

A Novel Phenolate “Constrained Geometry” Catalyst System. Efficient Synthesis, Structural Characterization, and α -Olefin Polymerization Catalysis

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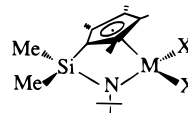
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This paper reports the convenient “one-pot” synthesis of a bifunctional $\text{Me}_4\text{Cp}^{\text{--}}$ phenolate $^{\text{--}}$ ligand and the efficient “one-step” synthesis of the corresponding Ti^{IV} and Zr^{IV} complexes. The reaction of 2-bromo-4-methylphenol with 2 equiv of $n\text{BuLi}$ followed by addition of 2,3,4,5-tetramethyl-2-cyclopentenone produces the bifunctional mono-Cp phenol ligand precursor 2-(tetramethylcyclopentadienyl)-4-methylphenol ((TCP)H₂, **1**). Reaction of **1** with $\text{Ti}(\text{CH}_2\text{Ph})_4$ at 60 °C in toluene cleanly generates (TCP)/ $\text{Ti}(\text{CH}_2\text{Ph})_2$ (**2**), while the corresponding reaction with $\text{Zr}(\text{CH}_2\text{Ph})_4$ at higher temperatures affords the chelated C_2 -symmetric zirconocene (TCP)₂Zr (**3**). In solution at room temperature, the two benzyl groups of **2** are magnetically equivalent, however, in the solid state, X-ray diffraction reveals that one benzyl group is coordinated in a normal η^1 -fashion and the other in an η^2 -mode. The small Cp-(centroid)–Ti–O angle of 107.7(2)° in **2** indicates sterically open features in common with amido-based “constrained geometry” polymerization catalysts. Low-temperature NMR-scale reactions of **2** with $\text{B}(\text{C}_6\text{F}_5)_3$ and $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ indicate the formation of the corresponding cationic complexes (TCP)/ $\text{TiCH}_2\text{Ph}^+\text{PhCH}_2\text{B}(\text{C}_6\text{F}_5)_3^-$ (**4**) and (TCP)/ $\text{TiCH}_2\text{Ph}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ (**5**). Upon activation with $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$, complex **2** is highly active for ethylene, propylene, and styrene polymerization.

Introduction

Ligand modifications have played a key role in developing new “single-site” group 4 metallocene catalyst precursors for optimizing polymerization activity as well as polymer properties such as stereoregularity, molecular weight, thermal/rheological characteristics, bulky and polar comonomer incorporation, and microstructure.¹ In particular, complexes of bifunctional monocyclopentadienyl ligands having an appended heteroatom donor have attracted considerable attention,² as exemplified by “constrained geometry” catalysts having the formula $\text{Me}_2\text{Si}(\eta^5\text{-Me}_4\text{C}_5)(\text{tBuN})\text{MX}_2$ (CGC-MX₂; M = Ti, Zr, Hf; X = Cl, Me, CH₂Ph).³ These catalysts have a covalently attached amide donor



CGCMX₂; M = Ti, Zr, Hf; X = Cl, Me, CH₂Ph

ligand which stabilizes the electrophilic metal center electronically, while the short $\text{Me}_2\text{Si}<$ bridging group considerably opens the metal coordination sphere vis-à-vis a conventional metallocene. The result upon activation with a variety of cocatalysts is a new generation of catalysts which, among other features, efficiently produce ultra-low-density elastomeric ethylene–octene copolymers.^{3c}

Given the impact of the Cp-appended heteroatom donor groups on the catalytic performance of such complexes, ligand design remains a very active and challenging area of olefin polymerization research, and much attention has been focused on the design of new N,^{2,4} and O-containing ligands.^{2,5} In addition, developing more efficient syntheses of useful ligands as well as of the corresponding metal complexes has attracted

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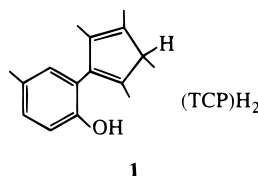
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both scientific and technological interest.^{3a,6} In view of the importance of the aforementioned issues, we report here a convenient "one-pot" synthesis of a new bifunctional mono-Cp ligand containing an appended phenolate group (ligand **1**; (TCP)H₂) as well as efficient one-step syntheses of the corresponding C_s-symmetric Ti and chiral C₂-symmetric Zr complexes.⁷ Attractive features



of the new ligand system include a simple synthetic procedure as well as great intrinsic steric and electronic flexibility introducible via modification of the aryl fragment. We also report the solution and solid state structure, cocatalyst abstraction/activation chemistry, and the performance in olefin polymerization of the Ti dibenzyl complex.

