chelating phenoxide and binaphthoxide titanium and zirconium species, in the presence of an aluminum cocatalyst are active for the oligo-polymerization of α-olefins. For the polymerization of ethylene, rates of up to 4740 kg of PE/mol of catalyst·h (100 kg/g of Ti·h) were obtained. They are active for the polymerization of butadiene and the catalytic cyclotrimerization of terminal acetylenes to 1,2,4- and 1,3,5-trisubstituted benzenes. This ratio of benzenes is dependent on the steric bulk of the ancillary binaphthol ligands. Steric modifications also have a clear influence on the degree of 1-hexene polymerization as well as the tacticity of poly(1-hexene). In particular, the chelating alkoxide ligand framework can induce stereoregularity. For **1** and **2**, with methylaluminoxane as cocatalyst, regioregular and stereospecific polymerization of 1-hexene is observed to give high molecular weight isotactic polyhexene. Related ligand-dependent differences in polymer microstructure are observed in the polymerization of butadiene. Cationic complexes have been synthesized. [$(C_{10}H_5SiPh_3O)_2Zr(CH_2Ph)$]$BPh_4$ (**21**), and zwitterionic $(C_{10}H_5SiPh_3O)_2Zr(CH_2Ph)(\eta^6\text{-}PhCH_2)B(C_6F_5)_3$ (**22**) were made by treatment of **8** with [$PhNMe_2H$]BPh_4 and $B(C_6F_5)_3$, respectively. They are active for the polymerization of ethylene.

Introduction

The catalytic reactivity of homogeneous early transition metal metallocenes with ethylene and α-olefins has recently attracted considerable attention.[1] This is because of their ability to produce narrow molecular weight distribution polymers, with controllable stereoregularity and molecular weight. Efficient catalyst systems have utilized two-component homogeneous, chiral titanium-, zirconium-, and hafnium-bridged metallocenes together with a cocatalyst, typically methylaluminoxane (MAO), for the stereospecific polymerization of α-olefins.[2] By application of appropriate bridged metallocenes, the molecular architecture of the resultant polyolefin can be tuned, and appreciable understanding and control of the factors which influence

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(1) (a) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325. (b) Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57. (c) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355. (d) Kaminsky, W.; Külper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem.* **1985**, *97*, 507. (e) Kaminsky, W. *Angew. Makromol. Chem.* **1986**, *145*, 149. (f) Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728. (g) Jordan, R. F.; Dasher, W. E.; Echols, S. F. *J. Am. Chem. Soc.* **1986**, *108*, 1718. (h) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99. (i) Resconi, L.; Piemontesi, F.; Franciscono, G.; Abis, L.; Fiorani, T. *J. Am. Chem. Soc.* **1992**, *114*, 1025. (j) Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1991**, *10*, 840.

(2) Horton, A. D. *Trends Polym. Sci.* **1994**, *2*, 158. This is a useful and insightful review of α-olefin polymerization by metallocene catalysts.

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propagation and termination kinetics has been achieved. Ligand modifications, with retention of the Cp_2 framework, to such metallocene complexes have been performed and have afforded polymers with new stereostructures including syndiotactic,[3a] hemiisotactic,[3b] stereoblock,[3c] and high molecular weight isotactic polypropene (PP).[3d]

The investigation of alternative ligands for olefin polymerization is relatively unexplored. Despite the diversity of environments recently discovered,[4-7] few new ligand types have proved amenable to α-olefin polymerization. Despite the expected compatibility of chelating phenoxides with early transition metals, relatively little research in this area[8,9] has been performed. Sterically hindered binaphthol and chelating biphenols also possess C_2 symmetry and can provide a stereochemically rigid framework for a metal center. They should therefore afford the stereochemically rigid ligand framework necessary for stereospecific transformations, including the stereoregular polymerization of α-olefins. Their intrinsic chirality is due to the lack of free rotation about the C−C bond between the two naphthyl rings. Furthermore, their chelating nature inhibits possible disproportionation reactions of $LL'MX_2$ (M = Ti, Zr; L,L′ ≠ Cp) mixed-ligand species. Sterically hindered auxiliary groups on the binaphthols or biphenols allow the degree of shielding to be tuned without significantly altering the electronic characteristics of the ligand. Furthermore, the influence of the number of atoms between the alkoxide oxygens in such ligands can also be studied. Such ligands, as well as protecting the often electronically and coordinatively unsaturated metal center, are also important in controlling stereoregular olefin insertion. Increasing steric bulk serves to increase the difference in energy between the two diastereoisomers ($\Delta\Delta G$) allowing effective discrimination[10] between the two α-olefin enantiofaces required for enantiomorphic site control. By the application of catalysts possessing ligands of varying steric bulk, it should be possible to tune the degree of polymerization as well as the polymer microstructure.

Indeed, chelating oxygen donor ligands have proven to be useful chiral auxiliaries in enantiospecific organic synthesis[11] with early and late transition metals. In particular, chiral binaphthol, albeit unhindered, titanium species have recently attracted attention as in-situ generated chiral Lewis acids.

Terminal alkoxides in Ti and Zr chemistry have been used.[12] Of particular relevance, the kinetics and thermodynamics of intra- and intermolecular rearrangement of alkoxides in binaphtholate Ti(IV) complexes[8b] have been studied. Chiral molybdenum alkylidene initiators containing a binaphtholate or biphenolate ligand for the stereoselective ring opening metathesis polymerization (ROMP) of norbornadiene have been reported.[8c] Recently, an ill-defined chelating phenoxide titanium species, formulated as $S(4\text{-Me, }6\text{-}{}^tBuC_6H_2O)_2TiCl_2$, has been reported to be highly active for olefin polymerization.[9] No ligand variations were investigated.

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(4) Much recent patent literature from Dow and Exxon documents (cyclopentadienylamido)MCl_2 (M = Ti, Zr, Hf)/MAO catalysts for olefin (co)polymerization. See: (a) Canich, J. M. European Patent 420436, 1991. (b) Canich, J. M.; Hlatky, G. G.; Turner, H. W. U.S. Patent 542236, 1990. (c) Stevens, J. C.; Timmers, F. J.; Wilson, D. R.; Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. W.; Lai, S. European Patent 416815, 1990. (d) Campbell, R. E., Jr. U.S. Patent 5066741, 1991. (e) LaPointe, R. E. European Patent 468651, 1991. (f) LaPointe, R. E.; Rosen, R. K.; Nickias, P. N. European Patent 495 375, 1992. (g) Formation of tactic polypropene by such catalysts has also been reported. $\{Me_2Si(fluorenyl)NR\}MMe_2$ (M = Ti, Zr, Hf; R = ${}^tBu$, $C_{12}H_{23}$), activated by $PhNMe_2H[B(C_6F_5)_4]$, yielded syndiotactic polypropene (M_w = ca. 2000, 60−90% r diads). Turner, H. W.; Hlatky, G. G.; Canich, J. M. PCT Int. Appl. WO 93/19103 filing date March 16, 1992. (h) In contrast, $\{Me_2Si(fluorenyl)N{}^tBu\}ZrCl_2$ is reported to polymerize propene to isotactic polypropene Canich, J. M. U.S. 5026798.

(5) The bis(amide) system $\{(Me_3Si)_2N\}_2ZrCl_2$/MAO has been claimed to polymerize propene to i-PP (90% m diads). Canich, J. M.; Turner, H. W. PCT Int. Appl. WO 92/12612 filing date December 26, 1991.

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(10) Such a rationale is valid in all types of asymmetric catalysis. For example, high enantiomeric excesses in asymmetric organic synthesis are indicative of high enantiomorphic discrimination between catalyst and substrate.

(11) (a) For example, in the asymmetric hetero-Diels−Alder reaction, the asymmetric ene reaction, the asymmetric Claisen rearrangement, and as chiral auxiliaries for aluminum reducing agents. Enantioselective and diastereoselective aldol reactions catalyzed by the chiral Lewis acids (*R*)-$(C_{10}H_5O)_2TiCl_2$ have also been reported. Maruoka, K.; Hoshino, Y.; Shirasaka, T.; Yamamoto, H. *Tetrahedron Lett.* **1988**, *29*, 3967. Maruoka, K.; Araki, Y.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 2650. Maruoka, K.; Nonoshita, K.; Banno, H.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 7922. Noyori, R.; Tomino, I.; Tanimoto, Y. *J. Am. Chem. Soc.* **1979**, *101*, 3129. Noyori, R. *Pure Appl. Chem.* **1981**, *53*, 2315. Narasaka, K.; Inoue, M.; Yamada, T. *Chem. Lett.* **1986**, 1967. Kitagawa, O.; Hanano, T.; Tanabe, K.; Shiro, M.; Taguchi, T. *J. Chem. Soc., Chem. Commun.* **1992**, 1005. Mikami, K.; Terada, M.; Motoyama, Y.; Nakai, T. *Tetrahedron: Asymmetry* **1991**, *2*, 643. Schmidt, B.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1321. (b) The elegant and well-documented enantioselective epoxidation of allylic alcohols by ${}^tBuOOH$ uses Ti^{4+} complexes of chiral tartaric acid derivatives. Duthaler, R. O.; Hafner, A. *Chem. Rev.* **1992**, *92*, 807. (c) Reaction of optically pure 2-*exo*,3-*exo*-camphanediols (derived from (1*S*)-camphorquinone) with $TiCl_4$ gave the homochiral dimer. (d) Bachland, B.; Wuest, J. W. *Organometallics* **1991**, *10*, 2015. (e) In the titanate-mediated enantioselective addition of $ZnEt_2$ to aldehydes, reaction of $Ti(O{}^iPr)_4$ with tetraaryldioxolanedimethanols gives a chiral spirotitanate that is highly selective in catalyzing this reaction. (f) Corey, E. J.; Matsumura, Y. *Tetrahedron Lett.* **1991**, *32*, 6289.

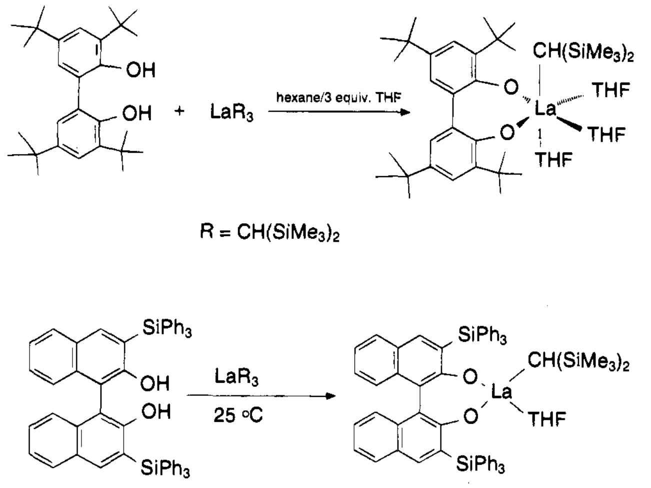
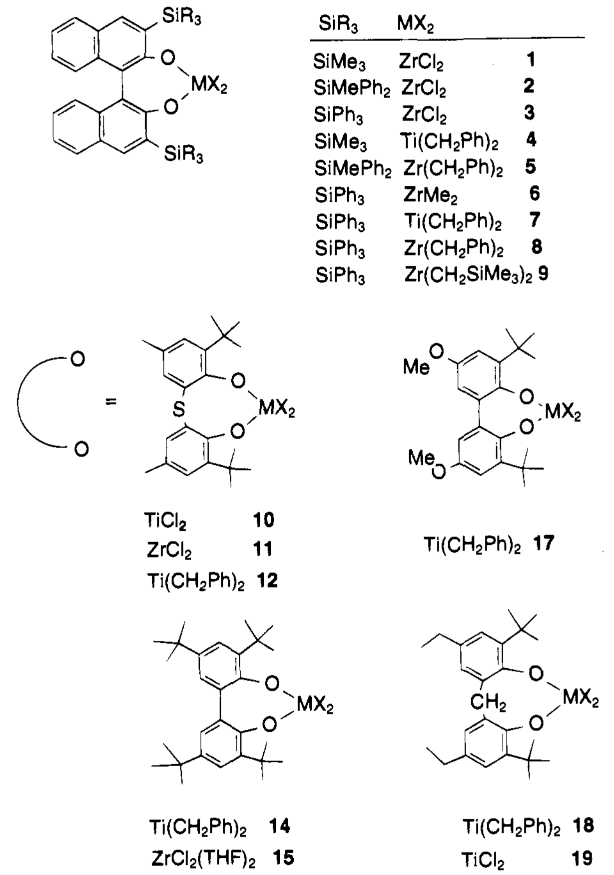


Figure 1.

We have previously examined the use and effect of terminal alkoxides as ancillary ligands in organoyttrium chemistry[13] and have undertaken preliminary studies on binaphthol ligands in organolanthanide chemistry.[14] However, in this latter area, only $\{1,1'\text{-}(2,2',3,3'\text{-}OC_{10}H_5SiPh_3)\}_2LaCH(SiMe_3)_2\cdot THF$[14] and crystallographically characterized $2,2'\text{-}(4,6\text{-}{}^tBu_2OC_6H_2)_2LaCH(SiMe_3)_2(THF)_3$[14] could be prepared; the corresponding hydride could not be isolated (Figure 1).

Intrigued by reports[9] of a highly active olefin polymerization catalyst, and our previous studies[14] in organolanthanide chemistry, we began an investigation on the effect of chelating alkoxide ligands on the efficacy and regio- and stereoregularity of olefin polymerization. Chelating biphenolates and binaphtholates allow changes in steric hindrance to be simply accomplished.

We report[15] here the synthesis and structure of a new type of titanium and zirconium catalysts for the efficient oligo- and polymerization of α-olefins and polymerization of dienes. The degree of polymerization and polymer microstructure (regio- and/or stereoregular) are shown to be ligand dependent. Dibenzyl species $(O-O)M(CH_2Ph)_2$ ($(O-O)$ = chelating phenoxide or binaphthoxide) without cocatalyst are active for the catalytic cyclotrimerization of terminal acetylenes.



SiR3	MX2	
SiMe3	ZrCl2	1
SiMePh2	ZrCl2	2
SiPh3	ZrCl2	3
SiMe3	Ti(CH2Ph)2	4
SiMePh2	Zr(CH2Ph)2	5
SiPh3	ZrMe2	6
SiPh3	Ti(CH2Ph)2	7
SiPh3	Zr(CH2Ph)2	8
SiPh3	Zr(CH2SiMe3)2	9

$TiCl_2$ **10**
$ZrCl_2$ **11**
$Ti(CH_2Ph)_2$ **12**

$Ti(CH_2Ph)_2$ **17**

$Ti(CH_2Ph)_2$ **14**
$ZrCl_2(THF)_2$ **15**

$Ti(CH_2Ph)_2$ **18**
$TiCl_2$ **19**

Figure 2.

