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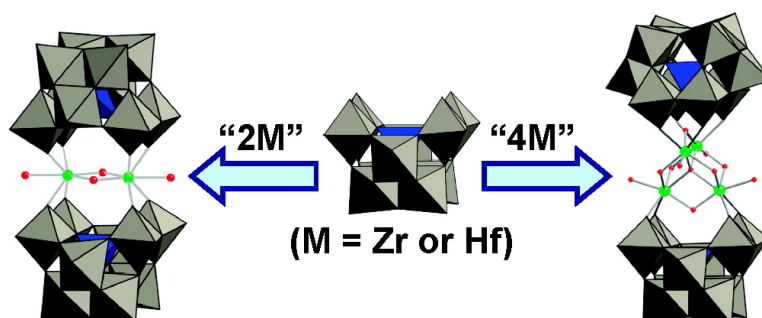# Synthesis and Catalysis of Di- and Tetranuclear Metal Sandwich-Type Silicotungstates [(#-SiWO)M(µ-OH)]⁻ and [(#-SiWO)M(µ-O)(µ-OH)] (M = Zr or Hf)

Yuji Kikukawa, Syuhei Yamaguchi, Kazutaka Tsuchida, Yoshinao Nakagawa, Kazuhiro Uehara, Kazuya Yamaguchi, and Noritaka Mizuno

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Synthesis and Catalysis of Di- and Tetranuclear Metal Sandwich-Type Silicotungstates [(γ-SiW$_{10}$O$_{36}$)$_2$M$_2$(μ-OH)$_2$]$^{10-}$ and [(γ-SiW$_{10}$O$_{36}$)$_2$M$_4$(μ$_4$-O)(μ-OH)$_6$]$^{8-}$ (M = Zr or Hf)

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Abstract: The di- and tetranuclear metal sandwich-type silicotungstates of Cs$_{10}$[(γ-SiW$_{10}$O$_{36}$)$_2${Zr(H$_2$O)}$_2$(μ-OH)$_2$]·18H$_2$O (**Zr2**, monoclinic, C2/c (No. 15), a = 25.3315(8) Å, b = 22.6699(7) Å, c = 18.5533(6) Å, β = 123.9000(12)°, V = 8843.3(5) Å^3, Z = 4), Cs$_{10}$[(γ-SiW$_{10}$O$_{36}$)$_2${Hf(H$_2$O)}$_2$(μ-OH)$_2$]·17H$_2$O (**Hf2**, monoclinic, space group C2/c (No. 15), a = 25.3847(16) Å, b = 22.6121(14) Å, c = 18.8703(11) Å, β = 124.046(3)°, V = 8974.9(9) Å^3, Z = 4), Cs$_8$[(γ-SiW$_{10}$O$_{36}$)$_2${Zr(H$_2$O)}$_4$(μ$_4$-O)(μ-OH)$_6$]·26H$_2$O (**Zr4**, tetragonal, P4$_1$2$_1$2 (No. 92), a = 12.67370(10) Å, c = 61.6213(8) Å, V = 9897.78(17) Å^3, Z = 4), and Cs$_8$[(γ-SiW$_{10}$O$_{36}$)$_2${Hf(H$_2$O)}$_4$(μ$_4$-O)(μ-OH)$_6$]·23H$_2$O (**Hf4**, tetragonal, P4$_1$2$_1$2 (No. 92), a = 12.68130(10) Å, c = 61.5483(9) Å, V = 9897.91(18) Å^3, Z = 4) were obtained as single crystals suitable for X-ray crystallographic analyses by the reaction of a dilacunary γ-Keggin silicotungstate K$_8$[γ-SiW$_{10}$O$_{36}$] with ZrOCl$_2$·8H$_2$O or HfOCl$_2$·8H$_2$O. These dimeric polyoxometalates consisted of two [γ-SiW$_{10}$O$_{36}$]$^{8-}$ units sandwiching metal–oxygen clusters such as [M$_2$(μ-OH)$_2$]$^{6+}$ and [M$_4$(μ$_4$-O)(μ-OH)$_6$]$^{8+}$ (M = Zr or Hf). The dinuclear zirconium and hafnium complexes **Zr2** and **Hf2** were isostructural. The equatorially placed two metal atoms in **Zr2** and **Hf2** were linked by two μ-OH ligands and each metal was bound to four oxygen atoms of two [γ-SiW$_{10}$O$_{36}$]$^{8-}$ units. The tertanuclear zirconium and hafnium complexes **Zr4** and **Hf4** were isostructural and consisted of the adamantanoid cages with a tetracoordinated oxygen atom in the middle, [M$_4$(μ$_4$-O)(μ-OH)$_6$]$^{8+}$ (M = Zr or Hf). Each metal atom in **Zr4** and **Hf4** was linked by three μ-OH ligands and bound to two oxygen atoms of the [γ-SiW$_{10}$O$_{36}$]$^{8-}$ unit. The tetra-nuclear zirconium and hafnium complexes showed catalytic activity for the intramolecular cyclization of (+)-citronellal to isopulegols without formation of byproducts resulting from etherification and dehydration. A lacunary silicotungstate [γ-SiW$_{10}$O$_{34}$(H$_2$O)$_2$]$^{4-}$ was inactive, and the isomer ratio of isopulegols in the presence of MOCl$_2$·8H$_2$O (M = Zr or Hf) were much different from that in the presence of tetranuclear complexes, suggesting that the [M$_4$(μ$_4$-O)(μ-OH)$_6$]$^{8+}$ core incorporated into the POM frameworks acts as an active site for the present cyclization. On the other hand, the reaction hardly proceeded in the presence of dinuclear zirconium and hafnium complexes under the same conditions. The much less activity is possibly explained by the steric repulsion from the POM frameworks in the dinuclear complexes.

