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Article

Anisole–Diphenoxide Ligands and Their Zirconium Dichloride and Dialkyl Complexes

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Linear triphenol $H_3[^{R}O_3]$ (2,6-bis(3-*tert*-butyl-5-methyl-2-hydroxybenzyl)-4-R-phenol; R = Me, ^{t}Bu) was found to undergo selective mono-deprotonation and mono-*O*-methylation. Deprotonation of $H_3[^{R}O_3]$ with 1 equiv of ^{n}BuLi resulted in the formation of $Li\{H_2[^{R}O_3]\}(Et_2O)_2$ (R = Me (**1a**), ^{t}Bu (**1b**)), in which the central phenol unit was lithiated. Treatment of $H_3[^{R}O_3]$ with methyl *p*-toluenesulfonate in the presence of K_2CO_3 in CH_3CN gave the corresponding anisol-diphenol $H_2[^{R}O_2O]$ (2,6-bis(3-*tert*-butyl-5-methyl-2-hydroxybenzyl)-4-R-anisole; R = Me (**2a**), ^{t}Bu (**2b**)). Reaction of $H_2[^{R}O_2O]$ with 2 equiv of ^{n}BuLi gave the dilithiated derivatives $Li_2[^{R}O_2O]$. The lithium salts were reacted with $ZrCl_4$ in toluene/THF to obtain the dichloride complex $[^{R}O_2O]ZrCl_2(thf)$ (R = Me (**3a**), ^{t}Bu (**3b**)). **3b** underwent dimerization along with a loss of THF to generate $\{[^{tBu}O_2O]ZrCl_2\}_2$ (**4**), whereas **4** was dissolved in THF to regenerate the monomer **3b**. Alkylation of **3** with MeMgBr, $PhCH_2MgCl$, and Me_3SiCH_2MgCl gave $[^{Me}O_2O]ZrMe_2(thf)$ (**5**), $[^{R}O_2O]Zr(CH_2Ph)_2$ (R = Me (**6a**), ^{t}Bu (**6b**)), and $[^{tBu}O_2O]Zr(CH_2SiMe_3)_2$ (**7**), respectively. Reaction of **3b** with $LiBHEt_3$ produced the hydride-bridged dimer $[Li_2(thf)_4Cl]\{[^{tBu}O_3]Zr\}_2(\mu\text{–}H)_3\}$ (**8**), in which demethylation of the dianionic $[^{tBu}O_2O]$ ligand took place to give the trianionic $[^{tBu}O_3]$ ligand. The X-ray crystal structures of **1b**, **2a**, **3a**, **4**, **6a**, and **7** were reported.

Introduction

The search for new ancillary ligands capable of supporting various inorganic/organometallic reactions is one of the challenging problems in coordination and organometallic chemistry. One approach involves the utilization of polydentate ligands to impose specific coordination geometries upon one or more metal centers.[1−4] Phenoxide groups are ubiquitous in polydentate ligands and are frequently used as components of mixed-donor sets.[5−8] Research regarding phenoxide-based polydentate ligand systems has been greatly

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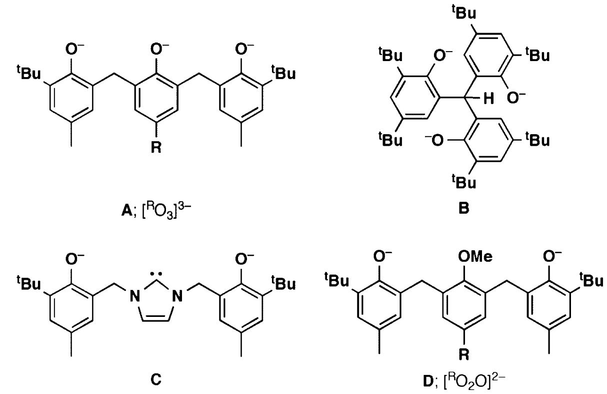
facilitated by their ease of synthesis. A large range of structures can be accessed, often requiring only a few steps from many commercially available phenol derivatives. For example, calixarenes can be readily prepared through condensation reactions of aldehydes and phenols.[9] These cyclic polyphenoxides provide a robust and well-defined O-donor coordination environment, and their metal complexes serve as models for reactive metal-oxide surfaces.[10] In particular, early-transition-metal derivatives of calix[4]arene possess the ability to activate small molecules such as dinitrogen and carbon monoxide.[11] Important examples of phenoxide-containing mixed-donor ligands are the heteroatom-bridged bisphenoxides, which support the metal centers capable of displaying efficient activity as catalysts for various reactions. Titanium complexes bearing sulfur-bridged diphenoxide ligands have proven to be versatile olefin polymerization catalyst precursors upon activated by methylaluminoxane,[12] whereas copper complexes have been shown to catalyze the aerobic oxidation of alcohols.[13] The considerable potential of these ligand systems in small-molecule activation and homogeneous catalysis prompts us to develop metal complexes supported by phenoxide-based polydentate ligands.

We previously reported the use of linear and tripodal triphenoxide ligands to support early transition metals (**A** and **B**; Chart 1).[14,15] In these ligands, three phenoxide units are connected at ortho positions through single carbon linkers. As part of a program aimed at developing new mixed-donor ligands, we recently described the examples of transition-metal complexes employing dianionic phenoxide-carbene ligands, in which an *N*-heterocyclic carbene group is flanked by two phenoxide groups (**C**).[16] Next, we examined the partial functionalization of the phenoxide groups of triphenoxide ligands via alkylation, giving ether-phenoxide mixed-donor ligands. This method has been successfully employed in the synthesis of calixarene derivatives.[9a,10c,d,17] The overall charge and steric demand can be tuned by the alkylation of polyphenoxide ligands. In addition, the neutral ether group can act as a weak donor as compared with an anionic phenoxide group. Herein, we report the methylation of the central phenoxide group of the triphenoxide **A**, giving an anisole−dianionic ligand, $[^{R}O_2O]^{2-}$ (**D**). The full details of the synthesis of zirconium complexes and their crystal structures are also described in this article. Preliminary results on the reactivity of the dibenzyl compounds supported by the $[^{R}O_2O]$ ligand have been communicated.[18]

Chart 1



Results and Discussion

Ligand Synthesis. Mono-deprotonation of $H_3[^{R}O_3]$ was examined to prepare the ether-diphenoxide ligands via alkylation of the resulting monoanionic species. The acidity of oligomeric phenolic compounds is important for selective substitution reactions and determined by the system of intramolecular hydrogen bonds.[19] The pK_{a1} values of ortho-connected phenolic oligomers are significantly reduced relative to those of the corresponding monomeric phenols, whereas the pK_{a2} values lie considerably higher.[20] We and others have previously reported that $H_3[^{R}O_3]$ could be fully deprotonated by a reaction with 3 equiv of ^{n}BuLi, and these tri-lithium salts serve as useful precursors for the synthesis of transition-metal derivatives.[6b,21] The triphenol $H_3[^{R}O_3]$ was found to be selectively monolithiated by the dropwise addition of 1 equiv of ^{n}BuLi in hexane to an Et_2O solution of the triphenol at 0 °C (Scheme 1). Evaporation of the solvent yielded $Li\{H_2[^{R}O_3]\}(Et_2O)_2$ (R = Me (**1a**), ^{t}Bu (**1b**)) as a white solid.

