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Synthesis of Zirconium Aryloxide Complexes Containing Pendent Vinyl Groups

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The attachment of pendent olefin groups to oxygen-ligated zirconium complexes using olefin-substituted phenols and alcohols and readily accessible zirconium reagents is described. Syntheses of three crystallographically characterizable complexes isolable in 55−90% yield are reported. Eugenol, $HOC_6H_3(OMe\text{-}2)(CH_2CH{=}CH_2\text{-}4)$ (HOAr) reacts with $[Zr(O^iPr)_4(HO^iPr)]_2$ in toluene to form $[(^iPrO)_2(ArO)Zr(\mu\text{-}O^iPr)]_2$, **1**. $CH_2{=}CHCH_2OH$ reacts with $[Zr(NMe_2)_4]_2$ in the presence of 2,6-dimethylphenol to form the mixed ligand salt, $\{Me_2NH_2\}\{[(2,6\text{-}Me_2C_6H_3O)_3Zr]_2(\mu\text{-}OCH_2CH{=}CH_2)_3\}$, **2**. The potassium salt derived from eugenol, KOAr, reacts with “$Zr(OEt)_4$” in THF to form $[K_2Zr(OAr)_4(OEt)]_2(O)$, **3**.

Introduction

The field of hybrid materials has grown enormously as advances in technology create needs for higher performance materials.[1] One area of current interest in the hybrid materials field is the synthesis of polymers which contain metals.[2] Such polymers have a variety of specialty applications depending on their composition and structure and several approaches to such materials are being pursued.

We report here efforts to make olefin-functionalized zirconium-containing monomers which could be incorporated into polyolefin-based plastics and films. Zirconium is of interest[3] due to the special properties of zirconia. The approach taken here involves the attachment of commercially available olefin-substituted alkoxide and aryloxide ligands to readily available zirconium precursors. Alkoxides and aryloxides were chosen as ligands since they provide strong metal oxygen bonds for zirconium and since suitable inexpensive alcohols and phenols are available. Results with 2-methoxy-4-allylphenol, $HOC_6H_3(OMe\text{-}2)(CH_2CH{=}CH_2\text{-}4)$ (HOAr), which is commonly called eugenol, and allyl alcohol, $HOCH_2CH{=}CH_2$, are reported here. $[Zr(O^iPr)_4(HO^iPr)]_2$,[4] $[Zr(NMe_2)_4]_2$,[5] and “$Zr(OEt)_4$”[6] were chosen as convenient zirconium precursors. The use of isoeugenol, 2-methoxy-4-propenylphenol, with titanium alkoxides has previously been described by Schubert.[7]

Experimental Section

The chemistry described below was performed under nitrogen using Schlenk, vacuum line, and glovebox techniques. Solvents were purified as previously described.[8] NMR spectra were recorded at 25 °C using a General Electric QE 300 or GN 500 spectrometer. Elemental analyses were performed by Analytische Laboratorien, Lindlar, Germany. Allyl alcohol (Aldrich) and eugenol (Aldrich) were purified by drying over molecular sieves and subsequent distillation. KOAr was obtained by reacting HOAr and KH in THF and was dried under high vacuum. $ZrCl_4$ (Strem), $[Zr(O^iPr)_4(HO^iPr)]_2$ (Aldrich), and “$Zr(OEt)_4$” (Aldrich) were used as obtained. $[Zr(NMe_2)_4]_2$ was prepared according to the literature procedure.[5]

$\{Zr(O^iPr)_2[(OC_6H_3)(OMe\text{-}2)(CH_2CH{=}CH_2\text{-}4)](\mu\text{-}O^iPr)\}_2$, 1. In the glovebox, eugenol, $HOC_6H_3(OMe\text{-}2)(CH_2CH{=}CH_2\text{-}4)$ (338 mg, 2.0 mmol) was added dropwise to a colorless solution of $[Zr(O^iPr)_4(HO^iPr)]_2$ (775 mg, 1.0 mmol) in 10 mL of toluene. The resultant pale yellow solution was stirred for 24 h and centrifuged to remove a small amount of insoluble material. The supernatant was evaporated to dryness on a rotary evaporator. Cooling a concentrated toluene solution at −40 °C produced X-ray-quality crystals of **1** (780 mg, 90%). Anal. Calcd for $C_{38}H_{64}O_{10}Zr_2$: C, 52.74; H, 7.44; Zr, 21.13. Found: C, 52.63; H, 7.31; Zr, 21.45. IR (Nujol): 2361 s, 2337 s, 1504 s, 1462 s, 1335 w, 1376 s, 1290 m, 1259 w, 1167 m, 1139 s, 1018 s, 909 w, 811 m, 724 m, 652 w cm^{-1}. ^1H NMR (C_6D_6): δ 6.98 (d, 2H, $OC_6H_3(OMe)(CH_2CH{=}CH_2)$), 6.74 (d, 2H, $OC_6H_3(OMe)(CH_2CH{=}CH_2)$), 6.67 (s, 2H, $OC_6H_3(OMe)(CH_2$-

