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Molecular Routes to Group IV Magnesium and Calcium Nanocrystalline Ceramics

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S Supporting Information

ABSTRACT: The effect of alkaline-earth-metal alkoxides on the protonolysis of Cp₂M'Cl₂ (M' = Ti, Zr, Hf; Cp = cyclopentadiene) was investigated. This approach enabled the design of compounds with well-defined molecular structures to generate high-purity binary metal oxides. Single-source molecular precursors with structures of $[M_2M'_2(\mu_3-OEt)_2(\mu-OE-t)_4(OEt)_6(EtOH)_4]$ with M = Mg and M' = Ti (1), Zr (2), and Hf (3), $[Ca_{\epsilon}Ti_4(\mu_{\epsilon}-O)_2(\mu_4-O)_2(\mu_2-OEt)_{12}(OEt)_{12}(EtOH)_{\epsilon}Cl_4]$ (4)



Hf (3), $[Ca_6Ti_4(\mu_6-O)_2(\mu_4-O)_2(\mu_3-OEt)_{12}(OEt)_{12}(EtOH)_6Cl_4]$ (4), and $[M_2M'_2(\mu_4-O)(\mu-OEt)_5(OEt)_4(EtOH)_4Cl]_n$ with M = Ca and M' = Zr (5) and Hf (6) were prepared via elimination of the cyclopentadienyl ring from $Cp_2M'Cl_2$ as CpH in the presence of M(OEt)_2 and ethanol (EtOH) as a source of protons. Meanwhile, similar reactions involving the initial substitution of Cl ligands by OEt groups in $Cp_2M'Cl_2$ (M' = Ti, Zr, Hf) resulted in the formation of $[M_2M'_2(\mu_3-OEt)_2(\mu-OEt)_4(OEt)_6(EtOH)_4]$ with M = Ca and M' = Ti (7), Zr (8), and Hf (9). The precursors were characterized by elemental analysis, NMR spectroscopy, and single-crystal X-ray structural analysis. Magnesium compounds 1–3 decomposed at 750–850 °C to give MgTiO_3 along with small amounts of Mg_2TiO_4, Mg_2Zr_5O_{12}, or Mg_2Hf_5O_{12} binary metal oxides. The thermolysis of calcium compounds 4 and 7–9 led to highly pure CaTiO_3, CaZrO_3, or CaHfO_3 perovskite-like oxide particles with diameters of 20–30 nm.

INTRODUCTION

In the last 2 decades, metal oxide nanoparticles with welldefined geometries exhibiting unique size- and shape-dependent phenomena have received huge interest for a wide range of applications. In particular, group IV alkaline-earth ceramics are attractive as functional nanomaterials in materials science and solid-state physics because of their unique properties. For example, alkaline-earth-metal perovskite oxides with the general formula $MM'O_3$, where M = Ca, Sr, or Ba and M' = Ti, Zr, or Hf, have sparked great interest in the fields of energy storage and conversion,¹ imaging technology,² electronics,³ and heterogeneous catalysis.⁴ Group IV calcium-based oxides are particularly desirable representatives of this type of material. For example, CaTiO₃ is used as a thermistor and refractory material with high resistance to caustic corrosion and as a biocompatible coating for medical Ti implants.⁵ CaZrO₃ has been studied as a thermal blanket with corrosion resistance to liquid lithium, and it can also be used as a red phosphor for white-light-emitting diodes (LEDs) upon doping with Eu^{3+,6}

In contrast, group IV beryllium, radium, and magnesium ceramics have been the subject of only a few studies in the area of materials chemistry. In the case of beryllium, there are no known compounds based on $BeO-M'O_2$ oxides, as verified by the phase diagrams showing only polymorphic temperature transitions of the individual components. The high cost and strong radioactivity of radium have precluded any investigations of RaO-M'O₂ systems.⁷ Meanwhile, in the MgO-TiO₂

system, three compounds have been established: MgTiO₃, MgTi₂O₅, and Mg₂TiO₄. MgTiO₃ has a high quality factor, low dielectric constant, and high thermal stability at high frequencies,⁸ so it has been employed in ceramic capacitors and resonators for use in antennas for communication, radar, or direct-broadcasting satellites.⁹

During the conventional sintering process of MgTiO₃, the formation of secondary phases of Mg2TiO4 and MgTi2O5 degrades the microwave dielectric properties of the obtained materials.¹⁰ The ratio of these materials can be controlled by the synthesis method and calcination temperature.¹¹ However, Mg₂TiO₄ has also attracted attention for use in integrated optics, as a substrate for the epitaxial growth of hightemperature superconducting thin films¹² and as an efficient red phosphor for white LEDs when doped with Mn⁴⁺.¹³ Mixedphase MgTiO₃-MgTi₂O₅ heterogeneous nanorods displayed excellent performance in high-efficiency photocatalytic dihydrogen production.¹⁴ Many papers have been published on the phase study of the MgO-ZrO₂ system, but most showed only a mixture of the individual oxide components.¹⁵ However, some literature data also described the formation of metastable Mg₂Zr₅O₁₂ and MgZr₆O₁₃ intermediate phases.¹⁶ It is also worth mentioning that MgZrO₃ obtained by a plasma-spray technique¹⁷ has been used as a thermal barrier coating on

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metallic surfaces for high-temperature applications in the automotive, aircraft, and aerospace industries.¹⁸

The MgO–HfO₂ system forms only Mg₂Hf₅O₁₂, which is not used industrially because of its instability at high temperature. However, Mg₂Hf₅O₁₂ films have been investigated as gate insulators for InGaZnO₄ thin-film transistors that operate at low voltage.¹⁹ It is also worth noting that hafnia (HfO₂) and hafnia-based materials are traditionally regarded as technologically important in the nuclear industry because of their exceptionally high neutron absorption coefficient.²⁰ This wide range of applications of group IV magnesium- and calcium-based ceramics creates a strong impetus for developing novel inexpensive methods for their synthesis.

