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Synthesis, characterization, and reactivity of titanium(IV) complexes supported by proximally bridged *p*-*tert*-butylcalix[4]arene ligands

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Abstract

Treatment of dilithium or dipotassium salt of *p*-*tert*-butylcalix[4]arene with $^{t}BuPCl_2$ or $PhPCl_2$ produced 1,2-alternate phosphorus-bridged *p*-*tert*-butylcalix[4]arene derivatives ($^{t}BuPC)H_2$ (1) and $(PhPC)H_2$ (**2**), respectively. An X-ray diffraction study of **2** showed that it exists in 1,2-alternate conformation. Reaction of **2** with sulfur gave $(PhSPC)H_2$ (**3**), which exists in cone conformation. Treatment of $TiCl_4$ with **1**–**3** produced the corresponding dichlorides L_2TiCl_2 [$L_2 = {}^{t}BuPC$ (**5**); PhPC (**6**); and PhSPC (**7**)]. Reaction of $R_2Mg{\cdot}2THF$ (R = Me or CH_2Ph) with $(DMSC)TiCl_2$ (**8**) yielded $(DMSC)TiMe_2$ (**9**) and $(DMSC)Ti(CH_2Ph)_2$ (**10**), respectively. Cationic derivatives $[(DMSC)Ti(NCCH_3)Me_2]BAr^F_4$ (**11**) and $[(DMSC)Ti(NCCH_3)(CH_2Ph)]BAr^F_4$ (**12**) were prepared from the respective reactions of **9** and **10** with $[Ph_3C]BAr^F_4$ [$Ar^F = (CF_3)_2C_6H_3$] in the presence of CH_3CN. Similarly, **9** and **10** reacted with $[Ph_3C]OTf$ (one equivalent) to yield $[(DMSC)Ti(OTf)Me_2]$ (**13**) and $[(DMSC)Ti(OTf)(CH_2Ph)]$ (**14**), respectively. NMR data showed that the more exposed *exo*-alkyl was abstracted. Complexes **5**–**10** and **14** showed modest ethylene polymerization activities at 25°C with 500 molar equivalents of methylalumoxane (MAO) as cocatalyst.

Keywords: Aryloxide ligand; Calix[4]arene ligand; Olefin polymerization; Titanium(IV)

1. Introduction

Recently, there has been increased interest in the chemistry of homogeneous early transition metal complexes supported by non-cyclopentadienyl ligands [1–19]. The expectation is that compounds with complementary or enhanced reactivity in comparison with early transition metal metallocenes can be developed. A number of ancillary ligand environments have been investigated in Group 4 metal chemistry including chelating diamides [1], aryloxides [2], carboranes [3], amidinates [4], porphyrins [5], tetradentate Schiff bases [6], boratabenzenes [7], and calixarenes [8–19]. While these studies have demonstrated the profound influence of ancillary ligands on the chemical properties of transition metals, tailoring of chemical reactivity remains difficult. As part of a research program aimed at exploring the influence of ancillary ligands on early transition metal-mediated organic transformations, we have been investigating the potential of *p*-*tert*-butylcalix[4]arene derivatives as ancillary ligands in Group 4 metal chemistry [20]. Calix[4]arenes [21] usually adopt one of four main conformations in solution. The degree of steric shielding and electronic stabilization provided by an ancillary calix[4]arene ligand can be influenced by the conformation it adopts. Recent reports by Floriani and co-workers described novel reactivities and bonding modes for a variety of organic fragments bonded to Group 4–6 metal complexes of *p*-*tert*-butylcalix[4]arene and its *O*-methylated derivatives in the cone conformation [8–16]. Our initial attraction to the calix[4]arene ligand system was motivated by the possibility of obtaining a chelating bis(aryloxide) ligand from the 1,2-alternate conformer of *p*-*tert*-butylcalix[4]arene and

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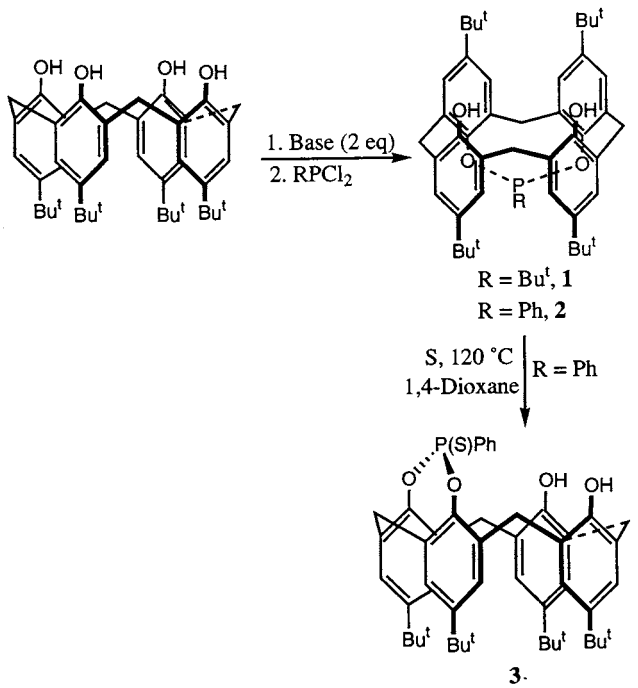
utilizing the ligand to sterically define the reaction sites at the metal center. When the 1,2-alternate conformation is secured by bridging proximal phenolic oxygen atoms, a pair of bulky ^{t}Bu groups and the attached pair of phenyl rings essentially project over the two remaining 'unbridged' phenolic oxygen atoms (Scheme 1). Thus, when the ligand is coordinated via the two donor oxygen atoms, it imposes this stereochemical environment at the metal center. In this paper, we report on the synthesis of titanium(IV) complexes containing *p-tert*-butylcalix[4]arene-derived chelating bis(aryloxide) ligands. In addition, we report herein results of a preliminary investigation of their catalytic reactivity with alkenes.

2. Experimental

2.1. General details

All experiments were performed under dry nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres glovebox. Toluene, ether, tetrahydrofuran, and benzene were distilled twice from sodium benzophenone ketyl. Pentane and hexane were distilled twice from sodium benzophenone ketyl with addition of 1 ml l^{-1} of tetraethyleneglycol dimethyl ether as a solubilizing agent. Methylene chloride and acetonitrile were distilled twice from CaH_2. 1,4-Dioxane and triethylamine were distilled from sodium. Deuterated solvents were distilled as necessary; benzene-d_6 from sodium benzophenone ketyl, methylene chloride-d_2, chloroform-d, acetonitrile-d_3 from CaH_2. All solvents were stored in the glovebox over 4 Å molecular sieves that were dried in a vacuum oven at 125°C for at least 48 h prior to use. Titanium(IV) chloride, dichlorodimethylsilane, benzylmagnesium chloride, methylmagnesium chloride, dimethylzinc, methyllithium, triphenylmethyl chloride, silver triflate, sodium tetrafluoroborate, 3,5-bis(trifluoromethyl)bromobenzene and Mg turnings were purchased from Aldrich and were used as received. *p-tert*-Butylcalix[4]arene was either purchased from Aldrich or synthesized by literature methods [22] and dried in a vacuum oven at 150°C for 48 h. The following compounds were prepared by literature methods: $[Ph_3C]OTf$ [23a], $Na[B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]$ [23b,24,25], $[Ph_3C][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]$ [24], and $[(Et_2O)_2H][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]$ [25]. Ethylene used in the polymerization experiments was purchased from Aldrich (99.8% purity) and was further purified by passage through consecutive columns packed with nickel–copper–barium catalyst (purchased as the oxide from BASF and reduced with H_2/N_2 mixture according to manufacturer's instructions), and 4 Å molecular sieves (dried as described above). NMR spectra were recorded on a Varian Gemini-200 or Varian VXR-400 spectrometer. ^{1}H and ^{13}C chemical shifts are reported relative to residual solvent signal while the ^{19}F-NMR spectra were referenced externally to $CFCl_3$. Mass spectra were recorded at the mass spectroscopy center of the University of Kentucky. Elemental analyses were performed by E + R Microanalytical Laboratory, Ithaca, NY.



Scheme 1.