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$CH{=}CH_2)$), 5.96 (m, 2H, $OC_6\mathit{H}_3(OMe)(CH_2CH{=}CH_2)$), 6.98 (d, 2H, $OC_6H_3(OMe)(CH_2C\mathit{H}{=}CH_2)$), 5.01 (m, 4H, $OC_6H_3(OMe)(C\mathit{H}_2CH{=}CH_2)$), 4.54 (m, 4H, $C\mathit{H}(Me)_2$), 4.44 (m, 2H, $C\mathit{H}(Me)_2$), 3.93 (s, 6H, OMe), 3.25 (d, 4H, $OC_6H_3(OMe)(CH_2CH{=}C\mathit{H}_2)$), 1.30 (m, 36H, $CH(C\mathit{H}_3)_2$). ^{13}C NMR (C_6D_6): δ 159.0, 138.0, 128.5, 126.7, 119.6, 115.3, 39.9, 35.5, 32.1, 31.7, 22.8, 17.6, 15.9, 14.1 ppm.

$\{Me_2NH_2\}\{[(2,6\text{-}Me_2C_6H_3O)_3Zr]_2(\mu\text{-}OCH_2CH{=}CH_2)_3\}$, 2. To a colorless solution of $[Zr(NMe_2)_4]_2$ (267 mg, 0.5 mmol) in 10 mL of hexane was added allyl alcohol (89 mg, 1.5 mmol) followed by 2,6-dimethylphenol (366 mg, 3 mmol). The resulting cloudy suspension was stirred for 1 h and evaporated to dryness. Recrystallization from THF/hexane at −40 °C gave colorless crystals of **2** (870 mg, 78%). Anal. Calcd for $C_{59}H_{70}NO_9Zr_2$: C, 63.29; H, 6.30; N, 1.25; Zr, 16.29. Found: C, 62.72; H, 6.93; N, 1.35; Zr, 18.20. IR (Nujol): 2361 m, 2336 s, 1457 s, 1376 m, 1276 s, 1233 m, 1088 w, 1018 m, 882 s, 760 m, 717 m, 668 w cm^{-1}. ^1H NMR (THF-d_8): δ 6.75 (d, 12H, $OC_6\mathit{H}_3Me_2$-2,6), 6.45 (t, 6H, $OC_6\mathit{H}_3Me_2$-2,6), 6.15 (m, 3H, $OCH_2C\mathit{H}{=}CH_2$), 4.71 (d, 6H, $OC\mathit{H}_2CH{=}CH_2$), 4.51 (d, 3H, $OCH_2CH{=}C\mathit{H}_{2,}$), 4.37 (d, 3H, $OCH_2CH{=}C\mathit{H}_{2,}$), 2.71 (s, 6H, H_2NMe_2), 2.25 (s, 36H, $OC_6H_3Me_2$). ^{13}C NMR (THF-d_8): δ 160.7, 141.7, 129.6, 117.9, 114.1 ($O\mathit{C}_6H_3Me_2$), 72.9 ($O\mathit{C}H_2CH{=}CH_2$), 35.7 ($OCH_2\mathit{C}H{=}CH_2$), 26.3 ($OCH_2CH{=}\mathit{C}H_{2,}$), 24.7($H_2NMe_2$), 19.0 ($OC_6H_3Me_2$).

$[K_2Zr[(OC_6H_3)(OMe\text{-}2)(CH_2CH{=}CH_2\text{-}4)]_4(OEt)]_2(\mu\text{-}O)$, 3. In the glovebox a freshly prepared sample of $KOC_6H_3(OMe\text{-}2)(CH_2CH{=}CH_2\text{-}4)$ obtained by mixing KH (160 mg, 4.0 mmol) and $HOC_6H_3(OMe\text{-}2)(CH_2CH{=}CH_2\text{-}4)]$ (592 mg, 4.0 mmol) in 10 mL of THF was added to a suspension of $Zr(OEt)_4$ (272 mg, 1.0 mmol) in 5 mL of THF. The mixture was stirred for 48 h and centrifuged to remove small amounts of insoluble material. The volume of the supernatant was reduced to 5 mL and the solution was layered with hexane and was cooled to −40 °C. After several days, colorless crystals of **3** (470 mg, 56%) were produced. Anal. Calcd for $C_{84}H_{106}O_{19}K_4Zr_2$: C, 60.05; H, 6.35; Zr, 10.86. Found: C, 57.67; H, 6.21; Zr, 9.98. IR (Nujol): 1504 m, 1456 s, 1377 s, 1296 m, 1148 m, 1148 m, 1034 w, 895 w, 820 m, 722 m cm^{-1}. ^1H NMR (C_6D_6): δ 7.14 (d, 16H, $OC_6\mathit{H}_3(OMe)(CH_2CH{=}CH_2)$), 6.64 (d, 16H, $OC_6\mathit{H}_3(OMe)(CH_2CH{=}CH_2)$), 6.00 (s, 8H, $OC_6\mathit{H}_3(OMe)(CH_2CH{=}CH_2)$), 5.08 (d, 16H, $OC_6H_3(OMe)(C\mathit{H}_2CH{=}CH_2)$), 5.00 (d, 8H, $OC_6H_3(OMe)(CH_2C\mathit{H}{=}CH_2)$), 3.81 (q, 6H, $OCH_2C\mathit{H}_3$), 3.53 (t, 4H, $OC\mathit{H}_2CH_3$), 3.31 (d, 16H, $OC_6H_3(OMe)(CH_2CH{=}C\mathit{H}_2)$), 3.12 (s, 12H, $OC_6H_3(OC\ \mathit{H}_3)(CH_2CH{=}CH_2)$), 3.07 (s, 12H, $OC_6H_3(OC\mathit{H}_3)(CH_2CH{=}CH_2)$). ^{13}C NMR (C_6D_6): 153.3, 149.7, 139.3, 122.4, 121.5, 114.6, 111.2, 61.2, 54.7, 40.5, 20.5.