Mixed-cation oxide ceramics are usually synthesized by conventional solid-state reactions involving oxides, carbonates, or nitrates at relatively high temperature (~1500 °C). These procedures are inefficient and give poor control over stoichiometry and phase purity, often leading to inhomogeneity and/or byproducts.²¹ We recently showed that reactions of heterometallic components and their transformation into a complex product in a single step are very attractive in the preparation of binary oxide nanomaterials.²² In such reactions, the composition of the oxide products after thermal treatment can be easily predicted from the ratio of the metals. This preparation technique focuses on elimination of the cyclopentadienyl ring (as CpH) from $Cp_2M'Cl_2$ (M' = Ti, Zr, Hf) in the presence of $M(OR)_2$ (M = Ca, Sr, Ba) and alcohol ROH as a proton source, providing crystalline precursors suitable to obtain group IV alkaline-earth oxides with high phase purity.²³ In this study, we prepare group IV magnesium or calcium oxide materials using $Cp_2M'Cl_2$ (M' = Ti, Zr, Hf) and M(OEt)₂ (M = Mg, Ca) as metal sources.

RESULTS AND DISCUSSION

Syntheses and Molecular Structures. We were interested in developing a new simple method to prepare welldefined single-source precursors (SSPs) containing all of the necessary elements and suitable stoichiometry to form highly pure binary oxide materials. According to our previous work, the reaction of Cp₂TiCl₂ with 2 equiv of metallic magnesium in ethanol (EtOH)/toluene (3:1) at room temperature gave colorless cyclopentadienyl-free crystals of $[Mg_2Ti_2(\mu_3-OEt)_2(\mu-OEt)_4(OEt)_6(EtOH)_4]$ (1, 62%).²⁴ Moreover, when zirconocene and hafnocene dichloride were used instead of Cp₂TiCl₂ under the same conditions, we obtained compounds $[Mg_2Zr_2(\mu_3-OEt)_2(\mu-OEt)_4(OEt)_6(EtOH)_4]$ (2, 70%) and $[Mg_2Hf_2(\mu_3-OEt)_2(\mu-OEt)_4(OEt)_6(EtOH)_4]$ (3, 73%), respectively, which are isostructural to 1 (Scheme 1).

In these reactions, metallocene dichlorides $Cp_2M'Cl_2$ (M' = Ti, Zr, Hf) undergo a transformation involving coordination of an EtOH molecule to the metal site, providing the proton

Scheme 1. Synthesis of 1-3



functionalities necessary for proton transfer from the OH group to the Cp ring and leading to CpH liberation with simultaneous coordination of an alkoxide ligand to the M' center and elimination of chloride ions by the formation of $[Mg(EtOH)_6]$ -Cl₂. These processes consequently led to the formation of heterometallic complexes 1–3, which were characterized by elemental analysis, ¹H and ¹³C NMR spectroscopy (Figures S1–S6), and single-crystal X-ray diffraction (XRD) analysis. The XRD data presented in Figure 1 show that the molecular



Figure 1. Molecular structures of $[M_2M'_2(\mu_3-OEt)_2(\mu-OE-t)_4(OEt)_6(EtOH)_4]$ with M = Mg and M' = Ti (1), Zr (2), and Hf (3) and M = Ca and M' = Ti (7), Zr (8), and Hf (9). The second disordered counterpart of the alkoxy group and H atoms are omitted for clarity [symmetry code: (i) -x + 1, -y + 1, -z + 1].

structures of the colorless cyclopentadienyl-free 1–3 consist of a centrosymmetric heterometallic cluster containing $Mg_2M'_2O_{16}$, where M' = Ti, Zr, Hf, as a double-open, faceshared dicubane core with two missing vertices. Octahedrally coordinated metal atoms surrounded by O_6 donor sets are held together by four μ - and two μ_3 -alkoxide ligands. The vertices of the common face of the defective dicubane units are occupied by the Mg1 and Mg1ⁱ ions, and the external vertices are M'1 and M'1ⁱ ions.

The need for a suitable simple method to prepare heterobimetallic magnesium complexes prompted us to also use metallic calcium instead of magnesium to obtain precursors of high-quality microwave dielectric materials.⁵ Unexpectedly, when we reacted Cp₂TiCl₂, 2 equiv of Ca, and an excess of EtOH in toluene, we obtained the colorless Cp-free chloro ethoxide heterometallic cluster $[Ca_6Ti_4(\mu_6-O)_2(\mu_4-O)_2(\mu_3-OEt)_{12}(OEt)_{12}(EtOH)_6Cl_4]$ (4, 21%; Scheme 2).

The composition and structure of 4 were confirmed by XRD, Fourier transform infrared (FT-IR) spectroscopy, and elemental analysis. The single-crystal XRD data presented in Figure 2 reveal that 4 contains a decametalate $Ca_6Ti_4O_{26}Cl_4$ core in which the metal ions are held together by 16 O-donor atoms from 12 μ_3 -OEt, two μ_4 -O, and two μ_6 -O groups. The Ti ions adopt octahedral coordination environments with O_6 donor sets, while Ca ions surrounded by O_8Cl , O_7 , or O_6Cl donors adopt tricapped trigonal-prismatic (Ca1) or capped octahedral (Ca2 and Ca3) geometry, as confirmed by continuous-shape-measures (CShM) calculation (Table S1).

The polyhedral representation of the central core in Figure 2b shows that it was formed exclusively by edge-sharing interactions. It is worth noting that the core of cluster 4 is

Scheme 2. Synthesis of 4-6



similar to that of the hexametalate complex $[Ca_4Ti_2(\mu_6 O)(\mu_3,\eta^2-OCH_2CH_2OMe)_8(\eta-OCH_2CH_2OMe)_2Cl_4]$ $(MeOCH_2CH_2OH = 2-methoxyethanol)$ that we previously reported.²⁵ The hexametalate compound was obtained from the reaction of Cp₂TiCl₂ with Ca(OCH₂CH₂OMe)₂ at a molar ratio of 1:2 in a MeOCH₂CH₂OH/toluene mixture (1:1). Unlike EtOH, MeOCH₂CH₂OH contains two donor atoms, namely, an alkoxo O atom and an ether O atom, separated by two C atoms. As shown in Scheme 3, the MeOCH₂CH₂OH ligand acted as a chelating agent and tethered in the $\mu_{\eta}\eta^2$ mode to create a $Ca_4Ti_2(\mu_6-O)$ octahedron in which two Ti atoms occupy axial positions, four Ca atoms are in the equatorial positions, and a μ_6 -O-encapsulated O atom resides at the center of the octahedron. Therefore, the core structure of 4 can be considered to be composed of two $\{Ca_4Ti_2(\mu_6-O)(\mu_3 OR_{10}Cl_4$ units that share two Ca atoms.

