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Synthesis of Heterometallic Compounds with Uncommon Combinations of Elements for Oxide Nanomaterials Using Organometallics

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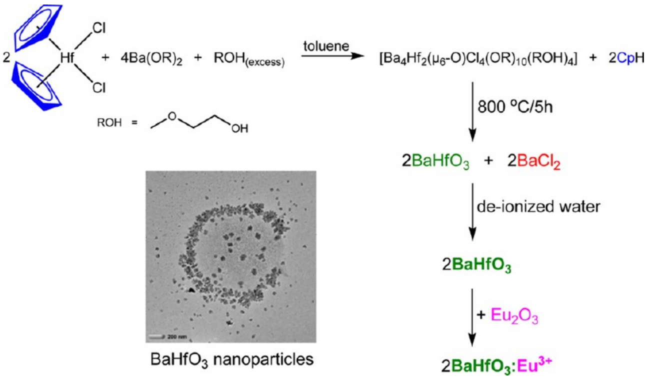

Oxide nanomaterials with interesting electronic and magnetic properties have applications including superconductors, magnetic core materials, high-frequency devices, and gas sensors. They can also serve as efficient oxide lattices for luminescent ions. Highly phase-pure $BaHfO_3$ nanopowders are extremely desirable as matrices for luminescent doping, and barium hafnate is an attractive host lattice for new X-ray phosphors, which are much more effective than the phosphors currently used in radiology and computed tomography.

This wide range of applications creates a strong impetus for novel and inexpensive methods for their synthesis. Classically, mixed-cation oxide ceramics are synthesized according to conventional solid-state reactions involving oxides, carbonates, or nitrates at relatively high temperatures (∼1500 °C). These procedures are inefficient and often lead to inhomogeneous by-products and poor control over the stoichiometry and phase purity. Among the new preparation techniques are those involving metal alkoxides and aryloxides with strictly defined metal stoichiometries at the molecular level.

In this Account, we describe several structurally interesting heterometallic alkoxoorganometallic compounds prepared via reactions of organometallic compounds (MMe_3 where M = Al, In, Ga) with group 2 alkoxides having additional protonated hydroxyl group(s) in the alcohol molecule present in the metal coordination sphere. Using lower temperatures than in the conventional solid-state thermal routes involving carbonate/oxide mixtures, we can easily transform these new complexes, with rarely found combinations of metallic precursors (Ba/In, Sr/Al, and Ba/Ga), into highly pure binary oxide materials that can be used, in a similar manner to perovskites and spinels, as host matrices for various lanthanide ions.

Furthermore, our studies on titanium, zirconium, and hafnium metallocenes showed them to be attractive and cheap precursors for an extensive range of novel molecular and supramolecular materials. This unique synthetic method comprises elimination of the cyclopentadienyl ring (as CpH) from Cp_2MCl_2 (M = Ti, Zr, Hf) in the presence of $M'(OR)_2$ (M' = Ca, Sr, Ba; ROH = $CH_3OCH_2CH_2OH$), in an alcohol as a proton source. The resulting compounds are suitable for obtaining highly phase-pure perovskite-like oxides including $BaTiO_3$, $BaHfO_3$, $SrHfO_3$, etc.

1. Introduction

The growing interest in the field of molecular precursor chemistry has arisen primarily from the tremendous growth in materials engineering, which has been spurred on by the discovery of high-temperature superconducting oxides and the important role of other metal oxides in technology. The

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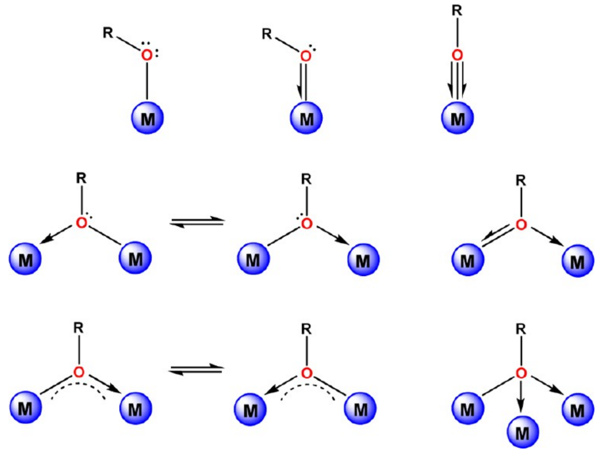
discovery by Müller and Bednorz from IBM that ceramic copper oxide exhibits superconductivity at 30 K has played an essential role in the development of new synthetic routes to these materials.[1]

For many years, it has been well-known that the structural arrangements[2] of coordination compounds play a key role in determining the properties of the final products,[3] and it is obvious that most of the major properties of complexes result from the incorporated elements and their mutual interactions. This is because the overall metal-based properties of a multimetallic compound are not a simple sum of the properties of the individual metal atoms. A perfect example is the cooperation of titanium, magnesium, and aluminum atoms in some olefin polymerization catalysts.[4] The procatalysts mainly comprise $TiCl_4$ and $MgCl_2$, and the cocatalyst is usually $AlEt_3$ or $Al(^iBu)_3$. Each of these components influences the catalyst and the polymer produced, but the procatalyst seems to have the greatest impact.[5] Simple and high-yield synthetic approaches to such compounds are therefore highly desirable.

In the literature, there are reports of a number of well-known routes for the preparation of mixed-metal oxides, for example, solid-state synthesis, reactions in molten salts, sol–gel processing of colloids, coprecipitation, the Pechini and citrate gel methods, sol–gel processing of metal–organic compounds, hydrothermal synthesis, nonaqueous liquid-phase reactions, and chemical vapor deposition (CVD).[6] Among these methods, the sol–gel and CVD techniques using metal alkoxides or aryloxides and their organometallic derivatives are the most valuable for obtaining highly phase-pure materials with low particle size distributions. These methods additionally guarantee good chemical homogeneity and fabrication of ceramic shapes other than powders. Such complexes as metal oxide precursors already have metal–oxygen bonds directly established at the molecular level, which is advantageous, but it should be emphasized that they may be of only incidental importance in the subsequent precursor thermal transformations.Thanks to these phenomena, thermal decomposition can be performed at relatively low temperatures compared with conventional methods, for example, using multicomponent mixtures of metal oxides and carbonates. The metal oxides derived from alkoxide-based compounds have specific properties such as high hardness, chemical and mechanical resistances, and high-temperature stability. They constitute a group of advanced ceramics, that is, the so-called high-tech ceramics, which are used as construction materials.[7] It is therefore of interest to develop a new synthetic strategy for incorporating alkali metals into M–OR systems to generate compounds containing the M–O(R)–M′ unit (M = transition metal, M′ = main group metal). In this context, the work of Bradley,[8a,b] Mehrotra and Singh,[8c] and Roesky et al.[9] on the synthesis and catalytic properties of alkoxo heterometallic complexes is noteworthy.