Results and Discussion

Synthesis of Chelating Alkoxide Group IV Species. Protonolysis of the readily available precursors $Zr(CH_2Ph)_2Cl_2$ or $M(CH_2Ph)_4$ (M = Ti, Zr)[16] with chelating biphenols[17] and binaphthols[18-20] at 20 °C yields $(O-O)MX_2$ (X = Cl or CH_2Ph) with concomitant liberation of toluene. See Figure 2 for the range of compounds prepared and the Experimental Section for the synthetic methodology. The auxiliary SiR_3 or ${}^tBu$ groups shield the metal center, and the degree of shielding can be judiciously tuned. This reaction pathway obviates salt coordination and avoids use of coordinating solvents.[21] A range of compounds is thus available by simple addition of the diol to the same Ti or Zr precursor. These can be regarded as the early transition metal analogues of the chiral late transition metal BINAP complexes used in asymmetric organic synthesis.[22] In general, compounds $(O-O)Zr(CH_2Ph)_2$ are less stable than their Ti counterparts. For example, in contrast to **4**, the Zr analogue

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[12] Terminal alkoxide Ti and Zr species have, of course, also attracted attention. (a) Burkhardt, T. J. *Abstracts of Papers*, 199th National Meeting of the American Chemical Society, Boston, MA, Spring 1990; American Chemical Society: Washington, DC, 1990; Abstract no. INORG 600. (b) Lubben, T. V.; Wolczanski, P. T.; van Duyne, G. D. *Organometallics* **1984**, *3*, 977. (c) Lubben, T. V.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1987**, *109*, 424. (d) Latesky, S. L.; Keddington, J.; McMullen, A. K.; Rothwell, I. P. *Inorg. Chem.* **1985**, *24*, 995. (e) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1991**, *10*, 15. (f) Durfee, L. D.; Latesky, S. L.; Rothwell, I. P.; Huffman, J. C.; Folting, K. *Inorg. Chem.* **1985**, *24*, 4569. (g) Minhas, R.; Duchateau, R.; Gamborotta, S.; Bensimom, C. *Inorg. Chem.* **1992**, *31*, 4933. (h) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1990**, *9*, 2211. (i) Wedler, M.; Gilje, J. W.; Pieper, U.; Stalke, D.; Noltemeyer, M.; Edelman, F. T. *Chem. Ber.* **1991**, *124*, 1163. (j) Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P. *Organometallics* **1985**, *4*, 902. Elegant studies on polyhedral oligometallasilsesquioxanes[12k] as models for silica-supported catalysts and cyclic metallasiloxanes of Ti, Zr, and Hf with 6−10-membered rings[12l] have been reported. (k) Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 3850. (l) See: Hossain, M. A.; Hursthouse, M. B.; Ibrahim, A.; Sullivan, A. C. *J. Chem. Soc., Dalton Trans.* **1989**, 2347 and references therein.

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[21] The activity of the solvated cations $[Cp_2MMe(L)]^+$ is often lowered due to competition between the (strongly) coordinated ligand (THF, $PhNMe_2$, THT) and the α-olefin.

[22] Miyashita, A.; Yasuda, A.; Tanaka, H.; Toriimi, K.; Ito, T.; Souchi, T.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 7932.

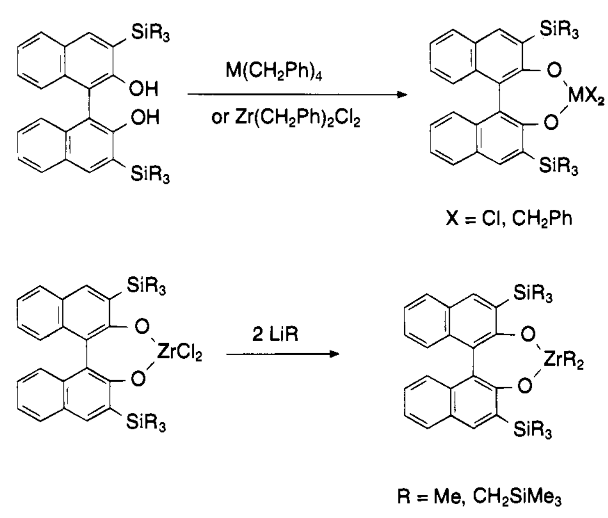

Figure 3.

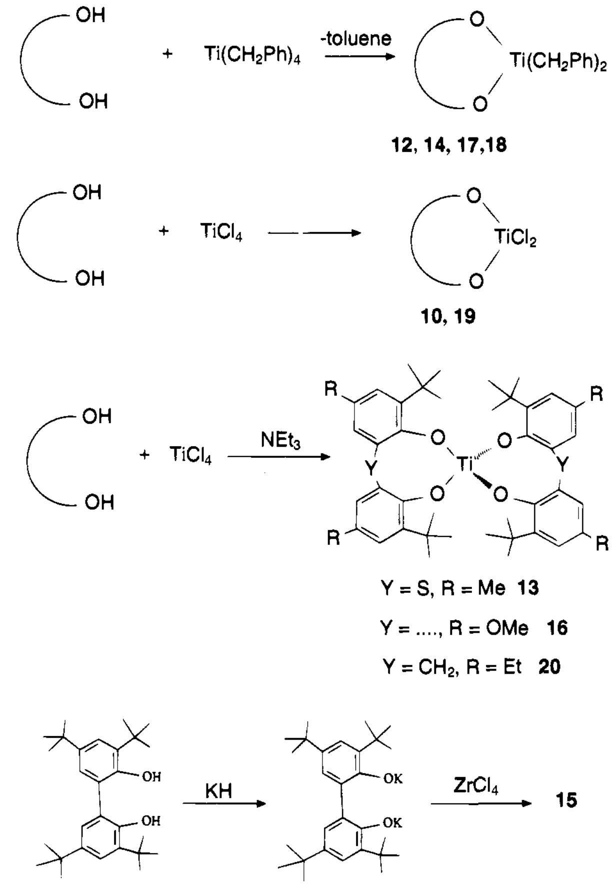

Figure 4.

$\{1,1'\text{-}(2,2',3,3'\text{-OC}_{10}\text{H}_5\text{SiMe}_3)\}_2\text{Zr(CH}_2\text{Ph)}_2$ could not be isolated in pure form. Figure 2 shows the compound numbering. Figures 3 and 4 summarize the general synthetic methods (see the Experimental Section for details).

Because $\text{Ti(CH}_2\text{Ph)}_2\text{Cl}_2$ is not synthetically accessible, (O−O)TiCl_2 species were prepared by addition of the biphenol or binaphthol to TiCl_4, in the *absence* of Et_3N. Addition of TiCl_4 to an ether solution of $2,2'\text{-S}(4\text{-Me},6\text{-}^t\text{BuC}_6\text{H}_2\text{OH})_2$ or $2,2'\text{-CH}_2(4\text{-Et},6\text{-}^t\text{BuC}_6\text{H}_2\text{OH})_2$ at −30 °C led to the evolution of HCl gas and formation of $2,2'\text{-S}(4\text{-Me},6\text{-}^t\text{BuC}_6\text{H}_2\text{O})_2\text{TiCl}_2$ (**10**) and $2,2'\text{-CH}_2(4\text{-Et},6\text{-}^t\text{BuC}_6\text{H}_2\text{O})_2\text{TiCl}_2$ (**19**), respectively. It might have been expected that use of a tertiary amine would assist in the removal of generated HCl. Surprisingly, reaction of TiCl_4 with 1 equiv of the biphenols $2,2'\text{-S}(4\text{-Me},6\text{-}^t\text{BuC}_6\text{H}_2\text{OH})_2$, $2,2'\text{-}(4\text{-OMe},6\text{-}^t\text{BuC}_6\text{H}_2\text{OH})_2$, or $2,2'\text{-CH}_2(4\text{-Et},6\text{-}^t\text{BuC}_6\text{H}_2\text{OH})_2$ in the *presence* of excess NEt_3 did not lead to anticipated (O−O)TiCl_2 but to a ≤50% yield of the bis(chelating alkoxide) species $\{2,2'\text{-S}(4\text{-Me},6\text{-}^t\text{BuC}_6\text{H}_2\text{O})_2\}_2\text{Ti}$ (**13**), $\{(4\text{-OMe},6\text{-}^t\text{BuC}_6\text{H}_2\text{O})_2\}_2\text{Ti}$ (**16**), or $\{\text{CH}_2(4\text{-Et},6\text{-}^t\text{BuC}_6\text{H}_2\text{O})_2\}_2\text{Ti}$ (**20**), respectively. See Experimental Section.

Having established synthetic routes to chelating alkoxide species, we were also interested in possible reactivity differences effected by the chelating thiolate analogs of the chelating phenoxides. Metal thiolates were expected to be inherently more electron-rich since S is less electronegative than O. Syntheses of sterically hindered chelating *binaphthiols*,[23] similar to the binaphthols above, have, however, yet to be reported in the literature. Despite much effort, we were unable to prepare crowded binaphthiols[23] starting from $\text{C}_{20}\text{H}_{10}(\text{SH})_2$[24] using similar methodology[18-20] for adding steric bulk to the analogous binaphthols. See the supplementary material.

Alkyl species, other than benzyl, are available via alkylation of (O−O)MCl_2. In this way, reaction of **3** with MeLi or $\text{Me}_3\text{SiCH}_2\text{Li}$ affords **6** or **9**, respectively. Compound **6** can be made using $\text{Me}_2\text{Mg(dioxane)}$ in toluene. Consistent with the enhanced π-donating ability of alkoxides, these alkylations only result in substitution of the chlorides, rather than the alkoxides.[12b]

These biphenolate and binaphtholate compounds are conveniently characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis (see the Experimental Section). In particular, the α-hydrogens of (O−O)$\text{M(CH}_2\text{R)}_2$ are potentially diastereotopic. They show differences in chemical shift dependent on the metal (Ti or Zr) and peak multiplicity depending on the ancillary ligand (Table 1). The ^{1}H NMR chemical shifts fall into several categories. The upfield ^{1}H NMR shifts of $\text{C}_\alpha H_2\text{Ph}$ in **7**, **8**, and **9** relative to $\text{M(CH}_2\text{Ph)}_4$ (1.56 ppm (M = Zr); 2.83 ppm (M = Ti)) can be attributed to ring current effects induced by the SiPh_3 binaphthol substituents. This is supported by the ^{1}H NMR chemical shifts in **4** (2.87, 2.35 ppm) which are less perturbed from that found in $\text{Ti(CH}_2\text{Ph)}_4$. In contrast to the binaphtholates, one singlet is observed for the benzyl α-CH_2s in biphenolates **14** and **17**, and two singlets for the benzyl group $\text{C}H_2$s are observed in sulfur-bridged **12** (3.26 and 3.32 ppm)[25] and CH_2-bridged[26] **18** (3.17 and 2.81 ppm). The apparent absence of stereochemical rigidity (nondiastereotopic α-$\text{C}H_2$-Ph) of the chelating biphenolate ligands in **12**, **14**, **17**, and **18** was also observed in organolanthanide chemistry.[14] A biphe-

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(23) The synthesis of the *unhindered* 1,1′-biphenyl-2,2′-dithiol $\text{C}_{12}\text{H}_8(\text{SH})_2$ and binaphthiols $\text{C}_{20}\text{H}_{10}(\text{SH})_2$ is described in the supplementary material on a 10 g scale. This is based upon, or is a modification of, literature procedures. (a) Schaefer, J. R.; Higgins, J. *J. Org. Chem.* **1967**, *32*, 1607. (b) Newman, M. S.; Karnes, H. A. *J. Org. Chem.* **1966**, *31*, 3980. (c) Snieckus, V.; Beaulieu, F. *Synthesis* **1992**, 113. (d) Di Furia, F. *Bull. Soc. Chim. Fr.* **1991**, *127*, 734. (e) Figuly, G. D.; Loop, C. K.; Martin, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 654. Block, E.; Eswarakrishnan, V.; Gernon, M.; Ofori-Okai, C. S.; Tang, K.; Zubieta, J. *J. Am. Chem. Soc.* **1989**, *111*, 658. Smith, K.; Lindsay, C. M.; Pritchard, G. J. *J. Am. Chem. Soc.* **1989**, *111*, 665.

(24) Reaction of 2,6-bis(trimethylsilyl)thiophenol with $\text{Zr(CH}_2\text{Ph)}_4$, $\text{Zr(CH}_2\text{Ph)}_2\text{Cl}_2$, or $\text{Ti(CH}_2\text{Ph)}_4$ did not proceed cleanly to give isolable products. However, reaction of $2,6\text{-C}_6\text{H}_3(\text{SiMe}_3)_2\text{SH}$ with TiCl_4 in the presence of excess NEt_3 or reaction of $2,6\text{-C}_6\text{H}_3{}^i\text{Pr}_2\text{SH}$ with $\text{Ti(CH}_2\text{Ph)}_4$ afforded dimeric $[\{2,6\text{-C}_6\text{H}_3(\text{SiMe}_3)_2\text{S}\}_2\text{TiCl}_2]_2$ (**23**) and monomeric $(2,6\text{-C}_6\text{H}_3{}^i\text{Pr}_2\text{S})_2\text{Ti(CH}_2\text{Ph)}_2$ (**24**), respectively. **23**: ^{1}H NMR (C_6D_6): 7.48 and 7.70 (dd, 4H, J = 7.4 Hz, 1.0 Hz), 7.08 (t, 2H, J = 7.4 Hz), 0.78 (s, 18H, Si*Me*$_3$), 0.37 ppm (s, 18H, Si*Me*$_3$). Addition of THF-d_8 resulted in monomer formation. ^{1}H NMR (C_6D_6): 7.45 (dd, 4H, J = 7.4 Hz, 1.0 Hz), 7.08 (t, 2H, J = 7.4 Hz), 0.37 ppm (s, 36H, Si*Me*$_3$). **24**: ^{1}H NMR (C_6D_6): 7.3−7.1, 6.6 (d, 4H, H_0), 3.8 (septet, 4H, CH), 3.05 (s, 4H, CH_2), 1.24 ppm (d, 12H, Me). ^{13}C NMR (C_6D_6, 25 °C): 149.22, 140.83, 138.8, 131.1, 130.75, 128.8, 127.3, 106.9 (CH_2), 33.05 (CH), 23.66 ppm (Me). **23** possesses terminal and bridging thiolates and terminal chlorides. With MAO as cocatalyst, it did not oligo/polymerize ethene.

(25) The singlets at 3.32 and 3.26 ppm were confirmed as two peaks (rather than a doublet) by measurement on a spectrometer of a different frequency.

Table 1. ^{1}H and ^{13}C NMR Chemical Shifts and $^1J_{CH}$ Coupling Constants of MCH_2Ph in (O−O)M(CH$_2$Ph)$_2$

	δ CH_2	$\delta$$CH_2$Ph	$^1J_{CH}$
Zr Binaphtholates			
{$C_{10}H_5SiMePh_2O$}$_2$Zr(CH$_2$Ph)$_2$ (**5**)	1.30, 0.91 (AB)	66.9	136
{$C_{10}H_5SiPh_3O$}$_2$Zr(CH$_2$Ph)$_2$ (**8**)	0.88, 0.64 (AB)	68.1	133
{$C_{10}H_5SiPh_3O$}$_2$Zr(CH$_2$SiMe$_3$)$_2$ (**9**)	0.50, −0.5 (AB)	67.6	
Ti Binaphtholates			
{$C_{10}H_5SiMe_3O$}$_2$Ti(CH$_2$Ph)$_2$ (**4**)	2.87, 2.35 (AB)		
{$C_{10}H_5SiPh_3O$}$_2$Ti(CH$_2$Ph)$_2$ (**7**)	1.40, 1.05 (AB)		
Ti Biphenolates			
(4,6-^{t}Bu$_2$C$_6$H$_2$O)$_2$Ti(CH$_2$Ph)$_2$ (**14**)	2.6 (s)	88.9	
(4-OMe, 6-^{t}BuC$_6$H$_2$O)$_2$Ti(CH$_2$Ph)$_2$ (**17**)	2.5 (s)	87.0	
Bridged Systems			
S (4-Me,6-^{t}BuC$_6$H$_2$O)$_2$Ti(CH$_2$Ph)$_2$ (**12**)	3.32 (s), 3.26 (s)		
CH$_2$(4-Et,6-^{t}BC$_6$H$_2$O)$_2$Ti(CH$_2$Ph)$_2$ (**18**)	3.17 (s), 2.81 (s)	84.0	136

nolate "flipping" mechanism in which the two enantiomers of the biphenolate unit could be exchanged was proposed.[14]

The ^{13}C NMR α-CH$_2$Ph chemical shifts and $^1J_{CH}$ coupling constants are also given in Table 1. The chemical shifts fall in two ranges for the Ti and Zr benzyl species.[12j] Zirconium dibenzyls (O−O)Zr(CH$_2$Ph)$_2$ exhibit Zr−CH$_2$Ph ^{13}C NMR chemical shifts at 66−68 ppm (cf. ca. 75 ppm for (ArO)$_n$-Zr(CH$_2$Ph)$_{4-n}$ (n = 2, 3)[12j]), and (O−O)Ti(CH$_2$Ph)$_2$ at 84−89 ppm. The α-CH$_2$Ph $^1J_{CH}$ coupling constants are 133−136 Hz and are indicative of an increase in sp^2 character. In comparison, the Zr methyl groups in **6** resonate at δ 46.04, $^1J_{CH}$ = 118 Hz. Although the data above are consistent with a weak η^2-CH$_2$Ph interaction, this is not reflected in the X-ray structure of **17** (vide infra). The ^{1}H NMR chemical shift of the Zr−CH$_2$Ph H$_{ortho}$ resonance is a better indication of an interaction between the phenyl π-system and Zr,[12j,27,28] a shift to relatively high field being indicative of such an interaction. Thus in monophenoxides (2,6-C$_6$H$_3$^{t}Bu$_2$O)Zr(CH$_2$Ph)$_3$[12j] and (^{t}Bu$_3$CO)Zr(CH$_2$Ph)$_3$,[12b] the benzyl H$_{ortho}$ resonates at 6.71 and ca. 6.6 ppm, respectively, indicative of a strong η^2-CH$_2$Ph interaction, whereas in bisphenoxide (2,6-C$_6$H$_3$^{t}Bu$_2$O)(2,6-^{t}Bu$_2$-4-OMe-C$_6$H$_2$O)Zr(CH$_2$-Ph)$_2$,[12j] the H$_{ortho}$ protons resonate at δ > 7.00. In compounds **5**, **7**, and **8**, benzyl H$_{ortho}$ resonates at 6.05, 6.45, and 5.70 ppm, respectively. However, these upfield ^{1}H NMR chemical shifts are *not* due to η^n (n > 1) benzyl coordination but to the ring currents induced by the SiPh$_3$ and SiMePh$_2$ ligand substituents. In comparison, benzyl H$_O$ in **4** resonates at >6.8 ppm. A high-field shifted benzyl C$_{ipso}$ ^{13}C NMR resonance has also been used as an indicator of η^2-benzyl coordination.[27b] Comparison of ^{13}C NMR data for **16** and **17** allowed assignment of benzyl C$_{ipso}$ (137.5 ppm) in **17**; this is at considerably lower field than that found for η^2-benzyl coordination in cationic [Cp$_2$ZrCH$_2$Ph]$^+$ and again indicates η^1-benzyl coordination.