Furthermore, the reaction of Cp₂M'Cl₂ (M = Zr, Hf) with 2 equiv of metallic Ca in a mixture of EtOH/toluene (3:1) conducted at room temperature, according to Scheme 2, gave colorless heterometallic $[Ca_2Zr_2(\mu_4-O)(\mu_2-OE-t)_5(OEt)_4(EtOH)_4Cl]_n$ (5, 75%) and $[Ca_2Hf_2(\mu_4-O)(\mu_2-OEt)_5(OEt)_4(EtOH)_4Cl]_n$ (6, 78%), respectively. XRD analysis revealed that both 5 and 6 have a one-dimensional linear coordination polymer structure based on tetranuclear Scheme 3. Comparison of the Central Core Structural Motifs of Products from the Reaction of Cp₂TiCl₂ and Ca in the Presence of Excess ROH (MeOCH₂CH₂OH or EtOH)



 $[Ca_2M'_2(\mu_4-O)(\mu-OEt)_5(OEt)_4(EtOH)_4Cl]$ units linked by μ -Cl bridges (Figure 3).

Each unit consists of two Ca and two Zr or Hf atoms bridged by one μ_4 -O and five μ -OEt ligands. The metal atoms adopt octahedral coordination environments, with O₆ donor sets for M' and O₅Cl for the Ca center. The central core of **5** and **6** is similar to that observed earlier for homometallic aluminum and titanium alkoxides of $[Al_4(\mu_4-O)(\mu-OiPr)_5(OiPr)(iPrOH)_4X_4]$ $(X = Cl, F),^{26} [Al_4(\mu_4-O)(\mu-OCH_2CF_3)_5(OCH_2CF_3)_5(CF_3-CH_2OH)],^{27}$ and $[Ti_4(\mu_4-OH)(\mu-OEt)_5(OEt)_{10}].^{28}$

Metal chloride compounds are described as corrosive agents because they evolve hydrochloride during calcination, and they also usually form multiphase systems.²⁹ To avoid the formation of complexes containing Cl ligands, we substituted the Cl ligands with OEt groups in Cp₂M'Cl₂ (M' = Ti, Zr, Hf). To the EtOH/toluene solution of EtONa synthesized in situ by reacting metallic Na with alcohol, we added Cp₂M'Cl₂ at a molar ratio of 2:1, leading to the separation of NaCl. As shown in Scheme 4, the direct addition of metallic Ca to the reaction mixtures resulted in the formation of $[Ca_2Ti_2(\mu_3-OEt)_2(\mu-OEt)_4(OEt)_6(EtOH)_4]$ (7, 22%), $[Ca_2Zr_2(\mu_3-OEt)_2(\mu-OEt)_4(OEt)_6(EtOH)_4]$



Figure 2. (a) Molecular structure of **4**. The second disordered counterpart of the alkoxy group and H atoms are omitted for clarity [symmetry code: (i) -x + 1, -y + 1, -z + 1]. (b) Polyhedral representation of the central Ca₆Ti₄O₂₆Cl₄ core structure in **4**.



Figure 3. Tetranuclear units of $[Ca_2M'_2(\mu_4-O)(\mu-OE-t)_5(OEt)_4(EtOH)_4Cl]_n$, where M' = Zr (5) or Hf (6). The H atoms, second disordered counterpart of Cl⁻, and, for 6, Ca and Hf atoms are omitted for clarity [symmetry code: (i) x - 0.5, -y + 1.5, z - 0.5].





t)₄(OEt)₆(EtOH)₄] (8, 82%), and $[Ca_2Hf_2(\mu_3-OEt)_2(\mu-OEt)_4(OEt)_6(EtOH)_4]$ (9, 64%), which are isostructural to 1–3.

Compounds 7–9 were characterized by elemental analysis, ¹H and ¹³C NMR spectroscopy (Figures S7–S12), and singlecrystal XRD. The deformation of the coordination geometry around the metal centers within the $[M_2M'_2(\mu_3\text{-OEt})_2(\mu OEt)_4(OEt)_6(EtOH)_4]$ series was also analyzed in terms of CShM.³⁰ The departure from an ideal octahedron is about 3 times larger for the coordination environment around the Ca ions in 7–9 than that around the Mg ions in 1–3, as confirmed by the metric shape parameters S(Oh) varying from 0.830 to 1.184 for Mg and from 2.662 to 3.199 for Ca. For Ti, Zr, and Hf ions, S(Oh) does not exceed 0.625 (Table S2).

Thermal Decomposition of 1–9 and Characterization of Oxides. Thermogravimetry–differential thermal analysis (TG/DTA) and powder XRD studies were conducted for compounds 1–9 to select the appropriate calcination temperatures to remove the organic component and crystallize pure oxide materials. Thermal decomposition of 1–9 upon heating from room temperature up to 800 °C at a heating rate of 10 °C min⁻¹ was investigated in air and N₂. These measurements clearly indicated that heterometallic ethoxide complexes 1–9 underwent a multistep transformation (Figures S13–S16). The TG/DTA curves for these compounds were all similar to that for precursor 9 presented in Figure 4. The weight losses in the temperature range of 200–800 °C were caused by the pyrolysis of coordinated ethoxide and EtOH ligands, as revealed by



Figure 4. TG/DTA curves for 9 under nitrogen measured at a heating rate of 10 $^\circ C$ min^{-1}.

exothermic peaks in the DTA curve, and no further weight change was observed above 800 $^\circ\mathrm{C}.$

Next, oxides were produced by heating precursors 1-9 at different sintering temperatures (usually from 700 to 900 °C) at a rate of 10 °C min⁻¹ for 1 h under air. The phase purity of the final residues was confirmed by powder XRD analysis, and their data are presented in Figures 5–9.