2.2. Synthesis of calix[4]arene derivatives **1–3**

2.2.1. [(^{t}BuPC)H_2] (**1**)

A 50 ml Schlenk flask was charged with *p-tert*-butylcalix[4]arene (1.948 g, 3.00 mmol), solid LDA (0.642 g, 6.00 mmol) and toluene (30 ml) /THF (10 ml). After stirring the suspension for 18 h, ^{t}BuPCl$_2$ (0.478 g, 3.00 mmol) was added and the reaction mixture was stirred for 24 h. The mixture was filtered, the filtrate was concentrated to dryness, and the resulting solids were extracted with methylene chloride. After separating the extract by filtration, volatiles were removed in vacuo. The residue was triturated with heptane and washed with pentane (5 ml). The solid product was dried under vacuum (0.830 g, 38%) and identified as **1** on the basis of the following data (**1** was pure enough to use for further reaction although acceptable microanalysis data could not be obtained): ^{1}H-NMR (C_6D_6): δ 7.34 (d, 2H, $J = 2$ Hz, arom. CH), 7.14 (d, 2H, arom. CH), 7.11 (d, 2H, arom. CH), 6.84 (d, 2H, arom. CH), 5.97 (s, 2H, OH), 4.60 (dd, $J_{H-H} = 13$ Hz, $J_{H-P} = 3$ Hz, 1H, calix–CH_2), 4.11 (d, $J = 13$ Hz, 1H, calix–CH_2), 4.08 (d, $J = 17$ Hz, 2H, calix–CH_2), 3.80 (d, $J = 17$ Hz,

2H, calix–CH_2), 3.22 (d, $J = 13$ Hz, 1H, calix–CH_2), 3.18 (d, $J = 13$ Hz, 1H, calix–CH_2), 1.30 (s, 18H, ^{t}Bu), 1.28 (s, 18H, ^{t}Bu), 0.73 (d, $J = 12$ Hz, 9H, P–C(CH_3)$_3$). ^{13}C-NMR (C_6D_6): δ 150.86, 150.35 (d, $J = 4$ Hz), 147.43, 142.72, 137.29 (d, $J = 2$ Hz), 131.47 (d, $J = 3$ Hz), 130.86, 127.14, 126.21, 125.75, 125.19, 123.80 (d, $J = 3$ Hz), 37.44 (calix–CH_2), 35.56 (d, $J = 17$ Hz, P–*C*(CH_3)$_3$), 34.22 (*C*(CH_3)$_3$), 34.11 (calix–CH_2), 33.88 (*C*(CH_3)$_3$), 31.58 (C(*C*H_3)$_3$), 31.42 (C(*C*H_3)$_3$), 30.80 (calix–CH_2), 23.86 (d, $J = 16$ Hz, P–C(*C*H_3)$_3$). ^{31}P-NMR (C_6D_6): δ 183.8. MS(EI): M^+ (734).

2.2.2. [(PhPC)H_2] (**2**)

p-tert-Butylcalix[4]arene (0.811 g, 1.25 mmol) in toluene (40 ml) was treated with KH (0.100 g, 2.50 mmol) and the suspension was stirred for 24 h. THF (5 ml) was introduced by syringe, the mixture was stirred for another 2 h, and $PhPCl_2$ (0.224 g, 1.25 mmol) was added to the mixture. After stirring for 48 h, the mixture was filtered, and the volatiles were removed from the filtrate under reduced pressure. The residue was triturated with heptane and washed with pentane. The product was dried under vacuum (0.590 g, 63%) and identified as **2** on the basis of the following data. ^{1}H-NMR (C_6D_6): δ 7.39 (d, 2H, $J = 2$ Hz, arom. CH), 6.90–7.25 (m, 9H, arom. CH), 7.11 (d, 2H, arom. CH), 6.80 (d, 2H, arom. CH), 5.73 (s, 2H, OH), 4.83 (dd, $J_{H-H} = 12$ Hz, $J_{H-P} = 3$ Hz, 1H, calix–CH_2), 4.24 (d, $J = 13$ Hz, 1H, calix–CH_2), 4.08 (d, $J = 17$ Hz, 2H, calix–CH_2), 3.79 (d, $J = 17$ Hz, 2H, calix–CH_2), 3.30 (d, $J = 12$ Hz, 1H, calix–CH_2), 3.27 (d, $J = 13$ Hz, 1H, calix–CH_2), 1.28 (s, 18H, ^{t}Bu), 1.21 (s, 18H, ^{t}Bu). ^{13}C-NMR ($CDCl_3$): δ 150.29 (d, $J = 4$ Hz), 149.53 (d, $J = 5$ Hz), 147.88, 143.71, 137.02 (d, $J = 2$ Hz), 130.82 (d, $J = 3$ Hz), 130.32, 130.07 (br), 129.37, 128.89, 127.68 (d, $J = 6$ Hz), 126.80, 125.75, 125.50, 125.31, 124.23 (d, $J = 3$ Hz), 38.02 (calix–CH_2), 34.27 (calix–CH_2), 33.98 (*C*(CH_3)$_3$), 33.73 (*C*(CH_3)$_3$), 31.40 (C(*C*H_3)$_3$), 31.31 (C(*C*H_3)$_3$), 30.74 (calix–CH_2). ^{31}P-NMR (C_6D_6): δ 165.2. Anal. Calc. for $C_{50}H_{59}O_4P$: C, 79.54; H, 7.88. Found: C, 79.67; H, 7.83. MS(EI): M^+ (754).

2.2.3. [(PhSPC)H_2] (**3**)

A 25 ml reaction vessel equipped with a Teflon stopcock was charged with **2** (1.000 g, 1.32 mmol), sulfur (0.047 g, 1.47 mmol), and 1,4-dioxane (15 ml). The vessel was closed and heated at 60–70°C for 18 h. After cooling to ambient temperature, the precipitate was filtered off, and the filtrate was concentrated under reduced pressure to give an oily residue. The residue was triturated with heptane, extracted with pentane (10 ml) and quickly filtered. The pentane solution was cooled at −30°C for 18 h; the precipitate was collected, dried under vacuum (0.760 g, 73%) and identified as **3** on the basis of the following data. ^{1}H-NMR (C_6D_6): δ 7.47–7.63 (m, 2H, PhP), 7.20 (br, 2H, arom. CH), 6.67–6.80 (m, 3H, PhP), 7.11 (d, 2H, arom. CH), 6.99 (d, 2H, arom. CH), 6.66 (d, 2H, arom. CH), 6.38 (s, 2H, OH), 4.94 (d, $J = 14$ Hz, 2H, calix–CH_2), 4.47 (d, $J = 14$ Hz, 1H, calix–CH_2), 3.95 (d, $J = 14$ Hz, 1H, calix–CH_2), 3.65 (d, $J = 14$ Hz, 1H, calix–CH_2), 3.60 (d, $J = 14$ Hz, 2H, calix–CH_2), 2.91 (d, $J = 14$ Hz, 1H, calix–CH_2), 1.20 (s, 18H, ^{t}Bu), 1.08 (s, 18H, ^{t}Bu). ^{13}C-NMR (C_6D_6): δ 150.75, 148.15 (d, $J = 6$ Hz), 147.74, 143.37, 138.26, 135.48, 133.90 (d, $J = 2$ Hz), 131.46 (br), 129.37 (br), 128.89 (d, $J = 1$ Hz), 128.72, 128.50 (br), 126.62, 125.74, 37.53 (calix–CH_2), 36.12 (calix–CH_2), 33.98 (*C*(CH_3)$_3$), 33.94 (*C*(CH_3)$_3$), 33.08 (calix–CH_2), 31.56 (C(*C*H_3)$_3$), 31.18 (*C*(CH_3)$_3$). ^{31}P-NMR (C_6D_6): δ 75.2. Anal. Calc. for $C_{50}H_{59}O_4PS$: C, 76.30; H, 7.56. Found: C, 76.32; H, 7.69. MS(EI): M^+ (786).