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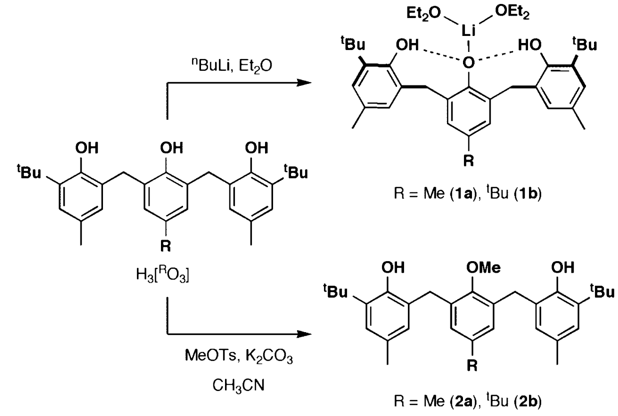
Scheme 1



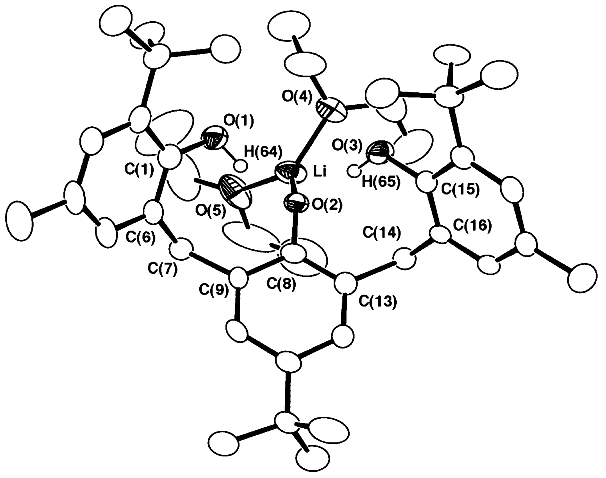


Figure 1. Molecular structure of $Li\{H_2[^{tBu}O_3]\}(Et_2O)$ (**1b**). Hydrogen atoms bound to carbon have been omitted for clarity. Selected bond distances (Å) and angles (deg): Li−O(2) 1.822(7), Li−O(4) 1.929(8), Li−O(5) 1.912(8), O(1)−C(1) 1.375(4), O(2)−C(8) 1.349(4), O(3)−C(15) 1.358(4), O(1)···O(2) 2.569(4), O(2)···O(3) 2.645(3), O(2)···H(64) 1.68, O(2)···H(65) 1.77, O(2)−Li−O(4) 114.9(3), O(2)−Li−O(5) 121.5(4), O(4)−Li−O(5) 121.5(4), C(8)−O(2)−Li 135.6(3), C(6)−C(7)−C(9) 117.0(3), C(13)−C(14)−C(16) 115.6(3), O(1)···O(2)···O(3) 93.3(1), O(1)−H(64)···O(2) 163, O(2)−H(65)···O(3) 172.

Single crystals of **1b**, grown from a saturated Et_2O solution, were examined by X-ray crystallography to confirm the monomeric nature and lithiation of the central phenolic group in the triphenol. The hydrogen atoms bound to O(1) and O(3) were located within the diffraction pattern and refined isotropically. The mono-deprotonated ligand is coordinated in a monodentate fashion to the lithium, which resides in a distorted trigonal-planar environment (sum of angles around Li = 357.9°) made up of one phenoxide oxygen [O(2)] and two Et_2O molecules [O(3) and O(4)]. The Li−O(2) distance of 1.822(7) Å is typical of lithium-phenoxide compounds[6a,b,22] and shows the expected shortening with respect to the Li−O(ether) distances of 1.929(8) and 1.912(8) Å. The ligand framework in **1b** adopts a U-shaped conformation with two short separations of 2.569(4) and 2.645(3) Å between the phenoxide [O(2)] and phenolic oxygen atoms [O(1), O(3)]. The proximity of phenoxide and phenolic groups promotes intramolecular hydrogen bonding.[23] The solid-state structure in **1b** discussed above is not observed in solution. The ^1H NMR spectra of the mono-lithium salts **1a** and **1b** in C_6D_6 at room temperature show the absence of molecular symmetry, as suggested by two inequivalent ortho ${}^tBu$ environments. The methylene protons linking the phenyl rings are broad, suggesting that a dynamic process is occurring in this system. The remaining OH resonances could not be assigned because of broadening and overlapping. The ^7Li NMR spectra of **1a** and **1b** in C_6D_6 exhibit a single resonance at 2.06 and 2.18 ppm, respectively.

The related mono-potassium salt of the sulfur-bridged diphenol $1,1'\text{-}S(2\text{-}KO)(2'\text{-}HO)(C_6H_2{}^tBu\text{-}3\text{-}Me\text{-}5)_2(Et_2O)$ underwent monoalkylation with methyl iodide to give the corresponding anisole-phenol.[24] However, attempts to prepare the ether-diphenols by alkylation of the mono-lithium salts **1a** and **1b** were unsuccessful. For example, treatment of **1b** with $PhCH_2Cl$ in THF at 60 °C and subsequent hydrolysis led to the recovered starting triphenol $H_3[^{tBu}O_3]$. As an alternative, we explored mono-*O*-alkylation of $H_2[^RO_2O]$ by using methyl *p*-toluenesulfonate (MeOTs) and a relatively weak base K_2CO_3. This follows the reports for selective dialkylation of calix[4]arenes in the 1,3-position.[25] The triphenol $H_3[^RO_3]$ reacted with MeOTs in the presence of 0.5 equiv of K_2CO_3 to afford the corresponding anisole-diphenol $H_2[^RO_2O]$ (R = Me (**2a**), ${}^tBu$ (**2b**)) in good yields. Although the synthesis of $H_2[^{Me}O_2O]$ was previously reported by the condensation reaction between 2-*tert*-butyl-4-methylphenol and 2,5-hydroxymethyl-4-methylanisole under acidic conditions, the yield was relatively low (12%).[20a] The ^1H NMR spectra of $H_2[^RO_2O]$ in $CDCl_3$ are consistent with a symmetrical molecule, and the phenolic protons reside at 6.32 for **2a** and 6.34 ppm for **2b**. A solution of $H_2[^RO_2O]$ in Et_2O reacted smoothly with 2 equiv of ${}^nBuLi$ at 0 °C to produce the dilithium salt $Li_2[^RO_2O]$, which could be utilized for subsequent transmetalation reactions without further purification.

A view of the molecular structure of $H_2[^{Me}O_2O]$ (**2a**) is shown in Figure 2. All of the hydrogen atoms were found and refined isotropically. The molecule is bisected by a crystallographic mirror plane containing the atoms O(2), C(8), C(11), C(17), and C(18). Like the monolithiated derivative **1b**, intramolecular hydrogen bonding interaction induces a U-shaped conformation of the $[^{Me}O_2O]$ backbone. However, the weakening of hydrogen bonding interactions in **2a** is reflected in O···O separations (3.029(2) Å) that are substantially greater than in the mono-lithium salt **1b** (2.269(4), 2.645(3) Å), consistent with a decrease in electron density on the O(2) atom upon alkylation. The three oxygen atoms of **2a** form a bent arrangement with the O(1)···O(2)···O(1′) angle of 83.79(4)°. This contrasts to an S-shaped

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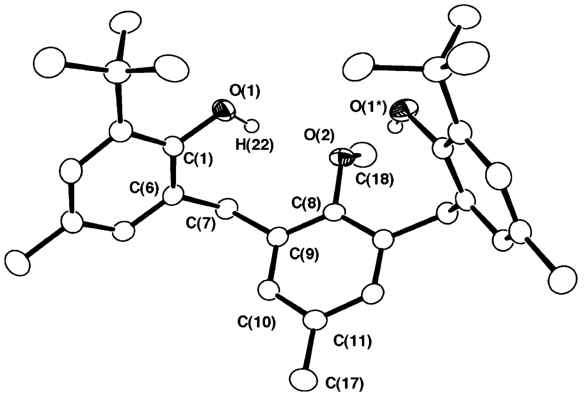
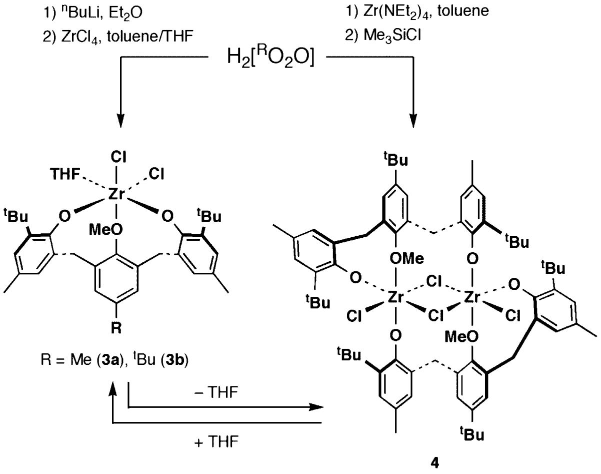


Figure 2. Molecular structure of $H_2[^{Me}O_2O]$ (**2a**). Hydrogen atoms bound to carbon have been omitted for clarity. Selected bond distances (Å) and angles (deg): O(1)−C(1) 1.382(1), O(2)−O(8) 1.408(2), O(2)−C(18) 1.452(3), O(1)···O(2) 3.039(2), O(2)···H(22) 2.18, C(8)−O(2)−C(18) 113.0(2), C(6)−C(7)−C(9) 111.9(1), O(1)···O(2)···O(1′) 83.79(1), O(1)−H(22)···O(2) 163.

