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Mono(pentamethylcyclopentadienyl)titanium and -zirconium Complexes Supported by Chiral Diolate Ligands. X-ray Crystal Structures of $[(\eta\text{-}C_5Me_5)TiCl(\mu\text{-}\eta^1,\eta^1\text{-}2\text{-}CF_3\text{-dpbd})]_2$ and $[HNEt_3][(\eta\text{-}C_5Me_5)_2Zr_2Cl_2(\mu\text{-}Cl)(\mu\text{-}\eta^1,\eta^2\text{-}3,5\text{-}Me_2\text{-dpbd})_2]$

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Reaction of optically pure (*S*,*S*)-butadiene diepoxide (**1**) with 2 equiv of Grignard reagent ArMgBr (Ar = $2\text{-}CF_3C_6H_4$ or $3,5\text{-}Me_2C_6H_3$) in the presence of copper(I) iodide produces the chiral substituted diphenylbutanediols (dpbd) (2*S*,3*S*)-$ArCH_2CH(OH)CH(OH)CH_2Ar$ (Ar = $2\text{-}CF_3C_6H_4$ (**2**), abbreviated $2\text{-}CF_3\text{-dpbdH}_2$; Ar = $3,5\text{-}Me_2C_6H_3$ (**3**), abbreviated $3,5\text{-}Me_2\text{-dpbdH}_2$). The mono(pentamethylcyclopentadienyl) halide complex $(\eta\text{-}C_5Me_5)TiCl_3$ reacts with 1 equiv of diol **2** in the presence of triethylamine to produce the dimeric species $[(\eta\text{-}C_5Me_5)TiCl(\mu\text{-}\eta^1,\eta^1\text{-}2\text{-}CF_3\text{-dpbd})]_2$ (**4**). An analogous reaction employing the zirconium halide $(\eta\text{-}C_5Me_5)ZrCl_3$ and the diol **3** leads to isolation of the salt complex $[HNEt_3][(\eta\text{-}C_5Me_5)_2Zr_2Cl_2(\mu\text{-}Cl)(\mu\text{-}\eta^1,\eta^2\text{-}3,5\text{-}Me_2\text{-dpbd})_2]$ (**5**). Compounds **4** and **5** have been subjected to single-crystal X-ray diffraction studies. The solid-state structure of **4** consists of two titanium metal centers, each bearing a pentamethylcyclopentadienyl ligand and a terminal chloride ligand, bridged by two diolate ligands such that a central 10-membered ring is formed. The terminal Ti−Cl bond length is 2.306(2) Å, and the Ti−O distances range from 1.783(4) to 1.830(5) Å. The two bridging diolate ligands adopt widely differing conformations such that one diolate ligand possesses Ti−O−C angles of 172.3(4) and 172.4(4)° while the other displays acute Ti−O−C angles of 125.2(4)°. The molecular geometry of the anion in **5** is comprised of two $(\eta\text{-}C_5Me_5)ZrCl$ moieties bridged by a single μ_2-Cl ligand and two diolate ligands. One oxygen atom within each diolate ligand acts as a μ_2 bridge between the zirconium metal centers whereas the other is bound in a terminal fashion to one metal center, thus forming a central Zr_2O_2 four-membered ring and two ZrO_2C_2 five-membered rings. Bridging Zr−Cl distances are 2.606(4) and 2.737(3) Å, and terminal Zr−Cl bond lengths are 2.499(4) and 2.584(4) Å. Terminal Zr−O distances are 1.989(9) and 1.972(9) Å, and bridging Zr−O distances range from 2.125(9) to 2.222(8) Å. Crystal data for **4** (at −90 °C): monoclinic space group $P2_1$, $a = 12.399(1)$, $b = 22.229(2)$, $c = 13.275(1)$ Å, $\beta = 111.208(6)°$, $V = 3411$ Å^3, $Z = 2$, $D_{calc} = 1.338$ g cm^{-3}. Crystal data for **5** (at −90 °C): orthorhombic space group $P2_12_12_1$, $a = 13.615(2)$, $b = 13.623(2)$, $c = 36.042(5)$ Å, $V = 6685$ Å^3, $Z = 4$, $D_{calc} = 1.246$ g cm^{-3}.

Introduction

The field of asymmetric catalysis is a rapidly expanding area of great current interest.[2] A wide range of ligand sets have been employed to produce an asymmetric environment around a metal center, including chiral phosphines, Schiff bases, tartrates, peptides, and alkaloids, to name but a few examples. Investigations of enantioselective catalysts bearing chiral diolate and triolate ligands have yielded a considerable number of publications in recent years, which have described the use of 2,2′-binaphthol,[3] TADDOL and its derivatives,[4] and a number of other examples.[5] Synthetic reactions facilitated by these catalysts have included asymmetric oxidation of aryl methyl sulfides,[3i,5f] asymmetric Mukaiyama aldol reactions,[3g] and asymmetric Meerwein−Ponndorf−Verley (MPV) reduction.[5g,6] In the majority of cases, the chiral diol ligands have been utilized in conjunction with an early transition metal, most frequently titanium, or a lanthanide metal center. Titanium diolate complexes are also implicated as the catalytically active species in the asymmetric epoxidation of allylic alcohols catalyzed by titanium *i*-propoxide/dialkyl tartrate.[7]

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Recently, Oh and co-workers described a simple synthetic procedure for the preparation of substituted butane-2,3-diols from optically active butadiene diepoxide.[8] They also described the use of a dichlorotitanium derivative of one of these diols as a moderately effective catalyst for the asymmetric Diels−Alder reaction. We wished to examine the structural chemistry of group IV derivatives of this class of 1,2-diol ligands and to assess the ability of these complexes to function as asymmetric catalysts. Here, we describe the synthesis and structural characterization of two mono(pentamethylcyclopentadienyl) diolate derivatives of titanium and zirconium.

Experimental Section

General Procedures and Techniques. All manipulations were carried out under an inert atmosphere of oxygen-free UHP-grade argon using standard Schlenk techniques or under oxygen-free helium in a Vacuum Atmospheres drybox. (η-C_5Me_5)$TiCl_3$ and (η-C_5Me_5)$ZrCl_3$ were purchased from Strem and used as received. (*S*,*S*)-Butadiene diepoxide was prepared from L-(+)-tartaric acid following the literature procedure.[8] 5-Bromo-*m*-xylene and 2-bromobenzotrifluoride were purchased from Lancaster and used as received. Triethylamine was purchased from Aldrich and degassed prior to use. Solvents were degassed and distilled from sodium benzophenone ketyl under nitrogen. Benzene-d_6 was degassed, dried over Na−K alloy, and then trap-to-trap distilled before use.