General Aspects of X-ray Data Collection, Structure Determination, and Refinement. Crystals were coated with Paratone oil, mounted on a glass fiber, and transferred to the nitrogen cold stream of a Siemens P4 or Siemens P4 rotating anode diffractometer. Determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix was carried out according to standard procedures.[9] Intensity data were collected at 163 K using a $2\theta-\omega$ scan technique with Mo Kα radiation. No significant decay was observed during data collection. Data were corrected for Lorentz and polarization effects and were placed on an absolute scale. The raw data were processed with a modified version of CARESS.[10a] All calculations were carried out using the SHELXTL program.[10b] The analytical scattering factors for neutral atoms were used throughout the analysis.[11] All of the structures were solved by direct methods and refined on F^2 by full-matrix least squares techniques. Details are given in Table 1 and in the Supporting Information.

$\{Zr(O^iPr)_2[(OC_6H_3)(OMe\text{-}2)(CH_2CH{=}CH_2\text{-}4)](\mu\text{-}O^iPr)\}_2$, 1. A colorless crystal of dimensions 0.30 × 0.30 × 0.50 mm was examined. There were no systematic absences nor diffraction symmetry other than Friedel condition. The centrosymmetric space group $P\bar{1}$ was assigned and later determined to be the correct choice. There are two molecules of the dimeric formula unit present. Each of the molecules is located about an inversion center resulting in the observed dimeric structure. Hydrogen atoms were included using a riding model. Atoms C(16), C(28), and C(29) are disordered and were included with two components each. Site occupancy factors were set at 0.65/0.35 for C(16)/C(16B) and 0.50 for the C(28) and C(29) components. At convergence, wR2 = 0.1086 and GOF = 1.056 for 448 variables against all 5626 unique data. As a comparison for refinement on *F*, R1 = 0.0413 for those 4605 data with $F > 4.0\sigma(F)$.

Table 1. Crystallographic Data for $[(^iPrO)_2(ArO)Zr(\mu\text{-}O^iPr)]_2$, **1**, and $[NH_2Me_2][(2,6\text{-}Me_2C_6H_3O)_3Zr(\mu\text{-}OCH_2CH{=}CH_2)_3$, **2**

	1	2
empirical formula	$C_{38}H_{64}O_{10}Zr_2$	$C_{75}H_{109}NO_{13}Zr_2$
fw	863.33	1415.07
space group	$P\bar{1}$	$P\bar{1}$
a, Å	10.132(2)	12.222(2)
b, Å	13.484(3)	14.161(3)
c, Å	16.408(3)	22.540(5)
α, deg	93.85(2)	99.75(3)
β, deg	101.17(2)	104.01(3)
γ, deg	99.69(2)	91.60(3)
Z	2	2
V, Å^3	2156.1(7)	3720.7(13)
d_{calcd}, g cm^{-3}	1.330	1.263
radiation, *λ*	0.71073	0.71073
μ, mm^{-1}	0.533	0.339
R1, $[I > 2\sigma(I)]$	0.0413	0.0660
wR2, all data	0.1086	0.1859
GOOF on F^2	1.056	1.013

$\{Me_2NH_2\}\{[(2,6\text{-}Me_2C_6H_3O)_3Zr]_2(\mu\text{-}OCH_2CH{=}CH_2)_3\}$, 2. A colorless crystal of dimensions 0.10 × 0.17 × 0.53 mm was mounted on a glass fiber and transferred to a Siemens P4 rotating anode diffractometer. There was no diffraction symmetry other than the Friedel condition nor any systematic absences. The centrosymmetric space group $P\bar{1}$ was chosen and determined to be correct. Carbon atoms C(29) and C(30) are disordered and were included with two components with site occupancy factors 0.55/0.45 for C(29)/C(29B) and 0.65/0.35 for C(30)/C(30B). Hydrogen atoms associated with C(29) and C(30) were not included. At convergence, wR2 = 0.1859 and GOF = 1.013 for 703 variables against all 6915 unique data. As a comparison for refinement on *F*, R1 = 0.0660 for those 5041 data with $F > 4.0\sigma(F)$.