SCHEME 1. Possible Coordination Modes of Alkoxo Ligand RO^- to Metal Center(s) M^{2a}



In this Account, we describe simple, high-yield, and less explored synthetic routes to mixed-metal compounds of high purity with fixed metal stoichiometries at the molecular level. Our starting point is metal alkoxides and aryloxides, which are considered to be attractive precursors for various oxide ceramics and fulfill the requirements for appropriate substrates for further reactions. Such complexes are used in reactions with organometallic species to form, after thermal decomposition, attractive binary matrices for lanthanide ions. All of these issues will be discussed in detail in this Account.

2. Most Frequently Used Ligands

Metal alkoxides display a wide range of nuclearities (Scheme 1).[10] In our studies, the choice of ligands is always dictated by the solubilities and crystallization abilities of specific compounds. This is why our efforts are mainly concentrated on O,O′- and O,N-functionalized ligands containing substituents such as $-OCH_3$ and $-N(CH_3)_2$ (Figure 1).[11] What is extremely important is that, being relatively strong δ-donors and generally weak π-acceptors, O,O′- and O,N-ligands are able to form bonds with various metal centers, as well as with organometallic moieties such as MR_2^+ (M = group 13 cation; R = Me, Et, etc.).

Such alcohols contain two and three donor atoms possessing free electron pairs that can be tethered between metallic atoms in μ_3-η^2, μ-η^2, μ_3-η^1, or μ-η^1 modes. Deprotonation of their hydroxide groups creates bi- or tridentate

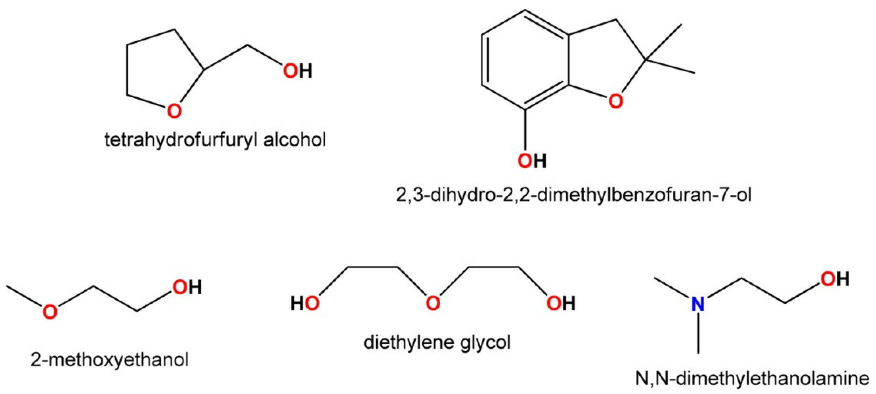
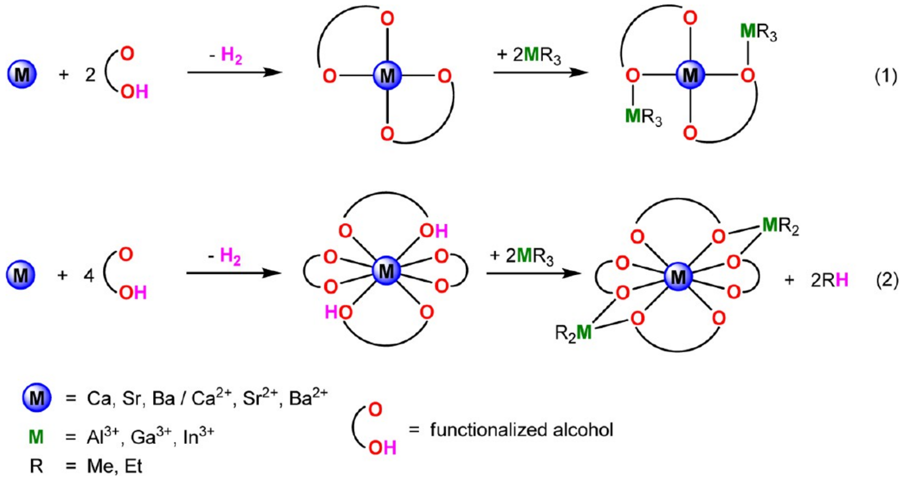


FIGURE 1. Functionalized alcohols as chelating ligands.

SCHEME 2. Cooperation of Group 2 Alkoxides or Aryloxides with Group 13 Organometallics in Synthesis of Heterometallic Complexes

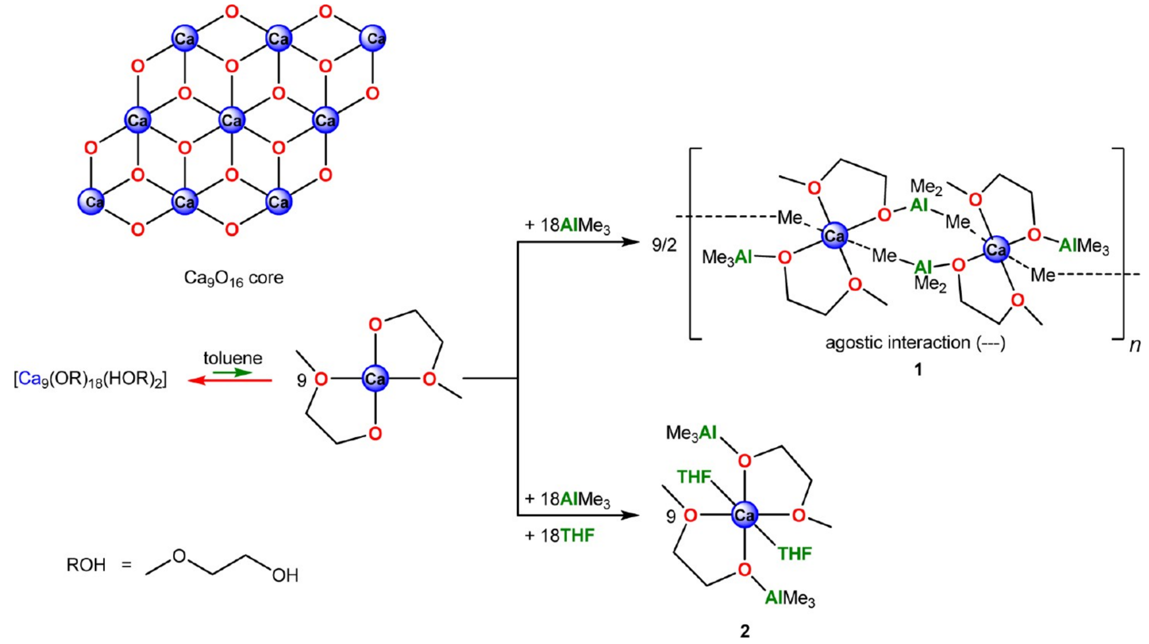


anions. The chelating ligands make it possible to obtain air- and moisture-stable complexes, although metal alkoxides are regarded as being highly susceptible to hydrolysis. Compared with simple alkoxo groups such as MeO^-, EtO^-, and $^iPrO^-$, most of these chelating ligands possess the inherent advantages of enhancing the solubilities and volatilities of the products by lowering their nuclearities as a result of steric factors and intramolecular coordination.[2a] These ligands form a family of moderately weak Lewis bases and are good leaving groups. It is worth noting that two factors, that is, solubility and volatility, are the properties of metal alkoxides and aryloxides that provide convenient methods for their purification, as well as making them suitable precursors for high-purity metal-oxide-based ceramic materials.