NMR spectra were recorded at 22 °C on Brüker WM300 or Varian Unity 300 spectrometers. All ^{1}H NMR chemical shifts are reported in ppm relative to the ^{1}H impurity in benzene-d_6 or chloroform-*d* set at δ 7.15 and 7.27, respectively. Infrared spectra were recorded on a Digilab FTS-40 spectrometer. Solid-state spectra were taken as Nujol mulls between KBr plates. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer. Elemental analysis samples were prepared and sealed in tin capsules in the glovebox prior to combustion.

1,4-Bis(2-trifluoromethylphenyl)butane-(2*S*,3*S*)-diol (2). To an argon-filled 250-mL Schlenk vessel containing 100 mL of dry THF was added 1.12 g (46.1 mmol) of magnesium turnings and a stir bar. 2-Bromobenzotrifluoride (10.3 g, 45.8 mmol) was then added to the flask in 1-mL portions over 1 h. When almost all of the magnesium had been consumed, the Grignard solution was cooled to −35 °C, and 0.3 g of copper(I) iodide was added. After the solution was stirred at −35 °C for 15 min, 2.00 g (23.2 mmol) of (*S*,*S*)-butadiene diepoxide was added dropwise, and the solution was allowed to warm to room temperature over 2 h. After being stirred for 18 h at room temperature, the reaction mixture was poured into 150 mL of $NaCl_{(sat)}$/0.1 M HCl. The organic layer was separated, and the aqueous phase was extracted with diethyl ether (2 × 75 mL). The combined organic phases were dried over $MgSO_4$, and all solvent was then removed in vacuo. The solid residue was dissolved in 150 mL of hot toluene and filtered, and the filtrate was reduced in volume to 75 mL, resulting in the precipitation of white solid. Hexane (50 mL) was added to the toluene slurry, and the solid was isolated on a frit and dried in vacuo. Yield: 4.74 g (55%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82−7.34 (m, 8 H, aromatic), 4.01 (d, J = 7 Hz, 2 H, CH), 3.86 (br, 2 H, OH), 3.28−2.98 (m, 4 H, CH_2). IR (cm^{-1}): 3364 (br, s), 1734 (w), 1609 (w), 1582 (w), 1495 (w), 1402 (w), 1316 (s), 1302 (sh, s), 1185 (sh, m), 1160 (s), 1110 (s), 1085 (sh, m), 1059 (s), 1040 (s), 1033 (sh, s), 955 (w), 924 (w), 885 (w), 871 (w), 764 (s), 740 (m), 723 (w), 653 (m), 597 (m), 518 (w). Anal. Calcd for $C_{18}H_{16}F_6O_2$: C, 57.15; H, 4.26. Found: C, 56.42; H, 4.39.

1,4-Bis(3,5-dimethylphenyl)butane-(2*S*,3*S*)-diol (3). Through the use of a procedure analogous to that for **2**, a Grignard solution prepared from 0.84 g (34.6 mmol) of magnesium turnings and 6.39 g (34.5 mmol) of 5-bromo-*m*-xylene in 100 mL of THF was cooled to −35 °C, and 0.25 g of copper(I) iodide was added. (*S*,*S*)-Butadiene diepoxide (1.50 g; 17.4 mmol) was then added dropwise, and the solution was allowed to warm to room temperature. The reaction mixture was quenched with 150 mL of $NaCl_{(sat)}$/0.1 M HCl, the organic layer was separated, and the aqueous phase was extracted with diethyl ether (2 × 75 mL). The combined organic phases were dried over $MgSO_4$, and all solvent then was removed in vacuo. The solid residue was dissolved in 150 mL of hot toluene and filtered, and the filtrate was cooled to 0 °C. The resulting solid was collected on a frit, washed with hexane, and dried in vacuo. Yield: 4.12 g (79%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23 (s, 2 H, *p*-H), 7.20 (s, 4 H, *o*-H), 4.11 (m, 2 H, CH), 3.16 (m, 4 H, CH_2), 2.65 (s, 12 H, Me), 2.51 (br, 2 H, OH). IR (cm^{-1}): 3345 (m), 3250 (br, s), 3013 (m), 1605 (s), 1406 (m), 1341 (m), 1306 (w), 1285 (w), 1231 (w), 1197 (w), 1153 (w), 1104 (m), 1067 (w), 1050 (m), 1032 (m), 973 (m), 959 (m), 919 (w), 841 (s), 769 (w), 723 (sh, m), 711 (s), 676 (m), 632 (w). Anal. Calcd for $C_{20}H_{26}O_2$: C, 80.50; H, 8.78. Found: C, 79.49; H, 8.54.

[(η-C_5Me_5)TiCl(μ-η^1,η^1-2-CF_3-dpbd)]$_2$ (4). To a mixture of solid (η-C_5Me_5)$TiCl_3$ (1.80 g, 6.23 mmol) and diol **2** (2.354 g, 6.23 mmol) was added toluene (50 mL), and the mixture was stirred for 5 min. Triethylamine (1.91 mL, 13.7 mmol) was added dropwise to this solution over 3 min. The reaction was stirred for 16 h, and much precipitate was formed. The mixture was filtered through Celite, which was washed with 5 mL of toluene, and then all volatiles were removed from the filtrate in vacuo. The residue was dissolved in toluene (20 mL) and cooled to −35 °C, resulting in the formation of yellow crystals overnight. The crystals were isolated on a frit, washed with cold toluene (3 mL), and dried under vacuum. A second crop was isolated after the mother liquor was concentrated and cooled to −35 °C. Yield: 3.13 g (81%). ^{1}H NMR (300 MHz, C_6D_6): δ 8.26 (d, J = 8 Hz, 2 H, Ar), 8.00 (d, J = 7 Hz, 2 H, Ar), 7.51 (d, J = 8 Hz, 2 H, Ar), 7.27 (m, 4 H, Ar), 7.10 (t, J = 8 Hz, 2 H, Ar), 6.85 (m, 4 H, Ar), 6.40 (d, J = 11 Hz, 2 H, CH), 4.71 (dd, J = 11, 4 Hz, 2 H, CH), 4.03 (t, J = 12 Hz, 2 H, CH_2), 3.64 (dd, J = 12, 4 Hz, 2 H, CH_2), 3.54 (t, J = 11 Hz, 2 H, CH_2), 3.41 (d, J = 12 Hz, 2 H, CH_2), 1.86 (s, 30 H, C_5*Me_5*). IR (Nujol, cm^{-1}): 1608 (w), 1572 (w), 1495 (w), 1351 (w), 1313 (s), 1294 (w sh), 1164 (s), 1106 (s br), 1078 (m), 1063 (m), 1033 (m), 1005 (w), 988 (w), 951 (w), 893 (m), 860 (w), 771 (s), 730 (s), 678 (w), 653 (s), 617 (w), 534 (w), 514 (m), 445 (m). Anal. Calcd for (partially desolvated) $C_{56}H_{58}Cl_2F_{12}O_4Ti_2\cdot(C_7H_8)_{0.2}$: C, 57.06; H, 4.97. Found: C, 57.09; H, 5.04.