X-ray Structure Determination of 2,2′-(4-OMe, 6-^{t}BuC$_6$H$_2$O)$_2$Ti(CH$_2$Ph)$_2$ (17·$^1/_2$OEt$_2$). Crystallization of **17** from ether/hexane at −40 °C afforded red block-like crystals of **17**·$^1/_2$OEt$_2$ which were suitable for X-ray diffraction analysis (Table 2). A perspective view of the molecular structure is shown in Figure 5. Atomic coordinates and selected bond distances and angles are given in Tables 3 and 4.

Table 2. Crystal Data and Data Collection Parameters for **17**·$^1/_2$OEt$_2$

Crystal Data	
chemical formula	$C_{38}H_{47}O_{4.5}Ti$
mol wt	623.7
crystal system	triclinic
space group, No.	$P\bar{1}$, No. 2
a Å	8.737(9)
b Å	11.840(10)
c Å	17.135(17)
α, deg	98.28(7)
β, deg	90.53(8)
γ, deg	101.38(7)
V, Å^3	1718(3)
Z	2
D_{calcd}, g cm^{-3}	1.205
F(000) electrons	666
μ(Mo Kα) cm^{-1}	2.88
approx cryst dim. mm	0.3 × 0.35 × 0.4
Data Collection	
temperature (K)	213
$\theta/2\theta$ range	4.0° < 2θ < 40.0°
scan method	Wyckoff ω
total data	6021
total unique data	3336 (R_{int} = 0.089)
Refinement	
no. of refined parameters	171
weighting factor, a	0.10
$R1^a$	0.103^b
wR2^a	0.227^b
goodness of fit, S	1.15
min/max residual densities in final Fourier map e/Å^3	−0.45, 0.46
mean shift/esd in final cycle	0.001

[a] $wR2 = [\sum w\Delta^2/\sum wF_o^4]^{0.5}$, $\Delta = F_o^2 - F_c^2$, and $R1 = \sum|F_o - F_c|/\sum|F_o|$. [b] For 1626 data with $F^2 > 2\sigma(F^2)$.

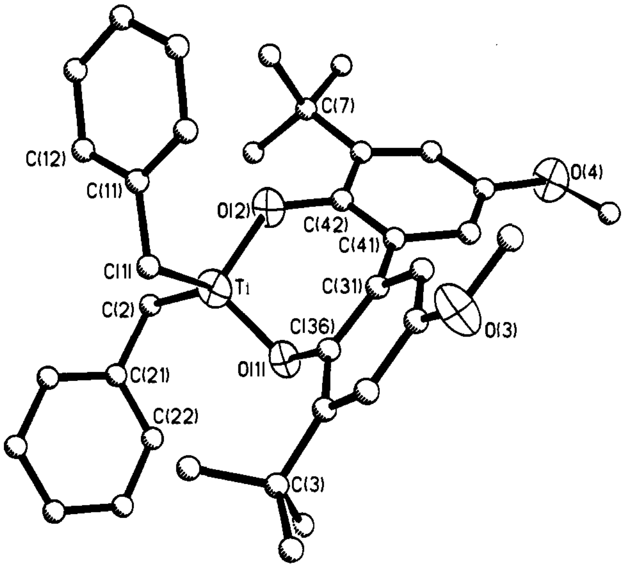

Figure 5. Perspective view of the molecular structure of **17**·$^1/_2$OEt$_2$.

The four-coordinate titanium is ligated by the chelating alkoxide and two σ-bonded benzyl groups. The coordination geometry at titanium is distorted from tetrahedral with the O−Ti−O angle markedly smaller than the C−Ti−C angle [O1−Ti−O2 = 102.0(3)°, O2−Ti−C1 = 104.8(4)°, O1−Ti−C1 = 114.6(4)°, O1−Ti−C2 = 112.4(4)°, O2−Ti−C2 110.4(4)°, C1−Ti−C2 = 111.9(5)°]. The two Ti−O (alkoxide) distances [Ti−O1 = 1.821(8), Ti−O2 = 1.799(7) Å] should be regarded

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[26] (a) A similar ligand has been used in Ti(IV), Zr(IV), and V(V) chemistry. Floriani, C.; Corazza, F.; Lesueur, W.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 66. {CH$_2$(4-Me,6-^{t}BuC$_6$H$_2$O)$_2$}-M(BH$_4$)$_2$ (M = Ti, Zr),[26b] (CH$_2$(4-Me,6-^{t}BuC$_6$H$_2$O)$_2$}V(THF)$_2$Cl,[26c] and {CH$_2$(4-Me,6-^{t}BuC$_6$H$_2$O)$_2$}V(O)Cl[26d] have also been synthesized and characterized by X-ray diffraction. (b) Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1991**, *30*, 145. (c) Mazzanti, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1989**, 1793. (d) Toscano, P. J.; Schermerhorn, E. J.; Dettelbacher, C.; Macherone, D.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1991**, 933.

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Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Factors ($Å^2 \times 10^3$) for **17**$\cdot{}^1/_2OEt_2$

	x	*y*	*z*	*U*(eq)
Ti	2661(3)	1302(2)	−3131(1)	37(1)[b]
O(1)	3270(8)	2646(6)	−2444(4)	31(2)[b]
O(2)	2695(8)	212(6)	−2504(4)	35(2)[b]
O(3)	9472(9)	2927(7)	−1626(4)	46(2)[b]
O(4)	3112(9)	591(7)	737(4)	41(2)[b]
C(1)	4251(13)	999(9)	−3990(6)	31(3)
C(2)	423(14)	1137(10)	−3617(7)	44(4)
C(3)	5595(14)	4558(10)	−2884(6)	36(3)
C(4)	4991(14)	4038(10)	−3714(6)	40(3)
C(5)	7023(15)	5516(10)	−2947(7)	56(4)
C(6)	4399(14)	5188(10)	−2463(7)	45(4)
C(7)	702(13)	−1556(10)	−1758(6)	31(3)
C(8)	−155(14)	−2337(10)	−1188(7)	44(3)
C(9)	1636(15)	−2300(11)	−2297(7)	56(4)
C(10)	−532(14)	−1198(10)	−2247(7)	45(4)
C(12)	3068(8)	−1034(6)	−4529(4)	35(3)
C(13)	2999(8)	−2225(6)	−4580(4)	46(4)
C(14)	4124(10)	−2635(5)	−4185(5)	52(4)
C(15)	5319(8)	−1854(7)	−3738(5)	61(4)
C(16)	5389(8)	−662(6)	−3687(4)	51(4)
C(11)	4263(9)	−252(5)	−4082(4)	33(3)
C(22)	581(10)	3263(7)	−3643(3)	55(4)
C(23)	899(10)	4228(5)	−4036(4)	50(4)
C(24)	1306(9)	4096(6)	−4821(4)	51(4)
C(25)	1394(10)	3000(7)	−5214(3)	55(4)
C(26)	1076(10)	2036(5)	−4822(4)	47(4)
C(21)	669(9)	2167(6)	−4036(4)	36(3)
C(31)	5183(13)	1998(9)	−1692(6)	26(3)
C(32)	6723(13)	2037(9)	−1476(6)	30(3)
C(33)	7916(15)	2840(10)	−1765(7)	39(3)
C(34)	7475(13)	3626(10)	−2200(6)	32(3)
C(35)	5969(13)	3652(9)	−2419(6)	28(3)
C(36)	4792(13)	2744(9)	−2180(6)	28(3)
C(37)	9917(14)	2147(10)	−1173(7)	44(4)
C(41)	3977(12)	1199(9)	−1292(6)	20(3)
C(42)	2825(12)	317(9)	−1688(6)	23(3)
C(43)	1841(13)	−523(9)	−1306(6)	30(3)
C(44)	1990(13)	−318(9)	−488(6)	28(3)
C(45)	3102(13)	557(9)	−67(6)	27(3)
C(46)	4111(13)	1316(9)	−462(6)	32(3)
C(47)	4289(15)	1430(10)	1176(7)	47(4)
O(5)	5640	4911	−24	133(10)[a]
C(50)	7315	5200	−79	229(31)[b]
C(51)	7790	4624	402	150(17)[a]
C(52)	5349	4442	226	68(9)[a]
C(53)	6790	5391	253	119(14)[a]

[a] Occupancy 0.5. [b] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **17**$\cdot{}^1/_2OEt_2$

Ti−O(2)	1.799(7)	Ti−O(1)	1.821(8)
Ti−C(2)	2.080(12)	Ti−C(1)	2.075(11)
O(1)−C(36)	1.379(12)	O(2)−C(42)	1.386(11)
O(3)−C(33)	1.359(14)	O(3)−C(37)	1.397(12)
O(4)−C(45)	1.372(12)	O(4)−C(47)	1.406(13)
C(1)−C(11)	1.469(11)	C(2)−C(21)	1.484(12)
O(2)−Ti−O(1)	102.0 (3)	O(2)−Ti−C(2)	110.4(4)
O(1)−Ti−C(2)	112.4(4)	O(2)−Ti−C(1)	104.8(4)
O(1)−Ti−C(1)	114.6(4)	C(2)−Ti−C(1)	111.9(5)
C(36)−O(1)−Ti	109.9(6)	C(42)−O(2)−Ti	130.2(7)
C(33)−O(3)−C(37)	117.2(9)	C(45)−O(4)−C(47)	116.5(8)
C(11)−C(1)−Ti	106.5(6)	C(21)−C(2)−Ti	100.0(7)

as identical, as should the Ti−C_α (benzyl) distances [Ti−C1 = 2.075(11), Ti−C2 = 2.080(12) Å]. The large esd's are due to poor crystal quality (see the Experimental Section for details). The Ti−phenoxide distances are unexceptional.[8b,12e,h,26a,b] The phenyl rings of the bis-phenoxide ligand are twisted, the mean planes of the two phenyl rings forming an angle of 57.6° with a torsion angle C36−C31−C41−C42 of 62.0(1)°. As a consequence of the smaller Ti−O1−C36 angle (109.9(6)°) than Ti−O2−C42 (130.2(7)°), C36 is much closer to Ti (2.64 Å) than C42 (2.90 Å). The two benzyl ligands in **17** can be regarded as being σ-bound to Ti with Ti−C1−C11 = 106.5(6)° and Ti−C2−C21 = 100.0(7)° and with Ti···C(11) = 2.87 Å and Ti···C(21) = 2.76 Å. This η^1-benzyl coordination mode was also found in the related bis(alkoxide) $(2,6\text{-}C_6H_3{}^tBu_2O)(2,6\text{-}{}^tBu_2\text{-}4\text{-}OMe\text{-}C_6H_2O)Zr(CH_2Ph)_2$.[12j] *Mono*-phenoxide $(2,6\text{-}C_6H_3{}^tBu_2O)Zr(CH_2Ph)_3$[12j] indicated a strong η^n ($n > 1$) phenyl π-interaction between the phenyl ring (of the benzyl group) and zirconium. In comparison with **17**, related crystallographically characterized $\{CH_2(4\text{-}Me,6\text{-}{}^tBuC_6H_2O)_2\}TiCl_2$[26a] has Ti−O = 1.760(4), 1.742(4) Å with O−Ti−O = 106.5°, and $\{CH_2(4\text{-}Me,6\text{-}{}^tBuC_6H_2O)_2\}TiMe_2$[26a] has Ti−O = 1.799(3) Å, O−Ti−O = 112.7°, with Ti−Me = 2.090(9), 2.03(1) Å and Me−Ti−Me = 105.8°. The structure of the much less sterically hindered methyl-substituted $\{(C_{20}H_{10}Me_2O_2)Ti(O^iPr)_2\}_2$[8b] is dimeric with terminal isopropoxides and asymmetrically bridging binaphthoxide groups. A range of *un*hindered binaphthoxide coordination modes in Ti(IV) species has been found.[8b]

α-Olefin Polymerization. Having developed synthetic pathways to a range of new titanium and zirconium species with varying steric requirements, the influence of the ligand environment on their catalytic activity toward unsaturated hydrocarbons including α-olefins, butadiene, and acetylenes was studied.

Polymerization of Ethene. Table 5 displays the ethene polymerization activity of these chelating alkoxide species, with 500 (based on $(AlMeO)_n$) molar equiv methylaluminoxane (MAO) as cocatalyst, polyethene molecular weight data as determined by gel permeation chromatography (GPC), and melting points as determined by differential scanning calorimetry (DSC). No oligomers were detected in the liquid phase by GC. Activities of up to 4740 kg of PE/mol of catalyst·h (PE = polyethylene) (equivalent to 100 kg/g of metal·h (metal = Ti, Zr; ≠ Al)) were obtained for the polymerization of ethylene. Use of other cocatalysts, such as Et_2AlCl, resulted in much poorer activity than with MAO. These activities at 25 °C compare to those (2−22 kg of PE/mmol of Zr·h) obtained for various substituted $(indenyl)_2ZrCl_2$/MAO ([MAO]/[Zr] = 2000:1, toluene, 25 °C)[29a] but are much less than found for Kaminsky's $(C_5H_5)_2ZrCl_2$/MAO.[29b] In α-olefin polymerization with $(C_5H_5)_2ZrCl_2$/MAO or *rac*-$(CH_2CH_2)(indenyl)_2ZrCl_2$/MAO, typically 1000−15000 equiv of MAO is used. Because of the high cost of cocatalyst in potential applications, efforts were made to reduce the high MAO/Zr ratios. For this reason, 500 equiv of MAO was (arbitrarily) chosen and used throughout for consistency. This lower [MAO]/[Zr] (or [Ti]) ratio may be reflected in a possibly reduced activity of these catalyst systems. An increase of catalytic activity with increasing [MAO]/[Zr] ratio has been observed.[29c]

A few qualitative polymerization trends can be observed (Table 5). The less sterically hindered **1**/MAO is slightly less active than **2**/MAO or **3**/MAO. Comparison of the series (O−O)MR_2 shows that **6**−**9**/MAO, containing the most sterically hindered $SiPh_3$-substituted binaphthol ligand, are less active than the less sterically hindered **4**/MAO or **5**/MAO. The activity of **10**/MAO, under our polymerization procedures (see Experimental Section) at least, is less (100 kg of PE/g of Ti·h) than that (820 kg of PE/g of Ti·h) previously reported.[9a,c] The molecular weight distribution (M_w/M_n = 11.9) is much broader

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(29) (a) Lee, I.-K.; Gauthier, W. J.; Ball, J. M.; Iyengar, B.; Collins, S. *Organometallics* **1992**, *11*, 2115. (b) Kaminsky, W.; Steiger, R. *Polyhedron* **1988**, 7, 2375. (c) Llinas, G. H.; Day, R. O.; Rausch, M. D.; Chien, J. C. W. *Organometallics* **1993**, *12*, 1283. See also ref 32 for ethylene polymerization activities of Cp_2ZrR_2/MAO.