Introduction

Polyoxometalates (POMs) are attractive compounds and used in the fields of analytical chemistry, medicine, electrochemistry, photochemistry, and catalysis.[1] POMs have especially received much attention in the area of catalysis because their chemical properties such as redox potentials, acidities, and solubilities can be finely tuned by choosing constituent elements.[1] In addition, the advantages of POMs in catalysis are their inherent stability toward oxidation and hydrolysis. Recently, interest in the catalysis of partially metal-substituted POMs, which are synthesized by the introduction of substituent metal ions into the vacant site(s) of lacunary POMs, has been growing because of the unique reactivities depending on the compositions and structures of the active sites.[1] Since the syntheses of the dilacunary [γ-SiW$_{10}$O$_{36}$]$^{8-}$ and [γ-PW$_{10}$O$_{36}$]$^{7-}$ were reported by Hervé and co-workers,[2] several dimetal-substituted POMs with the γ-Keggin framework have been reported.[3,4]

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[‡] Japan Science and Technology Agency.

Table 1. Crystallographic Data for **Zr2**, **Hf2**, **Zr4**, and **Hf4**

compound	Zr2	Hf2	Zr4	Hf4
formula	$Cs_{10}O_{78}Si_2W_{20}Zr_2$	$Cs_{10}O_{86}Si_2W_{20}Hf_2$	$Cs_8O_{95.25}Si_2W_{20}Zr_4$	$Cs_8O_{76}Si_2W_{20}Hf_4$
fw	6492.62	6795.15	6685.24	7062.32
cryst syst	monoclinic	monoclinic	tetragonal	tetragonal
space group	$C2/c$ (No. 15)	$C2/c$ (No. 15)	$P4_12_12$ (No. 92)	$P4_12_12$ (No. 92)
a (Å)	25.3315(8)	25.3847(16)	12.67370(10)	12.68130(10)
b (Å)	22.6699(7)	22.6121(14)	12.67370(10)	12.68130(10)
c (Å)	18.5533(6)	18.8703(11)	61.6213(8)	61.5483(9)
α (deg)	90.0000	90.0000	90.0000	90.0000
β (deg)	123.9000(12)	124.046(3)	90.0000	90.0000
γ (deg)	90.0000	90.0000	90.0000	90.0000
V (Å^3)	8843.3(5)	8974.9(9)	9897.78(17)	9897.91(18)
Z	4	4	4	4
d_{calcd} (g cm^{-3})	4.876	5.029	4.486	4.739
μ (mm^{-1})	30.332	31.974	26.596	30.363
no. of params refined	529	552	378	361
$R1$ ($I > 2\sigma(I)$)	0.074 (for 6089 data)	0.064 (for 6787 data)	0.076 (for 8447 data)	0.083 (for 9730 data)
$wR2$	0.270 (for all 11303 data)	0.211 (for all 11790 data)	0.230 (for all 10926 data)	0.213 (for all 11363 data)

Zirconium and hafnium compounds including their oxides have unique chemical and physical properties leading to their applications such as oxygen sensors, fuel cells, catalysts, and catalyst–supports.[5] In particular, they are very useful Lewis acid catalysts.[6] As the properties and reactivities are strongly dependent on their structures, the syntheses of zirconium and hafnium compounds with structurally well-defined sites are very important, and structurally characterized zirconium- and hafnium-containing POMs are one of the least reported compounds. The first example of the zirconium-containing POM is a trinuclear zirconium containing Knoth-type sandwich silicotungstate [$Zr_3(\mu_2$-$OH)_3(A$-β-$SiW_9O_{34})_2]^{11-}$ reported by Finke and co-workers in 1989.[7a] Successively, zirconium-containing POMs with Keggin- (not γ-type), Wells−Dawson-, and Lindqvist-type structures

have been reported.[7] Very recently, Hill and co-workers reported the chiral zirconium containing Wells−Dawson-type POMs functionalized with enantiomerically pure dicarboxylates such as tartrate and malate.[7g,h] Structurally characterized hafnium-containing POMs are still novel and there are only two examples of hafnium-containing POMs such as α-Keggin-type mono-hafnium-containing dimer [$Hf(\alpha$-$PW_{11}O_{39})_2]^{10-}$ and Wells−Dawson-type monohafnium-containing dimer [$Hf(\alpha_2$-P_2W_{17}-$O_{61})_2]^{16-}$.[7d]

In this paper, we report the synthesis, structural characterization, and catalytic intramolecular cyclization of (+)-citronellal of a series of novel di- and tetranuclear zirconium or hafnium-containing POMs with γ-Keggin silicotungstate units of $Cs_{10}[(\gamma$-SiW_{10}-$O_{36})_2\{Zr(H_2O)\}_2(\mu$-$OH)_2]\cdot18H_2O$ (**Zr2**), $Cs_{10}[(\gamma$-$SiW_{10}O_{36})_2\{Hf$-$(H_2O)\}_2(\mu$-$OH)_2]\cdot17H_2O$ (**Hf2**), $Cs_8[(\gamma$-$SiW_{10}O_{36})_2\{Zr(H_2O)\}_4(\mu_4$-$O)(\mu$-$OH)_6]\cdot26H_2O$ (**Zr4**), and $Cs_8[(\gamma$-$SiW_{10}O_{36})_2\{Hf(H_2O)\}_4(\mu_4$-$O)(\mu$-$OH)_6]\cdot23H_2O$ (**Hf4**).

Results and Discussion

Dinuclear Zirconium- and Hafnium-Containing POMs. The single crystals of **Zr2** and **Hf2** suitable for X-ray crystallographic analyses were obtained by the reaction of $K_8[\gamma$-$SiW_{10}O_{36}]$ with *1 equiv* of $ZrOCl_2\cdot8H_2O$ or $HfOCl_2\cdot8H_2O$ with respect to $K_8[\gamma$-$SiW_{10}O_{36}]$ (see Experimental Section, and Tables 1 and 2). As shown in Figure 1, the molecular structures of the anion parts of dizirconium (**Zr2**) and dihafnium (**Hf2**) complexes were intrinsically isostructural: The anions consisted of two γ-Keggin [$SiW_{10}O_{36}]^{8-}$ units, and the metal atoms were linked in the equatorial plane via oxygen atoms.