2.3. Synthesis of titanium compounds **5**–**14**

2.3.1. [(^{t}BuPC)$TiCl_2$] (**5**)

A solution of $TiCl_4$ (0.214 g, 1.13 mmol) in pentane (8 ml) was added dropwise to a suspension of **1** (0.829 g, 1.13 mmol) in ether (30 ml) at −40°C. The flask was allowed to warm gradually up to room temperature and left stirring for 24 h. Volatiles were removed in vacuo, the residue was washed with pentane (3 × 10 ml), and the product was dried under vacuum. The light-red solid (0.860 g, 89%) was identified as **5** on the basis of the following data. ^{1}H-NMR (C_6D_6): δ 7.22 (d, 2H, $J = 2$ Hz, arom. CH), 7.11 (d, 2H, arom. CH), 7.01 (d, 2H, arom. CH), 6.83 (d, 2H, arom. CH), 4.69 (dd, $J = 14$ Hz, $J = 1$ Hz, 1H, calix–CH_2), 4.43 (d, $J = 14$ Hz, 1H, calix–CH_2), 3.76 (s, 4H, calix–CH_2), 3.24 (d, $J = 14$ Hz, 1H, calix–CH_2), 3.21 (d, $J = 14$ Hz, 1H, calix–CH_2), 1.38 (s, 18H, ^{t}Bu), 1.21 (s, 18H, ^{t}Bu), 0.62 (d, $J = 11.5$ Hz, 9H, P–C(CH_3)$_3$). ^{13}C-NMR (C_6D_6 = THF): δ 163.61, 149.54, 146.39, 145.28, 139.91, 137.45, 131.46, 127.22 (br), 126.13, 125.38, 125.15, 125.15, 40.58 (calix–CH_2), 37.50 (calix–CH_2), 34.88 (calix–CH_2), 35.63 (d, $J = 18$ Hz, P–*C*(CH_3)$_3$), 34.15 (*C*(CH_3)$_3$), 33.92 (*C*(CH_3)$_3$), 31.62 (C(*C*H_3)$_3$), 31.32 (C(*C*H_3)$_3$), 24.66(d, $J = 16$ Hz, P–C(*C*H_3)$_3$). ^{31}P-NMR (C_6D_6 = THF): δ 179.4. Anal. Calc. for $C_{48}H_{61}Cl_2O_4PTi$: C, 67.68; H, 7.22; Cl, 8.32. Found: C, 67.29; H, 7.14; Cl, 8.21. MS(EI): M^+ (850).

2.3.2. [(PhPC)$TiCl_2$] (**6**)

A solution of $TiCl_4$ (0.128 g, 0.67 mmol) in pentane (5 ml) was added dropwise to a suspension of **2** (0.507 g, 0.67 mmol) in ether (20 ml) at −78°C. The flask was allowed to warm gradually up to room temperature and left stirring for 24 h. Volatiles were removed in vacuo, the residue was washed with pentane (3 × 5 ml), and the product was dried under vacuum (0.550 g, 87%). An analytically pure sample was obtained as a CH_3CN

adduct by recrystallization from CH_3CN/CH_2Cl_2. **6** was identified on the basis of the following data: ^{1}H-NMR (C_6D_6): δ 7.86–8.00 (br m, 3H, Ph–P), 7.24 (d, 2H, $J = 2$ Hz, arom. CH), 7.04 (d, 2H, arom. CH), 6.99 (d, 2H, arom. CH), 6.82–6.94 (m, 2H, Ph–P), 6.66 (d, 2H, arom. CH), 6.38 (d, $J = 13$ Hz, 1H, calix–CH_2), 5.33 (d, $J = 13$ Hz, 2H, calix–CH_2), 3.71 (d, $J = 13$ Hz, 1H, calix–CH_2), 3.56 (d, $J = 13$ Hz, 2H, calix–CH_2), 3.41 (d, $J = 13$ Hz, 1H, calix–CH_2), 2.97 (d, $J = 13$ Hz, 1H, calix–CH_2), 1.10 (s, 18H, ^{t}Bu), 1.00 (s, 18H, ^{t}Bu), 0.65 (3H, CH_3CN). ^{13}C-NMR (C_6D_6): δ 161.69, 148.08, 146.66 (d, $J = 18$ Hz), 145.20, 141.47, 134.76 (d, $J = 4$ Hz), 134.33, 132.10, 131.01 (d, $J = 12$ Hz), 128.94 (d, $J = 2$ Hz), 128.30, 126.87, 126.38, 125.36 (br), 118.18 (CH_3CN), 36.76 (calix–CH_2), 36.00 (calix–CH_2), 34.19 ($C(CH_3)_3$), 34.14 ($C(CH_3)_3$), 33.00 (calix–CH_2), 31.30 (C(CH_3)$_3$), 31.25 (C(CH_3)$_3$), 0.72 (CH_3CN). ^{31}P-NMR (C_6D_6): δ 124.0. Anal. Calc. for (**6** · CH_3CN) $C_{52}H_{60}Cl_2NO_4PTi$: C, 68.42; H, 6.63; Cl, 7.77; N, 1.53. Found: C, 68.81; H, 7.28; Cl, 7.32; N, 1.08.

2.3.3. [(PhSPC)TiCl$_2$] (7)

A solution of $TiCl_4$ (0.170 g, 0.89 mmol) in pentane (5 ml) was added dropwise to a suspension of **3** (0.700 g, 0.89 mmol) in ether (20 ml) at -78°C. The flask was allowed to warm gradually up to room temperature and left stirring for 24 h. Volatiles were removed in vacuo, the residue was washed with pentane (3×10 ml) and the product was dried under vacuum. The light-brown solid (0.710 g, 88%) was identified as **7** on the basis of the following data. NMR data established that **7** exists as a 3.5:1 mixture of 1,2-alternate:cone isomers at room temperature: ^{1}H-NMR (1,2-alternate, **7a**) (C_6D_6): δ 7.34–7.48 (m, 2H, Ph–P), 7.22 (m, 4H, arom. CH), 7.11 (d, 2H, arom. CH), 6.91 (d, 2H, arom. CH), 6.66–6.74 (m, 3H, Ph–P), 4.61 (d, $J = 14$ Hz, 1H, calix–CH_2), 4.20 (d, $J = {}_18$ Hz, 2H, calix–CH_2), 4.09 (d, $J = {}_14$ Hz, 1H, calix–CH_2), 4.05 (d, $J = {}_18$ Hz, 2H, calix–CH_2), 3.44 (d, $J = 14$ Hz, 1H, calix–CH_2), 3.06 (d, $J = 14$ Hz, 1H, calix–CH_2), 1.32 (s, 18H, ^{t}Bu), 1.25 (s, 18H, ^{t}Bu). 1H-NMR (cone, **7b**) (C_6D_6): δ 7.24–7.38 (m, 2H, Ph–P), 7.12 (d, 2H, arom. CH), 6.92 (d, 2H, arom. CH), 6.81 (d, 2H, arom. CH), 6.64–6.77 (m, 3H, Ph–P), 6.52 (d, 2H, arom. CH), 5.88 (d, $J = 15$ Hz, 1H, calix–CH_2), 5.06 (d, $J = 14$ Hz, 2H, calix–CH_2), 3.65 (d, $J = 16$ Hz, 1H, calix–CH_2), 3.37 (d, $J = 14$ Hz, 2H, calix–CH_2), 3.33 (d, $J = 15$ Hz, 1H, calix–CH_2), 2.86 (d, $J = 16$ Hz, 1H, calix–CH_2), 1.09 (s, 18H, ^{t}Bu), 0.97 (s, 18H, ^{t}Bu). ^{13}C-NMR (C_6D_6, 75 °C) (1,2-alternate, **7a**): δ 164.21, 148.50, 148.33, 138.15, 130.69, 130.54, 130.48, 129.41 (d), 128.33 (br), 128.28, 126.85, 126.16, 125.74, 124, 31, 39.04 (calix–CH_2), 38.51 (calix–CH_2), 36.43 (calix–CH_2), 34.51 ($C(CH_3)_3$), 34.32 ($C(CH_3)_3$), 31.59 (C(CH_3)$_3$), 31.47 (C(CH_3)$_3$). ^{31}P-NMR (C_6D_6): δ 69.0 (1,2-alternate, **7a**); 74.2 (cone, **7b**). Anal. Calc. for $C_{50}H_{57}Cl_2O_4PSTi$: C, 66.44; H, 6.36; Cl, 7.84. Found: C, 66.12; H, 6.44; Cl, 7.99. MS(EI): M^+ (902).