Experimental Section

Materials and Methods. All manipulations of air-sensitive materials were performed with rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual-manifold Schlenk line or interfaced to a high-vacuum line (10⁻⁶ Torr) or in a nitrogen-filled Vacuum Atmospheres glovebox with a high-capacity recirculator (<1 ppm O₂). Argon, hydrogen (Matheson, prepurified), ethylene, and propylene (Matheson, polymerization grade) were purified by passage through a supported MnO oxygen-removal column and an activated Davison 4A molecular sieve column. Ether solvents were purified by distillation from Na/K alloy/benzophenone ketyl. Hydrocarbon solvents (toluene and pentane) were distilled under nitrogen from Na/K alloy. All solvents for high-vacuum line manipulations were stored *in vacuo* over Na/K alloy in Teflon-valved bulbs. Deuterated solvents were obtained from Cambridge Isotope Laboratories (all ≥99 atom %D), freeze-pump-thaw degassed, dried over Na/K alloy, and stored in resealable flasks. Other non-halogenated solvents were dried over Na/K alloy, and halogenated solvents were distilled from P₂O₅ and stored over activated Davison 4A molecular sieves. C₆F₅Br (Aldrich) was vacuum distilled from P₂O₅. Styrene (Aldrich) was dried over CaH₂ and vacuum-transferred into a storage tube containing activated 4A molecular sieves. TiCl₄, ZrCl₄, PhCH₂MgCl (1.0 M in diethyl ether), ⁿBuLi (1.6 M in hexanes), 2-bromo-4-methylphenol, and 2,3,4,5-tetramethyl-2-cyclopentenone were purchased from Aldrich. Ti(CH₂Ph)₄,⁸ Zr(CH₂Ph)₄,⁸ B(C₆F₅)₃,⁹ and

Ph₃C⁺B(C₆F₅)₄^{-10a} were prepared and purified according to literature procedures.

Physical and Analytical Measurements. NMR spectra were recorded on either Varian VXR 300 (FT 300 MHz, ¹H; 75 MHz, ¹³C) or Germini-300 (FT 300 MHz, ¹H; 75 MHz, ¹³C; 282 MHz, ¹⁹F) instruments. Chemical shifts for ¹H and ¹³C NMR spectra were referenced to internal solvent resonances and are reported relative to tetramethylsilane. ¹⁹F NMR spectra were referenced to external CFCl₃. NMR experiments on air-sensitive samples were conducted in Teflon valve-sealed sample tubes (J. Young). Elemental analyses were performed by Oneida Research Services, Inc., Whitesboro, NY. ¹³C NMR assays of polymer microstructure were conducted in C₂D₂Cl₄ at 120 °C. Melting temperatures of polymers were measured by DSC (DSC 2920, TA Instruments, Inc.) from the second scan with a heating rate of 20 °C/min. GPC analyses of polymer samples were performed at L. J. Broutman & Associates Ltd., Chicago, on a Waters 150C GPC relative to polystyrene standards.

One-Pot Synthesis of 2-(Tetramethylcyclopentadienyl)-4-methylphenol, (TCP)H₂ (1). Into a 1 L Schlenk flask were charged 50.0 g (267 mmol) of 2-bromo-4-methylphenol and 250 mL of THF, and then 350 mL of ⁿBuLi (560 mmol, 1.6 M in hexanes) was added dropwise with stirring at 0 °C. A white precipitate formed, and the resulting mixture was allowed to warm to room temperature and stirred for another 2 h. The solution was next cooled to -78 °C, and 2,3,4,5-tetramethyl-2-cyclopentenone (40.2 mL, 36.9 g, 267 mmol) was added dropwise over 30 min. The resulting solution was then allowed to warm to room temperature and stirred overnight. The reaction mixture was next treated with 20 mL of water followed by 120 mL of concentrated HCl. The organic layer was separated and treated 3 times with 40 mL of concentrated HCl. Volatiles were removed by rotary evaporation, and the oily residue was distilled under vacuum at 150 °C/15 Torr to yield 28.5 g of the title ligand as a dark brown crystalline solid. Yield: 46.8%. ¹H NMR (C₆D₆, 23 °C): δ 6.88 (s, 1 H, Ar), 6.78 (m, 2 H, Ar), 3.00 (s, 1 H, OH), 2.50 (q, J_{H-H} = 6.6 Hz, 1 H, Cp-H), 2.18 (s, 3 H, Ar-CH₃), 1.63 (s, 3 H, Cp-CH₃), 1.48 (s, 3 H, Cp-CH₃), 1.28 (s, 3 H, Cp-CH₃), 1.00 (d, J_{H-H} = 7.2 Hz, 3 H, Cp-CH₃). ¹³C NMR (C₆D₆, 23 °C): δ 157.11, 138.57, 132.63, 129.18, 129.00, 125.40 (Ar), 109.88, 101.36, 58.37, 51.40 (Cp), 24.86 (Ar-CH₃), 21.00, 20.45, 12.27, 9.63 (Cp-CH₃). Anal. Calcd for C₁₆H₂₀O: C, 84.16; H, 8.83. Found: C, 84.37; H, 8.94.