The existence of ten cesium cations per the anion in **Zr2** and **Hf2** implies that the charges of these cluster anions are
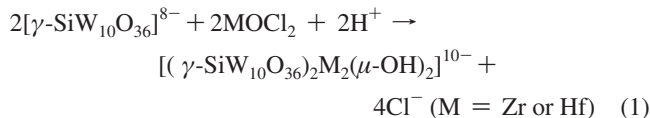
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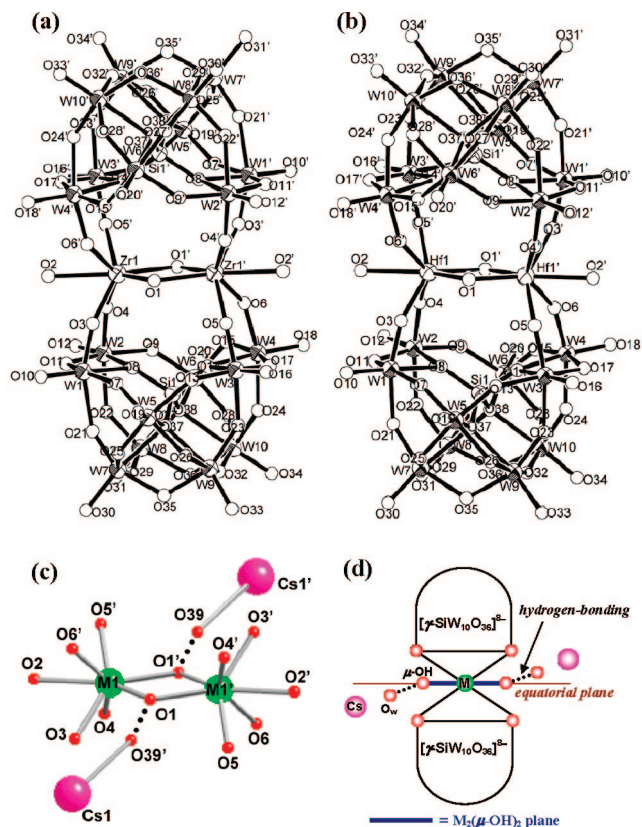
Table 2. Selected Bond Lengths and Angles in **Zr2** and **Hf2** (Lengths in Å and Angles in deg)

	Zr2 (M = Zr)	**Hf2** (M = Hf)
	Bond Length	
M(1)−O(1)	2.208(17)	2.117(14)
M(1)−O(1′)	2.12(2)	2.121(19)
M(1)−O(2)	2.48(2)	2.461(16)
M(1)−O(3)	2.123(19)	2.116(18)
M(1)−O(4)	2.11(2)	2.104(17)
M(1)−O(5)	2.11(2)	2.09(2)
M(1)−O(6)	2.13(2)	2.13(2)
M(1)···M(1′)	3.579(3)	3.5758(16)
O(1)···O(39′)	2.72(3)	2.68(2)
	Bond Angle	
M(1)−O(1)−M(1′)	111.7(8)	115.1(7)
O(1)−M(1)−O(1′)	68.3(7)	64.9(6)

−10. The thermogravimetric analysis showed the presence of twenty and nineteen water molecules in **Zr2** and **Hf2**, respectively. The bond valence sum (BVS)[8] values of zirconium or hafnium (3.77 for **Zr2**, 3.82 for **Hf2**), tungsten (5.72–6.83 for **Zr2**, 5.82–6.38 for **Hf2**), and silicon (4.02 for **Zr2**, 3.63 for **Hf2**) in dinuclear complexes indicate that the respective valences are +4, +6, and +4. The BVS values of O(1) (or O(1′)) and O(2) (or O(2′)) were 1.09 and 0.37 for **Zr2**, suggesting that O(1) and O(1′) are monoprotonated (hydroxo ligands) and that O(2) and O(2′) are diprotonated (aquo ligands). All these results and the elemental analysis data show that the formulas of **Zr2** and **Hf2** are $Cs_{10}[(\gamma\text{-}SiW_{10}O_{36})_2\{Zr(H_2O)\}_2(\mu\text{-}OH)_2]\cdot 18H_2O$ and $Cs_{10}[(\gamma\text{-}SiW_{10}O_{36})_2\{Hf(H_2O)\}_2(\mu\text{-}OH)_2]\cdot 17H_2O$, respectively. Compounds **Zr2** and **Hf2** are formed according to the following equation:

$$2[\gamma\text{-}SiW_{10}O_{36}]^{8-} + 2MOCl_2 + 2H^+ \rightarrow$$
$$[(\gamma\text{-}SiW_{10}O_{36})_2M_2(\mu\text{-}OH)_2]^{10-} +$$
$$4Cl^- \quad (M = Zr \text{ or } Hf) \quad (1)$$

Zirconium and hafnium centers in **Zr2** and **Hf2** were *seven-coordinated*[7c,j,9] to four oxygen atoms of two [γ-Si$W_{10}O_{36}$]$^{8-}$ units, two μ-OH ligands, and one aquo ligand. The overall coordination geometries around zirconium and hafnium centers were distorted *monocapped trigonal* prismatic. The Zr−$O_{hydroxo}$ (average 2.16 Å) and Hf−$O_{hydroxo}$ (average 2.12 Å) bonds were almost equidistant and the bis-μ-hydroxo-dimetal $M_2(\mu\text{-}OH)_2$ (M = Zr or Hf) cores in **Zr2** and **Hf2** had a slightly distorted diamond shape, and the anions had approximately D_{2h} inherent symmetry. The M···M distances (3.579(3) Å for **Zr2**, 3.5758(16) Å for **Hf2**) were similar to those of [$Zr_2(\mu\text{-}OH)_2(\alpha\text{-}PW_{11}O_{39})_2$]$^{8-}$ (3.568 Å)[7c] and [$Zr_2(\mu\text{-}OH)_2(W_5O_{18})_2$]$^{6-}$ (3.633 Å).[7j] The M-O_{aquo} bond lengths (2.48(2) Å for **Zr2**, 2.461(16) Å for **Hf2**) were longer than those previously reported for zirconium and hafnium complexes[10] and tetra-nuclear **Zr4** and **Hf4** (see later), and the aquo ligands in **Zr2** and **Hf2** were weakly coordinated to the metal centers. The hydroxo species between metal atoms were hydrogen-bonded to the water molecules in the vicinity of cesium ions (O_w: O(39) and O(39′)

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Figure 1. ORTEP representations of the anion parts of (a) **Zr2** and (b) **Hf2**. The illustrations c and d show the ball-and-stick representation around the $M_2(\mu\text{-}OH)_2$ core in these anions and the schematic representative view of these anions along the M···M axis, respectively.