2.3.4. [(DMSC)TiMe$_2$] (9)

Solid Me_2Mg·2THF (0.113 g, 0.57 mmol) was added to a suspension of (DMSC)$TiCl_2$ (**8**) [20] (0.469 g, 0.57mmol) in toluene (20 ml) and 1,4-dioxane (2 ml). After stirring for 2.5 h, the suspension was filtered through Celite, and volatiles were removed from the filtrate in vacuo. The solid residue was treated with pentane (15 ml), stirred for 15 min and cooled at -20°C for 1 h. The precipitate was collected by filtration and washed with pentane (2×5 ml). Toluene (7 ml) and pentane (20 ml) were introduced and the suspension was kept at -20°C overnight. After filtration, the pale-yellow precipitate was dried under vacuum. The product (0.330 g, 74%) was identified as **9** on the basis of the following data. ^{1}H-NMR (C_6D_6): δ 7.34 (d, $J = 2.5$ Hz, 2H, arom. CH), 7.21 (d, $J = 2.5$ Hz, 2H, arom. CH), 7.07 (d, 4H, d = 2.5 Hz, arom. CH), 4.44 (d, $J = 14.3$ Hz, 1H, calix–CH_2), 4.32 (d, $J = 16.5$ Hz, 2H, calix–CH_2), 4.04 (d, $J = 16.5$ Hz, 2H, calix–CH_2), 3.31 (d, $J = 14$ Hz, 1H, calix–CH_2), 3.29 (d, $J = 14.5$ Hz, 1H, calix–CH_2), 3.20 (d, 14 Hz, 1H, calix–CH_2), 1.35 (s, 18H, ^{t}Bu), 1.31 (s, 18H, ^{t}Bu), 1.16 (s, 3H, *exo*-$TiCH_3$), 0.32 (s, 3H, *exo*-$SiCH_3$), 0.11 (s, 3H, *endo*-$TiCH_3$), -1.45 (s, 3H, *endo*-$SiCH_3$). ^{13}C-NMR (C_6D_6): δ 158.44, 149.49, 144.60, 144.12, 134.02, 130.38, 129.27, 128.29, 127.10, 126.32, 125.22, 64.26 (*exo*-$TiCH_3$), 53.13 (*endo*-$SiCH_3$), 40.58 (calix–CH_2), 36.06 (calix–CH_2), 35.75 (calix–CH_2), 34.06 ($C(CH_3)_3$), 34.00 ($C(CH_3)_3$), 31.62 (C(CH_3)$_3$), 4.18 (*exo*-$SiCH_3$), -2.67 (*endo*-$SiCH_3$) Anal. Calc. for $C_{48}H_{64}O_4SiTi$: C, 73.82; H, 8.26. Found: C, 73.79; H, 8.22.

2.3.5. [(DMSC)Ti(CH$_2$Ph)$_2$] (10)

Solid $(PhCH_2)_2Mg$·2THF (1.196 g, 3.40 mmol) was added to a suspension of (DMSC)$TiCl_2$ (**8**) [20] (2.808 g, 3.40 mmol) in ether (100 ml). After stirring for 1 h, the suspension was filtered through Celite, and volatiles were removed from the filtrate in vacuo. The light-orange residue was washed with pentane (5×5ml) and dried under vacuum. The product (2.840 g, 89%) was identified as **10** on the basis of the following data. ^{1}H-NMR (CD_2Cl_2): δ 6.85–7.30 (several multiplets, 8H, $PhCH_2$), 7.23 (d, $J = 2$ Hz, 2H, arom. CH), 7.14 (d, $J = 2$ Hz, 2H, arom. CH), 7.01 (d, 2H, d = 2 Hz, arom. CH), 6.96 (d, 2H, $J = 2$ Hz, arom. CH), 6.55 (d, $J = 8$ Hz, 2H, *o*-CH of *endo*-$PhCH_2$), 4.42 (d, $J = 14$ Hz, 1H, calix–CH_2), 4.24 (d, $J = 16.5$ Hz, 2H, calix–CH_2), 3.97 (d, $J = 16.5$ Hz, 2H, calix–CH_2), 3.36 (d, $J = 14$ Hz, 1H, calix–CH_2), 3.08 (d, $J = 14.5$ Hz, 1H, calix–CH_2), 2.97 (d, $J = 14.5$ Hz, 1H, calix–CH_2), 2.11 (s, 2H, *exo*-$TiCH_2Ph$) 1.28 (s, 18H, ^{t}Bu), 1.20 (s, 18H, ^{t}Bu), 0.92 (s, 2H, *endo*-$TiCH_2Ph$), 0.27 (s, 3H, *exo*-$SiCH_3$), -1.72 (s, 3H, *endo*-$SiCH_3$). ^{13}C-NMR (CD_2Cl_2): δ 159.41, 149.58, 147.48, 144.95, 144.22, 142.66, 134.48, 130.30, 129.73, 129.54, 129.41, 128.39, 127.31, 126.88, 126.68, 126.55, 126.48, 125.39, 124.52, 122.74, 86.83

(*exo*-$TiCH_2Ph$), 80.65 (*endo*-$TiCH_2Ph$), 40.25 (calix–CH_2), 36.43 (calix–CH_2), 35.15 (calix–CH_2), 34.31 ($C(CH_3)_3$), 34.13 ($C(CH_3)_3$), 31.63 ($C(CH_3)_3$), 31.54 ($C(CH_3)_3$), 3.98 (*exo*-$SiCH_3$), −2.72 (*endo*-$SiCH_3$). Anal. Calc. for $C_{60}H_{72}O_4SiTi$: C, 77.22; H, 7.78. Found: C, 76.98; H, 7.78.

2.3.6. [(DMSC)Ti(Me)(NCCH$_3$)]BAr$_4^F$ (11)

Compound **9** (7.8 mg, 10 mmol) and $[Ph_3C]BAr_4^F$ (11.1 mg, 10 mmol) were co-dissolved in CD_2Cl_2 in presence of an excess of CH_3CN; resulting in immediate formation of a red solution. Numerous attempts to isolate the product were unsuccessful due to decomposition upon crystallization and exposure to reduced pressure. The product was therefore characterized in solution in the presence of the by-product (Ph_3CCH_3) as follows. ^{1}H-NMR (CD_2Cl_2): δ 7.72 (*o*-Ar^F), 7.56 (*p*-Ar^F), 7.00–7.30 (m, 21H, $(C_6H_5)_3C$ and calix. arom. CH), 6.89 (d, $J = 2.5$ Hz, 2H, calix. arom. CH), 4.43 (d, $J = 14.5$ Hz, 1H, calix–CH_2), 4.20 (d, $J = 16.5$ Hz, 2H, calix–CH_2), 3.96 (d, $J = 16.5$ Hz, 2H, calix–CH_2), 3.77 (d, $J = 13$ Hz, 1H, calix–CH_2), 3.35 (d, $J = 14.5$ Hz, 1H, calix–CH_2), 3.18 (d, $J = 13$ Hz, 1H, calix–CH_2), 2.17 (Ph_3CCH_3), 1.97 (s, 3H, $NCCH_3$), 1.28 (s, 18H, ^{t}Bu), 1.22 (s, 18H, ^{t}Bu), 0.35 (s, 3H, *exo*-$SiCH_3$), −0.37 ($TiCH_3$), −1.57 (s, 3H, *endo*-$SiCH_3$).

2.3.7. [(DMSC)Ti(CH$_2$Ph)(NCCH$_3$)]BAr$_4^F$ (12)