Figure 5. Powder XRD patterns of the materials obtained by thermolysis of 1 at 750–900 °C for 1 h: (a) MgTiO₃ reference pattern (JCPDS 06-0494); samples sintered at (b) 750, (c) 800, (d) 850, and (e) 900 °C; (f) Mg₂TiO₄ reference pattern (JCPDS 25-1157).

XRD patterns of the powders obtained by calcination of 1 at different sintering temperatures (750–900 °C) are shown in Figure 5 along with that of the rhombohedral (hexagonal) structure of MgTiO₃ for comparison. When 1 was calcined at 750–850 °C, the major phase formed was perovskite oxide MgTiO₃ with a small amount of Mg₂TiO₄. When 1 was calcined at 900 °C, the peak intensities of the crystalline phase MgTiO₃ increased, and no contaminant phases like MgTi₂O₅ or Mg₂TiO₄ were detected. It is worth noting that producing phase-pure MgTiO₃ is very difficult and the subject of several papers using various methods.^{9,10} For instance, a solid-state reaction gives final materials that contain a certain amount of MgTi₂O₅ as a metastable phase, and the sintering temperature is high (over 1400 °C).

Thermal decomposition of **2** at 750–950 °C led to crystalline $Mg_2Zr_5O_{12}$, as shown in Figure 6. However, besides

the peaks of $Mg_2Zr_5O_{12}$, additional diffraction peaks corresponding to MgO also appear as a result of the stoichiometry of the molecular precursor.



Figure 6. Powder XRD patterns of the materials obtained by thermolysis of 2 at 750–800 °C for 1 h: (a) MgO reference pattern (JCPDS 65-476); (b) $Mg_2Zr_5O_{12}$ reference pattern (JCPDS 80-967); samples treated at (c) 750 and (d) 800 °C.

The XRD patterns obtained after calcination of 3 at 750–1100 °C presented in Figure 7 show that, at 800-850 °C,



Figure 7. Powder XRD patterns of the materials obtained by thermolysis of 3 at 800–1100 °C for 1 h: (a) $Mg_2Hf_5O_{12}$ reference pattern (JCPDS 33-0862); samples thermolyzed at (b) 800, (c) 850, (d) 900, (e) 1000, and (f) 1100 °C; (g) HfO₂ reference pattern (ICSD 638736).

 $Mg_2Hf_5O_{12}$ crystallized, similar to the behavior of the Zr compound 2. Meanwhile, the sample heated at 900 °C displayed peaks from $Mg_2Hf_5O_{12}$ and HfO_2 , and above 1000 °C, only HfO_2 was identified. Magnesium hafnates are unstable at high temperature, so they are not used in industrial applications and are not available commercially.

There are some reports proving that chloroalkoxide complexes are also suitable precursors for pure perovskite-type oxides with the structure $MM'O_3$.³¹ The only limitation is the proper ratio of elements M, M', and Cl in the molecular precursor. For instance, calcium–titanium chloroethoxide complex 4 possesses the right stoichiometry and thermally decomposes under proper conditions to give a CaCl₂/CaTiO₃ mixture in a 1:2 molar ratio (Scheme 5).

Scheme 5. Thermal Transitions of 4



Using the different water solubilities of CaCl₂ and CaTiO₃, they can be easily separated from each other. Thus, CaCl₂ was easily removed from the raw powder using deionized water to give pure CaTiO₃. In this case, the important factor in preparing pure perovskite-type oxides is choosing the appropriate thermal decomposition conditions by taking into consideration the melting point of CaCl₂ (772 °C).³² Crystalline single-phase CaTiO₃ derived from 4 as well as from the chloride-free precursor 7 gave XRD patterns consistent with the reference standard for the orthorhombic structure of CaTiO₃, which is presented in Figure 8.



Figure 8. Powder XRD patterns of (a) $CaTiO_3$ as a reference (JCPSD 78-1013) and the materials obtained by thermolysis of (b) 4 at 750 °C for 1 h and then leached with deionized water with subsequent heat treatment at 800 °C for 1 h and (c) 7 at 800 °C for 1 h.

The stoichiometry of Ca, M' (Zr or Hf), and Cl in **5** and **6** is not suitable for their use as precursors of pure oxide materials. Their thermolysis led to a mixture of various compounds, including CaM'O₃, M'O₂, and CaCl₂ (Figure S17). In contrast, the powder XRD results for **8** and **9** indicate that, during their calcination at 750–900 °C, they crystallized to give single-phase CaZrO₃ and CaHfO₃, respectively. Representative diffraction patterns of samples obtained by the heat treatment of **8** and **9** at 800 °C and their comparison with the reference standards for CaZrO₃ and CaHfO₃ are presented in Figure 9.

To investigate the microstructural morphology of the oxides, transmission electron microscopy (TEM) and scanning electron microscopy (SEM) measurements were carried out; the resulting images are shown in Figures 10 and 11. All of the crystallites are spherical and well-dispersed with a slight tendency to agglomerate. The representative TEM images of the MgTiO₃ powders presented in Figure 10a,b reveal polycrystalline particles with smooth surfaces and a crystallite size distribution of ~50 nm. The Mg₂Zr₅O₁₂ oxide materials consist of nanoscale crystallites with a grain size of about 20 nm, as shown in Figure 10d,e.



Figure 9. Powder XRD patterns of the materials obtained by the thermolysis of 8 and 9 at 800 °C for 1 h: (a) $CaZrO_3$ reference pattern (JCPDS 72-7551); (b) thermolyzed 8; (c) $CaHfO_3$ reference pattern (JCPDS 36-1473); (d) thermolyzed 9.



Figure 10. (a and b) TEM and (c) SEM images of $MgTiO_3$ calcined at 900 °C. (d and e) TEM and (f) SEM images of $Mg_2Zr_5O_{12}$ calcined at 800 °C.



