

# Synthesis of Zirconium(IV) and Hafnium(IV) isopropoxide and tert-butoxide

Evert Dhaene, Carlotta Seno, and Jonathan De Roo\*

*Department of Chemistry, University of Basel, Mattenstrasse 22, 4058 Basel, Switzerland*

E-mail: Jonathan.DeRoo@unibas.ch

## Abstract

Here we review the synthesis literature towards zirconium(IV) and hafnium(IV) isopropoxide isopropanol complex ( $M(OiPr)_4 \cdot iPrOH$ ,  $M = Zr, Hf$ ) and zirconium(IV) and hafnium(IV) tert-butoxide ( $M(OtBu)_4$ ,  $M = Zr, Hf$ ). We optimized the most convenient syntheses methods and compare the products with commercial sources. En route to the metal tert-butoxides, we synthesized the metal diethylamido complex ( $M(NEt_2)_4$ ,  $M = Zr, Hf$ ).

## Introduction

Chemical precursors need to be pure for several important reasons. The purity of a chemical precursor directly affects the reproducibility and consistency of chemical reactions. Impurities can lead to variations in reaction outcomes, making it difficult to achieve the desired results consistently. In many cases, chemical reactions are highly sensitive to the presence of impurities. Impurities can act as catalysis, inhibitors, or interfere with the desired reaction pathway. Pure precursors ensure that the reaction proceeds as intended, allowing for better control over the synthesis procedure. The purity of chemical precursors plays a

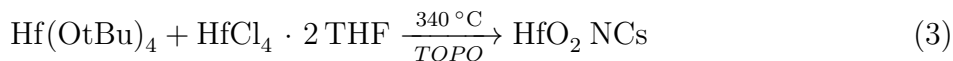
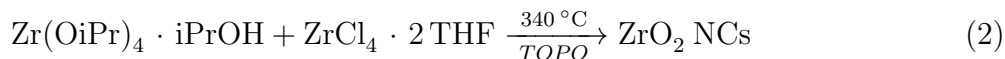
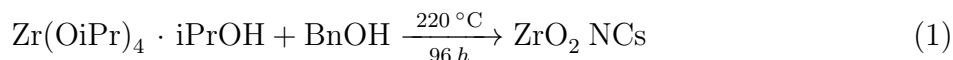
critical role in determining the quality of the final product. Impurities can negatively impact the properties and reliability of the synthesized products, e.g., impurities in semiconductor manufacturing can lead to defective electronic devices. In thin film deposition techniques, like chemical vapor deposition (CVD) and atomic layer deposition (ALD), precursor purity is crucial. Impurities can lead to unwanted reactions, film defects, non-uniformity, and poor adhesion of thin films to substrates. Overall, in research the reliability of experimental results is paramount. Impure precursors can introduce unexpected variables and confounding factors, making it difficult to draw accurate conclusions from experiments.

Group IV halide and alkoxide precursors, derived from elements such as titanium (Ti), zirconium (Zr), and hafnium (Hf), have gained significant attention in recent years as versatile and promising candidates for nanocrystal,<sup>1–23</sup> metal organic frameworks (MOFs),<sup>24,25</sup> and thin film<sup>26–29</sup> synthesis, as well as catalysts.<sup>30–34</sup> These halides and alkoxides are inorganic metal-organic compounds with the general formula  $\text{MX}_4$  and  $\text{M}(\text{OR})_4$ , where M represents the Group IV metal, X and R denotes a halide and organic group respectively.

Nanocrystals are a fascinating class of materials that exhibit unique properties due to their small size, typically ranging from 1 to 100 nanometers, and high surface-to-volume ratio.<sup>35,36</sup> These materials find applications in various fields, including electronics, catalysis, photonics, and biomedical research. One powerful method for synthesizing nanocrystals is through the controlled formation and growth of inorganic materials from solution-phase precursors.<sup>37</sup> The use of the halide and alkoxide functional groups, enable precise control over the size, shape, and composition of the resulting nanocrystals.<sup>38</sup> Furthermore, the use of Group IV alkoxides enables the incorporation of dopants into the nanocrystal lattice, leading to the development of functional materials with specific electronic, optical, or catalytic properties.<sup>4</sup> This capability is especially significant in the design of advanced nanocrystal-based devices and technologies.