Compound **10** (0.117 g, 125 mmol) was treated with CH_3CN (60 mg, 1.5 mmol) in CH_2Cl_2 (4 ml), followed with $[Ph_3C][BArF_4]$ (0.138 g, 125 mmol). After stirring the mixture for 10 min, most of the CH_2Cl_2 was removed in vacuo. The dark-red oily residue was triturated with 1:1 toluene–pentane (3 ml), washed with pentane (5 × 1 ml), and dried under vacuum; high solubility of the product in pentane resulted in substantial loss of product. The product (0.085g, 40%) was identified as **12** on the basis of the following data. ^{1}H-NMR (CD_2Cl_2) δ: 7.77 (*o*-Ar^F), 7.60 (*p*-Ar^F), 7.30–7.55 (m, 3H, m-,p-$C_6H_5CH_2$), 7.25 (d, $J = 2.5$ Hz, 2H, calix. arom. CH), 7.21 (d, $J = 2.5$ Hz, 2H, calix. arom. CH), 7.13 (d, $J = 2.5$ Hz, 2H, calix. arom. CH), 7.08 (d, $J = 2.5$ Hz, 2H, calix. arom. CH), 4.53 (d, $J = 14.5$ Hz, 1H, calix–CH_2), 4.22 (d, $J = 17$ Hz, 2H, calix–CH_2), 4.11 (d, $J = 17$ Hz, 2H, calix–CH_2), 3.51 (d, $J = 14.5$ Hz, 1H, calix–CH_2), 3.41 (d, $J = 14$ Hz, 1H, calix–CH_2), 2.83 (d, $J = 14$ Hz, 1H, calix–CH_2), 2.24 (s, 3H, $NCCH_3$), 1.32 (s, 18H, ^{t}Bu), 1.21 (s, 18H, ^{t}Bu), 1.18 (s, 2H, CH_2Ph), 0.47 (s, 3H, *exo*-$SiCH_3$), −1.50 (s, 3H, *endo*-$SiCH_3$). ^{13}C-NMR (CD_2Cl_2): δ 162.34 (q, $J = 50$ Hz, *ipso*-Ar^F), 161.26, 150.00, 147.15, 144.40, 138.59, 136.70, 135.34 (br s, *o*-Ar^F), 131.32, 130.84, 130.38, 130.26, 129.76, 129.13 (br s, m-Ar^F), 128.08, 127.18, 127.03, 126.77, 125.57, 125.13 (q, $J = 272$ Hz, CF_3), 118.00 (br s, *p*-Ar^F), 100.26 ($PhCH_2$), 40.74 (calix–CH_2), 36.54 (calix–CH_2), 36.17 (calix–CH_2), 34.60 ($C(CH_3)_3$), 34.20 ($C(CH_3)_3$), 31.52 ($C(CH_3)_3$), 31.49 ($C(CH_3)_3$), 4.51 (*exo*-$SiCH_3$), 3.49 ($NCCH_3$), −2.66 (*endo*-$SiCH_3$). ^{19}F-NMR ($CDCl_3$): δ −63.1. Anal. Calc. for $C_{87}H_{80}BF_{24}NO_4SiTi$: C, 59.84; H, 4.62; N, 0.80. Found: C, 59.61; H, 4.66; N, 1.02 (by NMR, contains ca. 1.2 CH_3CN per molecular unit).

2.3.8. [(DMSC)Ti(Me)(OTf)] (13)

To a solution of **9** (0.391 g, 0.500 mmol) in CH_2Cl_2 (15 ml) was added $[Ph_3C][OTf]$ (0.196 g, 0.500 mmol). A color change, from pale-yellow to brown, occurred immediately. After stirring the mixture for 1 h, volatiles were removed in vacuo. The orange–yellow solid obtained was triturated with heptane (5 ml), washed on a fritted funnel with pentane (4 × 5 ml) and dried in vacuo. The product (0.370 g, 81%) was identified as **13** on the basis of the following data: ^{1}H-NMR ($CDCl_3$): δ 7.09 (d, $J = 2.5$ Hz, 2H, arom. CH), 6.98 (d, $J = 2.5$ Hz, 2H, arom. CH), 6.91 (d, $J = 2.5$ Hz, 2H, arom. CH), 6.89 (d, $J = 2.5$ Hz, 2H, arom. CH), 4.42 (d, $J = 14$ Hz, 1H, calix–CH_2), 4.03 (d, AB, $J = 17$ Hz, 2H, calix–CH_2), 3.97 (d, AB, $J = 17$ Hz, 2H, calix–CH_2), 3.37 (d, $J = 14$ Hz, 1H, calix–CH_2), 3.10 (d, $J = 14$ Hz, 1H, calix–CH_2), 2.09 (br d, $J = 14$ Hz, 1H, calix–CH_2), 1.25 (s, 18H, ^{t}Bu), 1.17 (s, 18H, ^{t}Bu), 0.37 (s, 3H, *exo*-$SiCH_3$), 0.12 (s, 3H, $TiCH_3$), −1.61 (s, 3H, *endo*-$SiCH_3$). ^{13}C-NMR ($CDCl_3$ + THF): δ 159.84, 149.77, 145.18, 144.01, 137.02, 130.08, 130.02, 126.93, 126.58, 126.21, 125.93, 124.95, 80.34 ($TiCH_3$), 40.71 (calix–CH_2), 37.41 (s, calix–CH_2), 35.90 (s, calix–CH_2), 34.39 ($C(CH_3)_3$), 34.13 ($C(CH_3)_3$), 31.60 ($C(CH_3)_3$), 31.58 ($C(CH_3)_3$), 4.61 (*exo*-$SiCH_3$), −2.68 (*endo*-$SiCH_3$). Anal. Calc. for $C_{48}H_{61}F_3O_7SSiTi$: C, 63.01; H, 6.72; Cl, 0.00. Found: C, 62.78; H, 7.00; Cl, 0.00.

2.3.9. Synthesis of [(DMSC)Ti(CH$_2$Ph)(OTf)] (14)

To a solution of **10** (0.410 g, 0.440 mmol) in a 1:1 mixture of toluene/CH_2Cl_2 (15 ml) was added $[Ph_3C][OTf]$ (0.167 g, 0.440 mmol). A minor amount of insolubles was filtered off. After stirring for 1 h, the solution was concentrated almost to dryness under reduced pressure. The brownish solid residue was stirred in pentane (5 ml) for 3 min, filtered, and washed on a fritted funnel with pentane (2 × 5 ml). The product (0.160 g, 37%) was dried under vacuum (while the reaction is quantitative by ^{1}H-NMR, **14** was isolated in low yield because its solubility in hydrocarbon solvents is comparable to that of the by-product, Ph_3CCH_2Ph). **14** was identified on the basis of the following data. ^{1}H-NMR (CD_2Cl_2): δ 7.0–7.25 (m, 8H), 6.82–6.92 (m, 3H), 6.75 (d, $J = 7.5$ Hz, 2H, *o*-$C_6H_5CH_2$), 4.41 (d, $J = 15$Hz, 1H, calix–CH_2), 4.20 (d, AB, $J = 17$ Hz, 2H, calix–CH_2), 3.98 (d, AB, $J = 17$ Hz, 2H, calix–CH_2), 3.37 (d, $J = 15$ Hz, 1H, calix–CH_2), 3.06 (br d, $J = 14$ Hz, 1H, calix–CH_2), 2.35 (br d, $J = 14$ Hz, 1H, calix–CH_2), 1.32 (s, 18H, ^{t}Bu), 1.17 ($PhCH_2$), 1.10 (s,

18H, ^{t}Bu), 0.35 (s, 3H, *exo*-$SiCH_3$), −1.54 (s, 3H, *endo*-$SiCH_3$). ^{13}C-NMR ($CDCl_3$): δ 161.10, 149.77, 145.50, 144.24, 137.82, 136.89, 132.88, 129.92, 129.26, 129.22, 127.30, 126.72, 126.49, 125.26, 103.11 ($PhCH_2$), 40.16 (calix–CH_2), 36.42 (br s, calix–CH_2), 34.44 ($C(CH_3)_3$), 34.04 ($C(CH_3)_3$), 31.62 ($C(CH_3)_3$), 31.39 ($C(CH_3)_3$), 4.12 (*exo*-$SiCH_3$), −2.58 (*endo*-$SiCH_3$). ^{19}F-NMR ($CDCl_3$): δ −69.3. ^{19}F-NMR ($CDCl_3$ + excess of CH_3CN): δ −78.8. Anal. Calc. for (**14** · toluene) $C_{61}H_{73}F_3O_7SSiTi$: C, 67.63; H, 6.79; Cl, 0.00. Found: C, 67.45; H, 6.96; Cl, 0.00.

2.4. Ethylene polymerization

The catalyst precursor (20 mmol of Ti) was dissolved in toluene (40 ml) and treated with the excess of MAO (Al/Ti ratio 500/1). This solution was placed into a 100 ml Schlenk flask, the nitrogen atmosphere was replaced with ethylene, and ethylene pressure of 1 atm was maintained therefrom by slowly bubbling ethylene through the solution, controlling the pressure with the bubbler at the outlet. Polymerizations were quenched with MeOH (10 ml) and then 1 M HCl (30 ml), and the resulting suspension was vigorously stirred until both layers were colorless and clearly separated. Polyethylene was filtered off, washed with MeOH, 1 M HCl, acetone–aqueous HCl mixture, distilled water and acetone and then dried at 70°C for 48 h.