3. Synthesis of Polynuclear Precursors Using Organometallic Compounds

Heterometallic complexes are of interest not only because of their attractive structural chemistry, catalytic properties, and potential for industrial applications but also because they constitute a group of molecular precursors for various metal oxide materials. In heterometallic alkoxide- or aryloxide-based complexes, two or more different metals might be held together by alkoxo or aryloxo bridging ligands. Coordinated alkoxo or aryloxo groups and alcohol or phenol molecules both attach to the metal center, resulting in excellent anchors for organometallic compounds. Depending on the metal-to-alcohol ratio, it is easy to synthesize metal alkoxides with or without alcohols coordinated to the metal sphere (Scheme 2). This means that heterometallic complexes can be obtained in two ways. First, an organometallic agent can be bound directly to an alkoxide oxygen atom (Scheme 2, eq 1); second, when a metal alkoxide possesses coordinated alcohol molecules (Scheme 2, eq 2), the rapid evolution of a hydrocarbon leads to formation of an organometallic cation, e.g., MR_2^+, and attachment of the cation to the alkoxide core, resulting in a novel heterometallic complex.

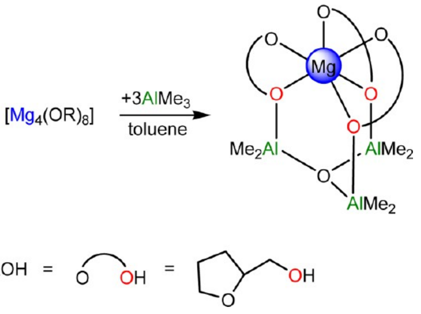
SCHEME 3. General Concept of Deoligomerization by Co-complexation Approach



3.1. Deoligomerization of Group 2 Alkoxides by Co-complexation with Group 13 Organometallic Agents. Calcium alkoxides are becoming important in the area of new biomaterials and are seeing increasing use as precursors for materials with numerous applications.[12] In the field of biodegradable polymers, such complexes are involved in lactide polymerization, which is promising in medicinal and pharmaceutical applications.[13] Calcium alkoxides are used in the production of bioactive glasses[14] for bone tissue engineering and environmentally friendly lubricants.[15] They are also of major importance in synthetic organic chemistry[16] and are highly desirable for the preparation of high-purity metal oxides.[17]

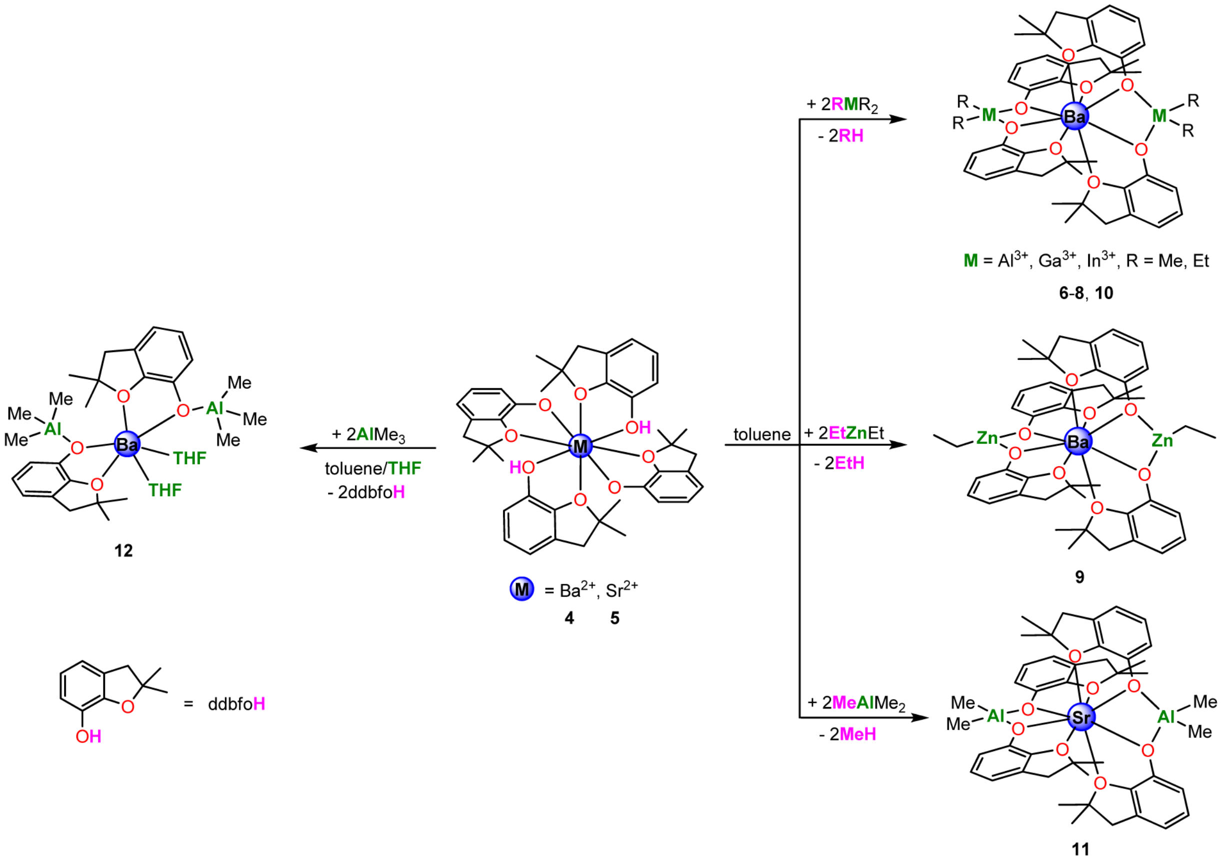
Nonramified and monodentate alcohol derivatives of calcium alkoxides often form large aggregates. The reaction of calcium with excess $CH_3OCH_2CH_2OH$ gives the nine-nuclear calcium complex $[Ca_9(CH_3OCH_2CH_2O)_{18}(CH_3OCH_2CH_2OH)_2]$.[18] Such a cluster structure is considered to be unattractive from many perspectives, such as in designing well-defined catalysts and in metal–organic CVD. In fact, the synthesis of calcium alkoxides of low nuclearity is cumbersome. This is because of the bridging ability of alkoxo oxygen atoms, which cause aggregation. A solid foundation for preventing agglomeration is the assumption that alkoxo-bridged oligomers partially dissociate in solution to low-nuclearity species, which can be "frozen" by coordination of additional organometallic moieties to the alkoxo oxygen atoms of functionalized O,O′- or O,N-ligands, which fill the calcium coordination sphere. This is called the "deoligomerization by co-complexation strategy" by our research group and is commonly used with great success (Scheme 3).[19]