Figure 11. TEM images of $CaTiO_3$ obtained from 4 (a) and 7 (b). TEM images of $CaZrO_3$ (c and d) and $CaHfO_3$ (e and f) calcined at 800 °C. TEM images of $CaHfO_3$ calcined at 900 °C (g and h).

Moreover, the microstructures of $CaTiO_3$ prepared from the chloride (4) and chloride-free (7) precursors are identical, as shown in Figure 11a,b. Electron microscopic analysis of the powders obtained by the calcination of 8 and 9 at 800 °C

(Figure 11c-f) confirmed that the single-phase perovskite oxides $CaZrO_3$ and $CaHfO_3$ consisted of nanoscale crystallites with particle sizes between 20 and 30 nm. It is also worth noting that the change of the grain size of the nanocrystallites resulted from decomposition of the precursors at different temperatures. Therefore, the particles obtained by calcination of **9** at 900 °C are larger than 50 nm, as illustrated in Figure 11g,h.

CONCLUSIONS

We presented a simple, high-yield synthetic route for the easily scaled preparation of well-defined SSPs to provide group IV alkaline-earth ceramics. The precursor compounds were prepared by the simple elimination of the Cp⁻ anion from $Cp_2M'Cl_2$ (M' = Ti, Zr, Hf) as cyclopentadiene in the presence of $M(OEt)_2$ using EtOH as a source of protons. We synthesized nine new heterometallic compounds that displayed three different arrangements of the central core structure to determine their influence on the phase purity and morphology of the obtained binary oxide nanoparticles. Under thermal treatment, the isostructural compounds $[M_2M'_2(\mu_3-OEt)_2(\mu_3-O$ $OEt_4(OEt_6(EtOH_4)]$, where M' = Ti, Zr, and Hf and M = Mg, led to a mixture of MgTiO₃/Mg₂TiO₄, Mg₂Zr₅O₁₂, or $Mg_2Hf_5O_{12}$ binary oxide nanomaterials. Meanwhile, for 7-9 (M = Ca), highly pure CaTiO₃, CaZrO₃, or CaHfO₃ perovskite-like oxides were obtained, respectively. The resulting particles were 20-30 nm in size. Furthermore, following a twostep strategy, compound 4 was thermally transformed into a double-phase CaTiO₃/CaCl₂ system, and then CaCl₂ was easily removed from the raw powder by washing with deionized water to give pure $CaTiO_3$. The molecular stoichiometry in 5 and 6 of $[Ca_2M'_2(\mu_4-O)(\mu-OEt)_5(OEt)_4(EtOH)_4Cl]_{n'}$ where M' = Zr and Hf, was not suitable for their use as precursors of pure oxide materials because their thermolysis led to mixtures of various compounds, including CaM'O₃, M'O₂, and CaCl₂. Overall, this study demonstrated that metal alkoxides and their organometallic derivatives can be used to synthesize molecular precursors for the preparation of numerous metal oxide materials at lower temperatures than those typically used in conventional solid-state thermal routes involving carbonate/ oxide mixtures.

EXPERIMENTAL SECTION

All reactions were performed under N_2 using standard Schlenk and vacuum-line techniques. All reagents were purchased from commercial sources: toluene, hexane, ethanol (EtOH), CDCl₃, calcium chips, and magnesium turnings were from Sigma-Aldrich and Cp₂TiCl₂, Cp₂ZrCl₂, and Cp₂HfCl₂ from ABCR. Reagents were purified using standard methods: toluene and hexane were distilled over Na, while EtOH was dried by reflux and distillation over metallic Mg.

NMR spectra were recorded at room temperature using a Bruker Avance 500 MHz spectrometer. Chemical shifts are reported in parts per million and referenced to the residual protons in deuterated solvents. FT-IR spectra (Nujol mulls) were recorded using a Bruker 66/s FT-IR spectrometer. Elemental analysis was performed using a PerkinElmer 2400 CHN elemental analyzer. Metal-ion concentrations were determined by inductively coupled plasma atomic emission spectroscopy using an ARL 3410 sequential spectrometer (Fisons Instruments). Cl analysis was performed according to Schoeninger's method using an Elementar Micro K analyzer. TG/DTA was performed under air using a SETSYS 16/18 system (Setaram) at a heating rate of 10 °C min⁻¹. Thermal decomposition was performed in a NT 1313 furnace equipped with a KXP3+ thermostat (Neotherm). Samples were heated in atmospheric air. The thermolysis products were characterized by powder XRD with a Bruker D8 Advance diffractometer equipped with a copper lamp [λ (Cu K α) = 1.5418 Å]. Measurements were performed in the 2 θ range of 5–90° in increments of 0.032° with a counting time of 0.3 s. The morphology of the prepared powders was examined by high-resolution TEM and SEM. TEM analysis was conducted using an FEI Tecnai G² 20 X-Twin microscope equipped with an EDS microanalyzer and operating at 200 kV (resolution = 0.25 nm). SEM analysis was performed on a Hitachi S-3400N microscope equipped with a Thermo Noran SIX EDS system.

XRD data were collected using an Xcalibur Ruby or Xcalibur PX diffractometer at 100 K for 1 and 8, 220 K for 2, 200 K for 3 and 7, 190 K for 4 and 9, and 90 K for 5 and $6^{.33}$ The experimental details and crystal data are summarized in Table S3. The crystal structures were solved using direct methods and refined by the full-matrix least-squares method on F^2 using the *SHELXTL* package.³⁴ Non-H atoms were refined with anisotropic thermal parameters. All H atoms were positioned geometrically and added to the structure factor calculations but were not refined. Molecular graphics were created using *DIAMOND* (version 3.1e).³⁵ Crystallographic data for the structural analyses reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as CCDC 1558845–1558853.