[$HNEt_3$][(η-C_5Me_5)$_2Zr_2Cl_2$(μ-Cl)(μ-η^1,η^2-3,5-Me_2-dpbd)$_2$] (5). To a mixture of solid (η-C_5Me_5)$ZrCl_3$ (0.516 g, 1.55 mmol) and diol **3** (0.460 g, 1.55 mmol) was added a mixture of toluene (70 mL) and THF (15 mL), and the solution was stirred for 2 min. Triethylamine (0.344 g, 3.41 mmol) was added dropwise to this solution over 1 min. The reaction was stirred at room temperature for 20 h, and much

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precipitate was formed. All volatiles were removed under vacuum, and the solid residue was washed with hexane (10 mL). Toluene (15 mL) was then added, the solution was filtered through Celite and concentrated to 3 mL, and hexane (2 mL) was added. The solution was cooled to −35 °C, resulting in a small amount of precipitate, which was separated by decanting the solution into another flask. An additional 10 mL of hexane was layered on top of the solution, and colorless crystals formed after standing at −35 °C for 24 h. Yield: 0.410 g (43%). ^{1}H NMR (300 MHz, C_6D_6): δ 8.38 (br, 1 H, *H*NEt$_3$), 7.12 and 6.80 (s, partially obscured by solvent, 12 H, *o*- and *p*-Ar), 5.02 (m, 2 H), 4.97 (m, 2 H), 3.68 (m, 4 H), 2.94 (m, 2 H), 2.53 (m, 2 H), 2.33 (s, 30 H, C_5Me_5), 2.32 (obscured by Cp* resonance) and 2.29 (2 × s, 24 H, $C_6H_3Me_2$), 2.19 (m, 6 H, NCH_2CH_3), 0.63 (t, J = 7 Hz, 9 H, NCH_2CH_3). IR (Nujol, cm^{-1}): 1604 (m), 1475 (m), 1442 (w), 1375 (w), 1328 (w), 1267 (w), 1202 (w), 1167 (w), 1154 (w), 1084 (s), 1045 (s), 1016 (m), 995 (w sh), 848 (s), 836 (s), 728 (m), 665 (m), 626 (w), 597 (m), 570 (m), 550 (w), 447 (m br). Anal. Calcd for $C_{66}H_{94}Cl_3NO_4Zr_2$: C, 63.20; H, 7.55; N, 1.12. Found: C, 63.19; H, 7.70; N, 1.13.

Crystallographic Studies. [(η-C$_5$Me$_5$)TiCl(μ-η^1,η^1-2-CF$_3$-dpbd)]$_2$·(C$_6$H$_5$CH$_3$)$_2$ (4). A yellow, rectangular block was mounted on a thin glass fiber using silicone grease. The crystal, which was mounted from a pool of mineral oil bathed in argon, was then immediately placed under a nitrogen coldstream on a Siemens P4/PC diffractometer. The radiation used was graphite monochromated Mo Kα radiation (λ = 0.710 69 Å). The lattice parameters were optimized from a least-squares calculation on 25 carefully centered reflections of high Bragg angle. The data were collected using ω scans with a 0.88° scan range. Three check reflections monitored every 97 reflections showed no systematic variation of intensities. Lattice determination and data collection were carried out using XSCANS version 2.10b software.[9] All data reduction, including Lorentz and polarization corrections and structure solution and graphics were performed using SHELXTL PC version 4.2/360 software.[9b] The structure refinement was performed using SHELX-93 software.[9c] The data were not corrected for absorption because of the low absorption coefficient (0.39 mm^{-1}).

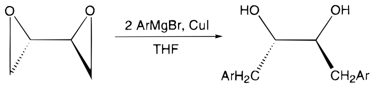
The space group $P2_1$ was chosen on the basis of systematic absences and chirality. Direct methods were used to locate the titanium, chlorine, and oxygen atoms. All remaining atoms were found from subsequent difference maps. The six-membered rings of the two lattice toluene molecules were refined as rigid bodies, with ring carbon−carbon distances fixed at 1.39 Å. All hydrogen atoms were fixed and refined in positions of ideal geometry. The C−H distances were fixed at 0.930 (ethyl), 0.970 (phenyl), or 0.960 Å (methyl). All hydrogen atoms were refined using the riding model in the HFIX facility in SHELX-93 and had their isotropic temperature factors fixed at 1.2 (ethyl, phenyl) or 1.5 (methyl) times the equivalent isotropic U of the atom to which they were bonded. The absolute structure was dictated by the diolate ligand conformation (*S*, *S*). The final refinement[10] included anisotropic thermal parameters on all non-hydrogen atoms except for the toluene carbon atoms and converged to $R1 = 0.0671$ and $R2_w = 0.1607$.

[HNEt$_3$][(η-C$_5$Me$_5$)$_2$Zr$_2$Cl$_2$(μ-Cl)(μ-η^1,η^2-3,5-Me$_2$-dpbd)$_2$] (5). A colorless prism was mounted on a thin glass fiber using silicone grease. The crystal, which was mounted from a pool of mineral oil bathed in argon, was then immediately placed under a nitrogen coldstream on a Siemens P4/PC diffractometer. The radiation used was graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). The lattice parameters were optimized from a least-squares calculation on 25 carefully centered reflections of high Bragg angle. The data were collected using ω scans with a 0.90° scan range. Three check reflections monitored every 97 reflections showed no systematic variation of intensities. Lattice determination and data collection were carried out using XSCANS version 2.10b software.[9a] All data reduction, including Lorentz and polarization corrections and structure solution and graphics, were performed using SHELXTL PC version 4.2/360 software.[9b] The structure refinement was performed using SHELX-93 software.[9c] The data were not corrected for absorption because of the low absorption coefficient (0.48 mm^{-1}).

The space group $P2_12_12_1$ was uniquely determined by the systematic absences. Direct methods were used to locate the zirconium, chlorine, and oxygen atoms. All remaining atoms were found from subsequent difference maps. All hydrogen atoms were fixed and refined in positions of ideal geometry. The C−H distances were fixed at 0.930 (ethyl), 0.970 (phenyl), or 0.960 Å (methyl). All hydrogen atoms were refined using the riding model in the HFIX facility in SHELX-93 and had their isotropic temperature factors fixed at 1.2 (ethyl, phenyl) or 1.5 (methyl) times the equivalent isotropic U of the atom to which they were bonded. Because of disorder, no hydrogen atoms were placed on the triethylammonium ion. The absolute structure was dictated by the diolate ligand conformation (*S*, *S*). The final refinement[11] included anisotropic thermal parameters on all non-hydrogen atoms and converged to $R1 = 0.0688$ and $R2_w = 0.1690$.