One-Step Synthesis of (TCP)Ti(CH₂Ph)₂ (2). Ti(CH₂Ph)₄ (1.01 g, 2.40 mmol), (TCP)H₂ (0.46 g, 2.0 mmol), and 50 mL of toluene were heated with stirring at 60–65 °C for 30 h in the absence of light. The solvent was removed *in vacuo*, and the black residue was extracted with 50 mL of pentane. The pentane extracts were then filtered, and the solvent was removed from the filtrate under vacuum. The resulting crude product was washed with 5 mL of cold pentane and dried to produce 0.46 g of the pure product as a brown solid. Yield: 50.4%. The product is very soluble in pentane. ¹H NMR (C₆D₆, 23 °C): δ 7.13 (d, J_{H-H} = 7.5 Hz, 4 H, Ph), 7.04 (d, J_{H-H} = 7.5 Hz, 4 H, Ph), 6.89 (d, J_{H-H} = 8.1 Hz, 2 H, Ar), 6.83 (t, J_{H-H} = 7.5 Hz, 2 H, Ph), 6.59 (d, J_{H-H} = 7.5 Hz, 1 H, Ar), 2.50 (d, J_{H-H} = 10.2 Hz, 2 H, CH₂Ph), 2.32 (d, J_{H-H} = 10.2 Hz, 2 H, CH₂Ph), 2.11 (s, 3 H, Ar-CH₃), 1.90 (s, 6 H, C₅Me₄), 1.44 (s, 6 H, C₅Me₄). ¹³C NMR (C₆D₆, 23 °C): δ 170.71, 147.87, 136.73, 130.50, 130.00, 129.76, 128.70 (Ar, Ph), 123.07, 121.18, 114.00 (Cp), 83.85 (t, J_{C-H} = 127.5 Hz, CH₂Ph), 20.73 (Ar-CH₃), 11.49 (C₅Me₄), 11.25 (C₅Me₄). Anal. Calcd for C₃₀H₃₂O₂·Ti: C, 78.93; H, 7.09. Found: C, 78.67; H, 6.83.

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One-Step Synthesis of (TCP)₂Zr (3). Zr(CH₂Ph)₄ (2.10 g, 4.60 mmol), (TCP)H₂ (0.840 g, 3.68 mmol), and 50 mL of toluene were heated with stirring at 110 °C for 12 h in the absence of light. Using the same work-up procedure as in the synthesis of (TCP)Ti(CH₂Ph)₂ above, 0.35 g of the title complex was isolated as a colorless crystalline solid. Yield: 35.0%. ¹H NMR (C₆D₆, 23 °C): δ 7.07 (d, *J*_{H-H} = 2.1 Hz, 2 H, Ar), 7.01 (dd, *J*_{H-H} = 7.8 Hz, *J*_{H-H} = 2.1 Hz, 2 H, Ar), 6.73 (d, *J*_{H-H} = 8.4 Hz, 2 H, Ar), 2.25 (s, 6 H, Ar-CH₃), 2.08 (s, 6 H, C₅Me₄), 1.78 (s, 6 H, C₅Me₄), 1.72 (s, 12 H, C₅Me₄). ¹³C NMR (C₆D₆, 23 °C): δ 173.89, 138.84, 129.91, 129.24, 129.18, 126.47 (Ar), 120.14, 118.42, 117.09, 115.83 (Cp), 20.83 (Ar-CH₃), 11.07, 10.56, 10.00, 9.52 (C₅Me₄). Anal. Calcd for C₃₂H₃₆O₂Zr: C, 70.67; H, 6.67. Found: C, 70.49; H, 6.73.

In Situ Generation of (TCP)TiCH₂Ph⁺PhCH₂B(C₆F₅)₃⁻ (4). (TCP)Ti(CH₂Ph)₂ (4.6 mg, 0.010 mmol) and B(C₆F₅)₃ (5.1 mg, 0.010 mmol) were loaded in the glovebox into a J. Young NMR tube, which was then attached to the high-vacuum line. CD₂Cl₂ (0.7–1 mL) was then vacuum-transferred into this tube at -78 °C. The NMR spectroscopy was carried out at -40 °C. ¹H NMR (CD₂Cl₂, -40 °C): δ 7.81 (t, *J*_{H-H} = 7.5 Hz, 1 H), 7.65 (t, *J*_{H-H} = 7.5 Hz, 1 H), 7.41 (t, *J*_{H-H} = 7.5 Hz, 1 H), 7.35 (t, *J*_{H-H} = 7.5 Hz, 1 H), 7.23 (d, *J*_{H-H} = 7.5 Hz, 1 H), 7.07 (t, *J*_{H-H} = 7.5 Hz, 2 H), 6.85 (t, *J*_{H-H} = 7.5 Hz, 2 H), 6.79 (t, *J*_{H-H} = 7.5 Hz, 1 H), 6.64 (d, *J*_{H-H} = 6.9 Hz, 2 H), 6.10 (d, *J*_{H-H} = 6.9 Hz, 1 H), 3.84 (d, *J*_{H-H} = 6.3 Hz, 1 H, Ti-CH₂Ph), 2.96 (d, *J*_{H-H} = 6.3 Hz, 1 H, Ti-CH₂Ph), 2.71 (s, br, 2 H, B-CH₂Ph), 2.44 (s, 3 H, Ar-CH₃), 2.33 (s, 3 H, C₅Me₄), 2.13 (s, 3 H, C₅Me₄), 2.04 (s, 3 H, C₅Me₄), 1.57 (s, 3 H, C₅Me₄). A small amount of dibenzyl (δ 2.84 ppm) was also detected in the NMR reaction. ¹⁹F NMR (CD₂Cl₂, -40 °C): δ -130.00 (s, br, 6 F, *o*-F), -162.30 (t, ³*J*_{F-F} = 21.4 Hz, 3 F, *p*-F), -165.30 (s, br, 6 F, *m*-F).