Synthesis of $[Mg_2Ti_2(\mu_3-OEt)_2(\mu-OEt)_4(OEt)_6(EtOH)_4]$ (1). A Schlenk flask was charged with Cp2TiCl2 (0.99 g, 3.98 mmol), Mg turnings (0.21 g, 8.64 mmol), EtOH (25 mL), and toluene (15 mL). The mixture was vigorously stirred at 65 °C until all metal was consumed (typically within 18 h). During the reaction course, the dark-red solution slowly changed to dark green, then navy blue, and finally light yellow. The resulting solution was filtered off. The filtrate volume was reduced under a vacuum to 20 mL, and then hexane (20 mL) was slowly added, forming a colorless layer over the solution. Colorless crystals of 1 were formed at room temperature within a few days (3-5). The crystals were collected, washed with a mixture of EtOH and hexane (1:5, 3×5 mL), and dried under vacuum. The resulting filtrate was concentrated to 10 mL and left to produce another portion of crystalline materials. Overall yield: 1.07 g, 1.23 mmol, 62%. Anal. Calcd for C₃₂H₈₄O₁₆Mg₂Ti₂: C, 44.21; H, 9.74; Mg, 5.59; Ti, 11.01. Found: C, 44.26; H, 9.76; Mg, 5.62; Ti, 11.03. IR (cm⁻¹, Nujol mull): 3289 (w), 3119 (w), 2955 (vs), 2922 (vs), 2853 (vs), 2705 (m), 2605 (w), 1462 (vs), 1376 (vs), 1283 (w), 1146 (vs), 1103 (vs), 1058 (vs), 925 (m), 892 (s), 720 (s), 558 (vs). ¹H NMR (500 MHz, CDCl₃, 300 K, ppm): δ [4.48, 4.34, 4.09, 4.02 (m, CH₂, 24H)], 3.71 (m, CH₂, 8H), [1.31, 1.25 (m, CH₃, 48H)]. ¹³C NMR (125 MHz, CDCl₃, 300 K, ppm): δ 58.2 (CH₂, 16C), 18.5 (CH₃, 16C).

Synthesis of $[Mg_2Zr_2(\mu_3-OEt)_2(\mu-OEt)_4(OEt)_6(EtOH)_4]$ (2). A Schlenk flask was charged with Cp2ZrCl2 (0.98 g, 3.35 mmol), Mg turnings (0.17 g, 6.99 mmol), EtOH (30 mL), and toluene (5 mL). The mixture was vigorously stirred at 65 °C until all metal was consumed (typically within 24 h). The resulting yellow solution was filtered off. The filtrate volume was reduced under a vacuum to 20 mL, and then hexane (20 mL) was slowly added, forming a colorless layer over the solution. Colorless crystals of 2 were formed at room temperature within a few days (1-2). The crystals were collected, washed with a mixture of EtOH and hexane (1:5, 3×5 mL), and dried under vacuum. The resulting filtrate was concentrated to 10 mL and left to produce another portion of crystalline materials. Overall yield: 1.12 g, 1.17 mmol, 70%. Anal. Calcd for C₃₂H₈₄O₁₆Mg₂Zr₂: C, 40.20; H, 8.86; Mg, 5.08; Zr, 19.08. Found: C, 40.26; H, 8.96; Mg, 4.97; Zr, 19.15. IR (cm⁻¹, Nujol mull): 3145 (m), 2954 (vs), 2924 (vs), 2854 (vs), 2710 (m), 2606 (w), 1459 (s), 1376 (vs), 1282 (w), 1162 (s), 1107 (s), 1063 (vs), 922 (m), 896 (s), 804 (w), 722 (m), 626 (s), 521 (vs). ¹H NMR (500 MHz, CDCl₃, 300 K, ppm): δ 3.99 (m, CH₂, 24H), 3.73 (q, J = 6.3 Hz, CH₂, 8H), 2.20 (s, OH, 4H), 1.24 (m, CH₃, 48H). ¹³C NMR (125 MHz, CDCl₃, 300 K, ppm): δ 58.3 (CH₂, 16C), 20.3, 18.5 (CH₃, 16C).

Synthesis of $[Mg_2Hf_2(\mu_3-OEt)_2(\mu-OEt)_4(OEt)_6(EtOH)_4]$ (3). A Schlenk flask was charged with Cp₂HfCl₂ (1.00 g, 2.63 mmol), Mg turnings (0.13 g, 5.35 mmol), EtOH (30 mL), and toluene (10 mL). The mixture was vigorously stirred at 65 °C until all metal was

consumed (typically within 24 h). The resulting yellow solution was filtered off. The filtrate volume was reduced under a vacuum to 20 mL, and then hexane (20 mL) was slowly added, forming a colorless layer over the solution. Colorless crystals of 3 were formed at room temperature within a few days (2-3). The crystals were collected, washed with a mixture of EtOH and hexane (1:5, 3×5 mL), and dried under vacuum. The resulting filtrate was concentrated to 10 mL and left to produce another portion of crystalline materials. Overall yield: 1.09 g, 0.96 mmol, 73%. Anal. Calcd for C₃₂H₈₄O₁₆Mg₂Hf₂: C, 34.00; H, 7.49; Mg, 4.30; Hf, 31.57. Found: C, 34.06; H, 7.56; Mg, 4.33; Hf, 31.66. IR (cm⁻¹, Nujol mull): 3126 (m), 2958 (vs), 2923 (vs), 2855 (vs), 2710 (m), 1463 (vs), 1375 (vs), 1282 (w), 1171 (vs), 1105 (vs), 1066 (vs), 922 (w), 893 (s), 874 (m), 721 (m), 640 (m), 517 (s), 465 (vs). ¹H NMR (500 MHz, CDCl₃, ppm): δ 5.36 (s, OH, 4H), 4.15, 4.07, 3.86 (m, CH_{2} , 24H), 3.73 (q, J = 6.7 Hz, CH_{2} , 8H), 1.23 (m, CH₃, 48H). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 64.6-59.2, 58.0 (CH₂, 16C), 21.6–18.8, 18.5 (CH₃, 16C).