SCHEME 4. Reaction of Magnesium 2-Tetrahydrofurfuroxide Tetrameric Compound with $AlMe_3$



As shown in Scheme 3 such a synthetic pathway enables us to obtain aluminum–calcium alkoxides such as the coordination polymer $[Ca\{(\mu\text{-}OCHH_2CH_2OCH_3)(\mu\text{-}CH_3)Al(CH_3)_2\}_2]$ (**1**) and the monomeric tetrahydrofuran (THF) compound $[Ca\{(\mu\text{-}OCHH_2CH_2OCH_3)Al(CH_3)_3\}_2(THF)_2]$ (**2**) starting from calcium 2-methoxyethoxide. The resulting complex **1**, which formally has four coordinated calcium atoms, is in fact a coordination polymer held together by γ-agostic interactions between the calcium atoms and the carbon atoms from the aluminum-centered methyl groups of neighboring units. The trimethylaluminum plays the role of both a Lewis acid and a neutral base, interacting through a methyl group. The polymeric structure can be easily destroyed by weak donors.

SCHEME 5. Synthesis of Group 2/Group 12 and 13 Aryloxo-Organometallic Compounds



Addition of THF to **1** leads to the formation of the molecular six-coordinated heterotrimetallic complex **2** (Scheme 3).[20] The crystalline **1** and **2** obtained in toluene solution possesses a 1:2 calcium-to-aluminum ratio that exactly matches the spinel-like $CaAl_2O_4$ composition. Similar coordination modes have been found, for example, in monomeric $(ArO)M[(\mu\text{-}OAr)(\mu\text{-}CH_3)Al(CH_3)_2]$ ($ArO = 2,6\text{-}{}^iPr_2C_6H_3O$; M = Y, Sm, and La),[21] cationic $[Ti(N^tBu)(Me_3[9]aneN_3)(\mu\text{-}CH_3)Al(CH_3)_2][BAr^F{}_4]$,[22] and $[(\eta\text{-}C_5Me_5)_2Ca(\mu\text{-}CH_3)_2Al(CH_3)(THF)]$ species.[23]

It is worth noting here that there is also the possibility of anchoring three $AlMe_2^+$ units to group 2 alkoxide carriers. For example, we have found that in the reaction of $AlMe_3$ with the tetrameric magnesium alkoxide $[Mg_4(thffo)_8]$ (thffoH is 2-tetrahydrofurfuryl alcohol), a molecular solid of formula $[Al_3Mg(\mu_3\text{-}O)(thffo)_3Me_6]$ (**3**) is formed (Scheme 4).[24]

This shows the various possibilities for creating novel heterometallic organometallic-based compounds with specific metal-to-metal ratios.

3.2. Reactions of Group 2 Aryloxides Possessing Coordinated Benzofuranol-Derived Molecules with Organometallic Species.

The wide ranges of applications of spinel-like binary oxides[25]provide a strong impetus to find novel and inexpensive methods for their synthesis. These materials are considered to be efficient oxide networks for luminescent materials.[26] For instance, strontium and barium aluminates ($SrAl_2O_4$ and $BaAl_2O_4$) represent some of the most studied and efficient host materials for long-lasting phosphorescence.[27] Conventionally, binary spinel ceramics are synthesized in solid-state reactions at relatively high temperatures, even >1500 °C. It is generally known that such protocols are largely inefficient and usually lead to multiphase contaminations.[28] Because of these disadvantages, mixed-metal alkoxides, hydridoalkoxides, alkoxo-organometallics, and related complexes, especially those that have strictly defined metal-to-metal stoichiometries, are attractive alternatives to the commonly used precursors. For instance, Kessler et al. reported a new class of metal–aluminum alkoxides of fixed spinel-like composition $[MAl_2(acac)_3(O^iPr)_4(OAc)]$ (M = Co, Zn; acac = acetylacetone; OAc = acetate).[29] Also, Veith and co-workers obtained well-defined $[Mg\{(O^tBu)_2AlH_4\}_2]$.[30]

When searching for a novel class of molecular precursors for binary ceramics, we found that group 2 aryloxides containing O,O′-coordinating 2,3-dihydro-2,2-dimethylbenzofuran-7-ol (dbbfoH), with a hydroxyl group at the metal site, are efficient anchors for various organometallic cationic fragments (Scheme 5).[31]

The crucial point is that the driving force for these reactions is removal of the hydroxyl protons from the coordinated benzofuranol molecules and the spontaneous liberation of alkanes, resulting in coordination of the aryloxo oxygens to an appropriate cationic organometallic moiety $M'R_x^+$ ($x = 1, 2$) to form $[M\{(\mu\text{-}OR)_2M'R_x\}_2]$-type (M = group 2 cation; M′ = group 12 or 13 cation; ROH = alcohol; R = alkyl group) complexes. For example, the reactions of group 2 aryloxides of composition $[M(ddbfo)_2(ddbfoH)_2]$ ($M = Ba^{2+}$ (**4**),[31a] Sr^{2+} (**5**)[31c]) with group 13 and group 12 organometallic species, such as $AlMe_3$, $AlEt_3$, $GaMe_3$, $InMe_3$, and $ZnEt_2$, result in the novel heterometallic aryloxo-organometallic $[M\{(\mu\text{-}ddbfo)_2M'R_x\}_2]$ (M/M′/R/x is Ba^{2+}/Al^{3+}/Me/2 (**6**),[31a] Ba^{2+}/Al^{3+}/Et/2 (**7**),[31b] Ba^{2+}/Ga^{3+}/Me/2 (**8**),[31b] Ba^{2+}/Zn^{2+}/Et/1 (**9**),[31b] Ba^{2+}/In^{3+}/Me/2 (**10**),[31c] Sr^{2+}/Al^{3+}/Me/2 (**11**)[31c]) compounds. In contrast, when a similar reaction is conducted in a toluene/THF mixture, the substitution of two ddbfoH molecules by the donor solvent is observed, the consequence of which is coordination of trimethylaluminum to the aryloxo oxygen atoms (Scheme 5). In this way, the barium–aluminum/THF adduct of formula $[Ba\{(\mu\text{-}ddbfo)AlMe_3\}_2(THF)_2]$ (**12**) was obtained.[31a] The complexes mentioned above have predesigned appropriate M and M′ ratios that exactly correspond to those of spinel-like oxides. These compounds underwent thermal decomposition in air, usually over 5 h, at specific temperatures. Selected examples are shown in Table 1 and Figure 2.