Scheme 2



conformation adopted by the triphenol $H_3[^RO_3]$, in which the corresponding arrangement in $H_3[^RO_3]$ is linear.[6b]

Synthesis of Zirconium Complexes. To probe the coordination ability of the anisole-diphenoxide ligands, we carried out the transmetalation reaction of $Li_2[^RO_2O]$ with $ZrCl_4$ (Scheme 2). Addition of an Et_2O solution of $Li_2[^RO_2O]$ to $ZrCl_4$ in toluene/THF at −78 °C and heating to 60 °C overnight afforded $[^RO_2O]ZrCl_2(thf)$ (R = Me (**3a**), ^{t}Bu (**3b**)) as a colorless solid (**3a**, 78% yield; **3b**, 64%). Upon dissolution in toluene/hexane, the THF adduct **3** gradually converted into THF-free **4**. Starting from **3b**, THF-free **4** could be isolated as colorless crystals. An X-ray study revealed **4** to be dimeric $\{[^{tBu}O_2O]ZrCl_2\}_2$ (vide infra). In agreement with the presence of a monomer−dimer equilibrium, the interconversion of **3** into **4** was shown to be reversible. Exposure of the colorless solid **4** to THF and evaporation of the solvent led to the clean formation of **3b**. For the preparation of **4**, we also made use of a sequence reaction in which initially $Zr(NEt_2)_4$ was reacted in toluene with 1 equiv of $H_2[^{tBu}O_2O]$, followed by the evaporation of NEt_2H and subsequent addition of excess Me_3SiCl.

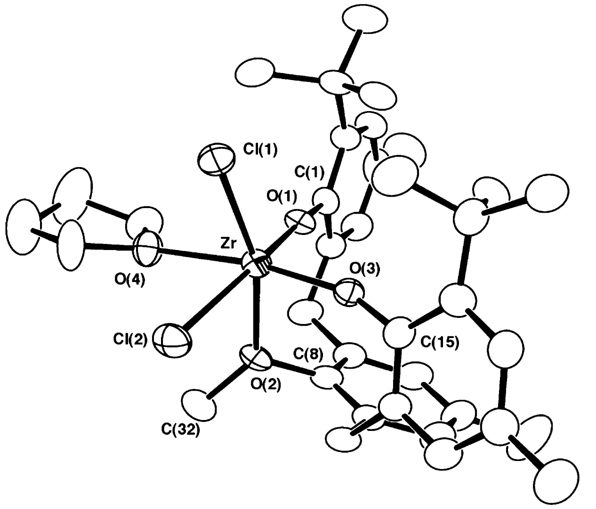


Figure 3. Molecular structure of $[^{Me}O_2O]ZrCl_2(thf)$ (**3a**). All of the hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Zr−Cl(1) 2.422(2), Zr−Cl(2) 2.491(1), Zr−O(1) 1.970(3), Zr−O(2) 2.250(3), Zr−O(3) 1.950(3), Zr−O(4) 2.287(3), Cl(1)−Zr−Cl(2) 90.56(5), O(1)−Zr−O(2) 85.6(1), O(1)−Zr−O(3) 101.4(1), O(2)−Zr−O(3) 92.4(1), Cl(1)−Zr−O(2) 163.52(9), Cl(2)−Zr−O(1) 161.5(1), O(3)−Zr−O(4) 170.8(1), C(8)−O(2)−C(32) 113.8(3), Zr−O(1)−C(1) 173.2(3), Zr−O(2)−C(8) 113.1(2), Zr−O(3)−C(15) 159.4(2).

Crystals of THF adduct **3a** were grown from a saturated toluene solution containing a small amount of THF and analyzed by single-crystal X-ray diffraction (Figure 3). The coordination geometry at zirconium is distorted octahedral, including the Zr−O(anisole) interaction of 2.250(3) Å. The tridentate $[^{Me}O_2O]$ ligand facially caps the metal in a U-shaped conformation, with the remainder of the coordination sphere occupied by one THF molecule and two mutually *cis*-chloride ligands. The obtuse Zr−O(phenoxide)−C_{ispo} angles (173.2(3), 159.4(2)°) are typical of d^0 metal phenoxide complexes, and the Zr−O(1) and Zr−O(3) distances of 1.970(3) and 1.950(3) Å are in agreement with those of the zirconium phenoxide complexes.[26−28] The THF ligand is trans to the phenoxide oxygen O(3) with an angle of 170.8(1)°, and the Zr−O(THF) distance of 2.287(3) Å is slightly elongated relative to the Zr−O(anisole) distance. The ready loss of the THF ligand from **3** to form **4** could be attributable to the trans labilizing ability of the phenoxide group. The Zr−Cl bond distances of 2.422(2) and 2.491(1) Å are within the previously found ranges.[27] The ^1H NMR spectra of **3a** and **3b** show a broadened AB system for the methylene protons and one single resonance for the ortho ^{t}Bu groups, indicating an average C_s symmetry and broad resonances for THF. This suggests reversible dissociation of coordinated THF on the NMR time scale. When an excess of THF was added to a solution of **2** in C_6D_6, only one set of average resonances for the THF protons was observed.

The zirconium centers in dimeric **4** (Figure 4) also possess

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(26) (a) Caselli, A.; Giannini, L.; Solari, E.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1997**, *16*, 5457−5469. (b) Chisholm, M. H.; Huang, J.-H.; Huffman, J. C.; Streib, W. E.; Tiedtke, D. *Polyhedron* **1997**, *16*, 2941−2949.

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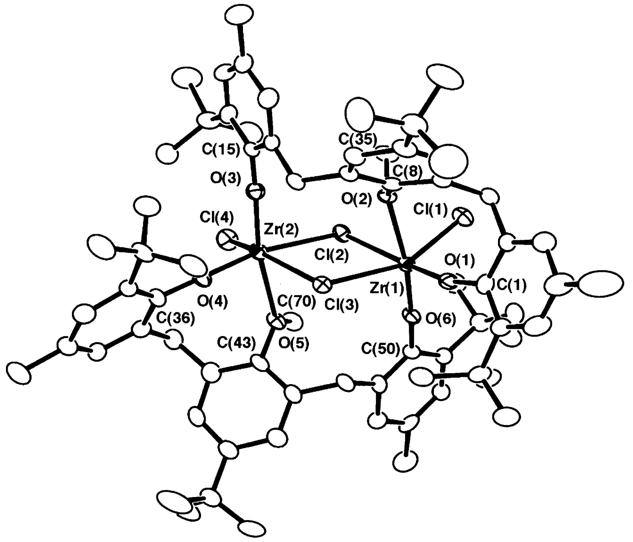
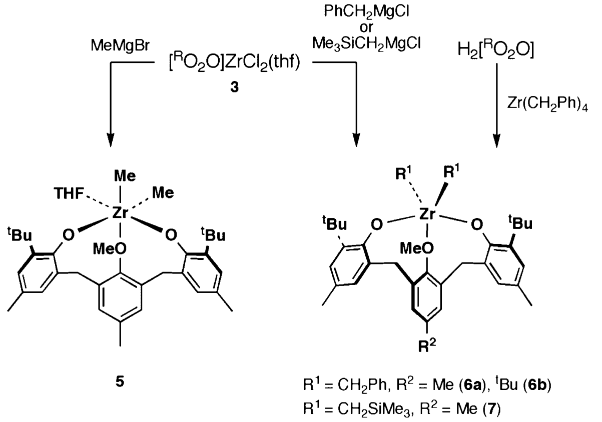