in Figure 1c). The distances between O(1) and O(39′) (2.72(3) Å for **Zr2**, 2.68(2) Å for **Hf2**) suggest the strong hydrogen-bonding interaction.[11]

Very recently, we have reported a tetra-*n*-butylammonium salt of a dizirconium-substituted silicotungstate **TBA-Zr2**.[12] The molecular shape of the anion part of **TBA-Zr2** was almost identical to that of **Zr2** (Figure 2).[12] On the other hand, the coordination geometry around zirconium centers in **TBA-Zr2** was different from that in **Zr2**. Each zirconium atom in **TBA-Zr2** was *six-coordinated* to two μ-OH ligands and four oxygen atoms of two lacunary [γ-Si$W_{10}O_{36}$]$^{8-}$ units, and the overall coordination geometry around each zirconium center was distorted *trigonal* prismatic. No aquo ligands were found on zirconium centers in **TBA-Zr2** in contrast with complexes **Zr2** and **Hf2**. The $Zr_2(\mu\text{-}OH)_2$ plane in **TBA-Zr2** was not placed in the equatorial plane and deviated from the equatorial plane by ca. 30° in sharp contrast with **Zr2** (Figure 2c). The water of crystallization was not observed around the $Zr_2(\mu\text{-}OH)_2$ core in **TBA-Zr2** and the hydrogen-bonding interaction was not observed. The hydrogen-bonding interaction between the hydroxo species (μ-OH) and the water molecules in the vicinity of cesium ions were observed for **Zr2** and would stabilize the $Zr_2(\mu\text{-}OH)_2$ cores in the equatorial plane.

Tetranuclear Zirconium- and Hafnium-Containing POMs. The single crystals of **Zr4** and **Hf4** suitable for X-ray crystallographic analyses were obtained by the reaction of $K_8[\gamma\text{-}$

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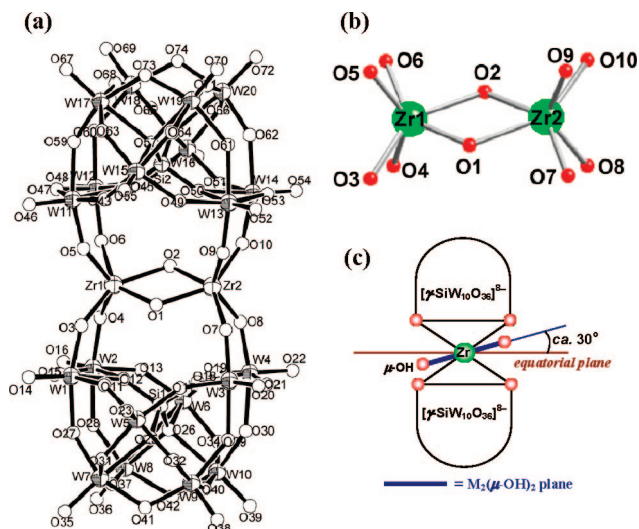
Figure 2. (a) ORTEP representation of the anion part of **TBA-Zr2**, (b) ball-and-stick representation around the $Zr_2(\mu\text{-OH})_2$ core, and (c) the schematic representative view along the $Zr\cdots Zr$ axis.

Table 3. Selected Bond Lengths and Angles in **Zr4** and **Hf4** (Lengths in Å and Angles in deg)

	Zr4 (M = Zr)	**Hf4** (M = Hf)
	Bond Length	
M(1)–O(1)	2.049(12)	2.16(2)
M(1)–O(2)	2.00(7)	2.13(2)
M(1)–O(3)	2.12(2)	2.14(2)
M(1)–O(5)	2.23(6)	2.24(2)
M(1)–O(7)	2.01(6)	1.98(8)
M(1)–O(8)	2.09(6)	2.25(2)
M(1)–O(9)	2.22(3)	2.15(2)
M(2)–O(1)	2.20(2)	2.077(13)
M(2)–O(3′)	2.12(3)	2.14(2)
M(2)–O(4)	2.12(3)	2.05(2)
M(2)–O(6)	2.30(3)	2.25(5)
M(2)–O(7)	2.03(6)	2.14(8)
M(2)–O(10)	2.13(2)	2.23(2)
M(2)–O(11)	2.28(2)	2.17(2)
M(1)···M(1′)	3.498(6)	3.487(2)
M(1)···M(2)	3.395(5)	3.386(2)
M(1)···M(2′)	3.509(5)	3.502(2)
M(2)···M(1′)	3.509(5)	3.502(2)
M(2)···M(2′)	3.489(5)	3.487(2)
	Bond Angle	
M(1)–O(1)–M(2)	105.9(7)	106.1(7)
M(1)–O(7)–M(2)	114(3)	111(4)
M(1)–O(1)–M(1′)	117.3(11)	107.6(10)
M(1)–O(2)–M(1′)	102(3)	110.2(11)
M(2)–O(1)–M(1′)	111.2(7)	111.4(7)
M(2)–O(3)–M(1′)	111.6(14)	109.8(12)
M(2)–O(1)–M(2′)	104.7(9)	107.6(10)
M(2)–O(4)–M(2′)	109.6(10)	117(2)

$SiW_{10}O_{36}]$ with 2 *equiv* of $ZrOCl_2 \cdot 8H_2O$ or $HfOCl_2 \cdot 8H_2O$ with respect to $K_8[\gamma\text{-}SiW_{10}O_{36}]$ (see Experimental Section, and Tables 1 and 3). The complexes **Zr4** and **Hf4** were intrinsically isostructural and the crystal structures of the anion parts consisted of two lacunary $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ units sandwiching the adamantanoid cages with a tetracoordinated oxygen atom in the middle (the $[M_4(\mu_4\text{-O})(\mu\text{-OH})_6]^{8+}$ cores, M = Zr or Hf, Figure 3). The central adamantanoid cages were distorted from the ideal tetrahedral symmetry and the anion possessed approximately C_2 symmetry.