Results and Discussion

Synthesis and Reactivity. Optically pure (*S*,*S*)-butadiene diepoxide (**1**) was prepared in five steps from L-(+)-tartaric acid following the procedure of Oh et al.[8] The low-temperature reaction of **1** with 2 equiv of Grignard reagent ArMgBr (Ar = 2-CF$_3$C$_6$H$_4$ or 3,5-Me$_2$C$_6$H$_3$) in THF in the presence of copper(I) iodide led to the ring opening of both epoxide moieties and the isolation of the substituted 1,4-diphenylbutane-2,3-diol (dpbdH$_2$) derivatives (eq 1).



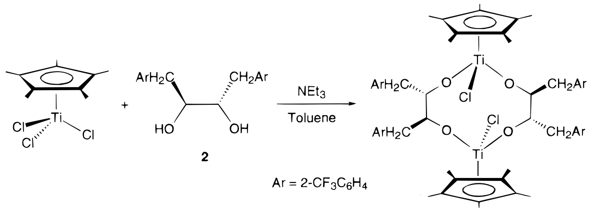
1

Ar = 2-CF$_3$C$_6$H$_4$ (**2**); 3,5-Me$_2$C$_6$H$_3$ (**3**)

(1)

The diols are obtained as microcrystalline white solids which are slightly soluble in hexane and soluble in most aromatic, ethereal, and halogenated solvents. ^{1}H NMR and IR spectroscopy, together with microanalytical data, established the formulation of the diols.

Reactions of either MCl$_4$ or (η-C$_5$H$_5$)MCl$_3$ (M = Ti, Zr) with the dilithium salts of the chiral diols failed to produce tractable products, and thus, we turned to a direct reaction between the diols and a metal halide complex, employing triethylamine as base to remove HCl. (Pentamethylcyclopentadienyl)titanium trichloride, (η-C$_5$Me$_5$)TiCl$_3$, was found to react with 1 equiv of the *o*-trifluoromethyl-substituted diol (2*S*,3*S*)-2-CF$_3$C$_6$H$_4$CH$_2$-CH(OH)CH(OH)CH$_2$C$_6$H$_4$-2-CF$_3$ [2-CF$_3$-dpbdH$_2$ (**2**)] at room temperature in toluene in the presence of triethylamine to produce the diolate complex [(η-C$_5$Me$_5$)TiCl(μ-η^1,η^1-2-CF$_3$-dpbd)]$_2$ (**4**) in good yield (eq 2).



2

Ar = 2-CF$_3$C$_6$H$_4$

4

(2)

4 may be isolated as yellow crystals following crystallization from toluene. Upon standing in the drybox atmosphere, the crystals rapidly become opaque and begin to powder. This

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[9] (a) XSCANS, 2.10b ed.; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1994. (b) Shledrick, G. M. *SHELXTL-PC*, version 4.2/360; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1994. (c) Sheldrick, G. M. *SHELXL-93: Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1993.

[10] $R(F_o) = \sigma||F_o| - |F_c||/\sigma|F_o|$ and $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. The parameter $w = 1/[\sigma^2(F_o^2) + (0.1012P)^2 + 0.3753P]$.

[11] $R(F_o) = \sigma||F_o| - |F_c||/\sigma|F_o|$ and $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. The parameter $w = 1/[\sigma^2(F_o^2) + (0.1216P)^2 + 12.4643P]$.

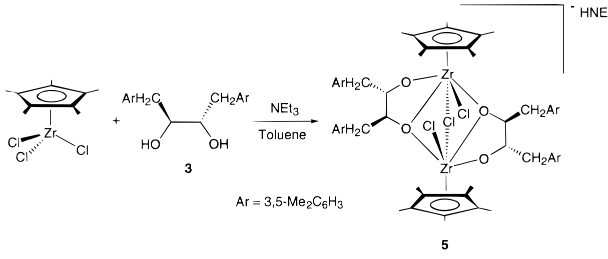
Table 1. Summary of Crystal Data

compound^a	**4**	**5**
empirical formula	$C_{70}H_{74}Cl_2F_{12}O_4Ti_2$	$C_{66}H_{94}Cl_3NO_4Zr_2$
space group	$P2_1$ (No. 4)	$P2_12_12_1$ (No. 19)
cell dim.		
a, Å	12.399(1)	13.615(2)
b, Å	22.229(2)	13.623(2)
c, Å	13.275(1)	36.042(5)
β, deg	111.208(6)	
temp, °C	−90	−90
Z, mol/unit cell	2	4
V, Å^3	3411	6685
D_{calc}, g cm^{-3}	1.338	1.246
λ (Mo Kα)	0.71069	0.71069
formula weight	1373.99	1254.29
abs coeff, cm^{-1}	3.91	4.75
$R(F_o)^b$	0.0671	0.0688
$R_w(F_o^2)^b$	0.1607	0.1690

^{a} **4** = $[(\eta\text{-}C_5Me_5)TiCl(\mu\text{-}\eta^1,\eta^1\text{-2-CF}_3\text{-dpbd})]_2$; **5** = $[HNEt_3][(\eta\text{-}C_5Me_5)_2Zr_2Cl_2(\mu\text{-Cl})(\mu\text{-}\eta^1,\eta^2\text{-3,5-Me}_2\text{-dpbd})_2]$. ^{b} $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w(F_o^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

likely is due to rapid loss of the two lattice toluene molecules observed in the X-ray structure of **4** (vide infra). ^{1}H NMR integration and microanalysis of samples of **4** which have been removed from mother liquor for several hours reveal the approximate formulation **4**·(toluene)$_{0.2}$.

A directly analogous reaction employing the 3,5-dimethylphenyl-substituted diol ligand 3,5-Me$_2$-dpbdH$_2$ (**3**) and (pentamethylcyclopentadienyl)zirconium trichloride led to isolation of the salt complex $[HNEt_3][(\eta\text{-}C_5Me_5)_2Zr_2Cl_2(\mu\text{-Cl})(\mu\text{-}\eta^1,\eta^2\text{-3,5-Me}_2\text{-dpbd})_2]$ (**5**), in which 1 equiv of triethylammonium chloride has been retained by the dimeric zirconium diolate species. Despite its formulation as a salt complex, **5** is found to be readily soluble in aromatic solvents such as benzene and toluene in addition to polar halogenated solvents such as methylene chloride (eq 3).



(3)

Reactions of $(\eta\text{-}C_5Me_5)TiCl_3$ with **3** and $(\eta\text{-}C_5Me_5)ZrCl_3$with **2** were also attempted, but in neither case could a pure product be obtained.