Figure 4. Molecular structure of $[^{t\mathrm{Bu}}\mathrm{O_2O}]_2\mathrm{Zr_2Cl_4}$ (**4**). All of the hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Zr(1)···Zr(2) 4.109(1), Zr(1)−Cl(1) 2.412(2), Zr(1)−Cl(2) 2.623(2), Zr(1)−Cl(3) 2.638(2), Zr(2)−Cl(2) 2.630(2), Zr(2)−Cl(3) 2.650(2), Zr(2)−Cl(4) 2.412(2), Zr(1)−O(1) 1.921(5), Zr(1)−O(2) 2.382(3), Zr(1)−O(6) 1.937(3), Zr(2)−O(3) 1.940(3), Zr(2)−O(4) 1.917(4), Zr(2)−O(5) 2.366(3), Cl(2)−Zr(1)−Cl(3) 77.68(5), Cl(2)−Zr(2)−Cl(3) 77.36(5), Zr(1)−Cl(2)−Zr(3) 102.95(6), Zr(1)−Cl(3)−Zr(2) 102.00(6), Cl(1)−Zr(1)−Cl(3) 155.74(4), Cl(2)−Zr(1)−O(1) 168.2(1), O(2)−Zr(1)−O(6) 170.53(18), Cl(3)−Zr(2)−Cl(4) 155.17(5), Cl(2)−Zr(2)−O(4) 168.3(1), O(3)−Zr(2)−O(5) 170.2(2), C(8)−O(2)−C(35) 108.1(3), C(43)−O(5)−C(70) 110.4(4), Zr(1)−O(1)−C(1) 166.0(4), Zr(1)−O(2)−C(8) 129.2(2), Zr(1)−O(6)−C(50) 175.9(4), Zr(2)−O(3)−C(15) 173.8(4), Zr(2)−O(4)−C(36) 167.8(4), Zr(2)−O(5)−C(43) 128.8(3).

a distorted octahedral geometry but this involves bridging chloride ligands forming a planar $\mathrm{Zr_2}(\mu{-}\mathrm{Cl})_2$ core. The $[^{t\mathrm{Bu}}\mathrm{O_2O}]$ ligands span two metals in an S-shaped conformation. It is noteworthy that the overall dimeric structure of **4** is different from those of the triphenoxide $[^{\mathrm{R}}\mathrm{O_3}]$ complexes, in which the complexes possess bridging central phenoxide groups of $[^{\mathrm{R}}\mathrm{O_3}]$ ligands rather than dimerizing via the chloride ligands.[21,29] This reflects a greater tendency for the central phenoxide group of the $[^{\mathrm{R}}\mathrm{O_3}]$ ligand to act as a bridging ligand. Each zirconium center is coordinated to three oxygen donors and one terminal and two bridging chloride ligands. Two oxygen donors (phenoxide and anisole) are provided by one $[^{t\mathrm{Bu}}\mathrm{O_2O}]$ ligand, whereas the third oxygen donor (phenoxide) arises from the other. These three oxygen atoms are arranged meridionally in each zirconium center. The molecule has approximate C_2 symmetry with the axis passing through two bridging chloride ligands. The geometrical parameters around the zirconium centers are within the expected ranges. The Zr−O(anisole) distances of 2.382(3) and 2.366(3) Å in **4** are substantially longer than those found in **3a**. This elongation can be accounted for by the difference between the trans influences between phenoxide and chloride ligands. The ^{1}H NMR spectrum of **4** is consistent with the solid-state structure. **4** exhibits two pairs of doublets due to methylene protons, which are diagnostic of an asymmetric environment adopted by the $[^{\mathrm{R}}\mathrm{O_2O}]$ ligand.

Scheme 3



Dichloride **3** complexes are useful precursors to zirconium phenoxide derivatives, and the synthesis of zirconium compounds derived from **3** is summarized in Scheme 3. Dialkyl compounds were prepared from a cold solution of **3** in toluene/THF and 2 equiv of Grignard reagents in $\mathrm{Et_2O}$. Reaction of **3a** with 2 equiv of MeMgBr afforded $[^{\mathrm{Me}}\mathrm{O_2O}]\mathrm{ZrMe_2(thf)}$ (**5**) as a colorless solid in 88% yield. In a manner like that of precursor **3**, the coordinated THF is labile in solution, the THF protons appearing as broad resonances in the NMR spectra. The ^{1}H NMR spectrum of **5** shows a singlet for the ortho ^{t}Bu groups (1.54 ppm), two singlets for the para Me groups (1.50 and 2.31 ppm in a 1:2 ratio), and a pair of doublets for the methylene protons of the $[^{\mathrm{R}}\mathrm{O_2O}]$ ligand (3.21 and 4.22 ppm, $J = 13.2$ Hz) along with two singlets for inequivalent Zr−Me groups (0.79 and 1.17 ppm), consistent with C_s symmetry in solution on the NMR time scale. In the $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectrum, the signals for the methyl groups on zirconium are coincidentally overlapping and appear as a broad peak at 44.9 ppm. On the basis of the X-ray study of **3a**, we presume that **5** has a facial geometry with the $[^{\mathrm{Me}}\mathrm{O_2O}]$ ligand adopting a U-shaped conformation (Scheme 3).

When the more sterically demanding $\mathrm{PhCH_2MgCl}$ and $\mathrm{Me_3SiCH_2MgCl}$ were used instead of MeMgBr, the THF-free alkyl complexes $[^{\mathrm{R}}\mathrm{O_2O}]\mathrm{Zr(CH_2Ph)_2}$ (R = Me (**6a**), R = ^{t}Bu (**6b**)) and $[^{t\mathrm{Bu}}\mathrm{O_2O}]\mathrm{Zr(CH_2SiMe_3)_2}$ (**7**) were obtained as a light-yellow solid and a colorless solid, respectively. Benzyl complexes **6a** and **6b** were also formed quantitatively by the protonolysis reactions of $\mathrm{H_2}[^{\mathrm{R}}\mathrm{O_2O}]$ with $\mathrm{Zr(CH_2Ph)_4}$ in toluene at 0 °C. Products **6** and **7** were isolated base-free as shown by NMR spectroscopy. The NMR data of **6** and **7** reveal two inequivalent alkyl groups on zirconium. In the solid-state (vide infra), two phenoxide rings are not equivalent, but in solution the resonances for a C_s symmetric $[^{\mathrm{R}}\mathrm{O_2O}]$ ligand environment are seen, although two broad resonances assigned to the methylene groups of the $[^{\mathrm{R}}\mathrm{O_2O}]$ ligand indicate a fluxional process in solution. Indeed, upon cooling of the NMR sample, a partial decoalescense of some of the ligand resonances is seen, most notably for these methylene resonances. However, this fluxional process could not be frozen out even at −40 °C. We assume that the fluxional process involves a phenoxide ring exchange via an intermediate having the U-shaped $[^{\mathrm{R}}\mathrm{O_2O}]$ ligand.

X-ray quality crystals of **6a** and **7** were obtained from their toluene/THF solutions. Because their structures are found

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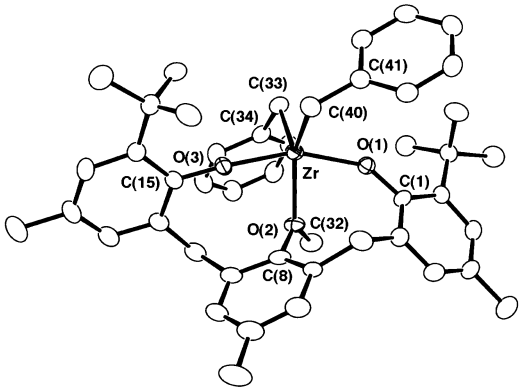
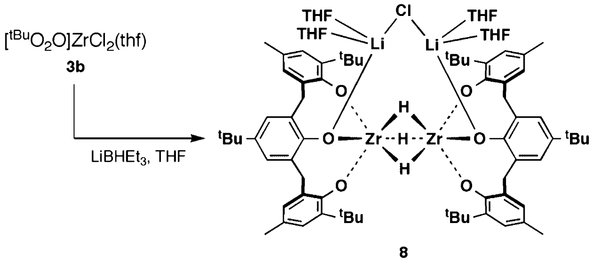