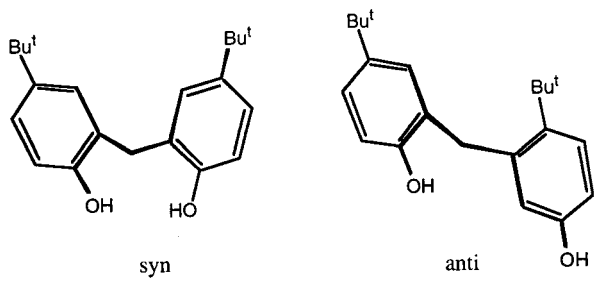
2.5. Crystal data

$C_{50}H_{59}O_4P$, triclinic, space group = $P\bar{1}$, a = 13.4485(2) Å, b = 13.5672(2) Å, c = 15.1013(2) Å, α = 66.236° (1), β = 82.248° (1), γ = 62.344° (1), U = 2229 Å^3, Z = 2, 7845 unique data (35683 measured, 1.48° ≤ 2θ ≤ 25.00°, R_{int} = 0.10), 532 parameters, R_1 = 0.0650, wR_2 (all data) = 0.1899. Single crystals suitable for X-ray diffaction were obtained by crystallization from toluene. A crystal with the dimensions 0.31 × 0.20 × 0.18 mm was mounted on a glass fiber in random orientation. Preliminary examination and data collection was performed using a Bruker SMART CCD X-ray diffractometer equipped with graphite monochromated Mo–K_α radiation (λ = 0.71073 A). Preliminary unit cell constants were determined with a set of 45 narrow frames (0.3° in ϖ) scans. A total of 4028 frames of intensity data were collected with a frame width of 0.3° in ϖ and counting time of 15 s frame^{-1} at a crystal to detector distance of 4.9 cm. The double-pass method of scanning was used to exclude any noise. The collected frames were integrated using orientation matrix determined from the narrow frame scans. The SMART software package (Bruker Analytical X-Ray, Madison, WI, 1997) was used for data collection and the SAINT package (Bruker Analytical X-Ray, Madison, WI, 1997) was used for frame integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by global refinement of *xyz* centroids of 8192 reflections. Structure solution and refinement were carried out using the SHELXTL-PLUS software package (Sheldrick, Bruker Analytical X-Ray Division, Madison, WI, 1997). The structure was solved by direct methods. Full matrix least-squares refinement was carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$. The non-hydrogen atoms were refined anisotropically to convergence. All hydrogen atoms were treated using appropriate riding models (AFIX m3).

3. Results and discussion

3.1. Ligand synthesis

Reaction of dilithium or dipotassium salt of *p-tert*-butylcalix[4]arene (generated *in situ*) with ^{t}BuPCl$_2$ or PhPCl$_2$ proceeded at room temperature to yield phosphorus-bridged *p-tert*-butylcalix[4]arene compounds (^{t}BuPC)H$_2$ (**1**) and (PhPC)H$_2$ (**2**), respectively (Scheme 1). The reaction of **2** with sulfur (1.1 equivalent) in 1,4-dioxane at 60–70°C for 18 h produced PhSP-bridged *p-tert*-butylcalix[4]arene (PhSPC)H$_2$ (**3**) in good yield (Scheme 1); no reaction occurred between **1** and sulfur under comparable conditions. The formulations given for **1**–**3** were confirmed by microanalysis and/or mass spectrometry. Their molecular structures were established by NMR data, and X-ray crystallography for **2**. In this regard, the bridging methylenes and the methyls from the ^{t}Bu groups are useful probes for deducing symmetry properties of *p-tert*-butylcalix[4]arenes [12,26]. Both **1** and **2** possess C_s symmetry and adopt the 1,2-alternate conformation in solution. Their ^{1}H-NMR spectra show two singlets for the ^{t}Bu groups, and two pairs of doublets and an AB system for the bridging methylene protons. The AB system integrates as four protons and represents the methylene groups not included in the mirror plane. In their ^{13}C-NMR spectra, three resonances are present at δ 30.80, 34.11, and 37.44 (doubly intense) (**1**) and δ 30.74, 34.27, and 38.02 (doubly intense) (**2**) for the bridging methylene carbons. These data are consistent with ^{13}C-NMR data for several calix[4]arenes reported by de Mendoza and co-workers [26] which showed that



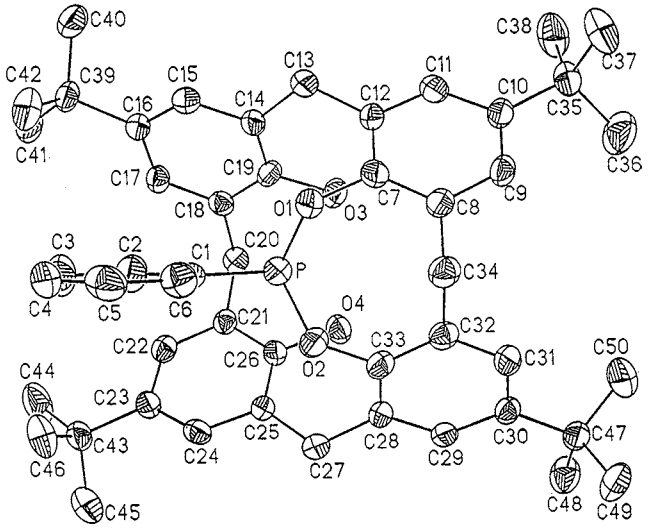


Fig. 1. Molecular structure of [(PhPC)H_2] (**2**), showing the atom labelling scheme.

Table 1
Selected bond distances (Å) and angles (°) for **2**

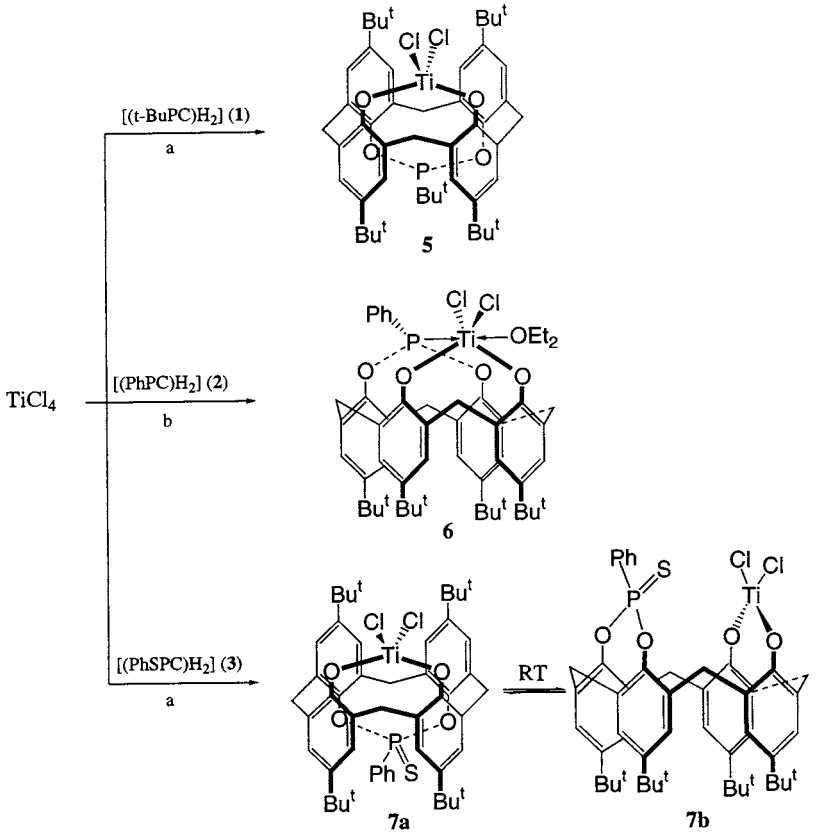
P–O(1)	1.662(2)
P–O(2)	1.663(2)
P–C(1)	1.816(3)
O(1)–C(7)	1.407(4)
O(2)–C(33)	1.409(4)
O(3)–C(19)	1.396(4)
O(4)–C(26)	1.401(4)
O(1)–P–O(2)	102.85(12)
O(1)–P–C(1)	95.59(13)
O(2)–P–C(1)	95.99(13)
C(7)–O(1)–P	117.7(2)
C(33)–O(2)–P	117.1(2)
C(8)–C(34)–C(32)	109.2(3)
C(18)–C(20)–C(21)	110.8(3)
C(12)–C(13)–C(14)	121.5(3)
C(28)–C(27)–C(25)	121.6(6)