The existence of eight counter cations (cesium ions) per anions shows that the charges of the anions are −8. The BVS
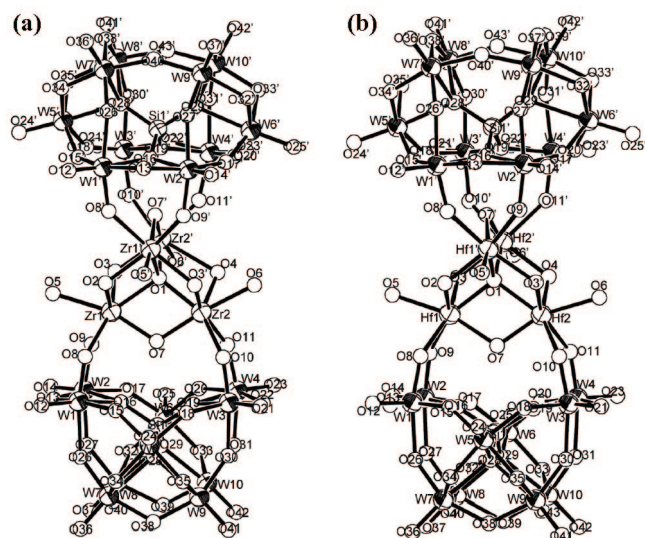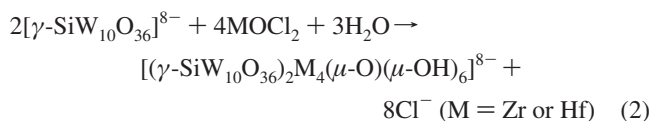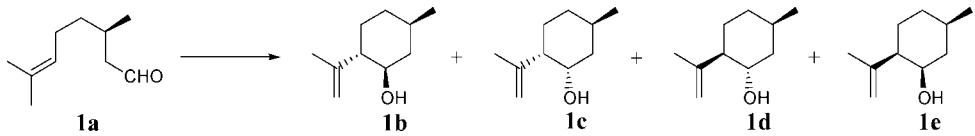

Figure 3. ORTEP representations of the anion parts of (a) **Zr4** and (b) **Hf4**. The illustration c shows the ball-and-stick representation around the distorted adamantanoid core in **Zr4** and **Hf4**.

values of zirconium or hafnium (3.85–4.59 for **Zr4**, 3.84–3.89 for **Hf4**), tungsten (5.75–6.99 for **Zr4**, 5.95–6.75 for **Hf4**), and silicon (3.66 for **Zr4**, 3.49 for **Hf4**) indicate that the respective valences in **Zr4** and **Hf4** are +4, +6, and +4. The BVS values of oxygen atoms (O(1) (2.46), O(2) (1.68), O(3) (1.22), O(4) (1.19), O(5) (0.45), O(6) (0.37), O(7) (1.59)) in **Zr4** suggest that two zirconium atoms are linked by one μ_4-oxo and three μ-OH ligands and had one aquo ligand. Two hafnium atoms in **Hf4** (O(1) (2.37), O(2) (1.14), O(3) (1.11), O(4) (1.42), O(5) (0.42), O(6) (0.41), O(7) (1.41)) were linked in the same manner as that of zirconium in **Zr4**. These BVS results, elemental analysis data, and thermogravimetric analysis data show that the formulas of **Zr4** and **Hf4** are $Cs_8[(\gamma\text{-}SiW_{10}O_{36})_2\{Zr(H_2O)\}_4(\mu_4\text{-O})(\mu\text{-OH})_6]\cdot 26H_2O$ and $Cs_8[(\gamma\text{-}SiW_{10}O_{36})_2\{Hf(H_2O)\}_4(\mu_4\text{-O})(\mu\text{-OH})_6]\cdot 23H_2O$, respectively. The formation of **Zr4** and **Hf4** is expressed by the following equation:[13]

$$2[\gamma\text{-}SiW_{10}O_{36}]^{8-} + 4MOCl_2 + 3H_2O \rightarrow$$
$$[(\gamma\text{-}SiW_{10}O_{36})_2M_4(\mu\text{-O})(\mu\text{-OH})_6]^{8-} +$$
$$8Cl^- \quad (M = Zr \text{ or } Hf) \quad (2)$$

The coordination geometry around metal centers in **Zr4** and **Hf4** was distorted *monocapped trigonal* prismatic and almost the same as those of dinuclear complexes **Zr2** and **Hf2** (Figures

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(13) When complex **Hf2** was reacted with 2 equiv of $HfOCl_2$ with respect to **Hf2**, complex **Hf4** was obtained in 44% yield, suggesting that the formation of tetranuclear complexes most likely proceeds via the formation of dinuclear complexes followed by the reaction with 2 equiv of metal cations (see Experimental Section).

Table 4. Intramolecular Cyclization of (+)-Citronellal[a]

entry	catalyst (mol%)	time (h)	conversion (%)	yield[b] (%)	isomer ratio (%)			
					1b	1c	1d	1e
1	**Zr4** (1.25)	24	92	70	70	27	1	2
2	**Hf4** (1.25)	24	97	91	79	16	1	4
3	**Zr2** (2.5)	24	no reaction					
4	**Hf2** (2.5)	24	18	6	75	20	1	5
5[c]	$[\gamma\text{-SiW}_{10}O_{34}(H_2O)_2]^{4-}$ (2.5)	24	no reaction					
6	ZrOCl$_2$·8H$_2$O (5)	4	>99	92	37	60	1	2
7	HfOCl$_2$·8H$_2$O (5)	4	83	79	32	66	1	1
8[d]	HCl (5)	1	>99	77	48	49	1	2
9	none	24	no reaction					

[a] Reaction conditions: **1a** (0.26 mmol), catalyst (1.25−5 mol%), nitromethane (0.8 mL), 348 K, 24 h, Ar atmosphere. Conversion and yield were determined by GC analysis using an internal standard. [b] Total yield of isopulegol isomers **1b**−**e**. [c] Tetra-*n*-butyl ammonium salt. [d] Reaction run using 4 M aqueous HCl solution.