Synthesis of $[Ca_6Ti_4(\mu_6-O)_2(\mu_4-O)_2(\mu_3-OEt)_{12}(OEt)_{12}(EtOH)_6Cl_4]$ (4). A Schlenk flask was charged with Cp₂TiCl₂ (1.66 g, 6.67 mmol), metallic Ca (0.53 g, 13.22 mmol), EtOH (30 mL), and toluene (5 mL). The mixture was vigorously stirred at 65 °C until all metal was consumed (typically within 2 h). During the reaction course, a darkred solution slowly changed to dark green, then brown, and finallylight yellow. The resulting solution was filtered off, and the filtrate was reduced under a vacuum to 20 mL and left to crystallize. After 12 h, colorless crystals of 4 were collected, washed with hexane $(3 \times 5 \text{ mL})$, and dried under vacuum. Yield: 0.56 g, 0.34 mmol, 21%. Calcd for C44H116O26Cl4Ca6Ti4: C, 32.32; H, 7.15, Cl, 8.67; Ca, 14.71; Ti, 11.71. Found: C, 32.30; H, 7.24, Cl, 8.68; Ca, 14.79; Ti, 11.78. IR (cm⁻¹, Nujol mull): 3290 (s), 2956 (vs), 2925 (vs), 2870 (vs), 2855 (vs), 2720 (w), 1922 (vw), 1636 (vw), 1457 (s), 1418 (m), 1378 (s), 1276 (vw), 1138 (vs), 1100 (s), 1073 (s), 1048 (vs), 923 (w), 886 (s), 751 (vs), 659 (vs), 569 (vs), 475 (vs). Compound 4 after isolation in crystalline form is not soluble in most conventional solvents; therefore, it was not possible to carry out an NMR study.

Synthesis of $[Ca_2Zr_2(\mu_4-O)(\mu_2-OEt)_5(OEt)_4(EtOH)_4Cl]_n$ (5). A Schlenk flask was charged with Cp₂ZrCl₂ (1.03 g, 3.52 mmol), metallic Ca (0.28 g, 6.99 mmol), EtOH (30 mL), and toluene (10 mL). The mixture was vigorously stirred at 65 °C until all metal was consumed (typically within 3 h). The resulting light-yellow solution was filtered off and concentrated under vacuum to 25 mL. After 24 h, colorless needle crystals of 5 were collected, washed with hexane $(3 \times 5 \text{ mL})$, and dried under vacuum. Another portion of crystalline 5 was obtained after a few days (2-3). Overall yield: 1.20 g, 1.33 mmol, 75%. Calcd for C₂₆H₆₉O₁₄Cl₁Ca₂Zr₂: C, 34.55; H, 7.69, Cl, 3.92; Ca, 8.87; Zr, 20.18. Found: C, 34.62; H, 7.78, Cl, 4.08; Ca, 8.99; Zr, 20.28. IR (cm⁻¹, Nujol mull): 3375 (s), 2955 (vs), 2923 (vs), 2854 (vs), 2725 (w), 1636 (vw), 1461 (vs), 1376 (s), 1263 (w), 1153 (m), 1103 (m), 1052 (s), 881 (m), 721 (m), 646 (s), 490 (s). Compound 5 after isolation in crystalline form is not soluble in most conventional solvents; therefore, it was not possible to carry out an NMR study.

Synthesis of $[Ca_2Hf_2(\mu_4-O)(\mu_2-OEt)_5(OEt)_4(EtOH)_4CI]_n$ (6). A Schlenk flask was charged with Cp₂HfCl₂ (1.01 g, 2.66 mmol), metallic Ca (0.21 g, 5.24 mmol), EtOH (30 mL), and toluene (10 mL). The mixture was vigorously stirred at 65 °C until all metal was consumed (typically within 4 h). The resulting light-yellow solution was filtered off and concentrated under vacuum to 25 mL. After 2-4 days, colorless needle crystals of 6 were collected, washed with hexane $(3 \times$ 5 mL), and dried under vacuum. Another portion of crystalline 6 was obtained after a few days (3-5). Overall yield: 1.12 g, 1.04 mmol, 78%. Calcd for C₂₆H₆₉O₁₄Cl₁Ca₂Hf₂: C, 28.96; H, 6.45, Cl, 3.29; Ca, 7.43; Hf, 28.96. Found: C, 28.99; H, 6.56, Cl, 3.28; Ca, 7.59; Hf, 28.98. IR (cm⁻¹, Nujol mull): 3369 (s), 2955 (vs), 2924 (vs), 2854 (vs), 2725 (w), 1636 (w), 1461 (s), 1378 (s), 1271 (s), 1149 (w), 1091 (m), 1051 (s), 877 (m), 725 (s), 450 (s). Compound 6 after isolation in crystalline form is not soluble in most conventional solvents; therefore, it was not possible to carry out an NMR study.

Synthesis of $[Ca_2Ti_2(\mu_3-OEt)_2(\mu-OEt)_4(OEt)_6[EtOH)_4]$ (7). A Schlenk flask was charged with metallic Na (0.43 g, 18.70 mmol), EtOH (10 mL), and toluene (10 mL). The mixture was vigorously

stirred until all metal was consumed (usually 1-2 h). The solution was evaporated to dryness to give a white powder of NaOEt. To the resulting solid was added Cp2TiCl2 (2.23 g, 8.96 mmol), EtOH (25 mL), and toluene (10 mL), and the mixture was stirred at 80 °C for 2 h. Stirring the dark-red solution resulted in a slow change of color to light yellow. The cloudly solution was filtered off, and the precipitate was washed with EtOH $(2 \times 5 \text{ mL})$ and dried to give a white powder of NaCl (0.95 g, 16.26 mmol, 91%). The filtrate was evaporated to dryness, and to the residue solid was added metallic Ca (0.47 g, 11.73 mmol), EtOH (25 mL), and toluene (5 mL). The mixture was stirred at 80 °C until all metal was consumed (usually 2 h). During the reaction, a green precipitate settled out. The solution was filtered off. The filtrate was reduced in volume under vacuum to 20 mL and left to crystallize at room temperature. After 4-6 days, colorless crystals of 7 were collected, washed with hexane $(3 \times 5 \text{ mL})$, and dried under vacuum. Yield: 0.88 g, 0.98 mmol, 22%. Anal. Calcd for C32H84O16Ca2Ti2: C, 42.66; H, 9.40; Ca, 8.90; Ti, 10.63. Found: C, 42.56; H, 9.46; Ca, 8.92; Ti, 10.57. IR (cm⁻¹, Nujol mull): 3345 (m), 2954 (vs), 2925 (vs), 2854 (vs), 2727 (w), 1640 (w), 1463 (vs), 1377 (s), 1099 (w), 1055 (m), 882 (m), 724 (s), 563 (s). ¹H NMR (500 MHz, CDCl₃, 300 K, ppm): δ 4.30 (s, CH₂, 24H), 3.74 (m, CH₂, 8H), 1.25 (m, CH₃, 48H). ¹³C NMR (125 MHz, CDCl₃, 300 K, ppm): δ 59.5, 58.5 (CH₂, 16C), 19.6, 18.6 (CH₃, 16C)