$[K_2Zr[(OC_6H_3)(OMe\text{-}2)(CH_2CH{=}CH_2\text{-}4)]_4(OEt)]_2(\mu\text{-}O)$, 3. A colorless crystal of dimensions 0.17 × 0.23 × 0.33 mm was analyzed on the P4 diffractometer. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The unit cell parameters were found to be $a = 13.933(3)$ Å, $b = 14.451(4)$ Å, $c = 15.924(4)$ Å, α = 82.06°, $\beta = 65.46°$, $\gamma = 67.51°$, and $V = 2694(1)$ Å^3. The molecule is located on an inversion center. Several carbon atoms are disordered and were included with two components with site occupancy factors of 0.60/0.40 for atoms C(9), C(10), C(29), C(41), C(42), and C(43) and 0.50/0.50 for C(44). Hydrogen atoms associated with disordered atoms or atoms directly bound to disordered atoms were not included. The remaining hydrogen atoms were included using a riding model. There is a disordered solvent molecule present, but a reasonable disordered model could not be determined and contributions from this molecule were not included in the calculations. The quality of the crystal was too poor to obtain detailed bond distances and angles, but the connectivity of the compound was established.

Results

$\{Zr(O^iPr)_2[(OC_6H_3)(OMe\text{-}2)(CH_2CH{=}CH_2\text{-}4)](\mu\text{-}O^iPr)\}_2$, 1. The readily available zirconium alkoxide precursor $[Zr(O^iPr)_4(HO^iPr)]_2$[4] reacts with two equivalents of eugenol, $HOC_6H_3(OMe\text{-}2)(CH_2CH{=}CH_2\text{-}4)$ (HOAr), in toluene over a 24 h period at room temperature to form a pale yellow solution which upon recrystallization from toluene gives **1** in 90% yield, eq 1.

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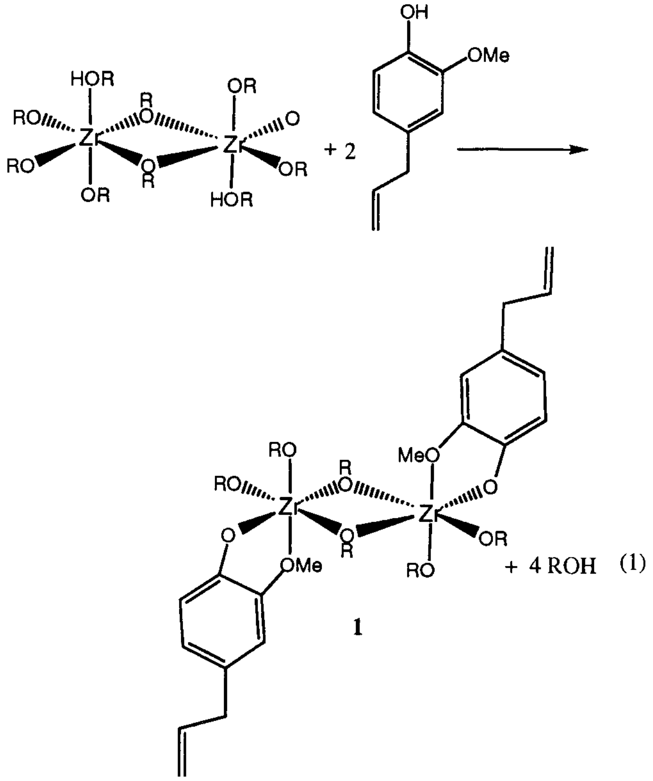
(9) *XSCANS Software Users Guide*, Version 2.1; Siemens Industrial Automation, Inc.: Madison, WI 1994.

(10) (a) Broach, R. W.; Argonne National Laboratory, IL 1978. (b) Sheldrick, G. M. Siemens Analytical X-ray Instruments, Inc.; Madison, WI, 1994.

(11) *International Tables for X-ray Crystallography*; Kluwer Academic Publishers: Dordrecht, 1992; Vol C.



1

The ^{1}H NMR spectrum of **1** in C_6D_6 is not structurally definitive but contains both ^{i}PrO and ArO resonances which are shifted downfield from the resonances of their precursors. X-ray crystallography revealed that **1** is a dimeric complex, Figure 1, in which two zirconium atoms are linked by two doubly bridging isopropoxide ligands. Each zirconium center is further ligated by two terminal isopropoxide ligands and one terminal bidentate eugenoxide moiety which chelates through the methoxy substituent. The overall geometry around zirconium is distorted octahedral, just as in the bimetallic $[Zr(O^iPr)_4(HO^i\text{-}Pr)]_2$ precursor.[4] The allyl groups of the eugenoxide ligands have neither intra- nor intermolecular interactions with zirconium. A consequence of the dimeric nature of this olefin-substituted compound is that it is effectively a diene. Retrospectively, the NMR spectrum is consistent with the solid-state structure.