Table 5. Ethene Polymerizations[a]

catalyst (mmol)	yield (g)	time (min)	rate (kg/mol cat·h)	rate (kg/g M·h)	M_w[b]	M_n[b]	M_w/M_n[b]	mp[c]
1 (0.054)	5.5	40	152	1.68	2×10^5	8300	24	125
2 (0.038)	4.5	35	203	2.2	3.6×10^5	24000	15	120
3	5.5	60	275	3.0				133
4[d]	1.5	25	180	3.75	4.2×10^5	39000	10.5	133
5	3.5	10	1050	11.5				133
6	0.9	60	45	0.49				
7	inactive							
8	inactive							
9	0.475	30	46	0.53				
10[e]	7.9	5	4740	100	3.5×10^5	29500	11.9	
11	inactive							
12[d] (0.023)	2.9	15	504	5.5	3.4×10^5	50000	7.0	117
13	3.2	25	384	8.0				
16 (0.05)	1.5	30	60	1.25				
17 (0.04)	1.1	90	18	0.38				
18	0.9	15	180	3.75				
19	1.3	10	390	8.1				

[a] 20 °C, 3 bar; 0.02 mmol of catalyst unless otherwise stated; 500 equiv of MAO in 200 mL of toluene. [b] By GPC. [c] By DSC. [d] Polymerization temperature 40 °C. [e] In all other polymerizations, an exotherm of 1−3 °C was normally observed on catalyst injection. In the case of **10**/MAO, an exotherm of 27 °C (25 to 52 °C) was observed.

than that originally reported ($M_w/M_n = 2$) for ethylene polymerization with **10**/MAO.[9a,c] Note that **11**/MAO, the Zr analogue of **10**/MAO, is inactive.

The significantly increased activity of S-bridged **10**/MAO compared to CH_2-bridged **19**/MAO may be due to increased ligand flexibility[30] and the effects of possible π-donation from S to Ti. Apart from these reasons, it remains a matter of conjecture, however, why **10**/MAO is an order of magnitude more active than all other tested biphenolate or binaphtholate ligands.

The melting point (DSC) of the polyethene produced a 117−133 °C, indicative of some degree of branching (Table 5). In comparison, melting points of LLDPE and HDPE are 119 and 136 °C, respectively. GPC results indicate that M_w is high ((2−4) × 10^5).[31] The origin of the broad molecular weight distribution (M_w/M_n = ca. 5−20)[32] is unclear. Although it is perhaps tempting to attribute it, at least partly, to precipitation (gelation) from toluene at 20 °C of the growing long chain M−(polyethylene) species, and thus catalyst heterogenization creating different catalyst sites, such an explanation of a purely physical phenomenon cannot be construed as valid, since high molecular weight PE of narrow M_w/M_n can be made in toluene.[29a,b] It would appear that for the polymerization of ethene, activation of the chelating phenoxides with MAO does not afford a single well-defined active species.

Polymerization of 1-Hexene. Use of 1-hexene as monomer ensures homogeneous polymerization conditions as a propagating M−(polyhexene) chain would be soluble in aromatic solvents. Significant differences in 1-hexene oligo-/polymerization are observed that can only be attributed to the varying steric hindrance of the ligands. Ligand-dependent trends of the degree of polymerization (oligomers to high molecular weight polymer) and stereoregularity (atactic to isotactic) are observed. An overview of this behavior is shown in Figure 6.

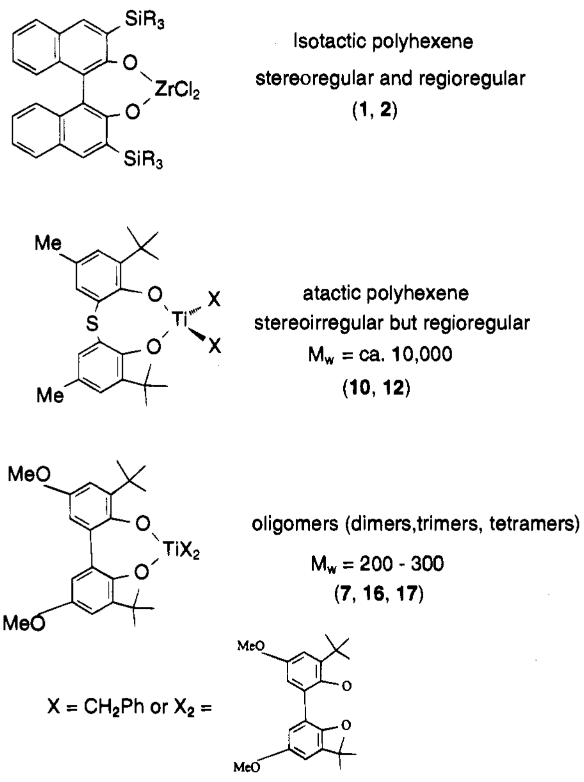

Figure 6.

Polymerization of 1-hexene by **1** and **2**, with MAO (100 equiv) as cocatalyst,[33] affords polyhexene with narrow polydispersity. Furthermore, polymerization of 1-hexene is both regio- and stereospecific, affording highly (>90%) tactic polyhexene. The tactic polyhexene from **2**/MAO has high molecular weight (M_w = 674 000)[34] and M_w/M_n = 2.23. The ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of polyhexene produced from **1**/MAO is shown in Figure 7. Clean resonances are observed at 40.24 (CH_2), 34.61 (CH_2), 32.38 (CH), 28.73 (CH_2), 23.25 (CH_2), and 14.21 (Me) ppm. In order to unequivocably determine whether this polyhexene is isotactic or syndiotactic,

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[30] Preliminary molecular modeling experiments on a Cache system indicate that 2,2′-S(4-Me,6-$^tBuC_6H_2O)_2MCl_2$ adopts a wedge-shaped structure with the sulfur at the apex and that the biphenolates and binaphtholates show the expected C_2 symmetry, as was determined by X-ray crystallography for **17**.

[31] Heterogeneous catalysts can give polyolefins with $M_w > 10^6$.

[32] Note that M_w/M_n of 3.3−12 have been found for the polymerization of ethylene by $[Cp_2ZrMe][(C_2B_9H_{11})_2Co]$. Hlatky, G. G.; Eckman, R. R.; Turner, H. W. *Organometallics* **1992**, *11*, 1413.

[33] Polymerization of 1-hexene by **1** and **2** has been investigated using both MAO solution (10% in toluene) and MAO powder (in which unbound $AlMe_3$ is largely removed under vacuum from the commercially available MAO in toluene solution) dissolved in toluene. No notable cocatalyst-related differences in polymerization behavior were observed. See: Resconi, L.; Bossi, S.; Abis, L. *Macromolecules* **1990**, *23*, 4489.

[34] It should be obvious from this very high M_w, compared to the amount of 1-hexene and **2** added, that not all of **2**/MAO can be active.

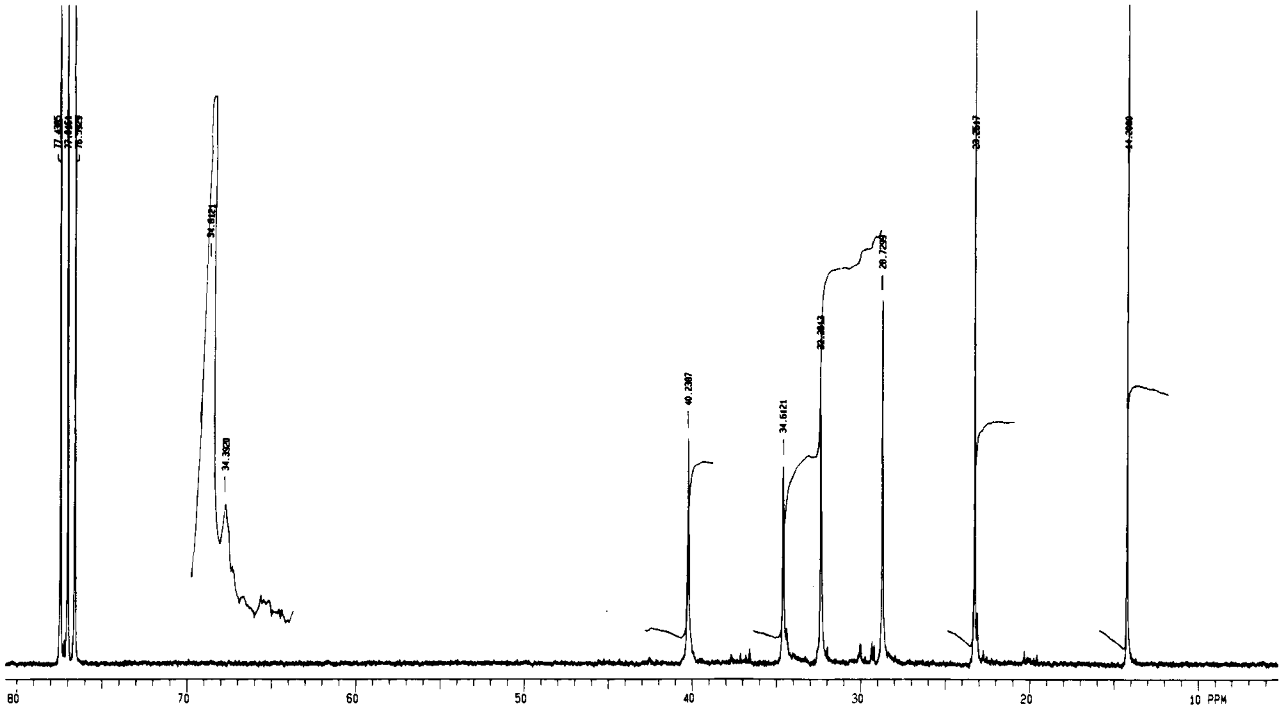

Figure 7. ^{13}C NMR ($CDCl_3$) of isotactic polyhexene from **1**/MAO.

1-hexene was polymerized in toluene at 25 °C with isospecific *rac*-$CH_2CH_2(indenyl)_2ZrCl_2$/MAO,[1d] and with syndiospecific $Me_2C(fluorenyl\text{-}Cp)ZrCl_2$/MAO,[3a] affording reference samples of isotactic (i-PH) and syndiotactic (s-PH) polyhexene, respectively. In comparison with their ^{13}C NMR chemical shifts,[35] the polyhexene produced by **1**/MAO or **2**/MAO best resembles i-PH.

For the wedge-shaped[30] S-bridged biphenolate complexes **10** and **12**, aspecific polymerization of hexene is observed with regioregular 1,2-insertion. The slightly bulkier coordination sphere (compared to biphenolates **16** and **17**, due to a larger bite angle)[30] in titanium species **10** and **12** (with MAO as cocatalyst) affords atactic polyhexene (**10**: $M_w = 7800$, $M_w/M_n = 1.78$. **12**: $M_w = 19\,000$, $M_w/M_n = 1.71$). As in the polymerization of ethylene, **11**/MAO did not polymerize 1-hexene. This ligand provides sufficient steric hindrance to suppress 2,1-insertion of 1-hexene. Stereoregular olefin insertion by enantiomorphic site control would be lost, should the rate of the above-mentioned "flipping mechanism" be of the same order as the rate of olefin insertion.

In contrast to **10** and **12**, the bis(phenolate) **16** and compound **17**, with MAO cocatalyst, produce only oligomers. The reactivity of titanium binaphthoxide **7**/MAO is apparently anomalous; it also affords only oligomers. In comparison, its Zr analogue **8**/MAO affords atactic polyhexene, suggesting that, in this case at least, molecular weight control may also be metal dependent. The oligomer distributions are given in Table 6. Significantly, ^1H and ^{13}C NMR end group analysis indicates that these oligomers are predominantly (>95%) *internal* olefins. Less than 5% of vinylidene ($H_2C{=}CRR'$) end groups, expected from a 1,2-olefin insertion/β-H elimination pathway, was observed. Allylic end groups ($H_2C{=}CHCH_2R$) due to 1,2 insertion/β-alkyl elimination were also not observed (^{13}C NMR).[36] A pathway to internal olefins involves 2,1 1-hexene insertion/β-H elimination.

Table 6. Oligomer Distribution (wt %)[a] for Oligomerization of 1-Hexene[b]

catalyst	7	16	17
dimers	31.8	61.4	48.1
trimers	47.3	32.0	35.3
tetramers	17.3	6.6	16.6
pentamers	3.6	0	0
end groups internal (%)	>95	98	100
vinylidene (%)	0	2	0

[a] By GC. Uncorrected for response factors. [b] MAO cocatalyst.

Oligomerization of 1-hexene by early[37] and late[38] transition metals, in the presence of an aluminum cocatalyst, has been reported. Oligomerization of 1-hexene by $Zr(O\text{-}n\text{-}Pr)_4/AlEt_2Cl$ afforded (C_{12} fraction) 2-butyl-1-octene, as well as (4 and/or 5)-dodecene.[37] Isomerization[39,40] also occurred, *cis*- and *trans*-2-hexene being explained by 2,1 insertion/β-H elimination.[37] Oligomerization of 1-hexene by *rac*-$CH_2CH_2(indenyl)_2ZrCl_2$/MAO was recently shown to lead to minor quantities of internal olefins.[37a] This was attributed[37a] to 2,1 insertion of 1-hexene and isomerization.

The olefinic ^{13}C NMR resonances for the oligomers were assigned on the basis of their relative intensities, in conjunction

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[35] In $CDCl_3$ at 25 °C, we have found that isotactic-PH (from *rac*-$CH_2CH_2(indenyl)_2ZrCl_2$/MAO) displays ^{13}C NMR resonances at 40.36, 34.70, 32.50, 28.80, 23.31, and 14.24 ppm. Syndiotactic-PH (from $Me_2(C_5H_4\text{-}fluorenyl)ZrCl_2$/MAO) has ^{13}C NMR resonances at 40.75, 34.03, 32.40, 28.75, 23.36, and 14.29 ppm. ^{13}C NMR chemical shifts of isotactic[35a–c,e] and syndiotactic[35d,e] polyhexene are also reported in the literature. (a) Babu, G. N.; Newmark, R. A.; Chien, J. C. W. *Macromolecules* **1994**, *27*, 3383. (b) Asakura, T.; Demura, M.; Nishiyama, Y. *Macromolecules* **1991**, *24*, 2334. (c) Coughlin, E. B.; Bercaw, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 7606. (d) Asanuma, T.; Nishimori, Y.; Ito, M.; Uchikawa, N.; Shiomura, T. *Polym. Bull.* **1991**, *25*, 567. This compares the ^{13}C NMR chemical shifts of various isotactic and syndiotactic poly(α-olefins). See also: (e) Asanuma, A.; Shiomura, T.; Nishimura, Y.; Uchikawa, N. Mitsui Chem. Co. European Pat. Appl. 403866.

[36] Resconi, L.; Piemontesi, F.; Franciscono, G.; Abis, L.; Fiorani, T. *J. Am. Chem. Soc.* **1992**, *114*, 1025.