methylene carbons of calix[4]arenes are characterized by a resonance around δ 31 when the attached phenol rings are in a *syn* orientation. In contrast, a resonance around δ 37 is characteristic when the phenol rings are *anti* oriented [26]. The authors attributed this difference to the different angles imposed at the methylene carbon in these two steric arrangements. Moreover, the ^{1}H and ^{13}C-NMR spectra of **1** and **2** are similar to those of 1,2-alternate dimethylsilyl-bridged *p-tert*-butylcalix[4]-arene derivative (DMSC)H_2 (**4**), recently reported by Lattman and colleagues [27]. Single-crystal X-ray analysis of **2** confirmed the structure assigned by spectroscopy: the molecule exists in the 1,2-alternate conformation. A thermal ellipsoid plot of **2** showing the atom labelling is presented in Fig. 1. As shown in the Figure, the geometry around phosphorus is pyramidal and the phenyl group points away from the 'unbridged' oxygen atoms. Thus, the lone pair on phosphorus points toward the center of the cavity. Selected bond distances and angles are listed in Table 1. The P–C and P–O bond lengths are comparable to those reported for other phosphorus-bridged calix[4]arenes [28]. The C(ring)–CH_2–C(ring) angles between *syn*- and *anti*-oriented phenol rings (Table 1) are in line with values expected for calix[4]arenes: the C(ring)–CH_2–C(ring) angle is always smaller for *syn* orientations (107–111°) than for anti orientations (111–118°) [26].

Complex **3** is also C_s symmetric, as shown by its ^{1}H- and ^{13}C-NMR spectra. Two singlets for the ^{t}Bu groups and three pairs of doublets for the methylene protons are present in its ^{1}H-NMR spectrum. However, the spectrum is distinctly different from the spectra of **1**, **2**, and **4**. The absence of an AB system is notable, and the J_{H-H} coupling constant for the doubly intense pair of doublets ($J_{H-H} = 14$ Hz) is smaller compared to the corresponding coupling constant of **1**, **2**, or **4** [27] ($J_{H-H} = 16–17$ Hz). In its ^{13}C-NMR spectrum, the bridging methylene carbons resonate at δ 37.53, 36.12, and 33.08 (doubly intense). Complex **3** evidently adopts the cone conformation in solution. Apparently, bridging a pair of phenolic oxygens results in a downfield shift of the resonances for the *syn*-connected methylene carbon, due probably to changes in angle at the methylene carbon [26]. These chemical shifts are comparable to those reported for the methylenes of doubly bridged calix[4]arene phosphate ester derivatives in the cone conformation (34–38 ppm) [28]. Ring-current effects from the phosphorus-bound phenyl groups could also cause a downfield shift of the *syn*-connected methylene carbons [29]. Variable-temperature ^{1}H-NMR studies show that **1**–**3** are conformationally stable up to 348 K.

3.2. Titanium(IV) complexes: synthesis and reactivity

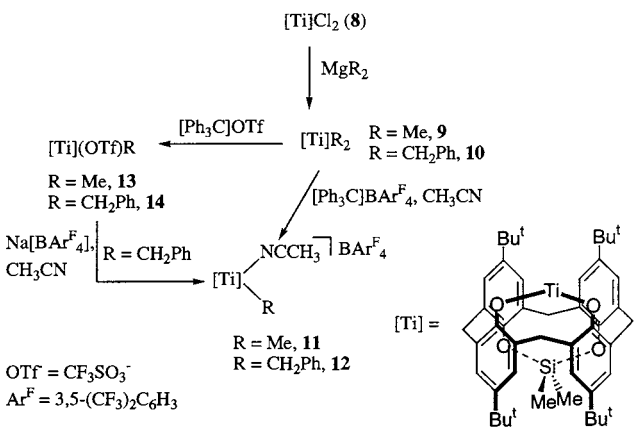
The reactions of **1**–**3** with $TiCl_4$ furnished titanium(IV) dichloride complexes L_2TiCl_2 (**5**–**7**) (L_2 = ^{t}BuPC, PhPC, or PhSPC, respectively) as air- and moisture-sensitive solids in moderate to excellent yield (Scheme 2). Each compound's proposed structure is consistent with all of its analytical and spectroscopic data (vide infra). The compounds are practically insoluble in aliphatic hydrocarbon solvents. However, (PhPC)$TiCl_2$ (**6**) and (PhSPC)$TiCl_2$ (**7**) are quite soluble in aromatic hydrocarbon solvents while (^{t}BuPC)$TiCl_2$ (**5**) is only sparingly soluble. Adding a few drops of a coordinating solvent, such as THF or CH_3CN, greatly improves the solubility of **5** in hydrocarbon solvents. This solubilizing effect of THF or CH_3CN was utilized in obtaining NMR spectra of some of the complexes (see Section 2). Dialkyl derivatives (DMSC)$TiMe_2$ (**9**) and (DMSC)Ti($CH_2Ph)_2$ (**10**) were obtained in good yield from reaction of



Scheme 2.

(DMSC)$TiCl_2$ (**8**) [20] with the appropriate dialkylmagnesium compound (Scheme 3). Their formulation and structure were confirmed by microanalysis and spectroscopic characterization (vide infra). **5**–**10** are thermally stable at 80°C in benzene, undergoing no significant decomposition for hours. Whereas, the reaction of **8** with dibenzylmagnesium is fast and facile at ambient temperature and relatively insensitive to the solvent choice, a significant amount of black precipitate is always formed in the reaction with dimethylmagnesium. It seems likely that the decomposition of **9** by Me_2Mg occurs during its preparation. This proposal finds support in the observation that toluene solutions of pure **9** and Me_2Mg turn black after a few minutes. The reaction of **8** with alkylating reagents such as alkyllithium and Grignard reagents produced complex mixtures. This is in contrast to the report by Floriani and coworkers [16] showing calix[4]arene-based titanium–alkyl complexes can be prepared by alkylation of the dichloride precursors with alkyllithium and Grignard reagents. A potential side-reaction involves competing displacement of the calix[4]arene ligand rather than the chloride ligands, yielding an unstable R_2TiCl_2 species which rapidly decomposes. It is reasonable to expect that the displacement of a tetradentate calix[4]arene ligand (Floriani's case) would be less facile than the displacement of a bidentate one. However, we cannot rule out reduction of **8** to an unknown Ti(III) species by alkyllithium and Grignard reagents.

Cationic metallocene alkyl complexes have been identified as the chain-propagating species in homogeneous Ziegler–Natta α-olefin polymerization [30–33]. Therefore, we attempted to generate the cationic derivatives of **9** and **10** by protolysis with $[(Et_2O)_2H]BAr^F_4$ (Ar^F =



Scheme 3.

$(CF_3)_2C_6H_3$). Unfortunately, the reactions were complicated by side-reactions that involved destruction of the dimethylsilyl calix[4]arene (DMSC) ligand structure[1]. However, alkyl abstraction with $[Ph_3C]BAr^F_4$ proceeded cleanly in the presence of CH_3CN in a variety of solvents including $CHCl_3$, CH_2Cl_2, and C_6H_6 to produce $[(DMSC)Ti(NCCH_3)Me]BAr^F_4$ (**11**) and $[(DMSC)Ti(NCCH_3)(CH_2Ph)]BAr^F_4$ (**12**) (Scheme 3). In solution, **11** and **12** are quite stable, undergoing no significant decomposition at room temperature over 24 h in methylene chloride. However, only **12** could be isolated as a solid; it is extremely soluble in polar and aromatic solvents and turns into an oil upon addition of any solvent. **11** decomposes gradually as the solvent is removed and all attempts to crystallize it at low temperature have failed, as have attempts to generate cationic complexes in the presence of other donor ligands such as PMe_3 or PCy_3[2]. Alkyl abstraction did not occur cleanly in the absence of a donor ligand in weakly coordinating solvents, although the corresponding organic product (Ph_3CMe or Ph_3CCH_2Ph) was always formed quantitatively (by ^{1}H-NMR). The cation, if ever formed, is presumably unstable and rapidly decomposes to unidentified products; consistent with its very low electron count and coordinative unsaturation. Treatment of **9** and **10** with $[Ph_3C]OTf$ ($OTf = CF_3SO_3^-$) in 1:1 molar ratio led to the alkyltriflato complexes [(DMSC)Ti(OTf)Me] (**13**) and [(DMSC)Ti(OTf)(CH_2-Ph)] (**14**) (Scheme 3). The reaction of **14** with $Na[BAr^F_4]$ in presence of CH_3CN produced **12** (Scheme 3). Under analogous conditions, **13** did not give **11** but instead decomposed, reflecting the greater stability of **12** compared to **11**. The triflate ligand in **14** is readily dissociated in the presence of a donor ligand. Thus, when CH_3CN is added to a benzene-d_6 solution of **14**, the resonance for the triflate group in the ^{19}F-NMR spectrum at δ −69.3 is shifted to δ −78.8, which corresponds to the chemical shift of the triflate anion in $[Ph_3C]OTf$.