Solid-State and Molecular Structures. Two mono(pentamethylcyclopentadienyl) diolate bridged complexes, **4** and **5**, have been examined by single-crystal X-ray diffraction techniques. A summary of data collection and crystallographic parameters is given in Table 1.

Table 2. Selected Bond Lengths (Angstroms) and Angles (deg) for $[(\eta\text{-}C_5Me_5)TiCl(\mu\text{-}\eta^1,\eta^1\text{-2-CF}_3\text{-dpbd})]_2$ (**4**)

Ti(1)−O(1)	1.791(5)	Ti(2)−O(2)	1.783(4)
Ti(1)−O(4)	1.830(5)	Ti(2)−O(3)	1.828(4)
Ti(1)−Cl(2)	2.306(2)	Ti(2)−Cl(1)	2.306(2)
Ti(1)−C(21)	2.404(6)	Ti(2)−C(31)	2.372(6)
Ti(1)−C(22)	2.362(7)	Ti(2)−C(32)	2.327(7)
Ti(1)−C(23)	2.318(7)	Ti(2)−C(33)	2.381(7)
Ti(1)−C(24)	2.376(7)	Ti(2)−C(34)	2.383(6)
Ti(1)−C(25)	2.384(7)	Ti(2)−C(35)	2.401(6)
O(1)−Ti(1)−O(4)	103.2(2)	Ti(1)−O(1)−C(3)	172.3(4)
O(1)−Ti(1)−Cl(2)	101.5(2)	Ti(1)−O(4)−C(1)	125.2(4)
O(4)−Ti(1)−Cl(2)	103.7(2)	Ti(2)−O(2)−C(4)	172.4(4)
O(2)−Ti(2)−O(3)	103.7(2)	Ti(2)−O(3)−C(2)	125.2(4)
O(2)−Ti(2)−Cl(1)	100.1(2)	O(3)−Ti(2)−Cl(1)	103.2(2)

$[(\eta\text{-}C_5Me_5)TiCl(\mu\text{-}\eta^1,\eta^1\text{-2-CF}_3\text{-dpbd})]_2\cdot(C_6H_5Me)_2$ (4). Crystals of **4** suitable for an X-ray diffraction study were grown by cooling a concentrated toluene solution to −35 °C. Selected bond lengths and angles are presented in Table 2. An ORTEP drawing giving the atom-numbering scheme used in Table 2 is shown in Figure 1. The molecule sits in a general position in the monoclinic space group $P2_1$, with two lattice toluene solvent molecules per unit cell. The overall molecular geometry consists of two titanium metal centers, each bearing a pentamethylcyclopentadienyl ligand and a terminal chloride ligand, bridged by two diolate ligands such that a central 10-membered ring is formed (Figure 1). Similar coordination geometries have been observed previously in the chemistry of the group IV metals, notably the titanium pinacolato species $[(\eta\text{-}C_5H_5)TiCl(\mu\text{-}OCMe_2CMe_2O)]_2$[12] and the zirconium dimethyl tartrate complex $[(\eta\text{-}C_5H_5)_2Zr(\mu\text{-}OCH(CO_2Me)(MeO_2C)HCO)]_2$.[13] Related complexes containing 10-membered $M_2O_4C_4$ rings have also been described previously in the chemistry of thorium,[14] vanadium,[15] molybdenum,[16] and tungsten.[17]

The geometry about the metal center approximates a three-legged piano stool, with Cp$_{\mathrm{centroid}}$−Ti−Cl and Cp$_{\mathrm{centroid}}$−Ti−O angles ranging from 111.3(3)° to 123.3(3)°. Terminal Ti−Cl bond lengths of 2.306(2) Å in **4** are comparable to those of 2.276(1), 2.325(2), and 2.3518(9) Å observed in $[(\eta\text{-}C_5H_5)TiCl_2]_2(\mu\text{-}OCMe_2CMe_2O)$,[18] $[CH_2CH_2(\eta\text{-}C_5Me_4)_2TiCl_2]$,[19] and $[(\eta\text{-}C_5Me_5)(\eta\text{-}C_5H_5)TiCl_2]$,[20] and Ti−O distances ranging from 1.783(4) to 1.830(5) Å are typical of those previously observed for terminal titanium alkoxide ligands.[21] One of the most notable features of the solid-state structure of **4** is the widely differing conformations adopted by the two bridging diolate ligands. In the two previously described examples of dimeric group IV species containing central 10-membered rings, the molecule resides on a center of symmetry, and the conformations of the two diolate ligands are thus rendered identical by symmetry constraints. In the case of **4**, however, one of the diolate ligands possesses very large Ti−O−C angles of 172.3(4) and 172.4(4)° whereas the other displays rather acute Ti−O−C angles of 125.2(4)°. The major manifestation of this within the two diolate ligands is that the O(4)−C(1)−C(2)−O(3) torsion angle is 169.0° while the O(1)−C(3)−C(4)−O(2) torsion angle is only 60.9°. Minor differences in Ti−O bond lengths are observed

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(12) Huffman, J. C.; Moloy, K. G.; Caulton, K. G. *Inorg. Chem.* **1988**, *27*, 2190.

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(21) See, for example: (a) Williams, I. D.; Pedersen, S. F.; Sharpless, K. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 6430. (b) Naiini, A. A.; Ringrose, S. L.; Su, Y.; Jacobson, R. A.; Verkade, J. G. *Inorg. Chem.* **1993**, *32*, 1290. (c) Sabat, M.; Gross, M. F.; Finn, M. G. *Organometallics* **1992**, *11*, 745. (d) Boyle, T. J.; Barnes, D. L.; Heppert, J. A.; Morales, L.; Takusagawa, F.; Connolly, J. W. *Organometallics* **1992**, *11*, 1112.