TABLE 1. Thermolysis Conditions and Compositions of Selected Spinels

precursor	temperature (°C)	product	color	ref
6	1300	$BaAl_2O_4$	white	31b
7	1300	$BaAl_2O_4$	white	31b
8	1430	$BaGa_2O_4$	white	31b
10	1400	$BaIn_2O_4$	light brown	31c
11	1200	$SrAl_2O_4$	white	31c

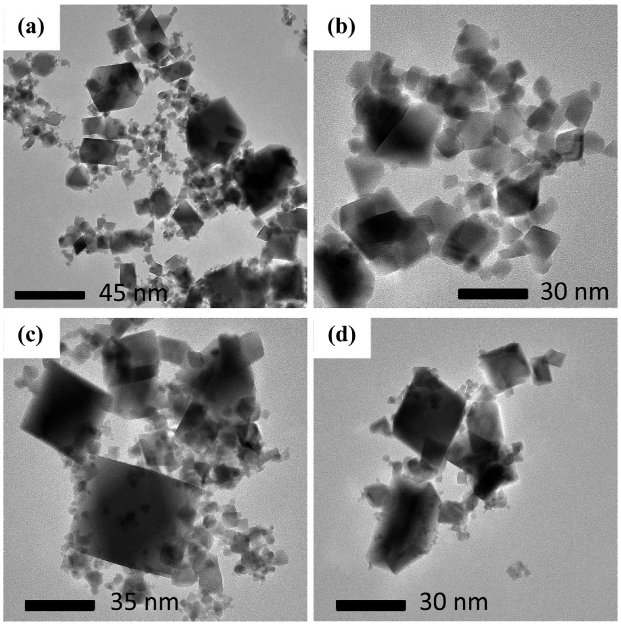


FIGURE 2. Transmission electron microscopy images of $BaGa_2O_4$ derived from **8** (a, b) and $BaIn_2O_4$ derived from **10** (c, d).

It should be mentioned that thermal decomposition of heterometallic aryloxides containing ramified ligands is much more challenging than that of simple alkoxo derivatives. Metal complexes containing chelating and bulky aryloxo groups are nonvolatile and much more stable than monodentate anions such as MeO^-, EtO^-, and $^iPrO^-$. Thermolysis of metal aryloxides is therefore much more complex and usually takes a long time. The resulting oxide materials exactly match the corresponding binary systems, and no residual diffraction peaks, for example, of group 2 carbonate contaminations, are observed in powder X-ray diffraction patterns.[31b]

Furthermore, some of the spinel-like metal oxides, for instance, $SrAl_2O_4$, constitute an attractive matrix for Eu-doped phosphors. For example, alkaline-earth aluminates have been widely studied in recent years because of their good luminescent properties such as longevity, high brightness, and chemical stability.[32] Because of these properties, they have many successful applications, for example, as display devices and in the lamp industry.[33] Our studies have clearly shown that phosphors based on $SrAl_2O_4$:Eu exhibit higher emission intensities than those obtained using conventional solid-state synthesis (Figure 3).[31c]

3.3. Convenient Route to Heterometallic Species via Cyclopentadienyl/Alkoxo Ligand Exchange in Group 4 Metallocenes. The studies mentioned above encouraged us to look for other organometallic starting materials as substrates for the synthesis of new binary combinations. Group 4 metal sandwich metallocenes have attracted considerable attention because of their applications in stoichiometric and catalytic reactions.[34] There are a number of books, articles, and reviews that cover the broad range of metallocene chemistry, from practical aspects and synthetic strategies to theoretical investigations.[35] This rich chemistry is dominated by their applications in olefin polymerization.[36] In most organometallic reactions of transition-metal complexes, the η^5-Cp ligand plays the role of spectator, staying tightly bound to the center throughout the reaction course. However, the capability of Cp as a leaving group in Cp_2MCl_2 metallocenes

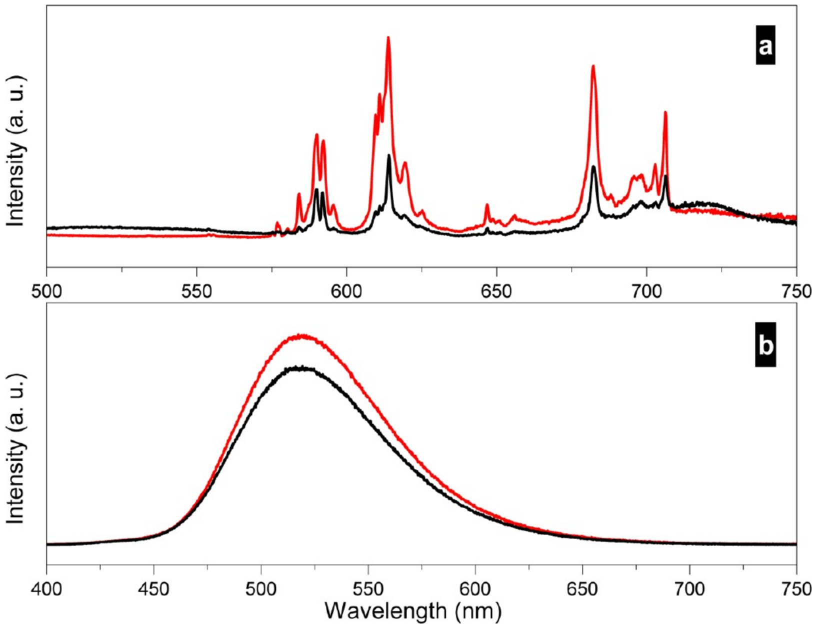
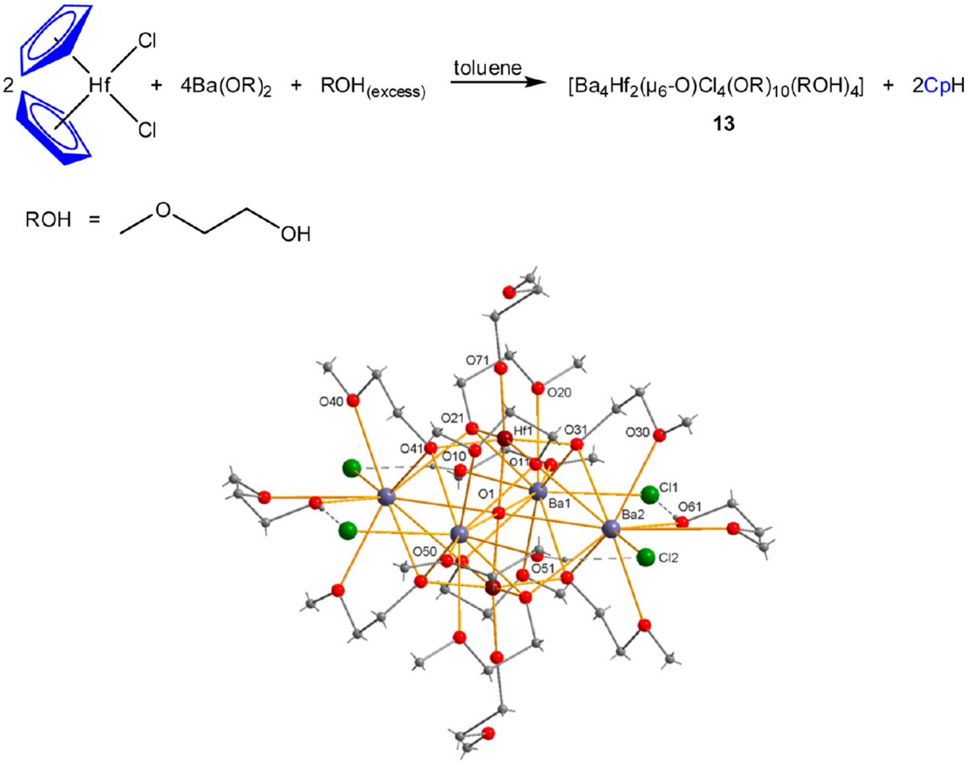