Figure 5. Molecular structure of $[^{Me}O_2O]Zr(CH_2Ph)_2$ (**6a**). All of the hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Zr−O(1) 1.987(2), Zr−O(2) 2.225(2), Zr−O(3) 1.994(2), Zr−C(33) 2.261(3), Zr−C(40) 2.253(3), Zr···C(34) 3.000(3), Zr···C(41) 3.180(3), O(1)−Zr−O(2) 77.05(10), O(1)−Zr−O(3) 154.60(11), O(2)−Zr−O(3) 81.85(10), O(2)−Zr−C(33) 116.50(12), O(2)−Zr−C(40) 136.82(12), C(33)−Zr−C(40) 106.61(15), Zr−O(1)−C(1) 146.2(2), Zr−O(2)−C(8) 118.5(2), Zr−O(3)−C(15) 172.1(2), Zr−C(33)−C(34) 104.5(2), Zr−C(40)−C(41) 114.4(2), C(8)−O(2)−C(32) 114.9(3).

to be similar,[30] that of **6a** is discussed in detail. The molecular structure of **6a** is presented in Figure 5. The compound is a distorted trigonal bipyramidal species with the S-shaped $[^{Me}O_2O]$ ligand adopting an approximately meridional coordination mode. The two phenoxide groups occupy the apical positions [O(1)−Zr−O(3) = 154.6(1)], and they are bent away from the side of the molecule that contains the anisole C(32) atom, as judged by the difference between O(1)−Zr−C(33) and O(1)−Zr−C(40) angles (12.1 °). The Zr−O bond distances are similar to the corresponding distances of **3a**. The two benzyl groups are bound to the metal in an η^1 fashion with the Zr−C−C_{ipso} angles of 104.5(2) and 114.4(2)°, and the Zr−C distances of 2.261(3) and 2.253(3) Å are comparable to those observed in other zirconium benzyl complexes incorporating phenoxide ligands.[27,28] The lack of any η^2 character in the benzyl groups indicates that the zirconium center supported by the $[^{R}O_2O]$ ligand is not particularly electrophilic.

Scheme 4



Hydride complexes containing hard, ancillary π-donor ligands such as phenoxides and siloxides have been found to display unique reactivity, for example undergoing catalytic all-cis hydrogenation of polynuclear aromatics and participating in the activation of small molecules.[31] We have previously reported the synthesis of the dihydride-benzylidene dizirconium complex $[^{R}O_2O]_2Zr_2(\mu{-}H)_2(\mu{-}CHPh)$ via the hydrogenation of benzyl **6**.[18b] In view of the success in the synthesis of the dihydride-benzylidene complex, we were interested in testing the versatility of the $[^{R}O_2O]$ ligand in stabilizing other zirconium hydride species. Methyl **5** was analogously treated under an atmosphere of H_2, but no reaction occurred according to ^{1}H NMR spectroscopy. This implies that the THF coordination prevents the complex from undergoing hydrogenation of the Zr−C bonds. On the other hand, prolonged exposure of THF-free **7** to H_2 resulted in a mixture of Me_4Si and uncharacterized zirconium compounds.

Some early-transition-metal hydrides have been synthesized by the addition of hydride reagents such as $LiBHEt_3$.[32] Treatment of the chloride **3b** with $LiBHEt_3$ in THF afforded $[Li_2(thf)_4Cl]\{[^{tBu}O_3]Zr\}_2(\mu{-}H)_3\}$ (**8**) as colorless crystals in 25% isolated yield (Scheme 4). Attempts to identify any other metal-containing products of this reaction were unsuccessful, but the generation of **8** was reproducible. Previously, we have found that the reaction of $[^{tBu}O_3]ZrCl(thf)_2$ with $LiBHEt_3$ gave **8** in 59% yield.[33] Demethylation associated with the formation of **8** is frequently observed in the interaction of methoxy-calix[4]arenes with early transition metals.[34] We suppose that coordination of the anisole group to zirconium facilitates demethylation of the $[^{R}O_2O]$ ligand via nucleophilic attack by the hydride reagent.

Summary. The linear triphenol $H_3[^{R}O_3]$ was found to undergo mono-deprotonation and mono-*O*-methylation, in which the central phenol unit was selectively functionalized to afford **1** and **2**. The readily available diphenol-anisole **2** provides a useful entry point to organometallic and coordination complexes of zirconium. A series of five- or six-coordinate derivatives have been prepared and crystallographically characterized. The preparation of hydride complexes through the addition of the hydride reagent $LiBHEt_3$ led to demethylation of the $[^{R}O_2O]$ ligand, yielding the trihydride-bridged dizirconium complex supported by the triphenoxide $[^{R}O_3]$ ligand. The anisole group of the $[^{R}O_2O]$ ligand not only functions as a weakly binding group, but it can also undergo facile demethylation to generate the corresponding $[^{R}O_3]M$ fragment. We are continuing to explore the early-transition-metal chemistry of the $[^{R}O_2O]$ ligand systems, and this work will be reported in due course.

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(30) Crystal data for **7**: formula = $C_{50}H_{76}O_3Si_2Zr$; M = 872.54; monoclinic; space group, $P2_1/n$ (no. 14); a = 11.453(6), b = 18.622(9), c = 24.540(13) Å, β = 104.754(7)°, V = 5061(4) Å^3; Z = 4; D_{calcd} = 1.145 g cm^{-3}; Mo Kα = 3.009 cm−1; collected reflns = 39 998; unique reflns = 11 485; parameters = 542; R1[$I > 2\sigma(I)$] = 0.0883; wR2 (all) = 0.1933; GOF = 1.039; peak/hole (e Å^{-3}) = 6.64/−3.10. Additional crystallographic data are given in the Supporting Information (CIF format).

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Experimental Section

General Procedures. All of the manipulations of air- and/or moisture-sensitive compounds were performed under an inert atmosphere of argon or dinitrogen using standard Schlenk-line techniques. All of the dried solvents and chemicals commercially available were used as received without further purification. Linear-linked phenol trimers $H_3[^{R}O_3]$ were synthesized according to the literature procedures.[6b,28] Deuterated benzene (benzene-d_6, C_6D_6) and toluene (toluene-d_8, C_7D_8) were dried and degassed over a potassium mirror in vacuo prior to use. Deuterated chloroform (chloroform-d_1, $CDCl_3$) was distilled from calcium hydride prior to use. Air- and/or moisture-sensitive compounds were stored and weighted in a glovebox (MBraun Labmaster 130) filled with dinitrogen. Reactions in small quantities were performed in a glovebox. Nuclear magnetic resonance (NMR) measurements were carried out on JEOL Lambda-500, JNM-GX500, and LA-400 spectrometers at room temperature. Chemical shifts (δ) are given in parts per million. Chemical shifts (δ) for ^1H NMR spectra were referenced to residual protic solvents peaks (residual C_6D_5H in C_6D_6, $^1H(\delta) = 7.15$; residual C_7D_7H in C_7D_8, $^1H(\delta) = 2.09$; residual $CHCl_3$ in $CDCl_3$, $^1H(\delta) = 7.24$). The absolute values of the coupling constants are given in Hertz (Hz), regardless of their signs. Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), quartet (q), and broad (br). Elemental analyses (C, H, and N) were measured using YANACO MT-6 and MSU-32 microanalyzers.

Synthesis of $Li\{H_2[^{Me}O_3]\}(Et_2O)_2$ (1a). A solution of butyllithium (1.58 M in hexane, 1.35 mL, 2.13 mmol) was added dropwise to a solution of $H_3[^{Me}O_3]$ (1.00 g, 2.17 mmol) in diethylether (30 mL) at 0 °C, resulting in the immediate formation of a white precipitate. Evaporation of volatiles afforded $Li\{H_2[^{Me}O_3]\}(Et_2O)_2$ (**1a**) as a colorless solid in a quantitative yield. ^1H NMR (500.00 MHz, C_6D_6) δ 0.92 (br. s, 9 H, ^{t}Bu), 1.09 (t, $J = 7.0$ Hz, 12 H, Et_2O), 1.51 (br. s, 9 H, ^{t}Bu), 1.76 (br. s, 3 H, Me), 2.00 (br. s, 3 H, Me), 2.23 (br. s, 3 H, Me), 3.24 (q, $J = 7.0$ Hz, 8 H, Et_2O), 3.61 (br. s, 1 H), 3.9∼4.2 (overlapping, br. s, 2 H), 4.52 (br. s, 1 H), 4.96 (br. s, 1 H), 5.87 (br. s, 1 H), 6.58 (br. s, 1 H), 6.8∼7.1 (overlapping, br. s, 5 H). ^7Li NMR (194.25 MHz, C_6D_6) δ 2.06. Anal. Calcd for $C_{39}H_{59}LiO_5$: C, 76.19; H, 9.67. Found: C, 75.54; H, 9.30.