[37] (a) Liu, H. Q.; Deffieux, A.; Sigwalt, P. *Makromol. Chem.* **1991**, *192*, 2111. (b) Liu, H. Q.; Deffieux, A.; Sigwalt, P. *Makromol. Chem.* **1991**, *192*, 2125.

[38] Foulds, G. A.; Bennet, A. M. A.; Nivan, M. L.; Thornton, D. A.; Cavell, K. J.; Desjardins, S.; Peacock, E. J. *J. Mol. Catal.* **1994**, *87*, 117.

[39] A control experiment with the aspecific 1-hexene polymerization catalyst **10**/MAO did not result in the isomerization of 1-hexene.

[40] Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333. $Cp_2Zr(H)Cl$ reacts with 4-octene to give the thermodynamically most stable Zr-*n*-octyl product.

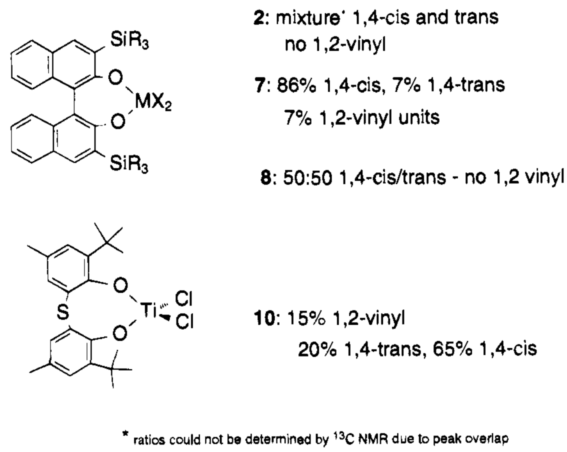

Figure 8.

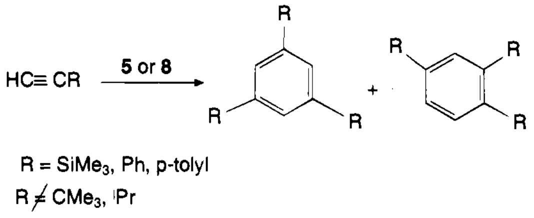

Figure 9.

with the oligomer ratios as given by GC (and GPC) data. These are dimer, 130.4 and 126.0 ppm; trimer, 136.3 and 124.6 ppm; and tetramer, 135.7 and 130.2 ppm. Note that only two olefinic resonances are observed for each oligomer, suggesting that 1-hexene insertion is regiospecific. The observed olefinic ^{13}C NMR chemical shifts for the 1-hexene dimer fraction are most consistent with *trans*-(4 or 5)-dodecene.[37] The structure of higher oligomers could not be unequivocably established. See the Experimental Section for analyses.

Polymerization of Butadiene. Many types of catalysts polymerize dienes, including Ziegler titanium compounds and allyl nickel species.[41] The attractive properties of natural rubber arise from the selective *cis* 1,4-polymerization of isoprene.[41] The polymerization of butadiene by chelating alkoxide Ti and Zr species shows that the polybutadiene microstructure is dependent on the ligand steric bulk. The sterically hindered binaphtholate compounds (**2**, **7**, and **8**), induced predominantly (86% *cis*-1,4, 7% *trans*-1,4, and 7% 1,2 vinyl units for **7**/MAO; 100% for **2**/MAO; 100% for **8**/MAO) 1,4-insertion. The smaller S-bridged ligand in **10** gave 15% 1,2-vinyl units. These reactivity modes are summarized in Figure 8. With **10**/MAO[42] an activity of 1.1 kg of polybutadiene/g of Ti·h was obtained. In our hands, **10**, **11**, and **12** were inactive for the polymerization of butadiene with $EtAlCl_2$ as cocatalyst.[42] The trends in regioselectivity can be rationalized as the bulkier ligands favoring a sterically less demanding 1,4-butadiene insertion mode.

Catalytic Cyclotrimerization of Acetylenes. The reactivity of acetylenes with late transition metals has been extensively investigated,[43] and cyclotrimerization is a common reaction pathway. Although the reactivity of early transition metals with acetylenes has been explored,[44] cyclic trimerization to substituted benzenes is rarely observed.[44] Dibenzyl species **5** and **8** proved to be active for the *catalytic* cyclotrimerization of terminal acetylenes in the absence of a cocatalyst (Figure 9).

Up to 200 equiv of HC≡CR (R = $SiMe_3$, Ph, *p*-tolyl) in toluene or C_6D_6 at 20 °C was selectively cyclotrimerized by **5** or **8** to a mixture of 1,2,4- and 1,3,5-trisubstituted benzenes. No acyclic oligomers were observed (GC and ^{1}H and ^{13}C NMR of reaction mixture). Cyclotrimerization of $Me_3SiC{\equiv}CH$ is qualitatively faster (200 equiv in minutes) than for PhC≡CH (40 equiv in hours). Internal acetylenes such as but-2-yne, as well as the more weakly acidic terminal acetylenes ^{i}PrC≡CH and ^{t}BuC≡CH, do not react with **5** or **8**, suggesting that the initial step is protonation of the dibenzylzirconium species. It was not possible to establish the mechanistic pathway for conversion of the bis(acetylide) $(O{-}O)Zr(C{\equiv}CR)_2$ to the putative intermediate (O−O)Zr(II), presumably necessary for zirconacyclopentadiene (ZrCP) formation, and subsequent acetylene cyclotrimerization. Liberation of toluene (GLC) was observed. $PhCH_2CH_2Ph$ was not observed (^{1}H NMR, GLC); however, the presence (^{1}H NMR, ^{13}C NMR, UV, GLC) of either RC≡CC≡CR[45,46] or RC≡CCH=CHR[47] as the probable organic species from reduction of $(O{-}O)Zr(C{\equiv}CR)_2$ to (O−O)Zr(II) could not be unequivocably determined.

The ligand-dependent product distribution in the catalytic cyclotrimerization of $Me_3SiC{\equiv}CH$ with **5** and **8** may be rationalized on steric grounds. A ligand-dependent mixture of 1,2,4- and 1,3,5-trisubstituted benzenes (ratios **5**, 1:1; **8**, 4:1) was observed. Assuming nonregioselective acetylene insertion into a ZrCP, the symmetrical 1,3,5-trisubstituted benzene is disfavored for the bulkier binaphthol complex **5**, as this would originate from a α,β'-ZrCP with a $SiMe_3$ group in a (presumably)[44] sterically unfavorable α-position.[44b]

It was not possible to distinguish between two possible pathways: one in which an equilibrium exists between the intermediate disubstituted zirconacyclopentadienes (α,α', α,β', or β,β') or a mechanism in which they are formed independently by kinetic control and in which they subsequently do not interconvert.

Catalytic acetylene trimerization by related species has been observed.[12h] Reduction of $Ti(O\text{-}2,6\text{-}C_6H_3Ph_2)_2Cl_2$ in the presence of 3-hexyne afforded the metallacyclopentadiene $Ti(O\text{-}2,6\text{-}C_6H_3Ph_2)_2(C_4Et_4)$. This slowly catalytically cyclotrimerized

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(41) Cooper, W. Polydienes by Coordination Catalysis in *The Stereo Rubbers*; Saltman, W. M., Ed.; Wiley: New York, 1977; pp 21−75.

(42) Compound **10**, with $EtAlCl_2$ as a cocatalyst, has been reported to polymerize butadiene to 98% 1,4-*cis*-polybutadiene. In our hands, use of $EtAlCl_2$ as a cocatalyst was unsuccessful. Variation of catalyst and cocatalyst concentrations as well as butadiene pressure did not result in any (polymerization) activity. Sumitomo Chemical Company Ltd. EP 433943 A2 filing date December 17, 1990.

(43) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539. McAlister, D. R.; Bercaw, J. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 1666.

(44) Smith, D. P.; Strickler, J. R.; Gray, S. D.; Bruck, M. A.; Holmes, R. S.; Wigley, D. E. *Organometallics* **1992**, *11*, 1275. Strickler, J. R.; Bruck, M. A.; Wigley, D. E. *J. Am. Chem. Soc.* **1990**, *112*, 2814. Heeres, H. J.; Heeres, A.; Teuben, J. H. *Organometallics* **1990**, *9*, 1508. Reduction of $Ta(OC_6H_3\text{-}2,6\text{-}^iPr_2)_2Cl_3{\cdot}OEt_2$ in the presence of $HC{\equiv}C^tBu$ gave the α,α'-disubstituted tantalacyclopentadiene as the kinetically favored product, which rearranged to the α,β' isomer as the thermodynamically favored product. (b) Assuming nonregioselective acetylene insertion into β,β'-ZrCP, this would yield a mixture of 1,2,4- and 1,2,3-trisubstituted benzenes. Presumably, the latter is not observed due to unfavorable sterics. Similarly, an α,β'-ZrCP would give 1,3,5- and 1,2,4-trisubstituted benzenes and α,α'-ZrCP 1,2,4-trisubstituted benzenes.

(45) Carbon−carbon bond formation between acetylides in $(C_5H_5)_2M(C{\equiv}CPh)_2$ (M = Ti, V)[45] has been reported to give a bimetallic M_2 species with a bridging diacetylide ligand.[46] Teuben, J. H.; De Liefde Meijer, H. J. *J. Organomet. Chem.* **1969**, *17*, 87. Related Group IV bis(acetylide) compounds include $(C_5H_5)_2Zr(C{\equiv}CMe)_2$: Erker, G.; Frömberg, W.; Benn, R.; Mynott, R.; Augermund, K.; Krüger, C. *Organometallics* **1989**, *8*, 911. $(C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2$: Lang, H.; Herres, M.; Zsolnai, L.; Imhof, W. *J. Organomet. Chem.* **1991**, *409*, C7.

(46) Stucky, G. D.; Sekutowsky, D. G. *J. Am. Chem. Soc.* **1976**, *98*, 1376. Teuben, J. H. Personal communication.

(47) For ^{1}H, ^{13}C NMR of enynes, see: Heeres, H. J.; Teuben, J. H. *Organometallics* **1991**, *10*, 1980. Horton, A. D. *J. Chem. Soc., Chem. Commun.* **1992**, 185. For UV−vis spectra of $Ph(C{\equiv}C)_nPh$, see: Armitrage, J. B.; Entwistle, N.; Jones, E. R. H.; Whiting, M. C. *J. Chem. Soc.* **1954**, 147.

(albeit at 110 °C) 3-hexyne to C_6Et_6. In comparison with the relatively rapid cyclotrimerization observed here, slow (1 turnover/day at 25 °C) catalytic cyclotrimerization of HC≡CH and HC≡CMe has been observed with the Zr(II) species $(C_5H_5)Zr(dmpe)_2X$ (X = Cl, Me).[48] Formation of the crystallographically characterized intermediate 2,4-zirconacyclopentadienes was selectively head-to-tail. However, a loss of selectivity was observed in the arene-forming step, giving a ca. 1:1 mixture of 1,2,4- and 1,3,5-mesitylenes similar to that observed here. This was attributed to a lack of steric hindrance.[48]

Cationic Complexes. Homogeneous transition metal catalysts for the polymerization of α-olefins are most commonly based on zirconocene/MAO systems.[1] The large excess of MAO necessary has inhibited close investigation of the active species involved in the catalytic cycle. In order to gain insight into the role of the metal center and the influence of ligand variations, much research has been undertaken on cationic systems, using "non-coordinating" anions such as substituted tetraphenylborates.[1-3]

Although frequently proposed, the cationic $[L_nM]B(Ar)_4$ (Ar = Ph, C_6F_5) species isolated and characterized have been almost exclusively limited to the metallocenes $[(C_5R_5)_2ZrR']B(Ar)_4$ (R = H, Me; R' = Me, CH_2Ph).[1-3] Exceptions are crystallographically characterized $Zr(CH_2Ph)_3\{(\eta^6\text{-}PhCH_2)B(C_6F_5)_3\}$,[49a] $(C_5Me_5)LaCH(SiMe_3)_2\{(\eta^n\text{-}C_6H_5)_2BPh_2\}$,[50] and $(C_5H_5)Zr(CH_2Ph)_2\{(\eta^6\text{-}CH_2C_6H_5)BPh_3\}$,[49b] in which the electron-deficient zirconium is stabilized by η^6-phenyl coordination from the benzyl group transferred from Zr to B.

To explore the possibility of cationic single-component catalysis, **8** was allowed to react with either $B(C_6F_5)_3$[51] or $[PhNMe_2H]B(Ar)_4$. Compound **8** was chosen, as the benzyl group in putative cationic $[(O{-}O)ZrCH_2Ph]^+$ could assist in stabilizing Zr by η^2-coordination.[27,52] Reaction of **8** with 1 equiv of $[PhNMe_2H]BPh_4$[53] in bromobenzene or C_6D_6 resulted in the formation of toluene (1 equiv) and free $PhNMe_2$ (1 equiv) and the appearance of a new AB quartet at 1.45 and 1.8 ppm (cf. those in neutral **8** at 1.25 and 0.96 ppm). The η^2-coordination of the benzyl phenyl group is indicated by H_O resonating at 5.9 ppm.

$$\mathbf{8} + [PhNMe_2H]BPh_4 \rightarrow \underset{\mathbf{21}}{[(C_{10}H_5SiPh_3O)_2Zr(CH_2Ph)]BPh_4} + PhNMe_2 + \text{toluene}$$

Given the asymmetry induced by the binaphtholate ligand environment in **21**, inequivalent naphthyl resonances are expected, as exemplified by the two naphthyl H4 singlets at 8.4 and 8.1 ppm. Although a clean reaction is observed in solution, it was not possible to isolate **21**. Its reactivity was, therefore, studied in situ. These reactions are summarized in Figure 10. Addition of THF (1 equiv) to **21** resulted in its strong coordination (2.95 and 0.75 ppm). These relatively high field ^1H NMR chemical shifts of coordinated THF are also due to ring current effects of the $SiPh_3$ groups. The benzyl CH_2 protons were shifted to 1.72, 1.48 ppm ($^3J_{HH}$ = 11.5 Hz) in **21**·THF. Due to the lack of stability in solution, characterization of **21** and **22** was only on the basis of their characteristic ^1H NMR resonances.

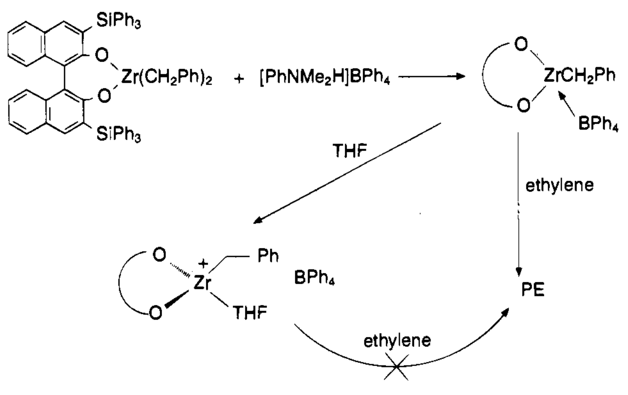

Figure 10.

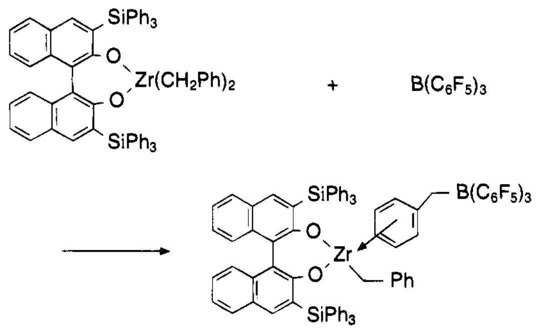

Figure 11.