1c and 2c). The coordination numbers of metal atoms in **Zr4** and **Hf4** were *seven* and the same as those of monoclinic ZrO$_2$[14] and HfO$_2$.[15] The M−O (M = Zr or Hf) bond lengths (2.00−2.12 Å for **Zr4**, 1.98−2.16 Å for **Hf4**) of the central adamantanoid cages in **Zr4** and **Hf4** were very close to those in the corresponding seven-coordinated compounds such as $[Zr_4(\mu_4\text{-}$O)$(\mu\text{-}O^nPr)_6]^{8+}$ (2.15−2.23 Å),[16] monoclinic ZrO$_2$ (2.05−2.27 Å),[14] {Hf$_4(\mu_4$-O)$(\mu$-OH)$_6$[(PO$_3$NH)$_3$]$_4$}$^{4-}$ (2.10−2.17 Å),[17] and monoclinic HfO$_2$ (2.03−2.25 Å).[15]

Intramolecular Cyclization of (+)-Citronellal. The cyclizations of citronellal derivatives such as (+)-citronellal (**1a**) and 3-methylcitronellal (**2a**) were carried out to investigate the acidic nature of the POM catalysts. The cyclization showed a complex selectivity pattern since **1a** and **2a** were converted into different diastereoisomers.[18] In the case of **1a**, the important feature of the cyclization is the diastereoselectivity toward (−)-isopulegol (**1b**) that is readily hydrogenated to the industrially important (+)-menthol.[19]

Cesium crown ether clathrate salts ([Cs(18-crown-6)]$^+$) of the POM catalysts were used for the dissolution in organic solvents.[20] The reaction conditions were optimized by changing the reaction temperature, solvent, and scale. The cyclization of
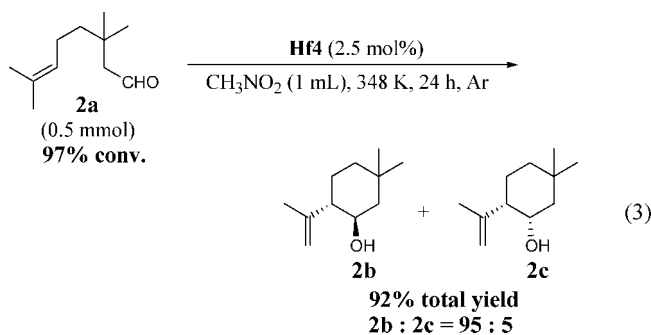
1a hardly proceeded in the absence of a catalyst (entry 9 in Table 4) or in the presence of a lacunary silicotungstate $[\gamma\text{-SiW}_{10}O_{34}(H_2O)_2]^{4-}$ (entry 5). Under the optimized conditions, tetranuclear complexes **Zr4** and **Hf4** showed high catalytic activity for the cyclization of **1a** and gave the corresponding isopulegol isomers (**1b**−**e**) in high yields (entries 1 and 2). In the present case, etherification and dehydration, which are frequently observed in the Brønsted acid-catalyzed reactions,[18j,k] could not be observed. On the other hand, the reaction hardly proceeded in the presence of dinuclear zirconium and hafnium complexes **Zr2** and **Hf2** under the same conditions (entries 3 and 4).

The diastereoselectivity to **1b** was high (>70%) in the presence of the tetranuclear complexes **Zr4** and **Hf4**. Among the catalysts tested, **Hf4** showed the highest diastereoselectivity to more valuable isomer **1b** (up to ca. 80%), and the value was higher than that with a typical Brønsted acid of HCl (entry 8) and with the catalyst precursor of HfOCl$_2$·8H$_2$O (entry 7). It is noted that the reaction of **2a** in the presence of **Hf4** also efficiently proceeded to give the corresponding methylisopulegol

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(20) The cesium salt of **Hf4** was completely insoluble in nitromethane and could be used as a solid catalyst. When the cyclization of (+)-citronellal was carried out with the cesium salt under the conditions in Table 4, the reaction efficiently proceeded to give the isopulegol isomers in 86% yield for 48 h (**1b**:**1c**:**1d**:**1e** = 71:24:1:4).

(21) An aqueous solution of TBAOH was used as a titrant because the methoxo derivatives of **Zr2** and **Hf4** were formed in methanol and the titrations became very complicated.

(22) López, M.; Bo, C.; Poblet, J. M. *J. Am. Chem. Soc.* **2002**, *124*, 12574. Nucleophilic species (substrate) would approach to the POM molecule along a path where the ESP is as high as possible. For **Zr4**, the regions close to the axial sites of the zirconium centers (the ESP value at the saddle point: −0.46 hartree/e) and the hydrogen atom site of the bridged μ-OH groups (−0.44 hartree/e) are calculated to be more electrophilic (acidic) than those of the polyoxotungstate regions (<−0.51 hartree/e). For **Zr2**, the regions close to the axial sites of the zirconium centers are calculated to be more electrophilic (−0.67 hartree/e) than the other sites including bridged μ-OH groups and the polyoxotungstate regions (<−0.68 hartree/e).

isomers **2b** and **2c** in high yields and the diastereoselectivity to trans isomer **2b** reached up to ca. 95% [eq (3)].

$$\text{(3)}$$

2a
(0.5 mmol)
97% conv.

Hf4 (2.5 mol%)
CH_3NO_2 (1 mL), 348 K, 24 h, Ar

2b   **2c**
92% total yield
2b : 2c = 95 : 5

A potentiometric titration of cesium crown ether clathrate salt of **Zr2** with tetra-*n*-butylammonium hydroxide (TBAOH)[21] in DMF showed an inflection point at 1.8 ± 0.2 equiv of OH^- with respect to **Zr2** (Figure S1a), in accord with the endpoint of the titration determined with phenolphthalein (2.2 ± 0.2 equiv of OH^- with respect to **Zr2**). A titration of **Hf4** in DMF showed a few inflection points (Figure S1b) and the end point of the titration determined with phenolphthalein was observed at 6.2 ± 0.2 equiv of OH^- with respect to **Hf4**. These results show that complexes **Zr2** and **Hf4** possess two and six titratable protons, respectively, and all μ-OH groups possibly act as Brønsted acid sites.[22]

As above-mentioned, tetranuclear complexes **Zr4** and **Hf4** showed high catalytic activity for the cyclization of **1a** and gave the corresponding isopulegol isomers in high yields. On the other hand, the reaction hardly proceeded in the presence of dinuclear complexes **Zr2** and **Hf2**. It has been reported that the cyclization is catalyzed by both Lewis and Brønsted acid sites.[18] Thus, the cyclization of **1a** in the presence of pyridine or 2,6-di-*tert*-butylpyridine was carried out to clarify the active sites on tetranuclear complexes. Pyridine can interact with both Brønsted and Lewis acid sites via protonation and coordination, respectively.[23] In contrast, 2,6-di-*tert*-butylpyridine can selectively interact with Brønsted acid sites and cannot interact with Lewis acid (metal) sites owing to the steric hindrance.[23,24] We also confirmed that 2,6-di-*tert*-butylpyridine cannot approach to the Lewis acid centers, but the μ-OH groups in **Hf4** (Figure S2). In addition, isopulegol can approach to the μ-OH groups in both these complexes. Therefore, if the μ-OH groups mainly act as active sites for the cyclization, the reaction rates in the presence of 2,6-di-*tert*-butylpyridine should be decreased.