Note that the successful synthesis of nanocrystals using Group IV precursors requires a thorough understanding of the underlying chemical mechanisms and precise control over

reaction parameters.<sup>39</sup> These precursors can undergo controlled hydrolysis reactions, leading to the formation of metal oxide gels with high surface areas. Subsequent thermal treatment under controlled conditions can then convert these gels into well-defined nanocrystals with precise crystalline structures.<sup>3,4,6-13,22</sup> Researchers must carefully optimize the reaction conditions, such as temperature, solvent choice, and reaction time, to achieve reproducible and scalable nanocrystal synthesis. Group IV alkoxide precursors also offer the advantage of being compatible with different synthesis techniques, such as solvothermal, sol-gel, and hydrothermal methods, allowing researchers to choose the most suitable approach for their specific nanocrystal synthesis goals.



Although most of these compounds are commercially available, their purity often varies significantly between producers and even between different precursor batches. In general, it is advised to purify these commercially received precursors by means of a recrystallization or vacuum distillation. On the other hand, the synthesis of these Group IV precursors are straightforward, easily to scale-up, and are all (in)directly made from the anhydrous metal chloride which is easy to store in big quantities, also for longer periods. However, the reactivity of these Group IV precursors can present challenges, such as their sensitivity to moisture, which can lead to premature hydrolysis. The synthesis of Group IV precursors requires careful handling, for which anhydrous and inert conditions are employed during the synthesis process to maintain the stability and purity of the products.

Group IV alkoxide precursors have emerged as valuable tools in the realms of catalysis and nanocrystal and thin film synthesis. Therefore, an overview of the synthesis of pure Group IV precursors is an important step in research, paving the way for innovative materials and

technologies in the future. Here, we review on previously reported and update the synthesis of frequently used Group IV metal alkoxide precursors. The synthesis of  $M(OiPr)_4 \cdot iPrOH$  complex,  $M(NEt_2)_4$  and  $M(OtBu)_4$  (with  $M = Zr$  and  $Hf$ ).

## Experimental

**Materials.** All manipulations are performed under rigorously anhydrous conditions via dry nitrogen or argon atmosphere and standard Schlenk and glovebox techniques unless otherwise mentioned. All chemicals are used as received unless otherwise mentioned. Hafnium(IV) chloride (99.9%), and Zirconium(IV) chloride (99.5%) were purchased from Strem Chemicals. Ammonia (2M in isopropanol), lithium diethylamide (95%), and anhydrous tert-butanol (99.5%) were purchased from Sigma-Aldrich. Isopropanol (extra dry over molecular sieves) was purchased from Thermo Scientific. Benzene- $d_6$  (99.5 atom%D) is purchased from Apollo Scientific. To remove residual water, 10% m/v of activated molecular sieves were added and left to stand for 3 days in the glovebox prior to use.

**Zr(OiPr) $_4$ ·iPrOH complex synthesis.** The protocol is inspired by the reports of Bradley et al. and Seienbaeva et al.<sup>40,41</sup> In a nitrogen filled glovebox, a 500 mL Schlenk flask is loaded with zirconium(IV) chloride (14.0 g, 60 mmol, 1.0 eq.) and toluene (150 mL), and air- and moisture-free transferred to the Schlenk line. The ammonia solution in isopropanol (2 M, 135 mL, 270 mmol, 4.5 eq.) is slowly and carefully dropwise added to the zirconium suspension while cooling with a water bath since the reaction is exothermic. After 1 hour of stirring at room temperature, the formed ammonium chloride is removed by means of Schlenk filtration (500 mL frit) to another 500 mL Schlenk flask. The solvent is removed under reduced pressure, and the product is redissolved in toluene (100 mL) to which ammonia solution in isopropanol (2 M, 30 mL, 60 mmol, 1.0 eq.) is added dropwise. If the previous exchange was incomplete, additional ammonium chloride precipitates. After 1 hour of stirring at room temperature, the additional ammonium chloride is removed by Schlenk filtration (250

mL frit) to a 250 mL Schlenk flask. The solvent is removed under reduced pressure. The resulting product is recrystallized to purity from a concentrated hot mixture (15 to 20 mL) of toluene and isopropanol (3:1 ratio by volume) where the hot solution is allowed to slowly crystallize overnight into colourless large crystals. The following day, the solvent is removed through a Cannula transfer. If needed a second recrystallization can be done under the same conditions. The product is vacuum dried at room temperature (at higher temperatures, the isopropanol adduct is removed under vacuum) to obtain a white crystalline product (15.1 g, 65 %) and is stored in the glovebox.  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  6.0-5.5 (s, 1H),  $\delta$  5.5-4.0 (s, 5H),  $\delta$  2.0-1.0 (s, 30H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  69.7, 26.6. SC-XRD confirms the identity of the product as reported by Vaartstra et al. (CSD ID: JETWOU) and hence is not reproduced.<sup>42</sup>