Addition (see the Experimental Section) of solid $B(C_6F_5)_3$ to a suspension of **8** in toluene resulted in an instantaneous change from a yellow suspension to an orange solution. The solution is stable for hours at 20 °C (^1H NMR). An AB pattern for $Zr{-}CH_2Ph$ is observed at 0.5 and 1.8 ppm, as well as isotropically shifted (ring current effects of the $SiPh_3$ groups) peak pattern [6.65 (d, 1H), 5.96 (t, 1H), 5.87 (d, 1H), 5.50 (t, 1H), 4.88 (t, 1H)]. Although NMR spectroscopy is insufficient to unequivocably establish the coordination mode, these resonances are characteristic[49] of a η^6-$PhCH_2$ group of a $\{(\eta^6\text{-}PhCH_2)B(C_6F_5)_3\}$ moiety. The binaphthol H4 resonances at 8.63 and 8.45 ppm are also consistent with the binaphthol ligand-induced asymmetry in $(C_{10}H_5SiPh_3O)_2Zr(CH_2Ph)\{(\eta^6\text{-}PhCH_2)B(C_6F_5)_3\}$ (**22**) (cf. these ^1H NMR resonances for **8**) (Figure 11). The $Zr{-}CH_2Ph$ H_{ortho} resonance at 6.00 ppm is possibly indicative of a weak interaction between the phenyl π-system and Zr,[12j,27] as given by the upfield chemical shift. In related $Zr(CH_2Ph)_3\{(\eta^6\text{-}PhCH_2)B(C_6F_5)_3\}$,[49a] a doublet−triplet−triplet pattern of resonances at 6.39, 5.66, and 5.40 ppm was observed for the ortho, meta, and para hydrogens, respectively, of the boron-bound benzyl group. Similar NMR patterns were observed in $Zr(CH_2Ph)_3\{(\eta^6\text{-}Ph)BPh_3\}$[54] and $[Cp'_2ZrMe]BPh_4$,[55] in which η^n-coordination of a boron phenyl group was proposed.

Conclusions

A new class of titanium and zirconium compounds has been developed which, with MAO cocatalyst, are active for the oligomerization or polymerization of α-olefins, the polymerization of butadiene, and the catalytic cyclotrimerization of

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(53) Initial attempts with $[PhNMe_2H]B(p\text{-}C_6H_4F)_4$ were unsuccessful. No clean reaction was observed; ^{19}F NMR spectroscopy showed decomposition to $B(C_6H_4F)_3$ and C_6H_5F. Lower reaction temperatures and use of other solvents such as benzene or 1,1,2,2-tetrachloroethane, instead of bromobenzene, also led to decomposition.

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certain terminal acetylenes. This class of L_2MCl_2 systems can be regarded as being analogous to the well-documented range of Group IV metallocenes. These catalysts contain bulky chelating biphenolate or binaphtholate ligands, thereby allowing control of steric hindrance by relatively simple synthetic modifications. For the polymerization of ethene, rates of up to 100 kg/g of metal·h (4740 kg/mol of catalyst·h) have been achieved, yielding high molecular weight ($M_w > 3 \times 10^5$) PE. The polydispersities are, however, very broad, indicating more than one active site. In contrast, polymerization of 1-hexene gives polyhexene with a narrow molecular weight distribution.

We have demonstrated that the sterically more demanding binaphthol ligands induced selective 1,4-insertion in the polymerization of butadiene. Steric modifications of the ligand also have a clear influence not only on the degree of polymerization (from oligomers to high molecular weight polyhexene) but also on the tacticity of poly(1-hexene). In particular, the isospecific polymerization of 1-hexene by **1**/MAO and **2**/MAO affords a very rare example[4g,4h,5] of stereocontrol in α-olefin polymerization with ligands other than those based on bis(cyclopentadienyl).

Experimental Section

All experiments were performed in an argon atmosphere using Schlenk-type glassware or in a Braun single station drybox equipped with a −40 °C refrigeration unit under a nitrogen atmosphere. Elemental analyses were performed at Analytische Laboratorien, Engelskirchen, West Germany. Nuclear magnetic resonance spectra were recorded on Varian XL-200, Varian VXR-300, or Bruker-500 MHz spectrometers. Chemical shifts are reported in parts per million and referenced to the residual protons in deuterated solvents. Coupling constants are reported in hertz. Solvents were p.a. grade and were dried over sodium wire and then distilled from the appropriate drying reagent (sodium benzophenone ketyl for ether and THF, sodium for hexane and toluene) under argon prior to use. Deuterated solvents were dried over 4 Å molecular sieves. 3,3′-Dibromo-1,1′-bi-2,2′-naphthol was prepared on a 20 g scale as described.[18] Binaphthol[18-20] and biphenol[17] ligands were prepared by modifications of literature procedures. Their synthesis and that of binaphthiol ($C_{20}H_{12}(SH)_2$) can be found in the supplementary material. 2,2′-S(4-Me,6-^{t}Bu$C_6H_2OH)_2$ (Irganox 1081) and 2,2′-CH_2(4-Me,6-^{t}Bu$C_6H_2OH)_2$ (Ionox 2246) are commercial antioxidants and were purchased from Ciba-Geigy and Shell, respectively. Acetylenes MeC≡CMe, HC≡CR (R = $SiMe_3$, Ph, ^{i}Pr, ^{t}Bu), and PhC≡CC≡CPh were obtained from Aldrich. $Zr(CH_2Ph)_2Cl_2(OEt_2)_2$ and $M(CH_2Ph)_4$ (M = Ti, Zr) were prepared according to literature methods.[16] Polymer melting points were determined by differential scanning calorimetry (DSC). High-temperature gel permeation chromatography (GPC) analyses were carried out at the Laboratoire des Hautes Polymeres, Catholic University of Louvain, Louvain-la-Neuve, Belgium, or performed on a Waters 150C equipped with a differential refractive index detector at KSLA for polymers soluble in THF or cyclohexane. The eluting solvent was cyclohexane, and the measurements were performed at room temperature. Methylaluminoxane was obtained from Witco Chemical Co. as a 10% solution in toluene.

Ethene Polymerization was performed in a 1 L jacket-cooled steel autoclave. After the autoclave was heated to 70 °C under vacuum for several hours and then allowed to cool under nitrogen to 25 °C, 500 equiv of MAO in 200 mL of toluene was injected. Three bar of ethene and then 0.02−0.05 mmol of Ti or Zr species were added. After a given time (see Table 5), ethene was vented and the polymerization quenched by emptying the solution through a tap in the bottom of the autoclave into MeOH/1 M HCl. After filtration, the PE was washed twice with 1 M HCl and then with acetone, MeOH, and hexane and subsequently dried (70 °C, vacuum oven, 16 h or to constant weight) and weighed.

1-Hexene Polymerization. Catalyst (20 μmol) was suspended in 5 mL of 1-hexene at 20 °C in the drybox. MAO (100 equiv) was added as a solution in 3 mL of toluene. The homogeneous solution formed was stirred for 16 h at 20 °C. Identification of polyhexene was by ^{1}H and ^{13}C NMR spectroscopy and GPC analysis. The end groups were identified by APT experiments and fully coupled ^{13}C NMR. DSC analysis (−40 to 100 °C) showed no T_g or T_m.

Identification[36,37] of Oligo/Polyhexene. Identification of the polymer was performed by ^{1}H and ^{13}C NMR and GPC. The molar mass of the polymers was determined by GPC. For NMR analysis, the oligomer or polymer was dissolved in $CDCl_3$. In the oligomerization of hexene, end groups were identified by APT and fully coupled ^{13}C NMR. The olefinic protons resonate at 5.0−5.5 ppm, and in the ^{13}C NMR olefinic resonances were observed only between 120 and 140 ppm; both these ^{1}H and ^{13}C NMR chemical shifts are typical of internal (R′CH=CHR) olefins. In comparison, olefinic resonances due to H_2C=CMeR″ end groups are at ^{1}H NMR 4.7 ppm (d); ^{13}C NMR 109 and 143 ppm);[36] the olefinic carbons of 2-butyl-1-octene (from 1,2-insertion/β-H elimination) resonate at 108.4 and 150.4 ppm.[37a]

1,3-Butadiene Polymerization. A 25 mL autoclave was charged with 20 μmol of catalyst, a 100-fold excess of methylaluminoxane (MAO), and 15 mL of toluene and pressurized with 1.5 bar of 1,3-butadiene. After 3 h, the autoclave was opened and the excess MAO was destroyed with methanol and then with 1 M HCl. Decanting the organic layer and evaporating the solvents yielded polybutadiene as a rubber-like material.

Identification[56] of Polybutadiene. The microstructure of polybutadiene was identified by ^{1}H and ^{13}C NMR. High-temperature GPC analysis was not possible due to its apparent insolubility in *o*-dichlorobenzene at 160 °C, indicative of oxidation and cross-linking in the dissolution process.[57] The ratio between 1,2-methylene and 1,4-*cis*/*trans* units was determined by ^{1}H NMR. To dissolve the polymer for NMR analysis, it was refluxed in $C_2D_2Cl_4$ for 1 h under an argon atmosphere. The insertion modes (1,2-, 1,4-*trans* and 1,4-*cis*) can be distinguished by the chemical shifts of the olefinic 1,2-vinyl protons and aliphatic methylene unit resonances. These appear respectively at 4.8 and 1.3 ppm (1,2 insertion), at 1.98 and 5.4 ppm (1,4-*trans*), and at 5.32 and 2.03 ppm (1,4-*cis*). The ratio between the three insertion modes can therefore be calculated from the integral of the individual peaks.

Cyclotrimerization. Excess Me_3SiC≡CH was added at 20 °C to a solution of **5** or **8** in C_6D_6. The solution changed color from light yellow to red and became warm. The ratio between 1,3,5- and 1,2,4-trisubstituted benzenes was determined by ^{1}H NMR spectroscopy, as well as GC and GC/MS. 1,3,5-Tris(trimethylsilyl)benzene. ^{1}H NMR (C_6D_6): 7.92, 0.32 ppm. ^{13}C NMR (C_6D_6): 140.16, 139.6, 0.18 ppm. 1,2,4-Tris(trimethylsilyl)benzene. ^{1}H NMR (C_6D_6): 8.04 (br s, 1H), 7.7 (d, 1H, AB), 7.5 (dd, 1H, AB), 0.41, 0.40, 0.31 ppm. ^{13}C NMR (C_6D_6): 147.5, 145.8, 141.3, 140.3, 135.9, 134.3, 3.26, 3.15, 0.00 ppm.

$Ti(CH_2Ph)_4$. A sample 2.74 g (14.42 mmol) of $TiCl_4$ was slowly added with vigorous stirring to 60 mL of ether cooled to −40 °C. This rapidly gave a bright yellow precipitate of $TiCl_4{\cdot}(OEt_2)_n$. This was once again cooled to −40 °C, and 8.1 g (2 equiv) of $Mg(CH_2Ph)_2{\cdot}$dioxane was added slowly as a solid. A rapid reaction ensued, and the yellow suspension instantly turned dark purple. This was allowed to warm to 20 °C and was stirred for 2 h. The solvent was removed in vacuo, and the solid was extracted with 4 × 50 mL of hexane. The combined hexane extracts were evaporated to dryness in vacuo to give 2.7 g of $Ti(CH_2Ph)_4$. ^{1}H NMR (C_6D_6, 25 °C): 7.1−6.8 (m, Ph), 6.62 (d, 8H, H_o), 2.83 (s, 8H, CH_2) ppm.

$\{1,1'\text{-}(2,2',3,3'\text{-}OC_{10}H_5SiMe_3)\}_2ZrCl_2$ (1). A sample of 0.494 g (1.00 mmol) of $Zr(CH_2Ph)_2Cl_2(OEt_2)_2$ was dissolved in 5 mL of toluene at 25 °C. To this solution was added 0.43 g (1.00 mmol) of 3,3′-bis(trimethylsilyl)-1,1′-bi-2,2′-naphthol dissolved in 5 mL of toluene. The solution was stirred for 16 h at 20 °C, the toluene was removed in vacuo from the clear yellow solution to give a yellow powder. Recrystallization from toluene/hexane layer diffusion at −40 °C afforded a yellow powder. This was washed with hexane and dried. Yield: 0.383 g, 73%. ^{1}H NMR (C_6D_6, 25 °C): 8.10 (s, 2H), 7.8−7.7 (d, 2H), 7.2−6.95 (m, 4H), 6.86−6.75 (m, 2H), 0.70 ppm (s, 18H, $SiMe_3$). ^{13}C NMR (C_6D_6): 158.1, 135.7, 129.6, 128.4, 128.3, 128.2,

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(57) Polymer dissolution at the Catholic University of Louvain was performed under air.

125.7, 124.7, 123.6, 111.4, −0.58 ppm (Si*Me*$_3$). Anal. Calcd for $C_{26}H_{28}O_2Si_2Cl_2Zr$: C, 52.86; H, 4.78; Si, 9.51; Cl, 12.00; Zr, 15.44. Found: C, 53.12; H, 5.04; Si, 9.20; Cl, 11.86; Zr, 15.30.

{1,1′-(2,2′,3,3′-OC$_{10}$H$_5$SiMePh$_2$)}$_2$ZrCl$_2$ (2). A sample of 0.48 g (0.975 mmol) of $Zr(CH_2Ph)_2Cl_2(OEt_2)_2$ was dissolved in 5 mL of toluene at 20 °C. To this was added 0.62 g (0.91 mmol) of 3,3′-bis(diphenylmethylsilyl)-1,1′-bi-2,2′-naphthol dissolved in 5 mL of toluene. After the solution was stirred for 2 h at 20 °C, a copious light yellow precipitate formed. The suspension was stirred for 16 h, and the yellow precipitate was separated by centrifugation. The yellow powder was washed with 5 mL of toluene followed by 5 mL of hexane. Drying under vacuum afforded 0.61 g (68% yield) of **2**. ^{1}H NMR (CD_2Cl_2, 25 °C): 7.75 (br, 6H), 7.62 (d, 2H), 7.52 (d, 2H), 7.43 (m, 6H), 7.27 (m, 6H), 7.17 (t, 2H), 7.06 (t, 2H), 6.73 (d, 2H), 1.17 ppm (s, 6H, *Me*). In C_6D_6/few drops THF-d_8: δ 1.40 ppm (s, 6H, Si*Me*). Anal. Calcd for **2**·OEt$_2$ ($C_{50}H_{46}O_3Si_2Cl_2Zr$): C, 65.76; H, 5.08; Si, 6.15; Cl, 7.76; Zr, 9.99. Found: C, 65.58; H, 5.14; Si, 6.19; Cl, 8.00; Zr, 10.10.

{1,1′-(2,2′,3,3′-OC$_{10}$H$_5$SiPh$_3$)}$_2$ZrCl$_2$ (3). A sample of 0.49 g (1.0 mmol) of $Zr(CH_2Ph)_2Cl_2(OEt_2)_2$ was dissolved in 10 mL of toluene at 20 °C. To this solution was added 0.80 g (1.0 mmol) of 3,3′-bis(triphenylsilyl)-1,1′-bi-2,2′-naphthol dissolved in 15 mL of toluene. The yellow suspension was stirred for 16 h, and the yellow precipitate was separated by centrifugation. The yellow powder was washed with 5 mL of toluene and then with 5 mL of hexane. Drying under vacuum gave **3** as a yellow powder (0.85 g, 82% yield). ^{1}H NMR (C_6D_6/THF-d_8, 25 °C): 8.07 (s, 2H), 8.0 (m, 12H), 7.35 (d, 2H), 7.25−7.15 (m, 18H), 7.35 (d, 2H), 6.86 (t, 2H, 7.7 Hz), 6.75 ppm (t, 2H, 7.7 Hz). ^{13}C NMR (CD_2Cl_2): 160.2, 142.1, 137.1, 137.0, 135.5, 129.9, 129.8, 128.6, 127.4, 126.8, 124.5, 124.0, 117.9 ppm. Anal. Calcd for **3**·OEt$_2$ ($C_{60}H_{50}O_3Si_2Cl_2Zr$): C, 69.47; H, 4.86; Si, 5.41; Cl, 6.48; Zr, 8.79. Found: C, 69.22; H, 5.04; Si, 5.30; Cl, 6.69; Zr, 8.61.