FIGURE 3. Comparison of emission spectra of $Sr_{0.99}Eu_{0.01}Al_2O_4$ obtained from molecular precursor **11** (red line) and ceramic method (black line) sintered in (a) air and (b) N_2 and H_2 mixture upon excitation at $\lambda_{ex} = 290$ nm and $\lambda_{ex} = 350$ nm, respectively.[31c]

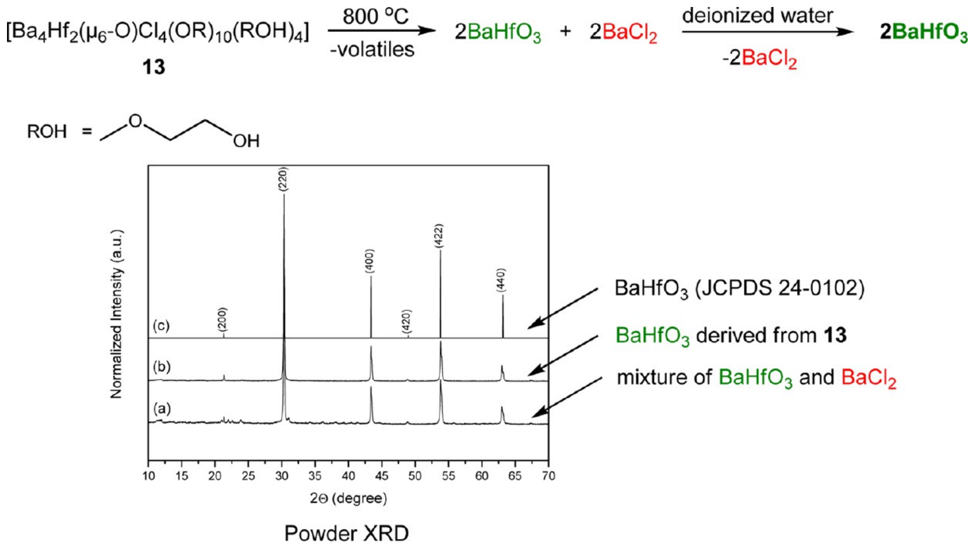
SCHEME 6. Synthesis and Molecular Structure of Barium–Hafnium Chloro-alkoxide $[Ba_4Hf_2(\mu_6\text{-}O)(\mu_3,\eta^2\text{-}OCHH_2CH_2OCH_3)_{10}Cl_4(CH_3OCH_2CH_2OH)_4]$



has been neglected, and, consequently, preparative applications remain unknown.[37]

Our studies on group 4 metallocenes showed that Cp_2MCl_2 (M = Ti^{4+}, Zr^{4+}, Hf^{4+}) are attractive and cheap precursors to an extensive range of novel polymetallic molecular and supramolecular materials. So, our efforts have been directed to molecular precursors of perovskite-like binary oxides. Such oxide ceramics, for example, barium

SCHEME 7. Transformations of **13** during Decomposition to $BaHfO_3$



hafnate ($BaHfO_3$), can act as effective networks for luminescent doping and are generally desirable. Among many possible heterobimetallic complexes, those which contain barium–hafnium compounds have become a cornerstone of advances in new materials. Barium-containing compounds are slightly scarcer, although some interesting examples have been reported recently. Their attractiveness lies in their much higher photofractions and absorption coefficients in the range of medical X-rays.[38] We have therefore developed an easily scaled-up synthetic pathway to well-defined perovskite nanopowders at low temperature, with simple control of the process parameters, high efficiency, and high yields.[39] This synthetic method involves elimination of the cyclopentadienyl ring from Cp_2MCl_2 (M = Ti, Zr, Hf) as CpH in the presence of $M'(OR)_2$ (M′ = Ca, Sr, Ba, Mn; ROH = $CH_3OCH_2CH_2OH$ or $Me_2NCH_2CH_2OH$) in an alcohol as a source of protons. For example, the reaction of Cp_2HfCl_2 with 2 equiv of $Ba(OR)_2$ and excess ROH (ROH = 2-methoxyethanol) in toluene at room temperature gave the colorless cyclopentadienyl-free heterometallic cluster compound $[Ba_4Hf_2(\mu_6\text{-}O)(\mu_3,\eta^2\text{-}OCHH_2CH_2OCH_3)_{10}Cl_4(CH_3OCH_2CH_2OH)_4]$ (**13**; Scheme 6). Our studies have shown the promoting effect of barium, strontium, or calcium alkoxide on the protonation of Cp groups of Cp_2MCl_2.

In these studies, we addressed the following question: can compounds containing chloride ligands be used as precursors for high-purity oxide materials? In the literature, chloride-containing compounds are described as corrosive agents, because of the evolution of chlorohydride, and it is reported that they usually form multiphase systems. However, there are some examples that contradict these rules and are safe for use in laboratory equipment. For instance, Mazhar et al. obtained a heterobimetallic acetate chloride, $[Zn_7(OAc)_{10}(\mu\text{-}OH)_6Cu_5(dmae)_4Cl_4]$ (dmaeH = *N*,*N*-dimethylethanolamine), which has been used in CVD to give $Cu_5Zn_7O_{12}$ with an exact metal-to-metal stoichiometry, as in a molecular compound.[40] Other examples are $[Co_2(acac)_2(\mu\text{-}OH)_4Cu_4(dmae)_4Cl_4]$ and $[Ni_2(acac)_2(\mu\text{-}OH)_2Cu_4(dmae)_4Cl_4]$, which give $Co_2Cu_4O_6$ and $Ni_2Cu_4O_6$ mixed-metal oxides, respectively.[41]

The thermal decomposition of **13** was investigated using thermogravimetric analysis under an air and N_2 atmosphere, and no signs of sublimation were observed. In our approach, we used two-step receiving. When heated from room temperature to 800 °C, **13** undergoes multistep transformations (Scheme 7).