In Situ Generation of (TCP)TiCH₂Ph⁺B(C₆F₅)₄⁻ (5). (TCP)Ti(CH₂Ph)₂ (4.6 mg, 0.010 mmol) and Ph₃C⁺B(C₆F₅)₄⁻ (9.2 mg, 0.010 mmol) were loaded in the glovebox into a J. Young NMR tube, which was then attached to the high-vacuum line. CD₂Cl₂ (0.7–1 mL) was then vacuum-transferred into this tube at -78 °C. The NMR spectroscopy was carried out at -60 °C. ¹H NMR (CD₂Cl₂, -60 °C): δ 7.81 (t, *J*_{H-H} = 7.5 Hz, 1 H), 7.65 (t, *J*_{H-H} = 7.5 Hz, 1 H), 7.43 (t, *J*_{H-H} = 7.5 Hz, 1 H), 7.40–6.90 (m, obscured by superimposed signals of Ph₃CCH₂Ph), 6.09 (d, *J*_{H-H} = 8.1 Hz, 1 H), 3.84 (d, *J*_{H-H} = 6.3 Hz, 1 H, Ti-CH₂Ph), 2.96 (d, *J*_{H-H} = 6.3 Hz, 1 H, Ti-CH₂Ph), 2.44 (s, 3 H, Ar-CH₃), 2.31 (s, 3 H, C₅Me₄), 2.13 (s, 3 H, C₅Me₄), 2.03 (s, 3 H, C₅Me₄), 1.59 (s, 3 H, C₅Me₄). A small amount of dibenzyl (δ 2.83 ppm) was also detected in the NMR reaction. ¹³C NMR (CD₂Cl₂, -60 °C): δ 82.56 (t, *J*_{C-H} = 150.8 Hz, Ti-CH₂Ph). ¹⁹F NMR (CD₂Cl₂, -60 °C): δ -131.86 (s, br, 8 F, *o*-F), -161.08 (t, ³*J*_{F-F} = 21.2 Hz, 4 F, *p*-F), -165.03 (s, br, 8 F, *m*-F).

Ethylene, Propylene, and Styrene Polymerization Experiments. Ethylene, propylene, and styrene polymerizations were carried out at room temperature in 250-mL flamed, round-bottomed flasks equipped with magnetic stirring bars and attached to the high-vacuum line. In a typical experiment, a 1:1 ratio of (TCP)Ti(CH₂Ph)₂:cocatalyst in 2 mL of toluene or 1,2-difluorobenzene (for those catalysts activated with Ph₃C⁺B(C₆F₅)₄⁻), freshly prepared in the glovebox, was quickly injected (using a gas-tight syringe equipped with a spraying needle) into a rapidly stirred flask containing a measured quantity of dry toluene, which was presaturated under 1.0 atm of rigorously purified ethylene or propylene. The solution was equilibrated at the desired reaction temperature using an external constant-temperature bath. For styrene polymerization, the toluene solution contained 2.0 mL of freshly distilled styrene under 1.0 atm of Ar. After a measured time interval, the polymerization was quenched by the addition of 2% acidified methanol. The polymer was then collected by filtration, washed with methanol, and dried on the high-vacuum line overnight to a constant weight.

X-ray Crystallographic Studies of (TCP)Ti(CH₂Ph)₂. Orange crystals of (TCP)Ti(CH₂Ph)₂ were grown by slow

Table 1. Summary of the Crystal Structure Data for (TCP)Ti(CH₂Ph)₂ (2)

| | |
|---|---|
| formula | C ₃₀ H ₃₂ TiO |
| fw | 456.48 |
| cryst color, habit | orange, platey |
| cryst dimens mm | 0.24 × 0.15 × 0.01 |
| cryst syst | triclinic |
| <i>a</i> , Å | 8.324(3) |
| <i>b</i> , Å | 10.432(4) |
| <i>c</i> , Å | 14.634(4) |
| α, deg | 85.67(3) |
| β, deg | 79.23(3) |
| γ, deg | 76.64(4) |
| <i>V</i> , Å ³ | 1213.9(8) |
| space group | <i>P</i> $\bar{1}$ (No. 2) |
| <i>Z</i> | 2 |
| <i>d</i> (calcd), g/cm ³ | 1.249 |
| μ, cm ⁻¹ | 3.72 |
| diffractometer | Enraf-Nonius, CAD4 |
| radiation | Mo Kα (λ = 0.710 69 Å), graphite monochromated |
| temperature, °C | -120 °C |
| scan type | ω-θ |
| 2θ range, deg | 2.0–45.9 |
| intensities (unique, <i>R</i> _i) | 3634 (3358, 0.114) |
| transmission factor range | 0.9543–0.9970 |
| secondary extinction | coefficient: 6.29514e-08 |
| intensities > 3σ(<i>I</i>) | 1335 |
| no. of params | 220 |
| <i>R</i> | 0.066 |
| <i>R</i> _w | 0.054 |
| max density in Δ <i>F</i> map, e ⁻ /Å ³ | 0.37 |