{1,1′-(2,2′,3,3′-OC$_{10}$H$_5$SiMe$_3$)}$_2$Ti(CH$_2$Ph)$_2$ (4). To 0.153 g (0.371 mmol) of $Ti(CH_2Ph)_4$ dissolved in 10 mL of toluene and cooled to −40 °C was added 0.16 g (0.372 mmol) of $(C_{10}H_5SiMe_3OH)_2$. The solution was allowed to warm to 20 °C and stirred for 15 h. The toluene was removed in vacuum to afford a red oil, which was recrystallized to give a red powder. ^{1}H NMR (C_6D_6, 25 °C): 8.17 (s, 2H), 7.7 (d, 2H), 7.2−6.8 (m), 2.87 (2H, AB, CH$_2$), 2.35 (AB, 2H, CH$_2$), 0.48 ppm (s, 18H, SiMe$_3$). **4** was not characterized further, since it was unstable in solution, presumably due to the relatively small binaphthol ligand.

{1,1′-(2,2′,3,3′-OC$_{10}$H$_5$SiMePh$_2$)}$_2$Zr(CH$_2$Ph)$_2$ (5). A sample of 0.904 g (1.33 mmol) of $\{C_{10}H_5(SiMePh_2)OH\}_2$ was added to 0.67 g of $Zr(CH_2Ph)_4$ in 30 mL of toluene. After the mixture was stirred at 20 °C for 16 h, the toluene was removed in vacuum to give a brown oil. This was washed with 2 × 10 mL of hexane and a small amount of ether to give a yellow powder (0.310 mg, 25% yield). Clean formation of **5** was observed by NMR. Attempts at crystallization from toluene/hexane or ether were unsuccessful. **5** decomposed after 24 h in solution. Selected ^{1}H NMR (CD_2Cl_2): 0.91 and 1.30 (AB, 9 Hz, 2H, ZrCH$_2$), 0.88 ppm (s, 6H, Si*Me*Ph$_2$). ^{13}C NMR (CD_2Cl_2): 66.9 ppm (t, 136 Hz, Zr*C*H$_2$).

{1,1′-(2,2′,3,3′-OC$_{10}$H$_5$SiPh$_3$)}$_2$ZrMe$_2$(ether)$_2$ (6). A sample of 0.896 g (0.83 mmol) of **3**·toluene was suspended in 60 mL of ether in a small Schlenk tube. This was cooled to −40 °C, and 2 equiv of MeLi (1.04 mL of 1.6 M solution) in ether was added dropwise. After 10 min, the orange suspension became a clear yellow solution and then began to turn cloudy. The solution was filtered, concentrated under vacuum, and crystallized at −40 °C to give **6** (yield 0.45 g, 49%) as a white crystalline solid. ^{1}H NMR (C_6D_6, 25 °C): 8.28 (s, 2H), 7.92 (m), 7.53 (m), 7.16 (m), 6.97 (m), 3.14 (q, 8H, ether), 0.78 (t, 12H, ether), −0.136 ppm (s, 6H, Me). ^{13}C NMR (C_6D_6): 159.86, 142.0 (d, 149 Hz), 138.2, 136.2, 129.3, 127.1, 125.8, 123.3, 118.2 (naphthyl and phenyl resonances), 66.1 (t, 141 Hz, ether), 46.04 (q, 118 Hz, *Me*), 14.22 ppm (q, 129 Hz, ether). Anal. Calcd for $C_{58}H_{66}O_4Si_2Zr$: C, 74.04; H, 6.21; Zr, 8.52. Found: C, 74.75; H, 5.32; Zr, 8.60; Li, 0.0; Cl, <0.2.

{1,1′-(2,2′,3,3′-OC$_{10}$H$_5$SiPh$_3$)}$_2$Ti(CH$_2$Ph)$_2$ (7). To 0.197 g (0.478 mmol) of $Ti(CH_2Ph)_4$ dissolved in 10 mL of toluene and 10 mL of hexane was added 0.411 g (0.51 mmol) of 3,3′-bis(triphenylsilyl)-1,1′-bi-2,2′-naphthol in 5 mL of toluene at 20 °C. After 4 h, the toluene was removed in vacuo and washed with 5 mL of hexane. This was crystallized from toluene/hexane at −40 °C to give **7** (yield 0.39 g, 79%). ^{1}H NMR (C_6D_6, 25 °C): 8.33 (s, 2H), 8.0−7.92 (m, 12H), 7.2−6.8 (m + C_6D_5H), 6.75 (m, 4H), 6.45 (m, 4H, benzyl H$_0$), 1.4 (AB, J_{AB} = 11 Hz, 2H, C*H*$_2$), 1.05 ppm (AB, J_{AB} = 11 Hz, 2H, C*H*$_2$). Anal. Calcd for $C_{70}H_{54}O_2Si_2Ti$: C, 81.53; H, 5.28; Ti, 4.64. Found: C, 81.24; H, 5.41; Ti, 4.75.

{1,1′-(2,2′,3,3′-OC$_{10}$H$_5$SiPh$_3$)}$_2$Zr(CH$_2$Ph)$_2$ (8). To 0.795 g (1.74 mmol) of $Zr(CH_2Ph)_4$ dissolved in 30 mL of toluene was added 1.40 g (1.74 mmol) of 3,3′-bis(triphenylsilyl)-1,1′-bi-2,2′-naphthol. After the solution was stirred for 16 h at 20 °C, the toluene was removed in vacuo. The resulting yellow oil was washed with hexane to give a yellow powder (yield 1.70 g, 91%). ^{1}H NMR (CD_2Cl_2, 25 °C): 8.15 (s, 2H), 7.75 (d, 2H), 7.65 (m, 10H), 7.35 (m, 24H), 6.78 (d, 2H), 6.55 (m, 6H), 5.70 (d, 4H, benzyl H$_0$), 0.88 (AB, 2H, 9.8 Hz), 0.64 ppm (AB, 2H, 9.8 Hz). ^{1}H NMR (C_6D_6, 25 °C): δ 8.41 (s, 2H), 7.85 (m, 10H), 7.2 (m, 24H), 7.0 (d, 2H), 6.60 (m, 6H), 5.95 (d, 4H, benzyl H$_0$), 1.25 (AB, 2H, 9.8 Hz), 0.96 ppm (AB, 2H, 9.8 Hz). ^{13}C NMR (CD_2Cl_2, 25 °C): 157.7, 143.9, 138.9, 137.5, 137.1, 134.9, 130.9, 130.0, 129.9, 128.3, 128.1, 127.5, 127.1, 125.9, 124.6, 124.3, 116.1, 68.1 ppm (t, *C*H$_2$, J_{CH} = 133 Hz). Anal. Calcd for $C_{70}H_{54}O_2Si_2Zr$: C, 78.24; H, 5.07; Zr, 8.49; Si, 5.23. Found: C, 72.2; H, 4.91; Zr, 9.63; Si, 5.88. We have no explanation for the low C analysis.

{1,1′-(2,2′,3,3′-OC$_{10}$H$_5$SiPh$_3$)}$_2$Zr(CH$_2$SiMe$_3$)$_2$ (9). A sample of 190 mg (0.186 mmol) of **3** was added to 35.1 mg (0.373 mmol) of Me_3SiCH_2Li dissolved in a 2:1 hexane:ether mixture to give a yellow suspension. After being stirred at 20 °C for 16 h, the solution became off-white, and a white precipitate formed. Filtration and removing the solvent in vacuum gave an off-white powder. Crystallization from ether/hexane gave **9** (yield, 50 mg, 25%) as a white powder. ^{1}H NMR (C_6D_6, 25 °C): 8.35 (s, 2H), 8.0−7.92 (m, 12H), 7.2−6.8 (m + C_6D_5H), 7.15 (d, 2H), 0.5 (AB, 2H, C*H*$_2$), −0.50 (AB, 2H, C*H*$_2$), −0.4 ppm (s, 18H, Si*Me*$_3$). ^{13}C NMR (CD_2Cl_2): 156.0, 142.9, 137.3, 137.0, 130.1, 130.0, 128.8, 128.7, 128.4, 128.0, 127.0, 126.1, 124.4, 117.2 (naphthyl and phenyl resonances), 67.6 (*C*H$_2$), 1.3 ppm (Si*Me*$_3$). Anal. Calcd for $C_{64}H_{62}O_2Si_4Zr$: C, 72.06; H, 5.86. Found: C, 64.56; H, 5.57. Compound **9** appeared to decompose during the analysis.

2,2′-S(4-Me,6-^{t}BuC$_6$H$_2$O)$_2$TiCl$_2$ (10). A sample of 0.665 g (1.86 mmol) of 2,2′-S(4-Me,6-^{t}BuC$_6$H$_2$OH)$_2$ was dissolved in 30 mL of ether and cooled to −30 °C. Then 0.353 g (1.86 mmol) of $TiCl_4$ was also cooled to −30 °C and slowly added to the ether solution of the ligand. This resulted in an immediate dark red solution. The dark red solution was allowed to warm to 20 °C and stirred for 2 h, during which time a dark red powder precipitated. The reaction flask was cooled to −40 °C, leading to further crystallization of dark red/purple microcrystalline solid (yield 0.66 g, 67%). ^{1}H NMR (C_6D_6/THF, 25 °C): 7.15 (d, 2 Hz, 2H), 6.95 (d, 2 Hz, 2H), 1.96 (s, 6H, Me), 1.47 ppm (s, 18H, ^{t}Bu). ^{13}C NMR (C_6D_6/THF): 165.7, 137.3, 132.2, 130.6, 130.2, 65.9 (ether), 35.5 (*C*Me$_3$), 29.8, 20.9, 15.6 ppm (ether). Anal. Calcd for $C_{22}H_{28}O_2Cl_2STi\cdot{}^1/_2OEt_2$: C, 56.26; H, 6.49; Cl, 13.84; S, 6.26; Ti, 9.34. Found: C, 56.61; H, 7.01; Cl, 13.81; S, 6.34; Ti, 9.28. Compound **10** is only sparingly soluble in benzene and therefore has a probable polymeric structure. Adding a drop of THF to a suspension in benzene resulted in immediate dissolution.

2,2′-S(4-Me,6-^{t}BuC$_6$H$_2$O)$_2$ZrCl$_2$ (11). A sample of 0.212 g (0.615 mmol) of 2,2′-S(4-Me,6-^{t}BuC$_6$H$_2$OH)$_2$ was added as a solid to 0.257 g (0.615 mmol) of $Zr(CH_2Ph)_2Cl_2$(ether) dissolved in 5 mL of toluene and cooled to −40 °C. After the mixture was stirred for 1 h at 20 °C, the toluene was removed in vacuo and the white powder was washed twice with hexane (yield 0.221 g, 60%). ^{1}H NMR (CD_2Cl_2, 25 °C): 7.19 (d, 2 Hz, 2H), 7.04 (d, 2 Hz, 2H), 2.22 (s, 6H, Me), 1.32 ppm (s, 18H, ^{t}Bu). ^{13}C NMR (C_6D_6): 162.8, 138.5, 131.8, 130.2, 130.1, 128.5, 35.3 (*C*Me$_3$), 29.6 (C*Me*$_3$), 20.6 ppm (*Me*). Anal. Calcd for $C_{22}H_{28}O_2Cl_2SZr$: C, 50.95; H, 5.44; Cl, 13.67; S, 6.18; Zr, 17.59. Found: C, 50.90; H, 5.68; Cl, 13.54; S, 5.96; Zr, 17.3.

2,2′-S(4-Me,6-^{t}BuC$_6$H$_2$O)$_2$Ti(CH$_2$Ph)$_2$ (12). A sample of 0.21 g of 2,2′-S(4-Me,6-^{t}BuC$_6$H$_2$OH)$_2$ dissolved in 2 mL of toluene was added to a cooled (−20 °C) solution of 0.24 g (0.583 mmol) of $Ti(CH_2Ph)_4$ in 3 mL of toluene and 5 mL of hexane. The red-purple solution was stirred for 1 h at 20 °C, and the solvent was removed under vacuum. Extraction with hexane gave a dark red, very hexane-soluble, slightly oily product. Recrystallization from hexane gave **12** as a red-brown powder (yield 0.20 g, 58%). ^{1}H NMR (C_6D_6, 25 °C): 7.45−6.8 (multiplets), 3.32 (s, 2H, CH$_2$) 3.26 (s, 2H CH$_2$), 1.94 (s, 6H, Me), 1.51 ppm (s, 18H, ^{t}Bu). Anal. Calcd for $C_{36}H_{42}O_2STi$: C, 73.70; H, 7.22; Ti, 8.16. Found: C, 73.68; H, 7.33; Ti, 8.09.

{2,2′-S(4-Me,6-^{t}BuC$_6$H$_2$O)$_2$}$_2$Ti (13). A sample of 1.0 g (5.26 mmol) of $TiCl_4$ was carefully and slowly added to 50 mL of ether with vigorous stirring to give $TiCl_4(ether)_n$ (exothermic reaction). This was cooled to −40 °C, whereupon excess (2 mL) Et_3N was added to the stirred solution. Subsequently, 1.88 g (5.26 mmol) of 2,2′-S(4-Me,6-^{t}BuC$_6$H$_2$OH)$_2$ dissolved in 10 mL of ether was added. The yellow suspension instantly became a dark red solution. After being stirred for 15 min at 20 °C, the pale-orange ether solution was centrifuged and decanted from the precipitate. This was also extracted with 2 × 50 mL of ether. Combining the ether extracts and removing the ether in vacuo gave a bright orange powder (yield 1.0 g, 40%) which was crystallized from ether. This is much more soluble than **10**. ^{1}H NMR (C_6D_6, 25 °C): 7.3 (dd, 2H), 7.04 (dd, 2H), 2.00 (s, 6H, Me), 1.61 (s, 9H, ^{t}Bu), 1.41 ppm (s, 9H, ^{t}Bu). In comparison, 2,2′-S(4-Me,6-^{t}BuC$_6$H$_2$OH)$_2$ has ^{1}H NMR (C_6D_6, 25 °C): 7.0 (m, 4H), 6.49 (s, OH), 1.92 (s, 6H, Me), 1.47 ppm (s, 18H, ^{t}Bu). ^{13}C NMR (C_6D_6) of **13**: δ 166.2, 164.3, 137.58, 137.50, 133.2 (CH), 131.7 (CH), 131.4, 130.9, 130.2 (CH), 130.1 (CH), 130.05, 127.5, 35.7 (*C*Me$_3$), 35.4 (*C*Me$_3$), 29.91 (C*Me*$_3$), 29.85 (C*Me*$_3$), 20.8 ppm (Me). Anal. Calcd for $C_{44}H_{56}O_4S_2Ti$: C, 69.45; H, 7.42; Ti, 6.29; Cl, 0.00. Found: C, 68.95; H, 7.50; Ti, 6.30; Cl, 0.66.

2,2′-(4,6-^{t}Bu$_2$C$_6$H$_2$O)$_2$Ti(CH$_2$Ph)$_2$ (14). A sample of 111 mg (0.27 mmol) of $Ti(CH_2Ph)_4$ dissolved in 5 mL of toluene was added to 111 mg (0.27 mmol) of 2,2′-bis(4,6-*tert*-butylphenol) dissolved in 2 mL of toluene. After the solution was stirred at 20 °C for 16 h, the toluene was removed in vacuo to afford an orange-red oil. Due to the high solubility of **14**, crystallization from hexane was unsuccessful. ^{1}H and ^{13}C NMR spectra showed only **14**. It was therefore not purified further. ^{1}H NMR (C_6D_6, 25 °C): 7.6 (d, 2.5 Hz, 2H), 7.4 (d, 2.5 Hz, 2H), 7.5−7.15 (m, 4H), 7.10−7.06 (dd, 4H), 6.99−6.92 (m, 2H), 2.6 (br, 4H, C*H*$_2$) (m), 1.53 (s, 18H, ^{t}Bu), 1.28 ppm (s, 18H, ^{t}Bu). ^{13}C NMR (C_6D_6): 156.2, 144.7, 141.8, 135.4, 129.9, 129.5, 129.4, 128.9, 124.9, 123.9, 88.9 (*C*H$_2$), 36.0 (*C*Me$_3$), 35.0 (*C*Me$_3$), 32.0 (C*Me*$_3$), 30.0 ppm (C*Me*$_3$).