Important bond distances and angles for **1** are listed in Table 2. The distortion of the octahedra around the zirconium centers in the two independent molecules in the unit cell can be evaluated by the range of the cis and trans O−Zr−O angles which are 69.51(11)−101.48(14)° and 151.69−167.43(12)°, respectively. The Zr−O(isopropoxide) distances are normal and the 1.920(9) Å average terminal distance is smaller than the 2.18(4) Å average bridging distance as expected. The 2.056(3) Å Zr−O(OAr) distance is similar to the 2.045(3) Å zirconium aryloxide distance in $Zr(acac)_3(OC_6H_4NO_2)$[12] and the 2.030(6) and 2.047(7) Å lengths in $Zr(OC_6H_3{}^tBu_2\text{-}2,6)_2({=}NPh)(Py)_2$.[13] The longest Zr−O distance in the molecule is the 2.429(4) Å distance arising from the donor bond formed by the chelating methoxide substituent. The C(9)−C(10) distance, 1.311(8) Å, is in the range of typical C=C bonds, but the analogous C=C bond in the other independent molecule in the unit cell was too disordered to obtain a reliable bond distance.

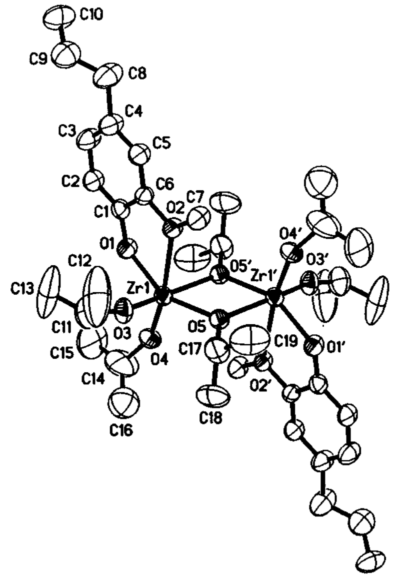
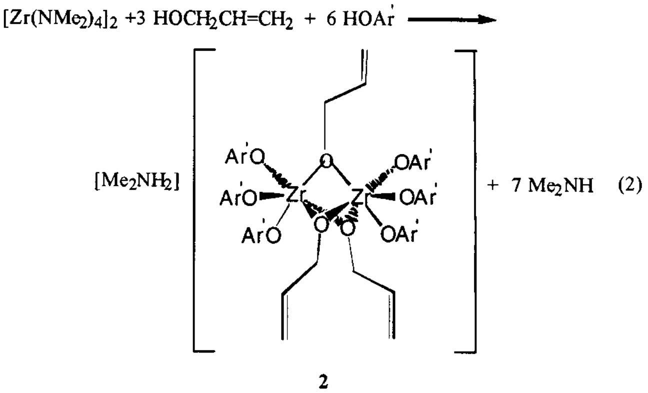


Figure 1. Structure of $[(^iPrO)_2(ArO)Zr(\mu\text{-}O^iPr)]_2$, **1**, where OAr = $OC_6H_3(OMe\text{-}2)(CH_2CH{=}CH_2\text{-}4)$. The thermal ellipsoid plot is shown at the 50% probability level.

$\{Me_2NH_2\}\{[(2,6\text{-}Me_2C_6H_3O)_3Zr]_2(\mu\text{-}OCH_2CH{=}CH_2)_3\}$, 2. In efforts to make olefin-functionalized zirconium alkoxides from allyl alcohol, $HOCH_2CH{=}CH_2$, it was desirable to start with an amide precursor instead of zirconium isopropoxide, since the difference of acidities of $HOCH_2CH{=}CH_2$ and $HNMe_2$ is more favorable for substitution than the difference between allyl alcohol and 2-propanol. Since the reaction of allyl alcohol with $[Zr(NMe_2)_4]_2$ gave an insoluble product, a mixed ligand reaction was examined. 2,6-Dimethylphenol, HOAr′, was chosen as the phenol since it has proven to be useful in the past in isolating crystalline compounds.[14] $[Zr(NMe_2)_4]_2$ reacts with 2 equiv of $HOCH_2CH{=}CH_2$ and 6 equiv of 2,6-dimethylphenol in hexane to form an oily product which is soluble in both toluene and THF and can be recrystallized from THF/hexane as $\{Me_2NH_2\}\text{-}\{[(2,6\text{-}Me_2C_6H_3O)_3Zr]_2(\mu\text{-}OCH_2CH{=}CH_2)_3\}$, **2**. After identifying **2** by X-ray crystallography, Figure 2, the synthesis was repeated with the stoichiometric amounts of reagents as shown in eq 2 to give a 78% yield.