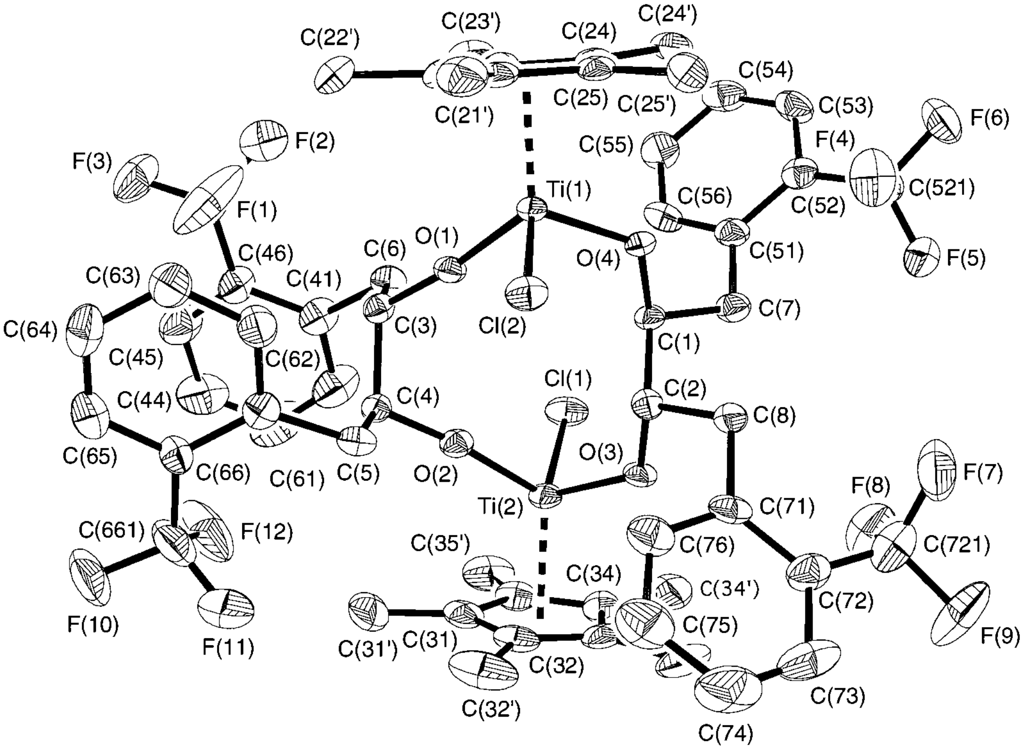


Figure 1. ORTEP plot (50% probability ellipsoids) showing the molecular structure of $[(\eta\text{-}C_5Me_5)TiCl(\mu\text{-}\eta^1,\eta^1\text{-}2\text{-}CF_3\text{-dpbd})]_2$ (**4**), giving the labeling scheme used in Table 2.

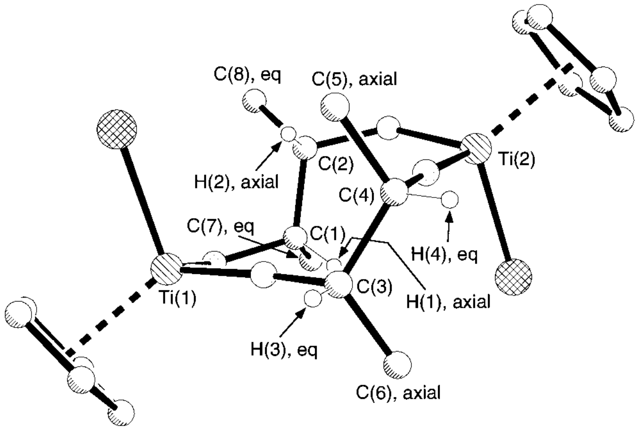


Figure 2. Ball-and-stick plot showing the cyclohexane chairlike conformation adopted by the central 10-membered $Ti_2O_4C_4$ core of $[(\eta\text{-}C_5Me_5)TiCl(\mu\text{-}\eta^1,\eta^1\text{-}2\text{-}CF_3\text{-dpbd})]_2$ (**4**).

between the diolate ligand with large Ti−O−C angles [Ti−O = 1.791(5) and 1.783(4) Å] as compared to the ligand with acute Ti−O−C angles [Ti−O = 1.830(5) and 1.828(4) Å]. The pairs of distances are in agreement with the generally accepted notion that a more obtuse M−O−C angle equates to greater O → M π donation and a shorter M−O bond length, although it should be noted that the difference lies only just outside the 3σ confidence interval of each bond distance. Despite the widely differing conformations of the diolate ligands, the central 10-membered $Ti_2O_4C_4$ core resembles a cyclohexane ring in a chair conformation (Figure 2), as was observed in the pinacolate complex $[(\eta\text{-}C_5H_5)TiCl(\mu\text{-}OCMe_2CMe_2O)]_2$.[12]

Table 3. Selected Bond Lengths (Angstroms) and Angles (deg) for $[HNEt_3][(\eta\text{-}C_5Me_5)_2Zr_2Cl_2(\mu\text{-}Cl)(\mu\text{-}\eta^1,\eta^2\text{-}3,5\text{-}Me_2\text{-dpbd})_2]$ (**5**)

Zr(1)−O(1)	2.208(8)	Zr(1)−C(42)	2.599(13)
Zr(1)−O(2)	1.989(9)	Zr(1)−C(43)	2.573(13)
Zr(1)−O(3)	2.125(9)	Zr(1)−C(44)	2.615(14)
Zr(2)−O(1)	2.150(9)	Zr(1)−C(45)	2.584(14)
Zr(2)−O(3)	2.222(8)	Zr(1)−Zr(2)	3.411(2)
Zr(2)−O(4)	1.972(9)	Zr(2)−C(51)	2.588(13)
Zr(1)−Cl(1)	2.606(4)	Zr(2)−C(52)	2.538(13)
Zr(1)−Cl(3)	2.584(4)	Zr(2)−C(53)	2.568(13)
Zr(2)−Cl(1)	2.737(3)	Zr(2)−C(54)	2.599(12)
Zr(2)−Cl(2)	2.499(4)	Zr(2)−C(55)	2.632(12)
Zr(1)−C(41)	2.611(13)		
O(1)−Zr(1)−O(2)	73.7(3)	O(1)−Zr(2)−O(3)	67.9(3)
O(1)−Zr(1)−O(3)	68.5(3)	O(1)−Zr(2)−O(4)	141.0(3)
O(2)−Zr(1)−O(3)	142.3(3)	O(3)−Zr(2)−O(4)	73.4(3)
O(1)−Zr(1)−Cl(1)	74.1(2)	Cl(1)−Zr(2)−Cl(2)	154.85(13)
O(2)−Zr(1)−Cl(1)	96.2(3)	Cl(1)−Zr(1)−Cl(3)	154.68(13)
O(3)−Zr(1)−Cl(1)	74.8(2)	Zr(1)−Cl(1)−Zr(2)	79.30(10)
O(1)−Zr(1)−Cl(3)	85.0(2)	Zr(1)−O(1)−Zr(2)	103.0(3)
O(2)−Zr(1)−Cl(3)	91.3(3)	Zr(1)−O(3)−Zr(2)	103.3(3)
O(3)−Zr(1)−Cl(3)	84.4(2)	Zr(1)−O(1)−C(1)	116.3(8)
O(1)−Zr(2)−Cl(1)	72.2(2)	Zr(2)−O(1)−C(1)	138.3(7)
O(3)−Zr(2)−Cl(1)	70.7(2)	Zr(1)−O(2)−C(2)	123.3(8)
O(4)−Zr(2)−Cl(1)	91.8(3)	Zr(1)−O(3)−C(19)	136.2(7)
O(1)−Zr(2)−Cl(2)	88.0(3)	Zr(2)−O(3)−C(19)	117.0(7)
O(3)−Zr(2)−Cl(2)	87.8(2)	Zr(2)−O(4)−C(18)	126.2(7)
O(4)−Zr(2)−Cl(2)	94.4(3)		