For the **Hf4**-catalyzed cyclization of **1a** at 293 K, the reaction rate ($R = 2.3$ mM·h^{-1}) and diastereoselectivity (76%) to **1b** in the presence of 1 equiv 2,6-di-*tert*-butylpyridine with respect to hafnium were the same as those in the absence (2.2 mM·h^{-1}, 76%). On the other hand, the addition of pyridine suppressed the reaction: The reaction rates decreased with an increase in

the amount of pyridine added and the reaction hardly proceeded in the presence of 1 equiv pyridine with respect to hafnium ($R = 0.081$ mM·h^{-1}). These results show that Lewis acid sites of Zr^{4+} and Hf^{4+} in tetranuclear complexes mainly promote the present cyclization reaction. The higher diastereoselectivities with **Zr4** and **Hf4** than those with Brønsted acids also support the idea. The much less activities of dinuclear complexes are possibly explained as follows: The substrate **1a** can not be cyclized on the active sites of the metal centers in **Zr2** and **Hf2** because of the steric repulsion from the $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$ frameworks (Figure S3).

Conclusion

The novel di- and tetranuclear metal sandwich-type silicotungstates **Zr2**, **Hf2**, **Zr4**, and **Hf4** have been synthesized by the reactions of $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$ with $ZrOCl_2 \cdot 8H_2O$ or $HfOCl_2 \cdot 8H_2O$ and their molecular structures were successfully determined. The dinuclear complexes **Zr2** and **Hf2** consisted of two $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$ units sandwiching bis-μ-hydroxo-dimetal core $[M_2(\mu\text{-OH})_2]^{6+}$ (M = Zr or Hf) with a distorted diamond shape. The $[M_2(\mu\text{-OH})_2]^{6+}$ cores in **Zr2** and **Hf2** were likely fixed in the equatorial plane by the hydrogen-bonding interaction between μ-OH moieties and the water of crystallization positioned in the vicinity of countercations. The complexes **Zr4** and **Hf4** were isostructual and consisted of two $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$ units sandwiching distorted adamantanoid clusters $[M_4(\mu_4\text{-O})(\mu\text{-OH})_6]^{8+}$ (M = Zr or Hf). The tetranuclear zirconium and hafnium complexes **Zr4** and **Hf4** showed high catalytic activity for the intramolecular cyclization of (+)-citronellal, while the dinuclear zirconium and hafnium complexes were inactive.

Experimental Section

General. IR spectra were measured on Jasco FT/IR-460 Plus using KBr disks. Liquid-state NMR spectra were recorded on JEOL JNM-EX-270. ^1H and $^{13}C\{H\}$ NMR spectra were measured at 270 and 67.8 MHz, respectively, with TMS as an internal standard. ^{29}Si NMR spectra were measured at 53.45 MHz with TMS as an external standard. $Na_2WO_4 \cdot 2H_2O$ and zirconium and hafnium salts were obtained from Wako or Kanto (reagent grade) and used as received. (+)-Citronellal (**1a**) and solvents were obtained from TCI (reagent grade) and were carefully purified before the use.[25] The dilacunary precursor of $K_8[\gamma\text{-SiW}_{10}O_{36}] \cdot 12H_2O$ was synthesized according to ref 2a. 3-Methylcitronellal (**2a**) was synthesized according to ref 26.

Synthesis of Dinuclear Zirconium- and Hafnium-Containing POMs (Zr2 and Hf2). Complex **Zr2** was synthesized as follows: $K_8[\gamma\text{-SiW}_{10}O_{36}] \cdot 12H_2O$ (1.0 g, 0.335 mmol) was disolved in deionized water (15 mL) and the pH of the solution was adjusted to pH 4.0 with 1 M aqueous HCl solution. Then, an aqueous solution of $ZrOCl_2 \cdot 8H_2O$ (70 mM, 5 mL) was added, and the pH of the solution was adjusted to 2.0 with an aqueous HCl solution (1 M). After 3 min, CsCl (0.56 g, 3.3 mmol) was added to the solution followed by stirring for 20 min at room temperature. The white precipitate of **Zr2** was collected by the filtration and washed with a small amount of water (0.94 g, 79% yield based on $K_8[\gamma\text{-SiW}_{10}O_{36}] \cdot 12H_2O$). The needle-like crystals of **Zr2** suitable for the X-ray crystallographic analysis were obtained by the recrystallization from hot water (323 K). Anal. Calcd for $Cs_{10}[(SiW_{10}O_{36})_2\{Zr(H_2O)\}_2(OH)_2] \cdot 18H_2O$ (**I**): Cs, 19.57; Si, 0.83; W, 54.14; Zr, 2.69. Found: Cs, 19.92; Si, 0.82; W, 54.14; Zr, 2.81. IR (KBr pellet; 2000–300 cm^{-1}): 1624, 1033, 999, 950, 924, 892, 867, 801, 734, 569, 539, 485, 386, 361,

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324. ^{29}Si NMR (53.45 MHz, D$_2$O, 298K, Li salt) δ -86.91. Complex **Hf2** was synthesized with the same procedure as that of **Zr2** except that HfOCl$_2$·8H$_2$O (0.13 g, 0.34 mmol) was used as a precursor (0.78 g, 67% yield based on K$_8$[γ-SiW$_{10}$O$_{36}$]·12-H$_2$O). Anal. Calcd for Cs$_{10}$[(SiW$_{10}$O$_{36}$)$_2$\{Hf(H$_2$O)\}$_2$(OH)$_2$]·17H$_2$O: Cs, 19.13; Si, 0.81; W, 52.92; Hf, 5.14. Found: Cs, 18.96; Si 0.84; W, 54.51; Hf, 5.28. IR (KBr pellet; 2000–300 cm^{-1}): 1623, 1031, 999, 950, 921, 897, 868, 800, 746, 690, 628, 569, 539, 485, 401, 386, 379, 362, 346, 330, 319. ^{29}Si NMR (53.45 MHz, D$_2$O, 298 K, Li salt) δ -86.98.