2

This combination of reagents, like those above, also generates a bimetallic complex containing six-coordinate zirconium with a distorted octahedral ligand environment. However, complex **2** differs from **1** in that there are three bridging ligands. With three bridging $OCH_2CH{=}CH_2$ groups and all of the ligands

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Table 2. Important Distances (Å) and Angles (deg) for $[(^iPrO)_2(ArO)Zr(\mu\text{-}O^iPr)]_2$, **1**, and $\{Me_2NH_2\}\{[(2,6\text{-}Me_2C_6H_3O)_3Zr]_2(\mu\text{-}OCH_2CH{=}CH_2)_3\}$, **2**

1		**2**	
	Terminal Zr−O		
Zr(1)−O(1)	2.049(3)	Zr(1)−O(1)	1.969(6)
Zr(1)−O(2)	2.426(3)	Zr(1)−O(2)	1.977(6)
Zr(1)−O(3)	1.923(3)	Zr(1)−O(3)	1.971(6)
Zr(1)−O(4)	1.920(3)	Zr(2)−O(7)	1.976(6)
Zr(2)−O(6)	2.063(3)	Zr(2)−O(8)	1.984(6)
Zr(2)−O(7)	2.432(3)	Zr(2)−O(9)	1.965(6)
Zr(2)−O(8)	1.930(3)		
Zr(2)−O(9)	1.908(3)		
	Bridging Zr−O		
Zr(1)−O(5)	2.141(3)	Zr(1)−O(4)	2.198(5)
Zr(1)−O(5)′	2.206(3)	Zr(1)−O(5)	2.194(5)
Zr(2)−O(10)	2.215(3)	Zr(1)−O(6)	2.197(5)
Zr(2)−O(10)′	2.144(3)	Zr(2)−O(4)	2.192(5)
		Zr(2)−O(5)	2.188(5)
		Zr(2)−O(6)	2.192(5)
	Miscellaneous		
Zr(1)- - -Zr(1)′	3.523(1)	Zr(1)- - -Zr(2)	3.215(1)
Zr(2)- - -Zr(2)′	3.543(1)	C(26)−C(27)	1.235(14)
C(9)−C(10)	1.311(8)	C(29)−C(30)	1.09(2)
C(28B)−C(29B)	1.11(2)	C(29B)−C(30B)	1.08(4)
		C(32)−C(33)	1.307(13)
	Angles		
O(1)−Zr(1)−O(2)	69.59(11)	O(1)−Zr(1)−O(2)	98.2(3)
O(1)−Zr(1)−O(3)	96.27(13)	O(1)−Zr(1)−O(3)	98.8(2)
O(1)−Zr(1)−O(5)	152.87(12)	O(1)−Zr(1)−O(4)	100.2(2)
O(2)−Zr(1)−O(3)	83.82(13)	O(1)−Zr(1)−O(5)	159.0(2)
O(2)−Zr(1)−O(4)	166.96(13)	O(1)−Zr(1)−O(6)	86.9(2)
O(2)−Zr(1)−O(5)	86.56(11)	O(2)−Zr(1)−O(3)	97.9(2)
O(3)−Zr(1)−O(5)	93.71(13)	O(2)−Zr(1)−O(4)	159.6(2)
O(3)−Zr(1)−O(5)′	161.56(13)	O(2)−Zr(1)−O(5)	88.0(2)
O(4)−Zr(1)−O(5)	105.21(13)	O(3)−Zr(1)−O(4)	87.9(2)
O(5)−Zr(1)−O(5)′	71.72(13)	O(3)−Zr(1)−O(5)	100.2(2)
O(6)−Zr(2)−O(7)	69.51(11)	O(3)−Zr(1)−O(6)	160.2(2)
O(6)−Zr(2)−O(8)	96.88(13)	O(4)−Zr(2)−O(5)	71.9(2)
O(6)−Zr(2)−O(9)	98.46(13)	O(4)−Zr(2)−O(6)	72.6(2)
O(6)−Zr(2)−O(10)	89.05(12)	O(4)−Zr(2)−O(7)	90.9(2)
O(6)−Zr(2)−O(10)′	151.69(12)	O(4)−Zr(2)−O(9)	160.6(2)
O(7)−Zr(2)−O(8)	84.08(13)	O(5)−Zr(2)−O(6)	72.4(2)
O(7)−Zr(2)−O(9)	167.43(12)	O(5)−Zr(2)−O(7)	98.3(2)
O(7)−Zr(2)−O(10)	80.41(11)	O(5)−Zr(2)−O(8)	160.8(2)
O(8)−Zr(2)−O(9)	101.48(14)	O(5)−Zr(2)−O(9)	89.4(2)
O(8)−Zr(2)−O(10)	160.61(13)	O(6)−Zr(2)−O(7)	162.9(2)
O(10)−Zr(2)−O(10)′	71.27(12)	O(6)−Zr(2)−O(8)	89.1(2)
		O(6)−Zr(2)−O(9)	97.2(2)
		O(7)−Zr(2)−O(8)	98.1(2)
		O(7)−Zr(2)−O(9)	97.1(2)
		O(8)−Zr(2)−O(9)	98.3(2)

monodentate, nine ligands are required to make octahedra around each zirconium. As a consequence, complex **2** is a face shared bioctahedron, whereas **1** is an edge shared bioctahedron. The nine anionic ligands require one proton for charge balance. In this $[Zr(NMe_2)_4]_2$-based reaction which provides dimethylamine as a byproduct, the proton is part of a dimethylammonium counterion.