**Hf(O*i*Pr)<sub>4</sub>.*i*PrOH complex synthesis.** Hafnium(IV) isopropoxide isopropanol complex is synthesized similar to Zr(O*i*Pr)<sub>4</sub>.*i*PrOH complex. Hafnium(IV) chloride (19.2 g, 60 mmol, 1.0 eq.) is added instead of zirconium(IV) chloride. After recrystallization a white crystalline solid is obtained (14.4 g, 51 %) and is stored in the glovebox.  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.5-7.0 (s, 1H),  $\delta$  5.5-4.0 (s, 5H),  $\delta$  2.0-1.0 (s, 30H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  69.7, 26.7. SC-XRD confirms the identity of the product as reported by Veith et al. (CSD ID: NAYDAS) and hence is not reproduced.<sup>43</sup>

**Zr(NEt<sub>2</sub>)<sub>4</sub> synthesis.** Tetrakis(diethylamido)zirconium(IV) complex is synthesized based on reports of Diamond et al., Kim et al., and Bradley et al.<sup>44-46</sup> In an nitrogen filled glovebox, a 250 mL round bottom flask is loaded with lithium diethylamide (8.70 g, 110 mmol, 4.23 eq.) and toluene (80 mL), to which zirconium(IV) chloride (6.06 g, 26 mmol, 1.00 eq.) is carefully and slowly added while stirring since the reaction is exothermic. After the addition, the flask is sealed with a septum and left stirring overnight at room temperature. The next day, the reaction mixture is filtered to remove the insoluble salts, and transferred to a 100 mL Schlenk flask to evaporate the solvent. Next, the Schlenk flask is transferred air- and moisture-free to the Schlenk line on which a predried vacuum distillation set-up is mounted.

During the distillation, the receiver Strauss flask is cooled with an ice bath which collects around 130 °C at 50 mtorr the colourless and transparent liquid product (6.6 g, 67 %) and is stored in the freezer of the glovebox.  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  3.36 (quad,  $J = 7.0$  Hz, 2H),  $\delta$  1.16 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  43.6, 16.3.

**Hf(NEt<sub>2</sub>)<sub>4</sub> synthesis.** Tetrakis(diethylamido)hafnium(IV) complex is synthesized similar to Zr(NEt<sub>2</sub>)<sub>4</sub>. Hafnium(IV) chloride (8.33 g, 26 mmol, 1.00 eq.) is added instead of zirconium(IV) chloride. During the distillation, the receiver Strauss flask is cooled with an ice bath which collects around 145 °C at 50 mtorr the colourless and transparent liquid product (9.3 g, 76 %) and is stored in the freezer of the glovebox.  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  3.37 (quad,  $J = 7.0$  Hz, 2H),  $\delta$  1.16 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  42.9, 16.3.

**Zr(OtBu)<sub>4</sub> synthesis.** Zirconium(IV) tert-butoxide is synthesized according to the procedure of Thomas et al.<sup>47</sup> In an nitrogen filled glovebox, a 100 mL Schlenk flask is loaded with tetrakis(diethylamido)zirconium(IV) (3.80 g, 3.70 mL, 10 mmol, 1 eq.) and toluene (40 mL), and a 25 mL Schlenk flask is loaded with tert-butanol (5.93 g, 7.65 mL, 80 mmol, 8 eq.) and toluene (10 mL). Both Schlenk flasks are transferred air and moisture free to the Schlenk line, where the zirconium containing flask is cooled with an ice bath. The tert-butanol solution is added dropwise to the zirconium suspension via Cannula transfer. Next, the ice bath is removed and the solution is allowed to heat to room temperature, and is stirred for 1.5 hours. Afterwards, the solvent is removed under reduced pressure prior to vacuum distillation. During the distillation, the receiver Strauss flask is cooled with an ice bath which collects around 45 °C at 50 mtorr the colourless and transparent liquid product (2.7 g, 71 %) and is stored in the freezer of the glovebox.  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  1.32 (s, 36H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  75.3, 33.1.

**Hf(OtBu)<sub>4</sub> synthesis.** Hafnium(IV) tert-butoxide is synthesized similar to Zr(OtBu)<sub>4</sub>. Tetrakis(diethylamido)hafnium(IV) (4.67 g, 3.74 mL, 10 mmol, 1 eq.) is used instead of tetrakis(diethylamido)zirconium(IV). During the distillation, the receiver Strauss flask is

cooled with an ice bath which collects around 30 °C at 50 mtorr the colourless and transparent liquid product (2.2 g, 46 %) and is stored in the freezer of the glovebox.  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  1.33 (s, 36H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  75.5, 33.2.