Synthesis of $Li\{H_2[^{tBu}O_3]\}(Et_2O)_2$ (1b). Addition of butyllithium (1.58 M in hexane, 2.5 mL, 4.00 mmol) to $H_3[^{tBu}O_3]$ (2.01 g, 4.00 mmol) in diethylether (Et_2O, 50 mL) at 0 °C gave a white precipitate. Workup similar to that above yielded $Li\{H_2[^{tBu}O_3]\}(Et_2O)_2$ (**1b**) as a white precipitate in quantitative yield. ^1H NMR (500.00 MHz, C_6D_6) δ 0.84 (br. s, 9 H, ^{t}Bu), 0.96 (br. s, 9 H, ^{t}Bu), 1.10 (t, $J = 7.0$ Hz, 12 H, Et_2O), 1.56 (br. s, 9 H, ^{t}Bu), 2.23 (br. s, 3 H, Me), 2.31 (br. s, 3 H, Me), 3.25 (q, $J = 7.0$ Hz, 8 H, Et_2O), 3.67 (br. s, 1 H), 4.0∼4.8 (overlapping, br. s, 3 H), 5.07 (br. s, 1 H), 5.80 (br. s, 1 H), 6.80 (br. s, 1 H), 6.85∼7.25 (overlapping, br. s, 4 H), 7.30 (br. s, 1 H). ^7Li NMR (194.25 MHz, C_6D_6) δ 2.18. Anal. Calcd for $C_{42}H_{65}LiO_5$: C, 76.79; H, 9.97. Found: C, 76.70; H, 9.71.

Synthesis of $H_2[^{Me}O_2O]$ (2a). A mixture of $H_3[^{Me}O_3]$ (5.01 g, 10.9 mmol), potassium carbonate (K_2CO_3, 775 mg, 5.61 mmol), and methyl *p*-toluenesulfonate (MeOTs, 2.10 g, 11.3 mmol) in CH_3CN (250 mL) was refluxed overnight. The mixture was poured into dichloromethane (CH_2Cl_2), hydrolyzed with dilute hydrochloric acid, and extracted with CH_2Cl_2. The organic layer was washed with water and dried over anhydrous sodium sulfate. After filtration, the solvent was removed in vacuo to give the crude product. Recrystallization from hexane/CH_2Cl_2 gave $H_2[^{Me}O_2O]$ (**2a**) as colorless crystals (5.09 g, 10.7 mmol, 98% yield). ^1H NMR (500.00 MHz, $CDCl_3$) d 1.32 (s, 18 H, ^{t}Bu), 2.16 (s, 3 H, Me), 2.22 (s, 6 H, Me), 3.83 (s, 4 H, CH_2), 4.00 (s, 3 H, OMe), 6.32 (br. s, 2 H, OH), 6.88 (s, 2 H, ArH), 6.91 (s, 2 H, ArH), 6.93 (s, 2 H, ArH). Anal. Calcd for $C_{32}H_{42}O_3$: C, 80.97; H, 8.92. Found: C, 80.49; H, 8.83.

Synthesis of $H_2[^{tBu}O_2O]$ (2b). The same procedure as used for $H_2[^{Me}O_2O]$ (**2b**) was followed. Reaction of $H_3[^{tBu}O_3]$ (10.0 g, 19.9 mmol), K_2CO_3 (1.40 g, 10.1 mmol), and MeOTs (3.95 g, 21.2 mmol) in CH_3CN (250 mL) afforded colorless crystals of **2b** in 98% yield (10.1 g, 19.5 mmol). ^1H NMR (500.00 MHz, $CDCl_3$) δ 1.18 (s, 9 H, ^{t}Bu), 1.34 (s, 18 H, ^{t}Bu), 2.22 (s, 6 H, Me), 3.87 (s, 4 H, CH_2), 3.98 (s, 3 H, OMe), 6.34 (br.s, 2 H, OH), 6.87 (s, 2 H, ArH), 6.93 (s, 2 H, ArH), 7.10 (s, 2 H, ArH). Anal. Calcd for $C_{35}H_{48}O_3$: C, 81.35; H, 9.36. Found: C, 81.15; H, 9.44.

Synthesis of $Li_2[^{R}O_2O]$. In a typical reaction, a solution of butyllithium (1.56 M in hexane, 5.4 mL, 8.4 mmol) was added dropwise to **2a** (1.95 g, 4.11 mmol) in Et_2O (70 mL) at 0 °C. The resulting colorless solutions of $Li_2[^{Me}O_2O]$ and analogously prepared $Li_2[^{tBu}O_2O]$ were used in the synthesis of **3a** and **3b** without further purification, respectively.

Synthesis of $[^{Me}O_2O]ZrCl_2(thf)$ (3a). To a slurry of $ZrCl_4$ (1.01 g, 4.33 mmol) in toluene (40 mL)/THF (10 mL) at −78 °C was added a Et_2O (70 mL) solution of $Li_2[^{Me}O_2O]$ (4.11 mmol). The mixture was allowed to warm up to room temperature, and then volatiles were removed in vacuo to give a white solid. The solid was dissolved in toluene (60 mL)/THF (10 mL) and stirred overnight at 60 °C. The mixture was centrifuged to remove an insoluble material. The supernatant was evaporated to dryness to yield a solid, which was washed with toluene/hexane to give 2.27 g of **3a** as a colorless solid (3.21 mmol, 78% yield). ^1H NMR (500.00 MHz, C_6D_6) δ 1.21 (br, 4 H, THF), 1.59 (s, 3 H, Me), 1.67 (br. s, 18 H, ^{t}Bu), 2.25 (br. s, 6 H, Me), 3.24 (br. s, 2 H, CH_2), 3.91 (s, 3 H, OMe), 4.23 (br. s, 6 H, overlapping CH_2 and THF), 6.75 (br. s, 4 H, ArH), 6.94 (s, 2 H, ArH). Anal. Calcd for $C_{36}H_{48}Cl_2O_4Zr$: C, 61.17; H, 6.84. Found: C, 61.04; H, 7.24.

Synthesis of $[^{tBu}O_2O]ZrCl_2(thf)$ (3b). A slurry of $ZrCl_4$ (1.02 g, 4.38 mmol) in toluene (30 mL)/THF (10 mL) was treated with $Li_2[^{tBu}O_2O]$ (4.37 mmol) in Et_2O (100 mL) as described for the synthesis of **3a**. The product **3b** was isolated as a colorless solid (2.09 g, 2.79 mmol, 64% yield). ^1H NMR (500.00 MHz, C_6D_6) δ 0.91 (s, 9 H, ^{t}Bu), 1.25 (br, 4 H, THF), 1.58 (br. s, 18 H, ^{t}Bu), 2.26 (br. s, 6 H, Me), 3.39 (br. s, 2 H, CH_2), 3.94 (s, 3 H, OMe), 4.26 (br. s, 6 H, overlapping CH_2 and THF), 6.99 (s, 2 H, ArH), 7.16 (br. s, 4 H, ArH). Anal. Calcd for $C_{39}H_{54}Cl_2O_4Zr$: C, 62.54; H, 7.27. Found: C, 62.65; H, 6.92.