Synthesis of $[Ca_2Zr_2(\mu_3-OEt)_2(\mu-OEt)_4(OEt)_6(EtOH)_4]$ (8). A Schlenk flask was charged with metallic Na (0.21 g, 9.13 mmol), EtOH (10 mL), and toluene (10 mL). The mixture was vigorously stirred until all metal was consumed (usually 1-2 h). The solution was evaporated to dryness to give a white powder of NaOEt. To the resulting solid was added Cp₂ZrCl₂ (1.29 g, 4.41 mmol), EtOH (20 mL), and toluene (10 mL), and the mixture was stirred at 80 °C for 2 h. After that time, the cloudly solution was filtered off, and the precipitate was washed with EtOH $(2 \times 5 \text{ mL})$ and dried to give a white powder of NaCl (0.42 g, 7.19 mmol, 82%). The filtrate was evaporated to dryness, to the residue solid was added metallic Ca (0.25 g, 6.24 mmol), EtOH (20 mL), and toluene (5 mL), and the mixture was stirred at 80 °C until all metal was consumed (usually 2 h). The colorless solution was filtered off, and the volume of filtrate was reduced to 10 mL and left to crystallize at room temperature. After 2 days, colorless crystals of 8 were collected, washed with hexane (3×5) mL), and dried under vacuum. Another portion of crystalline 8 was obtained after a few days (3-5) of standing at 10 °C. Overall yield: 1.22 g, 1.23 mmol, 56%. Anal. Calcd for C32H84O16Ca2Zr2: C, 38.92; H, 8.57; Ca, 8.12; Zr, 18.47. Found: C, 38.96; H, 8.66; Ca, 8.22; Zr, 18.49. IR (cm⁻¹, Nujol mull): 3306 (w), 2958 (vs), 2924 (vs), 2854 (vs), 2708 (w), 1942 (vw), 1636 (vw), 1461 (m), 1377 (s), 1161 (s), 1105 (s), 1058 (vs), 920 (w), 892 (m), 722 (w), 510 (s), 351 (s). ¹H NMR (500 MHz, CDCl₃, 300 K, ppm): δ 7.03 (s, OH, 4H), 3.97 (m, CH_{2} , 24H), 3.71 (q, J = 6.8 Hz, CH_{2} , 8H), 1.22 (m, CH_{3} , 48H). ¹³C NMR (125 MHz, CDCl₃, 300 K, ppm): δ 64.2–60.2, 58.1 (CH₂, 16C), 21.3-19.6, 18.5 (CH₃, 16C)

Synthesis of $[Ca_2Hf_2(\mu_3-OEt)_2(\mu-OEt)_4(OEt)_6(EtOH)_4]$ (9). A Schlenk flask was charged with metallic Na (0.46 g, 20.00 mmol), EtOH (15 mL), and toluene (10 mL). The mixture was vigorously stirred until all metal was consumed (usually 1-2 h). The solution was evaporated to dryness to give a white powder of NaOEt. To the resulting solid was added Cp₂HfCl₂ (3.43 g, 9.04 mmol), EtOH (30 mL), and toluene (10 mL), and the mixture was stirred at 80 °C for 2 h. After that time, a cloudly solution was filtered, and the precipitate was washed with EtOH $(2 \times 5 \text{ mL})$ and dried to give a white powder of NaCl (0.92 g, 15.74 mmol, 87%). The filtrate was evaporated to dryness, to the residue solid was added metallic Ca (0.43 g, 10.73 mmol), EtOH (25 mL), and toluene (5 mL), and the mixture was stirred at 80 °C until all metal was consumed (usually 2 h). The colorless solution was filtered, and the volume of filtrate was reduced to 20 mL and left to crystallize at room temperature. After 2-4 days, colorless crystals of 9 were collected, washed with hexane (3× 5 mL), and dried under vacuum. The filtrate was reduced in volume to 10 mL and gave, after 4 days of standing, another portion of crystalline material. Another portion of crystalline 9 was obtained after a few days (3-5) of standing at 10 °C. Overall yield: 3.36 g, 2.89 mmol, 64%.

Anal. Calcd for $C_{32}H_{84}O_{16}Ca_2Hf_2$: C, 33.07; H, 7.28; Ca, 6.90; Hf, 30.72. Found: C, 33.16; H, 7.36; Ca, 6.93; Hf, 30.66. IR (cm⁻¹, Nujol mull): 3307 (m), 2955 (vs), 2923 (vs), 2853 (vs), 2712 (vs), 1940 (vw), 1636 (vw), 1462 (vs), 1378 (vs), 1170 (s), 1106 (vs), 1060 (vs), 920 (w), 892 (m), 722 (m), 503 (m), 354 (s). ¹H NMR (500 MHz, CDCl₃, ppm): δ 7.86 (s, OH, 4H), 4.01 (m, CH₂, 24H), 3.71 (q, J = 7.0 Hz, CH₂, 8H), 1.22 (m, CH₃, 48H). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 63.0–60.4, 57.7 (CH₃), 21.5–19.1, 18.4 (CH₃, 16C).

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01772.

NMR, TG, powder XRD, and crystallographic data of 1–9 (PDF)

Accession Codes

CCDC 1558845–1558853 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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