2,2′-(4,6-^{t}Bu$_2$C$_6$H$_2$O)$_2$ZrCl$_2$(THF)$_2$ (15). The dipotassium salt (^{t}Bu$_2$C$_6$H$_2$OK)$_2$ was prepared from reaction of biphenol (^{t}Bu$_2$C$_6$H$_2$OH)$_2$ with excess KH in THF. Filtration and addition of 1 equiv of $ZrCl_4$ gave **15** (yield 1.75 g, 60%). ^{1}H NMR (C_6D_6, 25 °C): 7.59 (d, 2.6 Hz, 2H), 7.33 (d, 2.6 H, 2H), 4.1 (m, THF), 1.78 (s, 18H C*Me*$_3$), 1.34 (s, 18H, C*Me*$_3$), 1.2 ppm (m, THF). Anal. Calcd for $C_{36}H_{56}Cl_4O_2Zr$: C, 60.48; H, 7.89; Cl, 9.92; Zr, 12.76. Found: C, 60.21; H, 7.75; Cl, 10.07; Zr, 12.50.

{2,2′-(4-OMe,6-^{t}BuC$_6$H$_2$O)$_2$}$_2$Ti (16). A sample of 1.0 g (5.26 mmol) of $TiCl_4$ was slowly and carefully added to 50 mL of ether at 20 °C to give a yellow suspension of $TiCl_4(ether)_n$. Then 2 mL of Et_3N was added, resulting in a purple suspension. Immediately afterward, 1.86 g (5.26 mmol) of 2,2′-(4-OMe,6-^{t}BuC$_6$H$_2$OH)$_2$ was added in ether. The now orange suspension was stirred for 16 h at 20 °C. After filtration and removing the ether in vacuum, crystallization from ether at −40 °C afforded orange crystalline **16** (yield 0.9 g, 36%). ^{1}H NMR (C_6D_6, 25 °C): 7.21 ppm (d, 3.1 Hz, 2H), 6.75 (d, 3.1 Hz, 2H), 3.34 (s, 6H, O*Me*), 1.41 ppm (s, 18H, ^{t}Bu). ^{13}C NMR (C_6D_6): 156.1, 150.8, 140.4, 130.8, 115.5, 114.4, 55.2 (O*Me*), 35.7 (*C*Me$_3$), 30.5 ppm (C*Me*$_3$). Anal. Calcd for $C_{44}H_{56}O_8Ti$: C, 69.46; H, 7.42; Ti, 6.30. Found: C, 69.25; H, 7.71; Ti, 6.15.

2,2′-(4-OMe,6-^{t}BuC$_6$H$_2$O)$_2$Ti(CH$_2$Ph)$_2$ (17). A sample of 114 mg (0.275 mmol) of $Ti(CH_2Ph)_4$ in 5 mL of toluene was added to a suspension of 99 mg (0.275 mmol) of 2,2′-bis(3-*tert*-butyl-5-methoxyphenol) in 5 mL of toluene. After the solution was stirred for 16 h at 20 °C, the toluene was removed in vacuo. This afforded a purple-colored oil which could be crystallized from hexane or ether at −40 °C to give red block-like crystals (yield 0.12 g, 74%). ^{1}H NMR (CD_2Cl_2, 25 °C): 7.3−7.2 (m, 4H), 7.12−7.0 (m, 6H), 6.8 (d, 3.1 Hz, 2H), 6.55 (d, 2H, 3.1 Hz), 3.72 (s, 6H, O*Me*), 2.5 (s, 4H, C*H*$_2$), 1.31 ppm (s, 18H, ^{t}Bu). The ^{13}C NMR shifts attributable to the benzyl group can be assigned by comparison with the resonances of analog **16**. ^{13}C NMR (C_6D_6): 160.0, 155.0, 144.0, 137.5 (benzyl C_{ipso}), 130.0 (benzyl $C_{o/m}$), 129.0 (benzyl $C_{m/o}$), 128.8, 125.0 (benzyl C_p), 115.5, 115.0, 87.0 (Zr-*C*H$_2$), 55.0 (O*Me*), 35.5 (*C*Me$_3$), 31.0 ppm (C*Me*$_3$). Anal. Calcd for $C_{36}H_{42}TiO_4$: C, 73.71; H, 7.22; Ti, 8.16. Found: C, 69.43; H, 7.11; Ti, 7.82. Calcd for **17** minus CH$_2$Ph ($C_{29}H_{35}O_4Ti$): C, 70.3; H, 7.07; Ti, 9.70.

2,2′-CH$_2$(4-Et,6-^{t}BuC$_6$H$_2$O)$_2$Ti(CH$_2$Ph)$_2$ (18). A sample of 81 mg (0.20 mmol) of $Ti(CH_2Ph)_4$ in 5 mL of hexane was cooled to −40 °C and then added to a suspension of 72 mg (0.20 mmol) of 2,2′-CH$_2$(4-Et,6-^{t}BuC$_6$H$_2$OH)$_2$ in 5 mL of hexane, also cooled to −40 °C. After addition at −40 °C, the suspension was allowed to warm slowly to 20 °C. After being stirred for 2 h at 20 °C, the resulting red-colored solution was stripped under vacuum to give a red foam. Crystallization of a concentrated hexane solution at −40 °C gave microcrystalline **18** (yield 65 mg, 58%). ^{1}H NMR (C_6D_6, 25 °C): 7.4 (d, 2H), 7.3−7.2 (m, 2H), 7.1−6.75 (m), 3.27 (s, 1H, CH$_2$ bridge), 3.25 (s, 1H, CH$_2$ bridge), 3.17 and 2.81 (s, 2H, Ti-CH$_2$), 2.21 (q, 4H, C*H*$_2$), 1.58 (s, 18H, ^{t}Bu), 1.05 ppm (t, 6H, *Me*). ^{1}H NMR free ligand (C_6D_6, 25 °C): 7.08 (d, 2H), 6.93 (d, 2H), 5.54 (s, 2H, OH), 3.72 (CH$_2$ bridge), 2.45 (q, 4H, C*H*$_2$Me), 1.43 (s, 18H, ^{t}Bu), 1.13 ppm (t, 6H, CH$_2$*Me*). ^{13}C NMR (C_6D_6): 161.0, 146.5, 141.5, 138.3, 136.0, 135.5, 130.0, 129.5, 128.8, 127.4, 125.4, 124.6, 123.4, 84.0 (t, Ti-*C*H$_2$, 136 Hz), 35.0, 30.0, 29.0, 16.0 ppm. Anal. Calcd for $C_{39}H_{48}O_2Ti$: C, 78.50; H, 8.11; Ti, 8.02. Found: C, 78.31; H, 8.07; Ti, 7.88.

2,2′-CH$_2$(4-Et,6-^{t}BuC$_6$H$_2$O)$_2$TiCl$_2$ (19). A sample of 0.76 g (2.1 mmol) of 2,2′-CH$_2$(4-Et,6-^{t}BuC$_6$H$_2$OH)$_2$ in 30 mL of ether was cooled to −30 °C. To this was added 0.4 g (1 equiv) of $TiCl_4$. The solution immediately became dark red. This was stirred for 2 h at 25 °C, and then the ether was removed in vacuum to give an orange crystalline solid. This was recrystallized from ether to give **19** (yield 0.69 g, 68%). ^{1}H NMR (C_6D_6, 25 °C): 7.17 (s, 2H), 4.21 (AB, 14 Hz, bridge CH$_2$, 1H), 3.35 (AB, 14 Hz, bridge CH$_2$, 1H), 2.37 (q, CH$_2$, 4H), 1.43 (s, ^{t}Bu, 18H), 1.09 ppm (t, Me, 6H). ^{13}C NMR (C_6D_6, 25 °C): 165.1, 141.4, 138.5, 136.6, 127.7 (CH), 124.9 (CH), 35.6 (*C*Me$_3$), 35.4 (CH$_2$ bridge), 30.4 (C*Me*$_3$), 29.0 (*C*H$_2$Me), 16.0 ppm (Me). Anal. Calcd for $C_{25}H_{34}O_2TiCl_2$: C, 61.87; H, 7.06; Ti, 9.9; Cl, 14.61. Found: C, 61.71; H, 6.88; Ti, 9.97, Cl, 14.76.

{2,2′-CH$_2$(4-Et,6-^{t}BuC$_6$H$_2$O)$_2$}$_2$Ti (20). A sample of 0.40 g (2.1 mmol) of $TiCl_4$ was carefully added to 40 mL of ether cooled to −40 °C. A solution of 0.766 mg (2.1 mmol) of 2,2′-CH$_2$(4-Et,6-^{t}BuC$_6$H$_2$OH)$_2$ and 1 mL of NEt_3 dissolved in 8 mL of ether was added. After addition at −40 °C, a yellow precipitate formed immediately. The suspension was stirred at 20 °C for 3 h and centrifuged, and the light yellow precipitate (0.74 g) was extracted with 2 × 10 mL of ether. The ether extracts were combined, and the ether was removed in vacuum to give an orange foam. This was recrystallized from hexane at −40 °C to give **20** as a very soluble yellow/orange powder (yield 0.50 g, 50%). ^{1}H NMR (C_6D_6, 25 °C): 7.1 (d, 4H), 7.0 (d, 4H), 4.95 (d, 16 Hz, bridge CH$_2$, 2H), 3.9 (d, 16 Hz, bridge CH$_2$, 2H), 2.55 (q, CH$_2$, 4H), 2.45 (q, CH$_2$, 4H), 1.50 (s, ^{t}Bu, 18H), 1.44 (s, ^{t}Bu, 18H), 1.19 (t, Me, 6H), 1.10 ppm (t, Me, 6H). ^{13}C NMR (C_6D_6): 161.55, 161.06, 138.51, 138.27, 136.73, 136.61, 135.80, 134.49 (all quaternaries), 127.5 (CH), 125.14 (CH), 124.92 (CH), 35.51 (CH$_2$), 35.3 (*C*Me$_3$), 35.09 (CH$_2$), 30.61 (C*Me*$_3$), 30.41 (C*Me*$_3$), 29.0 (CH$_2$), 16.22 (Me), 16.17 ppm (Me). Anal. Calcd for $C_{50}H_{68}O_4Ti$: C, 76.90; H, 8.78; Ti, 6.13. Found: C, 76.35; H, 8.96; Ti, 6.54.

[(C$_{10}$H$_5$SiPh$_3$O)$_2$Zr(CH$_2$Ph)]BPh$_4$ (21). A sample of 107 mg (0.1 mmol) of **8** was dissolved in 10 mL of toluene at 20 °C and 44 mg of $[PhNMe_2H]BPh_4$ (0.1 mmol) was added, affording a clear yellow solution. The solvent was removed in vacuum to give a light yellow powder, which was washed with hexane to afford an off-white powder. Recrystallization by either layer diffusion from toluene/hexane or from an ether/hexane mixture was unsuccessful. Selected ^{1}H NMR (C_6D_6): δ 8.4 (s, 1H, naphthyl H4), 8.1 (s, 1H, naphthyl H4), 7.7−6.8 (Ph), 6.3 (m, 1H benzyl H_p), 5.9 (m, 1H, benzyl H_o), 1.8 (AB, $J_{HH} = 10.4$ Hz, 1H, ZrC*H*$_2$), 1.45 ppm (AB, $J_{HH} = 10.4$ Hz, 1H, ZrC*H*$_2$).

(C$_{10}$H$_5$SiPh$_3$O)$_2$Zr(CH$_2$Ph)(η^6-PhCH$_2$)B(C$_6$F$_5$)$_3$ (22). A sample of 104 mg of **8** was suspended in 4 mL of C_7D_8 at 20 °C to give a light yellow suspension. On addition of 50.4 mg (1 equiv) of $B(C_6F_5)_3$ as a white solid, an instant color change was observed from yellow to orange. ^{1}H NMR (C_7D_8, 25 °C): 8.63 (s, 1H), 8.45 (s, 1H), 6.00 ppm (d, 2H$_o$, Zr-CH$_2$Ph). η^6-PhCH$_2$ resonances at δ 6.65 (d, 1H), 5.96 (t, 1H), 5.87 (d, 1H), 5.50 (t, 1H), 4.88 (t, 1H). 1.8 (AB, 1H, 10 Hz, ZrC*H*$_2$), 3.16 (BC*H*$_2$), 0.50 ppm (AB, 1H, 10 Hz, ZrC*H*$_2$).

X-ray Structure Analysis for 17·$^1/_2$OEt$_2$. A single crystal of **17**·$^1/_2$OEt$_2$ was mounted under nitrogen in a thin-walled glass capillary under nitrogen and held in place using silicone grease. All diffraction experiments were carried out at 213 K on a Siemens R3/V four-circle diffractometer using graphite-monochromated Mo Kα X-ray radiation, $\lambda = 0.71073$ Å. Unit cell dimensions were determined from 22 centered reflections in the range $10.0° < 2\theta < 22.0°$. Details of crystal data collection and reduction are given in Table 3. A total of 6021 diffracted intensities, including check reflections, were measured in the whole of reciprocal space for $4.0° < 2\theta < 40.0°$ by Wyckoff ω scans. Two check reflections (2 −2 −1, 2 0 −4) remeasured after every 98 ordinary data showed a decay of 19% over the period of data collection; an appropriate correction was applied. Of the intensity data collected, 3336 unique observations remained after averaging of duplicate and equivalent reflections; of these, 3179 with $I > -2\sigma(I)$ were retained for use in structure solution and refinement. A semiempirical absorption correction was applied on the basis of 220 azimuthal scan data. Maximum and minimum transmission coefficients were 0.918 and 0.865, respectively. Lorentz and polarization corrections were applied. The titanium and oxygen atoms were assigned anisotropic displacement parameters. All other non-hydrogen atoms were assigned isotropic displacement parameters and all hydrogen atoms were assigned fixed (at 0.08 Å^2) isotropic displacement parameters and were constrained to idealized geometries (C−H, 0.96 Å; H−C−H, 109.5°). The ring carbon atoms of the benzyl group were treated as regular hexagons throughout the refinement. Solvent atoms were held at the positions in which they were located in difference electron density syntheses. Other non-hydrogen atoms were refined without positional constraints. Structure solution was by direct methods (Siemens SHELXTL PLUS) and refinement by full-matrix least squares (against F^2(SHELXL93). Weights, w, were set equal to $[\sigma_c^2(F_o^2) + (aP)^2]^{-1}$, where $P = [0.333 \max\{F_o^2,0\} + 0.667F_c^2]$, $\sigma_c^2(F_o^2)$ is the variance in F_o^2 due to counting statistics, and $a = 0.10$ was chosen to minimize the variation in S as a function of F_o. Final difference electron density maps showed features of +0.45 to −0.46 e Å^{-3}, the largest of these being close to the Ti atom. All calculations were carried out with Siemens proprietary software[58] and SHELXL-93[59] using complex neutral-atom scattering factors taken from ref 60.

The poor R factor is a result of poor crystal quality. The diffraction peaks were not only quite broad (0.5−0.6° full widths at half maximum in w) but the profiles appeared irregular, with some peaks showing pronounced shoulders. Furthermore, a rotation photograph showed that part of the sample was amorphous rather than single crystalline. Other crystal samples showed only powder diffraction patterns. Attempts to make the titanium and other atoms anisotropic were unsuccessful and resulted in nonpositive U_{ij}s, which, again, is due to the poor quality of the crystal and data.

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Supplementary Material Available: Synthesis of biphenol and binapththol ligands, assignment of ^{1}H and ^{13}C NMR binaphthol resonances from 2D COSY and HETCOR NMR, the synthesis of $C_{20}H_{10}(SH)_2$ and 2,2′-dithiol-1,1′-biphenyl, attempted synthetic routes to sterically hindered binaphthiols NMR spectra, and a complete listing of bond lengths and bond angles (22 pages). Observed and calculated structure factors (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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