Synthesis of $\{[^{tBu}O_2O]ZrCl_2\}_2$ (4). To a toluene (80 mL) solution of $H_2[^{tBu}O_2O]$ (**2b**) (1.00 g, 1.94 mmol) in toluene (80 mL) at 0 °C was added $Zr(NEt_2)_4$ (0.72 mL, 746 mg, 1.96 mmol). The mixture was stirred at room temperature overnight, and then volatiles were evaporated to leave a white solid. The solid was dissolved in toluene (60 mL) and treated with Me_3SiCl (1.0 mL, 7.87 mmol). The mixture was stirred at room temperature for 2 days. The reaction mixture was centrifuged to remove an insoluble material. Removal of volatiles in vacuo left a colorless solid, which was crystallized from toluene/hexane to afford **4** as colorless crystals (445 mg, 0.33 mmol, 34% yield). ^1H NMR (500.00 MHz, C_6D_6) δ 1.226 (s, 18 H, ^{t}Bu), 1.230 (s, 18 H, ^{t}Bu), 1.48 (s, 18 H, ^{t}Bu), 2.13 (s, 6 H, Me), 2.30 (s, 6 H, Me), 3.31 (d, $J = 13.7$ Hz, 2 H, CH_2), 3.40 (d, $J = 14.9$ Hz, 2 H, CH_2), 3.64 (s, 6 H, OMe), 5.34 (d, $J = 13.7$ Hz, 2 H, CH_2), 5.58 (d, $J = 14.9$ Hz, 2 H, CH_2), 6.63 (s, 2 H, ArH), 6.87 (s, 2 H, ArH), 6.90 (s, 2 H, ArH), 7.03 (d, $J = 2.2$ Hz, 2 H, ArH), 7.05 (s, 2 H, ArH), 7.13 (d, $J = 2.2$ Hz, 2 H, ArH).

Table 1. Crystallographic Data for **1b**, **2a**, **3a**, **4**, and **6a**

	1b	**2a**	**3a**·C_7H_8	**4**·1.5C_6H_{14}	**6a**·C_7H_8
formula	$C_{42}H_{65}O_5Li$	$C_{32}H_{42}O_3$	$C_{43}H_{56}O_4Cl_2Zr$	$C_{79}H_{113}O_6Cl_4Zr_2$	$C_{53}H_{62}O_3Zr$
M	656.91	474.68	799.04	1483.01	838.29
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1$/n (no. 14)	$P2_1$/m (no. 11)	$P2_1$ (no. 4)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a(Å)	13.256(6)	5.973(4)	12.018(7)	14.655(7)	9.311(3)
b(Å)	14.980(6)	25.500(15)	11.985(7)	17.712(9)	14.646(5)
c(Å)	20.820(9)	9.858(7)	14.529(9)	17.960(9)	17.238(6)
αdeg)				105.240(7)	95.777(7)
β(deg)	95.641(7)	113.752(9)	90.257(10)	103.929(6)	92.230(3)
γ(deg)				106.408(1)	102.844(7)
V(Å^3)	4114(3)	1374.2(16)	2093(2)	4057(3)	2275.8(14)
Z		4	2		2
D_{calcd}/g cm^{-3}	1.061	1.147	1.268	1.214	1.223
cryst size (mm)	0.50 × 0.10 × 0.10	0.30 × 0.20 × 0.20	0.40 × 0.20 × 0.16	0.35 × 0.20 × 0.05	0.30 × 0.10 × 0.05
μ(Mo Kα)/cm^{-1}	0.668	0.715	4.283	4.347	2.824
collected reflns	31 881	3135	4985	31 173	17 490
unique reflns	9388	3135	4985	17 296	9656
params	504	252	507	875	512
R1[$I > 2\sigma(I)$]^a	0.0984	0.0543	0.0630	0.0891	0.0714
wR2 (all)^b	0.2370	0.1140	0.0754	0.1915	0.1409
GOF	0.987	0.966	1.038	1.406	1.033
peak/hole (e Å^{-3})	0.84/−0.73	0.28/−0.31	1.14/−0.61	1.45/−0.68	1.45/−0.77

^{a} $R1 = \sum||Fo| - |Fc||/\sum |Fo|$. ^{b} $wR2 = [\sum(w(Fo^2 - Fc^2)^2/\sum w(Fo^2)^2)^{1/2}$.

Anal. Calcd for $C_{70}H_{92}Cl_4O_6Zr_2{\cdot}2C_6H_{14}$: C, 64.54; H, 7.93. Found: C, 64.89; H, 7.86.

Synthesis of [$^{Me}O_2O$]$ZrMe_2$(thf) (5). A solution of MeMgBr (3.0 M in Et_2O, 0.8 mL, 2.4 mmol) was added dropwise to **3a** (844 mg, 1.19 mmol) in toluene (30 mL)/THF (5 mL) at −78 °C. The colorless solution gradually turned light-yellow. The mixture was allowed to warm up to room temperature and stirred for 2 h. The solvent was removed in vacuo to leave a colorless solid. The residue was extracted into toluene (50 mL) and centrifuged to remove an insoluble material. The supernatant was evaporated to dryness, and the residue was washed with hexane, yielding 699 mg of **5** as a colorless solid (1.05 mmol, 88%). ^{1}H NMR (500.00 MHz, C_6D_6) δ 0.79 (s, 3 H, ZrMe), 1.17 (s, 3 H, ZrMe), 1.25 (br. s, 4 H, THF), 1.50 (s, 3 H, Me), 1.54 (s, 18 H, ^{t}Bu), 2.31 (s, 6 H, Me), 3.21 (d, J = 13.2 Hz, 2 H, CH_2), 3.48 (s, 3 H, OMe), 3.87 (br. s, 4 H, THF), 4.22 (d, J = 13.2 Hz, 2 H, CH_2), 6.71 (s, 2 H, ArH), 7.00 (s, 2 H, ArH), 7.19 (s, 2 H, ArH). ^{13}C{^{1}H} NMR (100.40 MHz, C_6D_6): δ 25.1 (THF), 44.9 (br. ZrMe), 65.6 (OMe), 71.1 (THF). Anal. Calcd for $C_{38}H_{54}O_4Zr$: C, 68.52; H, 8.17. Found: C, 68.09; H, 8.31.

Synthesis of [$^{Me}O_2O$]Zr(CH_2Ph)$_2$ (6a). Method A. A solution of $PhCH_2MgCl$ (1.0 M in Et_2O, 1.4 mL, 1.4 mmol) was added dropwise to a colorless solution of **4a** (0.50 g, 0.71 mmol) in toluene (30 mL)/THF (5 mL) at −78 °C. The solution gradually turned yellow, and it was allowed to warm up to room temperature. After 2 h of stirring, the solvent was evaporated in vacuo. The residue was extracted into toluene (60 mL) and centrifuged to remove an insoluble material. The supernatant was evaporated to dryness, and the residue was washed with hexane, yielding 0.45 g of **6a** as a light-yellow solid (0.60 mmol, 85%).

Method B. A solution of toluene (50 mL) and H_2[$^{Me}O_2O$] (**2a**) (1.41 g, 2.97 mmol) was added to a yellow-orange solution of tetrabenzylzirconium (Zr(CH_2Ph)$_4$, 1.35 g, 2.96 mmol) in toluene (60 mL) at 0 °C. The solution immediately turned light in color. After the mixture was allowed to warm up to room temperature and stirred for 2 h, the solvent was removed in vacuo to afford the product as a light-yellow solid in quantitative yield. Recrystallization from toluene/hexane gave 1.73 g of **6a** as light-yellow crystals (2.32 mmol, 78% yield).

Data for 6a. ^{1}H NMR (500.00 MHz, C_6D_6): δ 1.68 (s, 18 H, ^{t}Bu), 1.71 (s, 3 H, Me), 2.29 (s, 6 H, Me), 2.67 (s, 3 H, OMe), 2.77 (br.s, 2 H, $ZrCH_2$), 3.17 (br.s, 2 H, $ZrCH_2$), 3.26 (d, J = 14.0 Hz, 2 H, CH_2), 3.44 (d, J = 14.0 Hz, 2 H, CH_2), 6.58 (s, 2 H, ArH), 6.75 (t, J = 7.5 Hz, 1 H, benzyl(para)), 6.84 (t, J = 7.5 Hz, 1 H, benzyl(para)), 6.91 (d, J = 2.0 Hz, 2 H, ArH), 6.97∼7.13 (overlapping m, 6 H, benzyl(meta), benzyl(ortho)), 7.19 (d, J = 2.0 Hz, 2 H, ArH), 7.30 (d, J = 7.5 Hz, 2 H, benzyl(ortho)). ^{13}C{^{1}H} NMR (100.40 MHz, C_6D_6): δ 68.0 (OMe), 69.3 ($ZrCH_2$), 76.0 ($ZrCH_2$). Anal. Calcd for $C_{46}H_{54}O_3Zr{\cdot}C_6H_{14}$: C, 75.21; H, 8.34. Found: C, 75.19; H, 8.40.