cooling of a saturated pentane solution to -20 °C over several days. The solvent was decanted in the glovebox, and the crystals were quickly covered with a layer of Paratone-N oil (Exxon, dried and degassed at 120 °C/10⁻⁶ Torr for 24 h). The crystals were then mounted on thin glass fibers and transferred into the cold-steam (-120 °C) of the Enraf-Nonius CAD4 diffractometer. Final cell dimensions were obtained by a least-squares fit to the automatically centered settings for 25 reflections. Intensity data were all corrected for absorption, anomalous dispersion, and Lorentz and polarization effects. The space group was determined by statistical analysis of intensity distribution and successful refinement of the proposed structure. Crystallographic data are summarized in Table 1.

The structure was solved by direct methods¹¹ and expanded using Fourier techniques.¹² Owing to the paucity of data, atoms C17–C30 (the benzyl groups) were refined isotropically while the remaining non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in idealized positions. The final cycle of full-matrix least-squares refinement was based on 1335 observed reflections (*I* > 3.00σ(*I*)) and 220 variable parameters. All calculations were performed using the TeXsan crystallographic software package of Molecular Structure Corp.

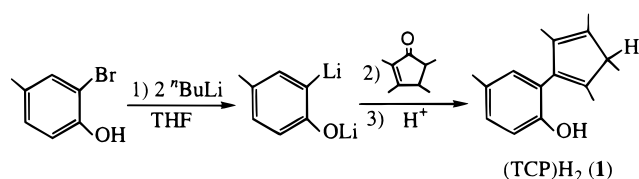
Results and Discussion

Synthesis of (TCP)H₂ (1), (TCP)Ti(CH₂Ph)₂ (2), and (TCP)₂Zr (3). The one-pot synthesis of the 2-(tetramethylcyclopentadienyl)-4-methylphenol ligand (TCP)-H₂ is depicted in Scheme 1. The reaction of commercially available 2-bromo-4-methylphenol with 2 equiv of *n*BuLi yields a dilithio salt, which is not isolated and is next reacted with 2,3,4,5-tetramethyl-2-cyclopentenone to produce ligand **1** (obtained as a single isomer judging from the NMR) as a brown crystalline solid after hydrolysis and subsequent vacuum distillation. This

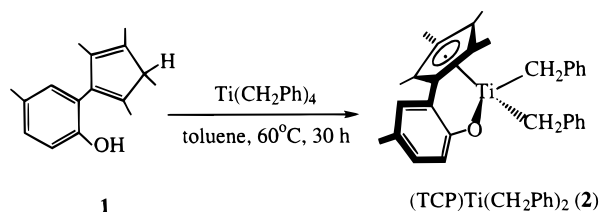
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Scheme 1



Scheme 2



approach can be compared to the conventional three-step synthesis of Me₂Si(C₅Me₄H)(BuNH)₂,^{4g,h} with the attraction of the present system being the efficient synthetic procedure as well as the great potential steric and electronic flexibility introducible via modification of the aryl fragment.

Interestingly, in attempts to synthesize the corresponding group 4 metal complexes from **1**, both the conventional metalation/salt elimination (double deprotonation with ⁿBuLi followed by metalation with MCl₄) and amine elimination approaches^{6c-h} (**1** + M(NMe₂)₄ at 110 °C for 3 days) gave complex mixtures of unidentified products. On the other hand, the alkane elimination approach reported^{3a} earlier for the efficient synthesis of group 4 constrained geometry catalysts afforded the desired complex **2** (Scheme 2) in 50% yield. In solution at room temperature, the ¹H NMR spectrum of **2** reveals two magnetically equivalent benzylic protons, each having diastereotopic benzylic protons at δ 2.50 and 2.32 ppm (*J*_{H-H} = 10.2 Hz). Although the observation of a normal Ph *ipso*-¹³C chemical shift at δ 147.87 ppm, a CH₂ ²*J*_{HH} value of 10.2 Hz, and a CH₂ ¹*J*_{CH} value of 127.5 Hz can be taken as evidence against significant ηⁿ-benzyl bonding,^{4f,13} the solid state structural results (see below) suggest rapid interconversion^{4f} of one η¹ and one ηⁿ group in solution at room temperature. The corresponding reaction of **1** with Zr(CH₂Ph)₄ under the same conditions yields a mixture of products. However, at higher reaction temperatures (110 °C for 12 h), the reaction yields a new, chiral chelated C₂-symmetric zirconocene¹⁴ (TCP)₂Zr (**3**; Scheme 3) which has been characterized spectroscopically and analytically. This salt-free synthetic/ligational approach which by design yields only the *rac* isomer may offer attractive features in the stereoselective synthesis of other precursors for *rac*-metallocene catalysts.