[1] In general, protonation of **10** led to somewhat cleaner reaction (by NMR) but in all cases it was evident that at least partial decomposition due to the destruction of the DMSC ligand structure tended to occur. This is supported by the fact that when a mixture formed by reacting **9** or **10** with $[(Et_2O)_2H]BAr^F_4$ in CH_2Cl_2/pentane was kept at −20°C for several weeks, $[(calix)_2Ti_2]$ [17] precipitated (calix = tetraanion of *p-tert*-butylcalix[4]arene).

[2] In the presence of PMe_3, alkyl abstraction proceeds over a period of days to produce several unknown calixarene-based products. The reaction can be monitored by appearance of Ph_3CR (R = Me or CH_2Ph) in the ^{1}H NMR spectrum. The formation of a strong $[Ph_3C–PMe_3]^+$ adduct which has very low degree of dissociation may explain this sluggishness. In support of this proposal, when PCy_3 is used instead of PMe_3, the reaction proceeds much faster (in minutes). $[Ph_3C–PCy_3]^+$ adduct, if formed, should be much less stable due to increased steric hinderance.

3.3. NMR analysis

The methyls of the ^{t}Bu groups and the bridging methylenes are useful spectroscopic probes for characterizing different symmetry properties and conformations of calix[4]arene-based metal complexes. Compounds **5**, **9**–**14** all exist in 1,2-alternate conformation and possess C_s symmetry. Their ^{1}H-NMR spectra contain two singlets for the ^{t}Bu groups, and two pairs of doublets and a broad singlet or an AB system (integrating as four protons) for the bridging methylene protons (see Section 2). Their ^{13}C-NMR spectra show *anti*-connected bridging methylenes at around 40 ppm while *syn*-connected bridging methylenes appear at around 36 ppm, consistent with the corresponding chemical shifts for 1,2-alternate doubly dimethylsilyl-bridged calix[4]arene (δ 39.9 and 35.6) [27] and the explanation by de Mendoza and co-workers [26]. The chemical shifts of the Me groups of the $SiMe_2$ unit and of the alkyl substituents on titanium are also diagnostic of 1,2-alternate conformation for the DMSC-based compounds **9**–**14**. For example, the '*endo*' Me group on silicon is located inside the calixarene cavity (above the centers of two aromatic rings), while the '*exo*' Me group is on the outside. Hence, *endo* and *exo* groups resonate as two separate signals in the ^{1}H- and ^{13}C-NMR spectra (see Section 2). NMR signals of the *endo* groups are strongly shielded compared to corresponding signals of the *exo* groups, due most likely to ring current effect [29]. This difference between the *exo*- and *endo*-substituents is also manifested in the reactivity of the compounds. Thus, **11**–**14** are formed by abstraction of the more exposed *exo*-alkyl. In other words, reaction occurs via the less hindered face; abstraction of the second alkyl by Ph_3C^+ is much slower (hours versus a few minutes for the first abstraction) and leads to decomposition. Unfortunately, our attempts to obtain single crystals of these compounds suitable for X-ray structure determinations have thus far been unsuccessful.

$[(PhPC)TiCl_2]$ (**6**) has C_s symmetry and adopts the cone conformation in solution. The molecular structure of **6** was characterized as follows: Its ^{1}H-NMR spectrum shows two singlets for the ^{t}Bu groups, and three pairs of doublets for the bridging methylene protons. Three resonances are present in its ^{13}C-NMR spectrum for the bridging methylene carbons (see Section 2), and the resonance at δ 33.00 is doubly intense. One resonance at δ 124.0 is observed in its $^{31}P\{^1H\}$-NMR spectrum. This represents an upfield shift from 'free **2**' (δ 165.2) and is likely indicative of an interaction between phosphorus and the electrophilic titanium center. $[(PhSPC)TiCl_2]$ (**7**) was isolated as a 3.5:1 mixture of 1,2-alternate and cone conformers. While the initial ratio of the conformers varies somewhat with the isolation procedure, solutions of **7** gradually equilibrate to this ratio. Variable-temperature NMR analysis of **7** from

Table 2
Ethylene polymerization at 25°C [a]

Catalyst	Catalyst (mmol)	Molar excess of MAO	Time (min)	Activity (Kg mol_{cat}^{-1} h^{-1})
5	0.02	500	30	9
6	0.02	500	30	70
7	0.02	500	30	15
8	0.02	500	30	35
9	0.02	500	30	15
10	0.02	500	30	25
14	0.02	500	30	24

[a] 1 atm C_2H_4 pressure bubbled through 40 ml toluene mixture of catalyst/MAO.

298 to 348 K in C_6D_6 showed the ratio of 1,2-alternate to cone conformer increased reversibly from 3.5:1 to 7:1 over this temperature range.

3.4. Ethylene polymerization

At 25°C with 500 molar equiv of methylalumoxane (MAO) as cocatalyst, **5**–**10** and **14** showed ethylene polymerization activities (Table 2) comparable to those reported for several noncyclopentadienyl-based Ti and Zr systems [2d]. With the exception of **6**[3], the compounds were inactive towards higher α-olefins, such as propene and 1-hexene, under comparable conditions; increasing the temperature did not promote polymerization. The modest ethylene polymerization activities may be due to several factors, including a low equilibrium concentration of the putative active cationic species. We were unable to generate cationic complexes from **9** and **10** by alkyl abstraction in the absence of a donor ligand (vide supra). Moreover, we observed no poly- or oligomerization of ethylene when either **9** or **10** was activated under an atmosphere of ethylene with $[Ph_3C]BAr_4^F$ in CD_2Cl_2 or C_6D_6. Other reasons for the modest activities observed may be MAO interaction with the O–E–O bridge (E = P or Si) of the calix[4]arene ligands and/or steric congestion at titanium. Coordination of MAO to the O–E–O bridge oxygens could disfavor formation of the cationic species by increasing the effective positive charge on the calix[4]arene ligand oxygens and thus the Ti center. An analogous explanation was proposed for the lower activity of methoxy-substituted bis(indenyl)zirconium complexes [34]. Alternatively, MAO interaction could disrupt the O–E–O bridge and thereby result in a loss of conformational rigidity[4]. It is interesting that **6**, which exists in cone formation and thus has an open face for reactivity, displayed the highest activity of the complexes (Table 2). However, stabilization of the cationic species by Ti–P interaction would lead to an increased concentration of the active catalyst and hence to higher activity. A similar Ti–S interaction has been proposed for the increased activity of an S-bridged biphenolate titanium (IV) dichloride complex [2d,2f,35].

4. Conclusions

In 1,2-alternate conformation, *p*-*tert*-butylcalix[4]arene-derived chelating bis(aryloxide) ligands sterically define reaction sites at the titanium center; substitution occurs at the sterically less hindered site. With MAO as co-catalyst, titanium derivatives **5**–**10** and **14** showed modest activities in ethylene polymerization. Studies of organic transformations mediated by these and related complexes are currently underway in our laboratory. Our results will be presented in future publications.

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 118419 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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[3] At 25°C with 500 molar equivalent MAO as cocatalyst, **6** oligomerizes 1-hexene. Efforts to characterize the products and enhance reactivity are in progress.

[4] Some decomposition occurs with apparent loss of DMSC ligand structure when $(DMSC)TiMe_2$ (**9**) is treated with an excess of $AlCl_3$ in benzene-d_6 under an atmosphere of ethylene. While these conditions are only a crude approximation of the polymerization conditions, the major product observed by ^{1}H-NMR was **8**. This suggests that alkyl/chloride exchange between Al and Ti may be preferred over attack on the Si–O bonds.

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