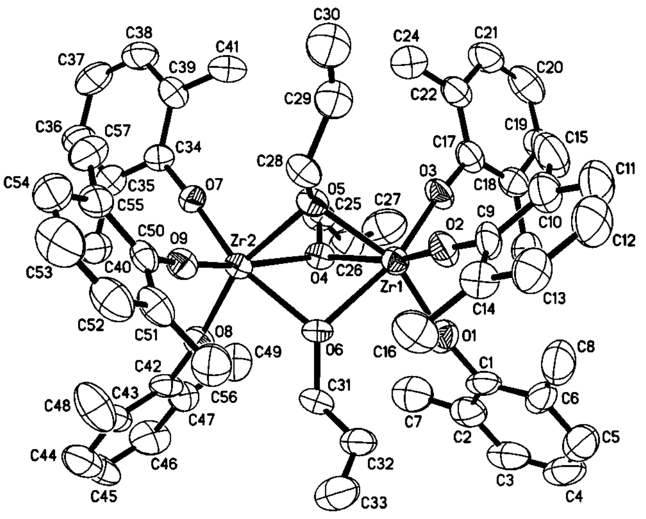

Figure 2. Structure of the anion in $\{Me_2NH_2\}\{[(2,6\text{-}Me_2C_6H_3O)_3Zr]_2(\mu\text{-}OCH_2CH{=}CH_2)_3\}$, **2**. The thermal ellipsoid plot is shown at the 50% probability level.

Important bond distances and angles for **2** are listed in Table 2. The O−Zr−O angles vary from 71.9(2) to 97.9(2)° for cis and 159.6(2) to 162.9(2)° for trans ligands. The six independent $Zr{-}O(\mu\text{-}OCH_2CH{=}CH_2)$ distances are very similar with a range of 2.188(5)−2.198(5) Å. This is similar to the 2.159(4)−2.180(4) Å range observed for the bridging isopropoxide $Zr{-}O(\mu\text{-}O^iPr)$ distances in **1** and $[Zr(O^iPr)_4(HO^iPr)]_2$.[4] The C═C distances were not precisely definable due to disorder. The 1.974(6) Å average Zr−O(OAr′) distance is smaller than the average zirconium aryloxide distances in **1**, 2.06(1) Å, in $Zr(acac)_3(OC_6H_4NO_2)$,[12] 2.045(3) Å, and in $Zr(OC_6H_3{}^tBu_2{-}2,6)_2({=}NPh)(py)_2$,[13] 2.030(6) and 2.047(7) Å.

$\{K_2Zr[(OC_6H_3)(OMe\text{-}2)(CH_2CH{=}CH_2\text{-}4)]_4(OEt)\}_2(\mu\text{-}O)$, 3. The zirconium starting material commercially sold as "$Zr(OEt)_4$" is insoluble in most solvents including THF and is reported to be a mixture of $Zr_3O(OEt)_{10}$ and $Zr_4O(OEt)_{14}$.[6] Interestingly it can be solubilized by addition of 1 equiv of eugenol in THF. Unfortunately, attempts to crystallize solids from this solution were unsuccessful. However, the potassium salt derived from eugenol, KOAr, reacts with a suspension of $Zr(OEt)_4$ in THF to produce a mixed ligand, mixed metal complex, $[K_2Zr(OAr)_4(OEt)]_2O$, **3**, which was identified by X-ray diffraction (Figures 3 and 4 and eq 3).

$$Zr_3O(OEt)_{10}/Zr_4O(OEt)_{14} + \text{excess KOAr} \rightarrow [K_2Zr(OAr)_4(OEt)]_2O \quad (3)$$

Complex **3** has inversion symmetry. The six metals, Zr_2K_4, are arranged in a distorted octahedral geometry around a μ_6-O ligand, O(10). The metals are also connected by the eight aryloxide oxygen atoms of the eight OAr ligands. Each of these oxygens is triply bridging and is located over a face of the octahedron of metals. The OMe oxygen atoms chelate only to potassium atoms. In addition, each zirconium atom has a terminal ethoxide and each potassium atom is attached to a THF molecule. As a result, each zirconium is octahedrally coordinated and the potassium atoms are eight coordinate.

The octahedron of metals is compressed along the Zr−O(10)−Zr axis which has 2.0169(8) Å Zr−O(10) distances compared to 2.965(2) and 2.928(2) Å K−O(10) lengths. Severe disorder in the THF and the allyl groups plus a disordered cocrystallized solvent molecule precludes detailed discussion of bond distances and angles.