Synthesis of [$^{tBu}O_2O$]Zr(CH_2Ph)$_2$ (6b). Method A. 6b was formed by a procedure analogous to that for **6a** in Method A, with $PhCH_2MgCl$ (1.0 M in Et_2O, 2.4 mL, 2.4 mmol) and **6b** (875 mg, 1.17 mmol) in toluene (45 mL)/THF (8 mL) at −78 °C. The volatiles were then removed in vacuo to leave a light-yellow solid. The residue was extracted into toluene (50 mL). The resulting solution was centrifuged and evaporated to dryness. Washing with a minimal amount of hexane yielded 773 mg of **6b** as a light-yellow solid (0.98 mmol, 84%).

Method B. 6b was formed by a procedure analogous to that for **6a** in Method B, with Zr(CH_2Ph)$_4$ (1.75 g in 80 mL of toluene, 3.84 mmol), and H_2[$^{tBu}O_2O$] (**2b**) (1.75 g in 60 mL of toluene, 3.84 mmol) at 0 °C. After evaporation of the volatiles, **6b** was obtained as a light-yellow solid in quantitative yield. The product was crystallized from hexane (2.15 g, 2.73 mmol, 72%).

Data for 6b. ^{1}H NMR (500.00 MHz, C_6D_6): δ 0.98 (s, 9 H, ^{t}Bu), 1.65 (s, 18 H, ^{t}Bu), 2.27 (s, 6 H, Me), 2.65 (br. s, 2 H, $ZrCH_2$), 2.71 (s, 3 H, OMe), 3.16 (br. s, 2 H, $ZrCH_2$), 3.37 (d, J = 14.5 Hz, 2 H, CH_2), 3.55 (d, J = 14.5 Hz, 2 H, CH_2), 6.75 (t, J = 7.5 Hz, 1 H, benzyl(para)), 6.87 (t, J = 7.5 Hz, 1 H, benzyl(para)), 6.96 (s, 2 H, ArH), 6.98∼7.13 (overlapping m, 8 H, ArH, benzyl(meta), benzyl(ortho)), 7.18 (d, J = 2.0 Hz, 2 H, ArH), 7.33 (d, J = 7.5

Hz, 2 H, benzyl(ortho)). $^{13}C\{^1H\}$ NMR (100.40 MHz, C_6D_6): δ 68.0 (OMe), 71.3 ($ZrCH_2$), 74.9 ($ZrCH_2$). Anal. Calcd for $C_{49}H_{60}O_3Zr\cdot 0.5\ C_6H_{14}$: C, 75.22; H, 8.18. Found: C, 75.16; H, 8.01.

Synthesis of [$^{tBu}O_2O$]Zr(CH_2SiMe_3)$_2$ (7). To **3a** in toluene (60 mL) at −78 °C was added a solution of Me_3SiCH_2MgCl (1.0 M in Et_2O, 4.6 mL, 4.6 mmol). The mixture was allowed to warm up to room temperature and stirred for 6 h. The solution was centrifuged and evaporated to dryness. Recrystallization from toluene afforded 1.66 g of **7** as colorless crystals (2.13 mmol, 92% yield). ^1H NMR (500.00 MHz, C_6D_6): δ −0.01 (s, 2 H, $ZrCH_2Si$), 0.10 (s, 9 H, $SiMe_3$), 0.21 (s, 9 H, $SiMe_3$), 0.29 (s, 2 H, $ZrCH_2Si$), 1.03 (s, 9 H, ^{t}Bu), 1.71 (s, 18 H, ^{t}Bu), 2.26 (s, 6 H, Me), 3.02 (s, 3 H, OMe), 3.40∼4.10 (br, 4 H, CH_2), 6.96 (s, 2 H, ArH), 7.11 (s, 2 H, ArH), 7.18 (s, 2 H, ArH). $^{13}C\{^1H\}$ NMR (100.40 MHz, C_6D_6): δ 2.7 ($SiMe_3$), 3.2 ($SiMe_3$), 61.7 ($ZrCH_2$), 63.4 ($ZrCH_2$), 66.3 (OMe). Anal. Calcd for $C_{43}H_{68}O_3Si_2Zr$: C, 66.18; H, 8.78. Found: C, 63.73; H, 8.68. We have been unable to obtain a satisfactory elemental analysis. For example, diffraction-quality crystals of **7** consistently gave a lower-than-expected carbon analysis, even when combustion aids were used. We believe that on the basis of the NMR spectra and the X-ray crystal structure that the compound is authentic and analytically pure but that either its lability on heating or incomplete combustion is responsible for the disappointing elemental analysis.

Reaction of 3b with $LiBHEt_3$. A solution of $LiBHEt_3$ (1.0 M in THF, 3.0 mL, 3.0 mmol) was added to a stirred solution of **3b** (621 mg, 0.83 mmol) in THF (20 mL) at −78 °C. The mixture was allowed to warm up to room temperature and stirred for 4 h. After evaporation of the solvent, the residue was dissolved in toluene (20 mL). After removal of an insoluble material by centrifugation, the supernatant was concentrated and stored at −30 °C to afford $[Li_2(thf)_4Cl]\{([^{tBu}O_3]Zr)_2(\mu\text{-}H)_3\}$ (**8**) as colorless crystals in 25% yield (159 mg, 0.10 mmol). ^1H NMR (500.00 MHz, toluene-d_8): δ 0.96 (s, 18 H, ^{t}Bu), 1.38 (br. s. THF), 1.48 (s, 36 H, ^{t}Bu), 2.30 (s, 12 H, Me), 3.54 (d, $J = 13.5$ Hz, 4 H, CH_2), 3.55 (br. s. THF), 4.98 (d, $J = 13.5$ Hz, 4 H, CH_2), 5.91 (s, 3 H, μ-H), 7.06 (s, 8 H, ArH × 2), 7.27 (s, 4 H, ArH).

X-ray Diffraction Studies for 1b, 2a, 3a, 4, 6a, and 7. Crystallographic data are summarized in Table 1. X-ray quality single crystals were obtained from Et_2O for **1b** as colorless blocks, hexane/CH_2Cl_2 for **2a** as colorless plates, toluene/THF for **3a**$\cdot C_7H_8$ as colorless blocks, hexane/toluene for **4**$\cdot$1.5 C_6H_{14} as colorless blocks, **6a**$\cdot C_7H_8$ as light-yellow blocks, and toluene for **7**$\cdot C_7H_8$ as colorless blocks. Crystals were immersed in Paraton-N oil on a nylon loop and transferred to a Rigaku Mercury (for **2a** and **7**$\cdot C_7H_8$) or Saturn (for **3a**$\cdot C_7H_8$, **4**$\cdot$1.5 C_6H_{14}, and **6a**$\cdot C_7H_8$) CCD diffractometer equipped with a Rigaku GNNP low-temperature device. Data were collected at −100(1) °C under a cold nitrogen stream using graphite monochromated Mo Kα radiation ($\lambda = 0.71070$ Å). Equivalent reflections were merged, and the images were processed with the CrystalClear (Rigaku) program. Corrections for Lorentz-polarization effects and absorption were performed.

All of the structures were solved by direct methods and refined on F^2 by the full-matrix least-squares method using the *CrystalStructure* (Rigaku) software package. Anisotropic refinement was applied to all non-hydrogen atoms. For **1b**, the hydroxy hydrogen atoms H(64) and H(65) were located from the difference Fourier map and were refined isotropically, and the remaining hydrogen atoms were put at calculated positions with C−H distances of 0.97 Å. All of the hydrogen atoms of **2a** were located from the different Fourier map and were refined isotropically. For **3a**, **4**, **6a**, and **7**, all of the hydrogen atoms were put at calculated positions with C−H distances of 0.97 Å. The crystal solvents of **4**$\cdot 1.5C_6H_{14}$ and **6a**$\cdot C_7H_8$were refined isotropically, in which no hydrogen atom was included. Additional crystallographic data are given in the Supporting Information (CIF format).

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Supporting Information Available: Listing for X-ray crystallographic files in CIF format for the compounds of **1b**, **2a**, **3a**, **4**, **6a**, and **7** as well as the molecular structure of **7** and the variable temperature ^1H NMR spectra of **6a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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