Thermolysis clearly indicates that when it is heated from room temperature to 800 °C within 1.5 h (step = 10 °C/min), **13** undergoes thermal transformations. The subsequent weight losses observed in thermogravimetric analysis experiments clearly correspond to a mixture of $BaCl_2$ and $BaHfO_3$ in a 1:1 molar ratio. In order to obtain pure perovskite-like $BaHfO_3$, the raw powder containing both phases was simply washed with deionized water to leach out barium dichloride. Such a strategy enables us to obtain nonporous materials (which are favorable in phosphors)[42] (Table 2) under mild conditions, at low temperature, with well-defined particle sizes ranging from 30 to 50 nm, and with simple control of the process parameters (Figure 4).[39] As can be seen, in this approach, the presence of chloride ligands is an advantage. Chloride ligands form water-soluble compounds, which can be easily washed out from the reaction system, so they do not have the chance to become corrosive

SCHEME 8. Formation of Heterometallic Species from Group 2 Alkoxides and Group 4 Metallocenes

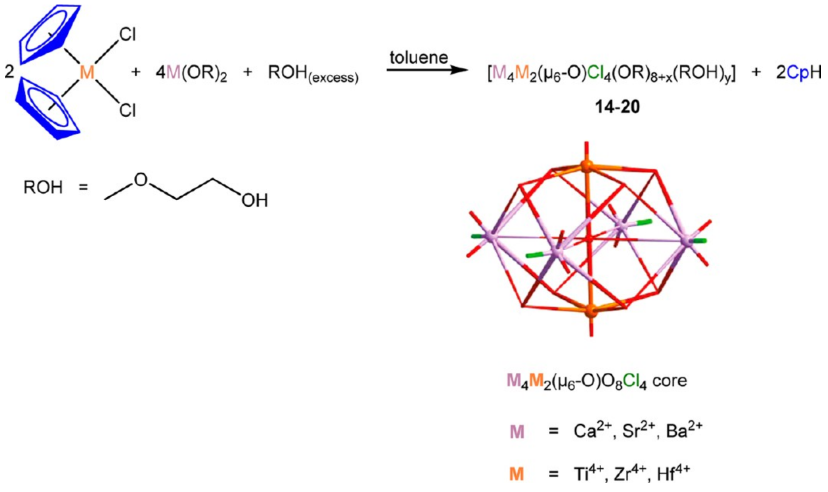


TABLE 2. Thermolysis Conditions and Compositions of Selected Perovskites

precursor	temp (°C)	product	color	ref
13	800	$BaHfO_3$	white	39
14	950	$BaZrO_3$	white	45
15	800	$BaTiO_3$	white	45
18	750	$CaHfO_3$	white	45
19	850	$SrTiO_3$	white	45
20	750	$CaTiO_3$	white	45

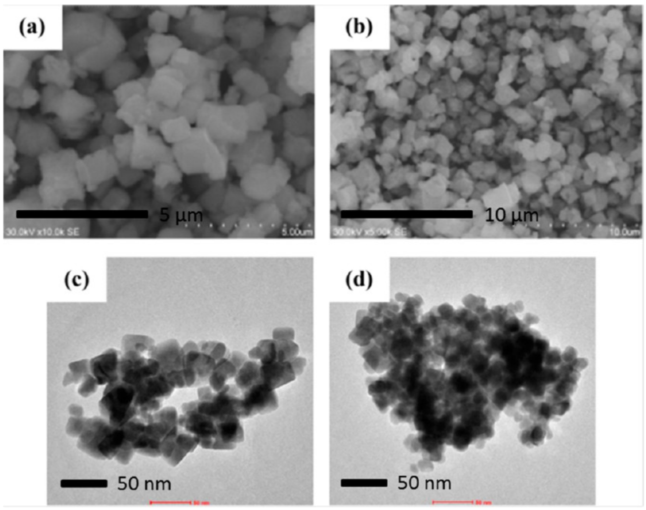


FIGURE 4. Scanning electron microscopy (a, b) and transmission electron microscopy (c, d) images of $BaHfO_3$ derived from **13**.

agents, because they do not decompose to technologically undesirable byproducts.

Furthermore, we proved that the resulting $BaHfO_3$ is an attractive host lattice for Eu-doped phosphors. The strong emission derived from the $^5D_0-^7F_2$ transition in the $BaHfO_3$ matrix has been observed for the first time as a dominant line and is particularly useful as a red-light-emitting phosphor (Figure 5).

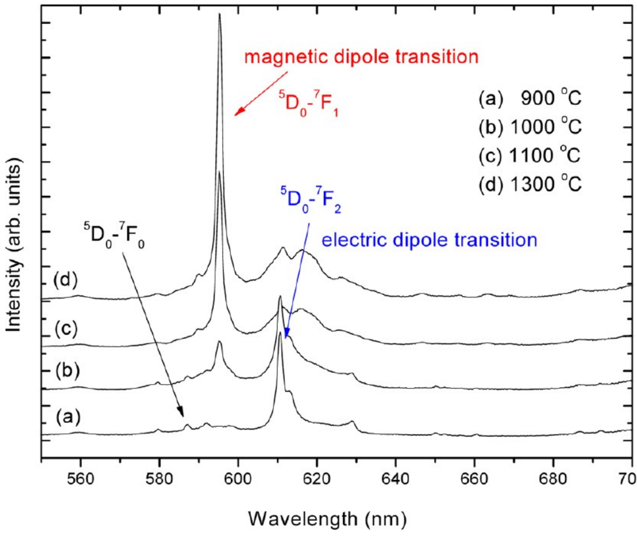
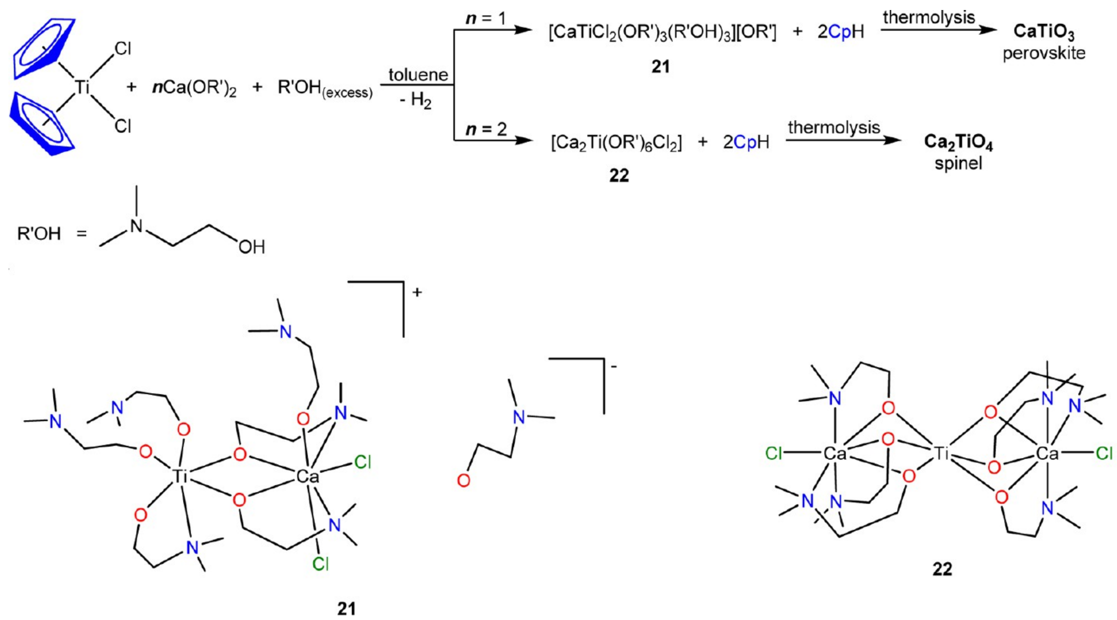