Crystal Structure of (TCP)Ti(CH₂Ph)₂ (2). The solid state structure of **2** as derived from single-crystal

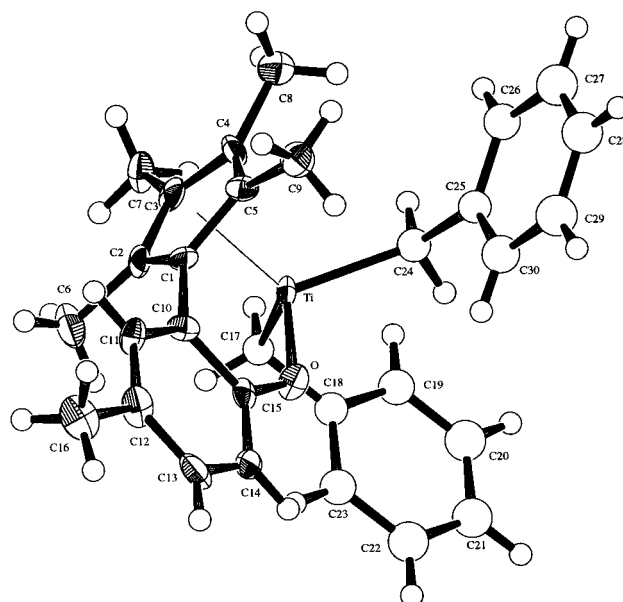


Figure 1. Perspective ORTEP drawing of the molecular structure of the complex (TCP)Ti(CH₂Ph)₂ (**2**). Thermal ellipsoids are drawn at the 50% probability level.

Scheme 3

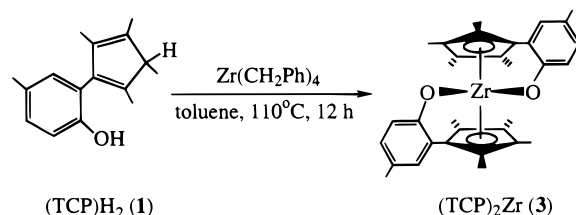


Table 2. Selected Bond Distances (Å) and Angles (deg) for (TCP)Ti(CH₂Ph)₂ (**2**)

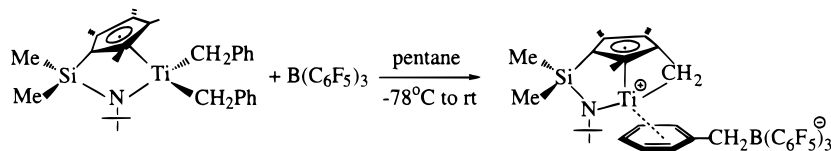
| Bond Distances | | | |
|-------------------|-----------|------------|-----------|
| Ti—O | 1.851(7) | Ti—C1 | 2.33(1) |
| Ti—C2 | 2.36(1) | Ti—C3 | 2.39(1) |
| Ti—C4 | 2.37(1) | Ti—C5 | 2.35(1) |
| Ti—C17 | 2.121(10) | Ti—C24 | 2.13(1) |
| Ti—C18 | 2.92(1) | C24—C25 | 1.50(1) |
| O—C15 | 1.36(1) | C17—C18 | 1.49(1) |
| Bond Angles | | | |
| O—Ti—C17 | 104.5(4) | O—Ti—C24 | 108.0(4) |
| Ti—O—C15 | 126.6(6) | Ti—C17—C18 | 106.7(7) |
| Ti—C24—C25 | 127.2(7) | O—C15—C10 | 116.6(10) |
| O—C15—C14 | 124(1) | C1—C10—C15 | 112.6(10) |
| C1—C10—C11 | 128(1) | C17—Ti—C24 | 101.1(4) |
| Cp(centroid)—Ti—O | 107.7(2) | | |

X-ray diffraction is shown in Figure 1, and important bond distances and angles are summarized in Table 2. The geometry around Ti is slightly distorted tetrahedral, with a Cp(centroid)—Ti—O angle of 107.7(2)° and a C17—Ti—C24 angle of 101.1(4)°. This acute Cp(centroid)—Ti—O angle is nearly identical to that of the Cp—Ti—N angle in Me₂Si(Me₄C₅)(BuN)TiCl₂ (107.6),^{3f} indicating similar sterically open features for both complexes as catalyst precursors. The Ti—C_{ring}(av) distance of 2.36(1) Å is probably slightly longer than the corresponding distance in Me₂Si(Me₄C₅)(BuN)TiCl₂ (2.340(5) Å).^{3f} The (phenyl)C10—C1(ring) vector in **2** is bent 15(1)° from the Me₄Cp ring mean-square plane, and the phenyl plane—Me₄Cp plane dihedral angle is 81(1)°. The Ti—O bond length in **2** (1.851(7) Å) is comparable to those reported for bent metallocene Ti^{IV} and Ti^{III} alkoxide complexes, such as Cp₂Ti(OCH=CH₂)₂