$[HNEt_3][(\eta\text{-}C_5Me_5)_2Zr_2Cl_2(\mu\text{-}Cl)(\mu\text{-}\eta^1,\eta^2\text{-}3,5\text{-}Me_2\text{-dpbd})_2]$ (5). Single crystals of **5** were grown from a layered toluene/hexane solution at −35 °C. Selected bond lengths and angles are presented in Table 3. An ORTEP drawing giving the atom-numbering scheme used in Table 3 is shown in Figure 3. The triethylammonium cation and zirconium-containing anion both occupy general positions in the orthorhombic space group $P2_12_12_1$. There appears to be a weak N−H···Cl hydrogen-bonding interaction between the triethylammonium cation and Cl(3), with an N(1)−Cl(3) distance of 3.10(2) Å (the N−H hydrogen itself could not be located). The overall molecular geometry of the zirconium-containing anion comprises two $(\eta\text{-}C_5Me_5)ZrCl$ moieties bridged by a single μ_2-Cl ligand and two diolate ligands. One oxygen atom within each diolate ligand acts as a μ_2-bridge between the zirconium metal centers whereas the other is bound in a terminal fashion to one metal center. The structure thus contains a central Zr_2O_2 four-

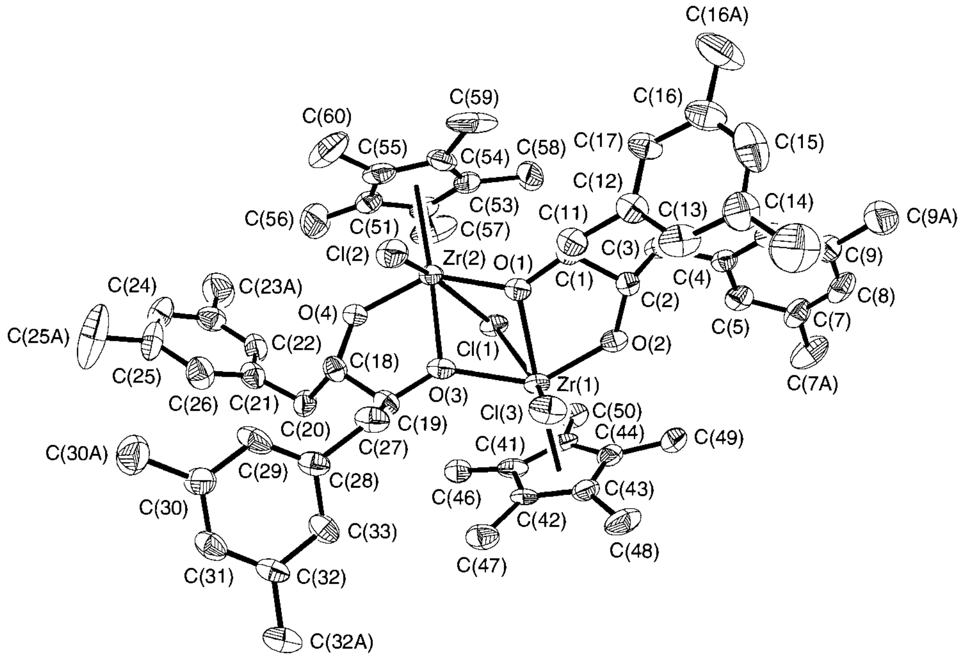
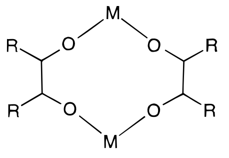


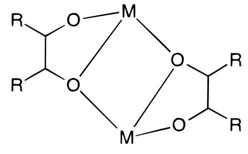
Figure 3. ORTEP representation (50% probability ellipsoids) of the anion of the salt complex $[HNEt_3][(\eta\text{-}C_5Me_5)_2Zr_2Cl_2(\mu\text{-}Cl)(\mu\text{-}\eta^1,\eta^2\text{-}3,5\text{-}Me_2\text{-}dpbd)_2]$ (**5**), giving the labeling scheme used in Table 3.

membered ring and two ZrO_2C_2 five-membered rings. The geometry about the zirconium metal centers may best be described as distorted octahedral, with the bridging oxygen atoms occupying positions effectively trans to the pentamethylcyclopentadienyl ligands. The Zr−O and Zr−Cl bonds cis to the pentamethylcyclopentadienyl ligand tend to distort away from it and define angles ranging from 99.9(5) to 116.8(5)° with the $Cp_{centroid}$−Zr vector. The bridging chloride ligand adopts a somewhat asymmetric position, having a Zr−Cl distance of 2.606(4) Å to Zr(1) and 2.737(3) Å to Zr(2). The asymmetry cannot be ascribed to a trans effect since both bridging Zr−Cl bonds lie effectively trans to a terminal chloride ligand. Both of the bridging Zr−Cl distances are, however, comparable to those found in other structurally characterized complexes containing Zr−Cl−Zr linkages.[22] Terminal Zr−Cl bond lengths are also substantially different from one another [Zr(1)−Cl(2) = 2.499(4) and Zr(1)−Cl(3) = 2.584(4) Å], with the shorter Zr−Cl distance being associated with the zirconium possessing the longer Zr−Cl bridging distance. However, the asymmetry also could be a result of the hydrogen-bonding interaction mentioned above. Both distances have structural precedent, being similar to the terminal Zr−Cl distances of 2.477(2), 2.4776(8), and 2.5610(11) Å found in $\{[(\eta\text{-}C_5Me_5)ZrCl(\mu_2\text{-}OH)]_3(\mu_3\text{-}OH)(\mu_3\text{-}O)\}$,[23] $[(\eta\text{-}C_5Me_5)_2ZrCl(OH)]$,[24] and $[(\eta\text{-}C_5H_4)CMe_2(\eta^3\text{-}C_{13}H_{10})Zr(\mu_2\text{-}H)Cl]_2$,[25] respectively. Terminal Zr−O distances of 1.989(9) and 1.972(9) Å are very similar to those observed in the zirconium tartrate complexes described by Erker et al.[13] and in the 1,2-cyclohexanediolate species $[ZrCl_3(THF)_2]_2(\mu\text{-}1,2\text{-}O_2C_6H_{10})$.[26] Bridging Zr−O distances are, as expected, longer than terminal Zr−O bond lengths and range from 2.125(9) to 2.222(8) Å. The central four-membered Zr_2O_2 ring deviates somewhat from planarity, with the internal angles summing to 342.7°, compared to 355.4° observed for the Zr_2O_2 ring in the diethyltartratozirconocene dimer $[(\eta\text{-}C_5H_5)_2Zr(\mu\text{-}\eta^1,\eta^2\text{-}OCH(CO_2Et)(EtO_2C)HCO)]_2$.[13b] The overall molecular geometry of **5** is very similar to that of the dimeric niobium complex $[(\eta\text{-}C_5H_4SiMe_3)_2Nb_2Cl_2(\mu\text{-}1,2\text{-}C_6H_4O_2)_2(\mu\text{-}O)]$,[27] which also features two (η-Cp)MCl(μ-diolate) moieties bridged by an additional μ_2 ligand to form a dimetallatricyclic system.