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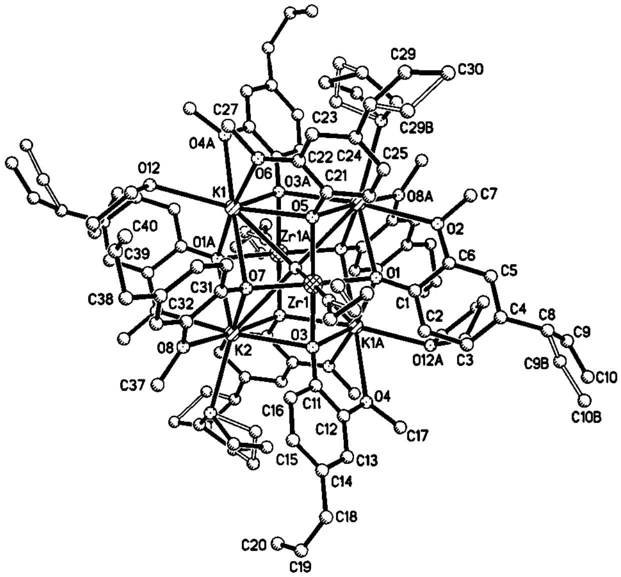

Figure 3. Ball and stick figure of $[K_2Zr(OAr)_4(OEt)]_2(O)$, **3**.

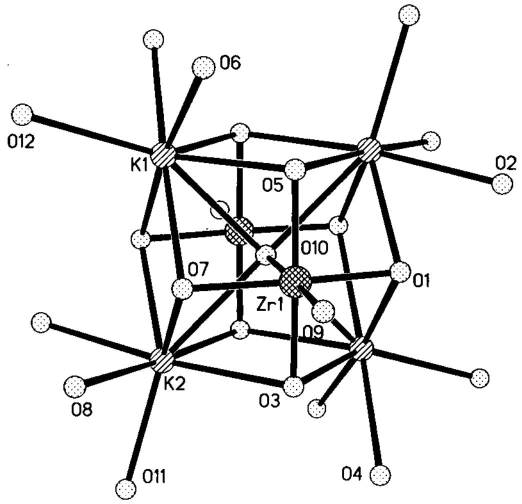

Figure 4. Metal oxygen framework of $[K_2Zr(OAr)_4(OEt)]_2(O)$, **3**.

Discussion

$[Zr(O^iPr)_4(HO^iPr)]_2$, $[Zr(NMe_2)_4]_2$, and the $Zr_3O(OEt)_{10}/Zr_4O(OEt)_{14}$ material called "$Zr(OEt)_4$" all function as suitable precursors for the formation of oxygen-ligated zirconium complexes containing pendent olefin groups when treated with either allyl phenols or allyl alcohol. As anticipated on the basis of previous studies, alcohol exchange, alcoholysis, and the addition of a metal alkoxide all can be used as reactions to make such complexes.[12−16]

Crucial to the success of these syntheses is the choice of a proper set of ligands which provides soluble crystalline complexes which can be definitively identified by X-ray crystallography. Unfortunately, too little is still known about zirconium alkoxide/aryloxide chemistry to be able to predict which combinations will have the appropriate macroscopic properties and success must still be achieved empirically. As shown here, highly soluble crystalline complexes can be obtained in good yields in this way.

Several general features can be discerned from the chemistry observed in these reactions. The zirconium centers in these complexes are typically six coordinate regardless of the nature of the starting material or the alcohol/phenol reagents involved. For tetravalent zirconium, six-coodination can be achieved either with bridging ligands, with bidentate chelating groups, or by forming anionic complexes. In the case of the anionic products formed from NMe_2-ligated precursors, charge balance can be achieved with protons residing in a dimethylammonium salt, rather than via hydrogen bonding to the alkoxide or aryloxide ligands. Hence, $[Zr(NMe_2)_4]_2$ offers some advantages as a precursor when anionic products are desired or anticipated. Small alkoxides, like $[OCH_2CH{=}CH_2]^-$, are generally good bridging ligands and can lead to insoluble compounds unless some other larger solubilizing co-ligands are present. Metal complexes containing pendent olefin functionalities derived from $[OCH_2CH{=}CH_2]^-$ appear to require larger co-ligands for solubility. On the other hand, the eugenoxide ligand, $[OAr]^-$, does not tend to be a bridging ligand, it is a bulky ligand in its own right, and it can provide a pendent olefinic group while occupying two coordination positions around the metal. It appears to be advantageous when neutral compounds with minimal bridging are desired.

Conclusion

The results described here show that readily available olefin-substituted alkoxides and phenoxides can be attached to zirconium complexes ligated by oxygen ligands starting from common zirconium precursors. Since highly soluble complexes can be synthesized in good yields, this provides a reasonable way to make precursors for hybrid inorganic/organic materials incorporating zirconium into polyolefins.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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