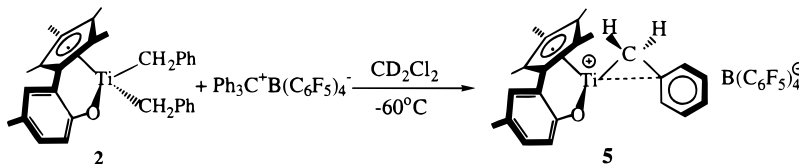
(13) (a) Bochmann, M.; Lancaster, S. J.; Hursthouse, M. B.; Malik, K. M. A. *Organometallics* **1994**, *13*, 2235–2243. (b) Bochmann, M.; Lancaster, S. J. *Organometallics* **1993**, *12*, 633–640. (c) Jordan, R. F.; LaPointe, R. E.; Baenziger, N. C.; Hinch, G. D. *Organometallics* **1990**, *9*, 1539. (d) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willet, R. J. *Am. Chem. Soc.* **1987**, *109*, 4111. (e) Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1985**, *4*, 902. (f) Mintz, E. A.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4692. (g) Davis, G. R.; Jarvis, J. A.; Kilburn, B. T. *J. Chem. Soc., Chem. Commun.* **1971**, 15111.

(14) For related chelated complexes having different ligand frameworks and prepared by different synthetic approaches, see refs 5c and 6h.

Scheme 4



Scheme 5

Table 3. Summary of α -Olefin Polymerization Catalyzed by $(\text{TCP})\text{Ti}(\text{CH}_2\text{Ph})_2$

| entry | cocatalyst | conditions | monomer ^a | polymer yield (g) | activity ^b | M_w^c | M_w/M_n | remarks |
|-------|---|---|----------------------|-------------------|-----------------------|--------------------|-----------|--|
| 1 | $\text{B}(\text{C}_6\text{F}_5)_3$ | 15 μmol of catalyst 100 mL of toluene, 30 min | ethylene | 0.11 | 1.47×10^4 | 1.27×10^6 | > 10 | $T_m = 142.5^\circ\text{C}$ |
| 2 | $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ | 15 μmol of catalyst 100 mL of toluene, 1 min | ethylene | 0.52 | 2.10×10^6 | 1.14×10^6 | > 10 | $T_m = 142.4^\circ\text{C}$ |
| 3 | $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ | 20 μmol of catalyst 50 mL of toluene, 5 min | propylene | 6.37 | 3.82×10^6 | 2.36×10^4 | 1.85 | $[\text{mm}] = 0.224$ $[\text{mr}] = 0.512$ $[\text{rr}] = 0.264$ atactic |
| 4 | $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ | 25 μmol of catalyst 5 mL of toluene, 5 min | styrene | 1.57 | 4.33×10^7 | 8.00×10^3 | 3.32 | |

^a Carried out at 25°C , 1 atm of ethylene, 1 atm of propylene, and 17.4 mmol of styrene. ^b Activities in units of g of polymer/(mole of catalyst \cdot atm \cdot h), except entry 4 in units of g of polystyrene/(mole of catalyst \cdot mole styrene \cdot h). ^c GPC relative to polystyrene standards.

(1.903(2) Å),^{15a} $\text{Cp}_2\text{Ti}(\text{OC}_2\text{H}_5)\text{Cl}$ (1.855(2) Å),^{15b} Cp_2TiO (2,6-Me₂C₆H₃) (1.892(2) Å),^{15c} $[\text{C}_5\text{H}_4(\text{CH}_2)_3\text{O}]\text{TiCl}_2$ (1.762(2) Å),^{5b} and $[\text{C}_5\text{Me}_4(\text{CH}_2)_3\text{O}]\text{TiCl}_2$ (1.767(1) Å),^{15d} where a partial Ti–O double-bond character involving oxygen π -donation to the metal in addition to the σ -interaction is associated with short Ti–O bond lengths. On the other hand, the present Ti–O–C15 angle ($126.6(6)^\circ$) is somewhat smaller than typical Ti–O–C angles, as in the above examples ($\sim 140^\circ$)¹⁵ where Ti–O multiple bonding is assumed operative, reflecting the great steric strain in **2**, also evidenced by the 15° bend of the (phenyl)C10–C1(ring) vector from the Me₄Cp ring mean-square plane.

The two benzyl ligands in complex **2** are inequivalent in the solid state, with one engaging in normal η^1 -bonding (Ti–C24 = 2.13(1) Å; $\angle\text{Ti–C24–C25} = 127.2(7)^\circ$) and the other in partial η^2 -bonding, with Ti–C17 and Ti–C_{ipso}(C18) distances of 2.121(10) and 2.92(1) Å, respectively, and a Ti–C17–C18 angle of $106.7(7)^\circ$ (Figure 1).