Spectroscopic Characterization. ^{1}H NMR Spectroscopy. Erker has previously noted the low-energy interconversions which are possible between the 10-membered cyclic structure **I** and the dimetallatricyclic structure **II**.[13] Formation of two



I



II

additional M−O bonds in **II** appears to compensate for the minor differences in energy between the two structural types. In the case of the zirconocene dialkyl tartrate complexes $\{(\eta\text{-}C_5H_5)_2Zr[OCH(CO_2R)(RO_2C)HCO]\}_2$, it was found that a seemingly minor alteration in the alkyl substituent from *i*-propyl to methyl brought about a change in solid-state structure from type **II** to type **I**.[13] Additionally, the dimethyltartrate complex appears to exhibit structural type **II** in solution and yet crystallizes into a structure of type **I**.

Ambient-temperature ^{1}H NMR spectra of $[(\eta\text{-}C_5Me_5)TiCl(\mu\text{-}\eta^1,\eta^1\text{-}2\text{-}CF_3\text{-}dpbd)]_2$ (**4**) reveal *two* distinct types of aromatic resonances, together with *two* methine resonances and diaste-

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(22) See, for example: (a) Erker, G.; Kropp, K.; Atwood, J. L.; Hunter, W. E. *Organometallics* **1983**, *2*, 1555. (b) Engelhardt, L. M.; Papasergio, R. I.; Raston, C. L.; White, A. H. *Organometallics* **1984**, *3*, 18. (c) Waymouth, R. M.; Santarsiero, B. D.; Coots, R. J.; Bronikowski, M. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 1427. (d) Cotton, F. A.; Diebold, M. P.; Kibala, P. A. *Inorg. Chem.* **1988**, *27*, 799.

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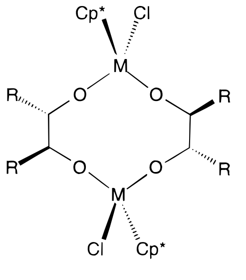
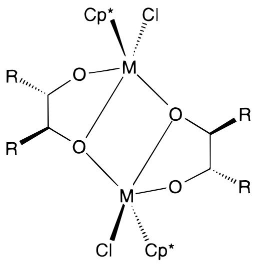
reotopic methylene resonances. Inequivalence of the methine protons and backbone substituents is a result of the C_2-symmetric chiral diolate ligands bridging metal centers which each bear two nonequivalent groups. No changes were observed in the ^{1}H NMR spectrum of **4** in the temperature range from 183 to 363 K in toluene-d_8. These observations are consistent with the maintenance of a 10-membered ring structure in solution (as shown schematically in **III**). A solution structure of type **II** (shown schematically in **IV**) would render all four methine protons inequivalent, which was not observed at any temperature studied. Two-dimensional ^{1}H$-$^{1}H COSY spectra were used to provide full assignment of resonances around the aromatic rings and to definitively establish the assignment of methine and methylene protons.

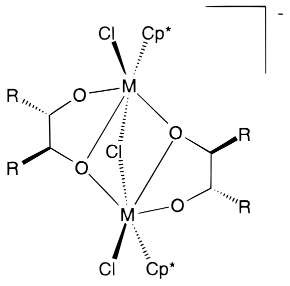


III



IV

In the case of the zirconium-containing anion $[(\eta\text{-}C_5Me_5)_2Zr_2Cl_2(\mu\text{-}Cl)(\mu\text{-}\eta^1,\eta^2\text{-}3,5\text{-}Me_2\text{-dpbd})_2]^-$ in **5**, structural type **II** is effectively "locked-in" by the presence of an additional bridging chloride ligand between the metal centers (**V**). The molecular structure of **5** (vide supra) revealed that both of the Cp* ligands are located on the same side of the molecule, which would be expected to produce two distinct types of methine protons, aromatic groups, and methylene protons. This is consistent with the ambient-temperature ^{1}H NMR spectrum of **5** in benzene-d_6.



V

Concluding Remarks

We have prepared and characterized two mono(pentamethylcyclopentadienyl) group IV complexes containing chiral 1,2-diolate ligands. As reported previously, oxametallacycles with ring size ≤5 are found to have a strong tendency toward dimerization,[13b] and this is consistent with our observations in this work. We have found the titanium diolate complex **4** to exhibit a dimeric structure with a central 10-membered ring, in which the coordination environment about the titanium metal centers approximates a three-legged piano stool. Variable-temperature NMR studies strongly suggested that a 10-membered ring structure (**III**) is maintained in solution and gave no indication of an equilibrium between **III** and its structural isomer **IV**. In the case of the zirconium complex (**5**), the larger zirconium metal center is able to accommodate an octahedral geometry which comprises a Cp* ligand, two bridging and one terminal alkoxide ligands, and one bridging and one terminal chloride ligand. In this case, the presence of the bridging chloride ligand effectively locks this molecule into the dimetallatricyclic structure (**V**).

Attempts were made to ascertain the utility of complexes **4** and **5** in asymmetric transformations of organic substrates. Reactions of **4** with 1 equiv of methylmagnesium bromide and benzylmagnesium bromide were carried out with the aim of preparing complexes of the type $(\eta\text{-}C_5Me_5)$TiR(diolate), which may be used to deliver an alkyl group enantioselectively to an aldehyde or ketone.[28] However, the reactions failed to yield any tractable products. Complexes **4** and **5** were also assessed as catalysts for the MPV reduction of acetophenone with 2-propanol[29] and the aldol reaction of 1-(trimethylsilyloxy)-1-phenylethylene with benzaldehyde.[30] In neither case was any catalytic activity observed. The use of ligands **2** and **3** in combination with lanthanide metal centers as catalysts in the MPV reduction of acetophenone was found to be effective and is the subject of work currently in progress.

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Supporting Information Available: Listings of fractional atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates for complexes **4** and **5** (20 pages). Files, in CIF format, are available on the Internet only. Ordering and access information is given on any current masthead page.

IC980645O

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