FIGURE 5. Emission spectra of $BaHfO_3:Eu^{3+}$ (3 mol %) sintered at different temperatures.

It is worth noting that the emission of the $BaHfO_3$:Eu lattice derived from molecular precursor emitted at lower temperatures compared with other host lattices reported in the literature and obtained in the solid-state approach.[43]

Such a synthetic approach can easily be extended to other group 4 metallocenes, resulting in various of cyclopentadienyl-free heterometallic complexes of formula $[M'_4M_2(\mu_6\text{-}O)Cl_4(OR)_{8+x}(ROH)_y]$ ($M_4'/M_2/x/y$ = Ba/Zr/2/4 (**14**), Ba/Ti/2/4 (**15**), Sr/Hf/2/4 (**16**), Ca/Zr/0/0 (**17**), Ca/Hf/2/0 (**18**), Sr/Ti/2/2 (**19**), Ca/Ti/2/2 (**20**); Scheme 8).[44,45] All of these complexes can be used as molecular precursors for binary perovskite-like metal oxides (Table 2).

SCHEME 9. Stoichiometric $Ca(OR)_2/Cp_2TiCl_2$ Ratio Effects on Compositions of Final Products



The stoichiometric ratio of the reactants and the nature of the alcohol involved also give practical control over the formula of the final complex. The ratio of a metal in the obtained precursor can be easily used to predict the composition of the oxide products after thermal decomposition. The reaction of Cp_2TiCl_2 with 1 or 2 equiv of $Ca(OCH_2CH_2NMe_2)_2$ in *N*,*N*-dimethylethanolamine results in the formation of the complexes $[CaTiCl_2(OCH_2CH_2NMe_2)_3(Me_2NCH_2CH_2OH)_3]$-$[OCH_2CH_2NMe_2]$ (**21**) and $[Ca_2Ti(OCH_2CH_2NMe_2)_6Cl_2]$ (**22**), respectively (Scheme 9).

4. Summary and Outlook

This Account highlights our synthetic strategies for heterometallic complexes, which are used for obtaining highly phase-pure binary metal oxides like perovskites and spinels. These studies have clearly shown that metal alkoxides $[M(OR)_x(ROH)_y]$ (M = group 2 cation, ROH = alcohol) and their organometallic derivatives $[M(OR)_{x+y}M'R'_{z-1}]$ (M′ = group 12 or 13 cation, R′ = alkyl group) are excellent molecular precursors for the preparation of numerous metal oxide materials. Furthermore, the promoting effect of metal alkoxides on the protonation of group 4 metallocenes was investigated. Such an approach enabled the design of compounds with predesigned molecular structures for the generation of high-purity binary metal oxides such as perovskites of formula ABO_3 (A = group 2 cation; B = group 4 cation) and spinels AB'_2O_4 (B′ = group 13 cation). This choice of elements is based on the subsequent uses of the oxide materials in the fabrication of superconducting materials and as host lattices for lanthanide-doped phosphors. The use of such molecular precursors enables the use of lower decomposition temperatures than those used in conventional solid-state thermal routes involving carbonate/oxide mixtures. The use of uncommon combinations of metallic precursors, for example, Ba/In, Sr/Al, Ba/Ti, Ba/Hf, and Sr/Ti, and thorough characterization of the resulting mixed-metal oxides sets this research apart from ordinary studies and makes them of interest to both inorganic and materials chemists. For example, strontium titanate ($SrTiO_3$), is an ideal substrate material for epitaxial growth of many functional materials, and as a result of its own high dielectric constant, thermal stability, and photocatalytic properties, it serves as one of the most versatile functional materials in a wide range of technological uses.[46] $BaHfO_3$ is an attractive host lattice for new X-ray phosphors, which are much more effective than the phosphors currently used in radiology and computed tomography, such as BaFBr:Eu, CsI:Tl, $CdWO_4$, and Gd_2O_2S:Tb.[47] Also, $SrAl_2O_4$ and $BaAl_2O_4$ are among the most studied and efficient host materials for long-lasting phosphorescence, and their synthesis and optical properties are worthy of investigation.[38] Finally, a very sharp first-order phase transition was observed in single-crystal barium titanate ($BaTiO_3$) and permitted thermal changes to be driven by a very small electric field. The resulting giant electrocaloric strength could be exploited in future cooling devices that operate at high frequency.[48]

The presented synthetic approach can easily be generalized, and other heterobi- or even heteropolymetallic compounds can be obtained. It is also possible that the presented methods will be very useful for the preparation of complexes with interesting magnetic properties, depending on the metal elements. We are sure that appropriate selection of starting materials and reaction conditions will result in the preparation of interesting materials with single-molecule magnetic properties.[48] Such reactions provide a gate to novel routes for the synthesis of heteropolynuclear compounds.

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Piotr Sobota received all of his degrees (M.Sc., 1966; Ph.D., 1973; Habilitation, 1978) from the University of Wrocław, Poland. After postdoctoral research with Professor Joseph Chatt at Sussex University in Brighton, U.K., he was promoted to head of a research group in 1980 and to full professor at the University of Wrocław in 1993. He has been a visiting professor at Indiana University (Bloomington, IN, USA), the University of Erlangen-Nürnberg (Germany), the Technical University of Trondheim (Norway), and the University of Lille (France). He was a consultant for Union Carbide and The Dow Chemical Company (USA). Since 2009, he is a Director of Novasome Pharmaceutical R&D Center (Poland). More than 300 articles, patents, and books record his research in inorganic, organometallic, and structural chemistry and catalysis.

FOOTNOTES

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The authors declare no competing financial interest.

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