Reaction Chemistry of $(\text{TCP})\text{Ti}(\text{CH}_2\text{Ph})_2$ with $\text{B}(\text{C}_6\text{F}_5)_3$ and $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$. The reaction of bis-Cp-type metallocene dibenzyls with $\text{B}(\text{C}_6\text{F}_5)_3$ and $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ often generates the corresponding cationic complexes with η^2 -bonding of the remaining benzyl group to the electrophilic metal center.^{3a,13a–c} In contrast, we previously found that the reaction of the $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{tBuN})\text{M}(\text{CH}_2\text{Ph})_2$ complexes with $\text{B}(\text{C}_6\text{F}_5)_3$ and $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ follows a different course.^{3a} While low-temperature NMR-scale reactions of $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{tBuN})\text{M}(\text{CH}_2\text{Ph})_2$ complexes with $\text{B}(\text{C}_6\text{F}_5)_3$ and

$\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ in CD_2Cl_2 indicate the formation of cationic monobenzyl species, preparative-scale reactions at higher temperature afford C–H activation products, i.e., intramolecularly ring-metallated η^1, η^6 -fulvene-type complexes (e.g., Scheme 4).^{3a} Likewise, the low-temperature NMR-scale reactions of $(\text{TCP})\text{Ti}(\text{CH}_2\text{Ph})_2$ with $\text{B}(\text{C}_6\text{F}_5)_3$ and $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ in CD_2Cl_2 clearly indicate the formation of the corresponding cationic monobenzyl species $(\text{TCP})\text{TiCH}_2\text{Ph}^+\text{PhCH}_2\text{B}(\text{C}_6\text{F}_5)_3^-$ (**4**) and $(\text{TCP})\text{TiCH}_2\text{Ph}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ (**5**), respectively, with identical cation structures based upon the NMR analyses (the formation of **5** is depicted in Scheme 5). The Ti–CH₂–Ph ¹H NMR signals of **5** are observed at δ 3.84 (d, $J_{\text{H–H}} = 6.3$ Hz) and 2.96 (d, $J_{\text{H–H}} = 6.3$ Hz) (CD_2Cl_2 , -60°C), which is 1.34 and 0.64 ppm down-field-shifted, respectively, from the benzyl resonances of neutral precursor **2** (δ 2.50 (d, $J_{\text{H–H}} = 10.2$ Hz) and 2.32 (d, $J_{\text{H–H}} = 10.2$ Hz) (C_6D_6 , 23°C)) as a consequence of cation formation. η^2 -Coordination of the benzyl ligand in the cationic complex is evidenced by a reduction of the value of $^2J_{\text{H–H}}$ for the diastereotopic CH₂Ph protons from 10.2 to 6.3 Hz, a high-field-shifted Ti–¹³CH₂Ph signal (δ 82.56 ppm in **5** vs 83.85 ppm in **2**), and a large CH₂ ¹J_{CH} value (150.8 Hz in **5** vs 127.5 Hz in **2**).¹³ However, despite the clean NMR-scale reactions at low temperatures, and unlike the case of the constrained geometry monobenzyls,^{3a} preparative-scale reactions at higher temperatures are accompanied by extensive decomposition and isolation of the cationic complexes could not be achieved in this case.

α -Olefin Polymerization Studies. Table 3 summarizes ethylene, propylene, and styrene polymerization activities of $(\text{TCP})\text{Ti}(\text{CH}_2\text{Ph})_2$ upon activation with $\text{B}(\text{C}_6\text{F}_5)_3$ and $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ as well as the properties of the resulting polymers. $(\text{TCP})\text{Ti}(\text{CH}_2\text{Ph})_2$ when activated with $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ is a highly active cata-

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lyst for ethylene, propylene, and styrene polymerization, producing high molecular weight ($>10^6$) polyethylenes with high melting transition temperatures ($T_m = 142^\circ\text{C}$), as well as atactic polypropylene and polystyrene. The open nature of the catalytic site can be associated with the low degree of polymerization stereocontrol, and the homopoly α -olefin products are generally atactic, similar to the performance of group 4 amido-based constrained geometry catalysts.^{3c} The broad polydispersities of the polyethylene products may be associated with the rapid decomposition of the cationic species at room temperature (possibly with the formation of η^1, η^6 "tuck-in" cations^{3a}) or slow initiation with respect to the fast propagation and significant inhomogeneity during the course of the catalytic reaction under the present ethylene polymerization conditions. In contrast, propylene polymerization mediated by **2** activated with $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ is both very rapid and produces a polymer having narrow polydispersity, which can be attributed to the structurally open nature of the cationic metal coordination sphere (catalytic activity is not affected by the steric encumbrance of monomer) and apparently greater stabilization of the catalytic sites in the presence of propylene. The substantial activity difference of identical cations having different counteranions (entry 1 vs 2) further demonstrates the significant influence of the anion identity on catalytic activity, as previously shown in detail by us and others.¹⁶

In summary, a novel phenolic bifunctional mono-Cp constrained geometry ligand framework and the Ti and Zr complexes thereof have been designed and synthe-

sized by one-pot/one-step syntheses. The solid state structure, cocatalyst activation chemistry, and performance for olefin polymerization of the titanium complex has been investigated in detail. The results considerably expand what is known about constrained geometry catalyst design and the consequent olefin polymerization performance.

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Supporting Information Available: Text giving complete X-ray experimental details and tables of crystal data, intensity measurements, structure solution and refinement, atomic coordinates, torsion angles, and bond lengths and angles, and ORTEP diagram of **2** (26 pages). Ordering information is given on any current masthead page.

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