Synthesis of Tetranuclear Zirconium- and Hafnium-Containing POMs (Zr4 and Hf4). Complex **Zr4** was synthesized as follows: An aqueous solution of ZrOCl$_2$·8H$_2$O (134 mM, 5 mL) was added to a suspension of K$_8$[γ-SiW$_{10}$O$_{36}$]·12H$_2$O (1.0 g, 0.335 mmol) in water (15 mL) and the mixture was stirred for 30 min at room temperature. Then, CsCl (0.56 g, 3.3 mmol) was added to the solution followed by the stirring for 30 min at room temperature. The white precipitate of **Zr4** was collected by the filtration and washed with a small amount of water (0.87 g, 75% yield based on K$_8$[γ-SiW$_{10}$O$_{36}$]·12H$_2$O). The needle-like crystals of **Zr4** suitable for the X-ray crystallographic analysis were obtained by the recrystallization from hot water (323 K). Anal. Calcd for Cs$_8$[(SiW$_{10}$O$_{36}$)$_2$\{Zr(H$_2$O)\}$_4$O(OH)$_6$]·26H$_2$O: Cs, 15.25; Si, 0.81; W, 52.74; Zr, 5.23. Found: Cs, 15.31; Si 0.77; W, 51.14; Zr, 5.21. IR (KBr pellet; 2000–300 cm^{-1}): 1617, 1023, 1015, 997, 949, 912, 874, 795, 700, 639, 565, 542, 484, 453, 403, 377, 372, 364, 321. ^{29}Si NMR (53.45 MHz, D$_2$O, 298 K, Li salt) δ -85.54. Complex **Hf4** was synthesized with the same procedure as that of **Zr4** except that HfOCl$_2$·8H$_2$O (0.26 g, 0.67 mmol) was used as a precursor (1.02 g, 84% yield based on K$_8$[γ-SiW$_{10}$O$_{36}$]·12H$_2$O). Anal. Calcd for Cs$_8$[(SiW$_{10}$O$_{36}$)$_2$\{Hf(H$_2$O)\}$_4$O(OH)$_6$]·23H$_2$O: Cs, 14.63; Si, 0.77; W, 50.60; Hf, 9.83. Found: Cs, 14.75; Si 0.74; W, 47.96; Hf, 9.43. IR (KBr pellet; 2000–300 cm^{-1}): 1624, 1025, 1016, 998, 949, 908, 875, 800, 703, 626, 566, 538, 483, 451, 401, 376, 372, 361, 321, 313. ^{29}Si NMR (53.45 MHz, D$_2$O, 298 K, Li salt) δ -85.58.

Reaction of Hf2 with HfOCl$_2$·8H$_2$O. HfOCl$_2$·8H$_2$O (0.060 g, 0.16 mmol) in water (5 mL) was added to a suspension of **Hf2** (0.50 g, 0.072 mmol) in water (15 mL) and the mixture was stirred for 15 min at 323 K. Then, CsCl (0.60 g, 3.5 mmol) was added to the solution followed by stirring for 30 min at room temperature. The white precipitate of **Hf4** was collected by the filtration and washed with water and diethylether (0.23 g, 44% yield based on **Hf2**).

Synthesis of Cesium Crown Ether Clathrate Salt. We attempted to synthesize the Zr and Hf complexes with organocations by the cation exchange of the cesium ions with organocations such as tetramethylammonium and tetra-*n*-butylammonium. However, our attempts to obtain the pure Zr and Hf complexes with organocations by the cation exchange have yet been unsuccessful. Therefore, cesium crown ether clathrate salts of the POM catalysts were used for the dissolution in organic solvents. A typical example for the synthesis of cesium crown ether clathrate salts was as follows: 18-Crown-6-ether (0.85 g, 3.2 mmol) was dissolved in

deionized water (10 mL). Then, the cesium salt of **Hf4** (0.42 g, 0.058 mmol) was added to the solution followed by stirring for 15 min at 323 K, and water was evaporated off at 323 K. The resulting white precipitate was washed with ethylether (ca. 20 mL) and collected by the filtration (0.49 g, 91% yield based on **Hf4**). Anal. Calcd for (C$_{12}$H$_{24}$O$_6$)$_9$Cs$_8$[(SiW$_{10}$O$_{36}$)$_2$\{Hf(H$_2$O)\}$_4$O(OH)$_6$]·7H$_2$O: C, 13.86; H, 2.63; Si, 0.60; W, 39.29; Hf, 7.63. Found: C, 13.56; H, 2.67; Si, 0.58; W, 38.30; Hf, 7.69.

X-ray Crystallography. Diffraction measurements were made on a Rigaku AFC-10 Saturn 70 CCD detector with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) at 93 K. Data were collected and processed using CrystalClear[27] for Windows software and HKL2000[28] for Linux software. Neutral scattering factors were obtained from the standard source. In the reduction of data, Lorentz and polarization corrections were made. The structural analysis was performed using CrystalStructure[29] and Win-GX for Windows software.[30] All structures were solved by SHELXS-97 (direct methods) and refined by SHELXH-97.[31]

Cyclization of (+)-Citronellal Derivatives. The catalytic cyclization was carried out with a glass tube reactor. All operations were carried out in a glovebox under Ar. Cesium crown ether clathrate salts of POMs, substrate, nitromethane, and naphthalene (internal standard) were successively placed into a glass tube reactor. A Teflon-coated magnetic stir bar was added, and the reaction mixture was stirred (800 rpm) at 343 K under Ar atmosphere. The conversion and yield were periodically determined by GC analysis. The products were confirmed by the comparison of GC retention times, mass spectra, and ^{1}H and ^{13}C NMR spectra with those of authentic samples. The isomer ratio was determined by GC and ^{1}H NMR analysis.

Supporting Information Available: Figures S1−S4 and crystallographic data for **Zr2**, **Hf2**, **Zr4**, and **Hf4** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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