**NMR Spectroscopy.** Nuclear magnetic resonance (NMR) spectra were recorded at 298.15 K on a Bruker UltraShield 500 spectrometer operating at a  $^1\text{H}$  frequency of 500.13 MHz. Regular  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were acquired using the standard pulse sequences with a 30 degree pulse with a recycle delay of 1.5 and 1.0 second from the Bruker library; zg30, zgpg30 respectively. All resonances were corrected prior to integration by subtracting a background from the measured intensity. Chemical shifts ( $\delta$ ) are given in parts per million (ppm), and the residual solvent peak was used as an internal standard ( $\text{C}_6\text{D}_6$ :  $\delta\text{H} = 7.16$  ppm,  $\delta\text{C} = 128.06$  ppm). The signal multiplicity is denoted as follows: s (singlet), d (doublet), t (triplet), quad (quadruplet), quin (quintet), and m (multiplet). Coupling constants are reported in Hertz (Hz).

## Results and Discussion

In our laboratory, we are producing oxide nanocrystals and oxo clusters from metal alkoxide precursors. While zirconium and hafnium isopropoxide and tert-butoxide compounds are commercially available, we experienced a high supplier-to-supplier and batch-to-batch variability in terms of color (slightly yellow instead of white solid) or purity (e.g., turbid instead of transparent liquid). In addition, such speciality chemicals are often back-ordered and long delivery times are normal. In order to secure a more reliable supply and to obtain more reproducible nanocrystal syntheses, we sought to synthesize the metal alkoxides in our laboratory from readily available precursors.

Many different synthetic routes have been reported for zirconium and hafnium alkoxides. The electrochemical route involves the dissolution of the metal anode in alcohol.<sup>48</sup> On the other hand, the reaction of the metal chloride with ethanol typically yields an incomplete

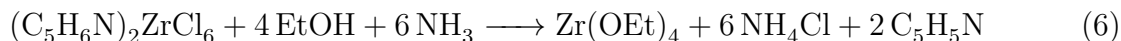
substitution.<sup>49</sup>



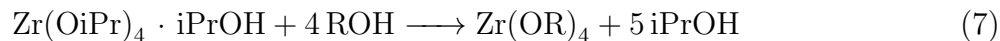
The reaction is driven to completion by anhydrous ammonia.<sup>40,50</sup>



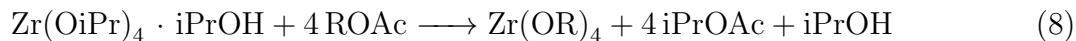
The use of sodium ethoxide is not recommended due to the formation of a heterobimetallic complex:  $\text{NaZr}(\text{OEt})_5 \cdot \text{HOEt}$ . The ammonia route also works well for zirconium isopropoxide, although some hydrolysis occurs due to reaction of HCl with isopropanol, generating water and isopropyl chloride.<sup>40,50</sup> The zirconium isopropoxide can be purified by recrystallization from isopropanol, yielding the  $\text{Zr}(\text{OiPr})_4 \cdot \text{iPrOH}$  complex. The metal alkoxides (ethoxide and isopropoxide) were also synthesized from pyridinium metal hexachloride in benzene.<sup>51,52</sup>



Given the convenience of purifying  $\text{Zr}(\text{OiPr})_4 \cdot \text{iPrOH}$  by crystallization, it is often used as starting point to synthesize other alkoxides by alcohol interchange, also called alcoholysis.<sup>40,50,51,53–55</sup>



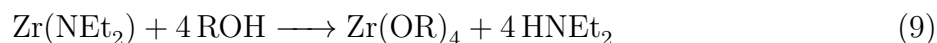
This is particularly successful when the incoming alcohol has a higher boiling point than isopropanol, e.g., amyl alcohols. In case of only slight differences in boiling points of the alcohols, transesterification can be helpful.<sup>56</sup> Taking the example of acetate esters:





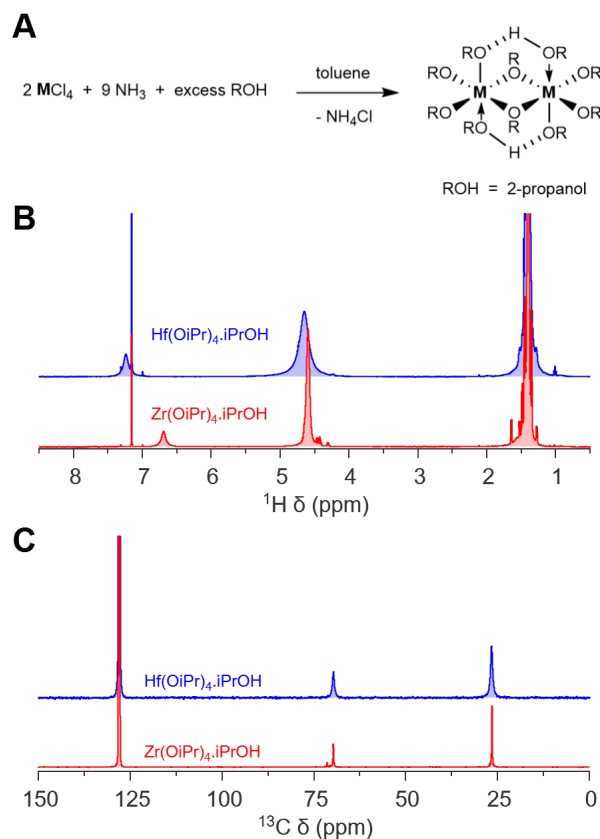
The method has been successful for n-butyl, sec-butyl and tert-butyl acetate, producing the respective zirconium alkoxides in semi-quantitative yields.<sup>56</sup> Since the isopropyl ester is more volatile, it can be fractionated out of the system. Especially for zirconium and hafnium tert-butoxides, the method is superior to alcohol exchange since the latter does not proceed further than metal tri-tert-butoxide mono-ethoxide.

Finally, one can readily generate alkoxides from metal amides, such as dialkylamides.<sup>47</sup>



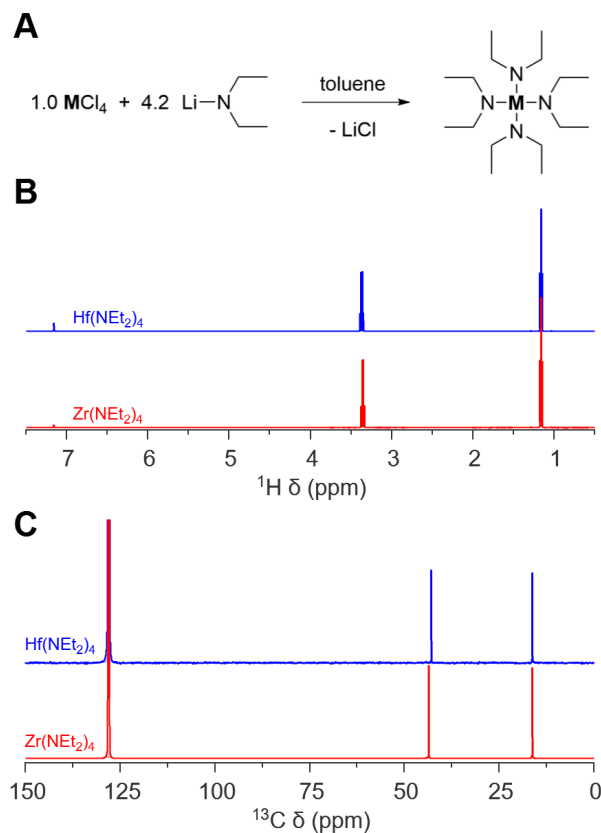
To prepare  $\text{Zr}(\text{OiPr})_4 \cdot \text{iPrOH}$ , we choose the ammonia route from  $\text{ZrCl}_4$  for several reasons. (1)  $\text{ZrCl}_4$  can be bought pure, in high quantities, and is an economical precursor. (2) Ammonia can be added to the mixture in either gas-form or as a 2M solution in isopropanol. (3) The excess of ammonia is easily removed due to its volatility. (4) The ammonium chloride byproduct precipitates from the reaction mixture and is easily removed by filtration.<sup>40,50-52</sup>  $\text{Zr}(\text{OiPr})_4 \cdot \text{iPrOH}$  is poorly soluble in pure isopropanol and thus requires large volume of solvent for recrystallization. Fortunately, recrystallization from a toluene/isopropanol (3:1) mixture is much more convenient.<sup>41</sup>

We thus synthesized  $\text{Zr}(\text{OiPr})_4 \cdot \text{iPrOH}$  and  $\text{Hf}(\text{OiPr})_4 \cdot \text{iPrOH}$  by dispersing the metal chloride in toluene, and slowly adding a 2M ammonia solution in isopropanol. After filtering off the ammonium chloride and a recrystallization, we obtain the pure white crystals. Their NMR spectra as shown in Figure 1. While both compounds are commercially available, their appearance varies from the desired white crystals to yellow-brown powder. It was already earlier advised to recrystallize the commercial precursors.<sup>41</sup>



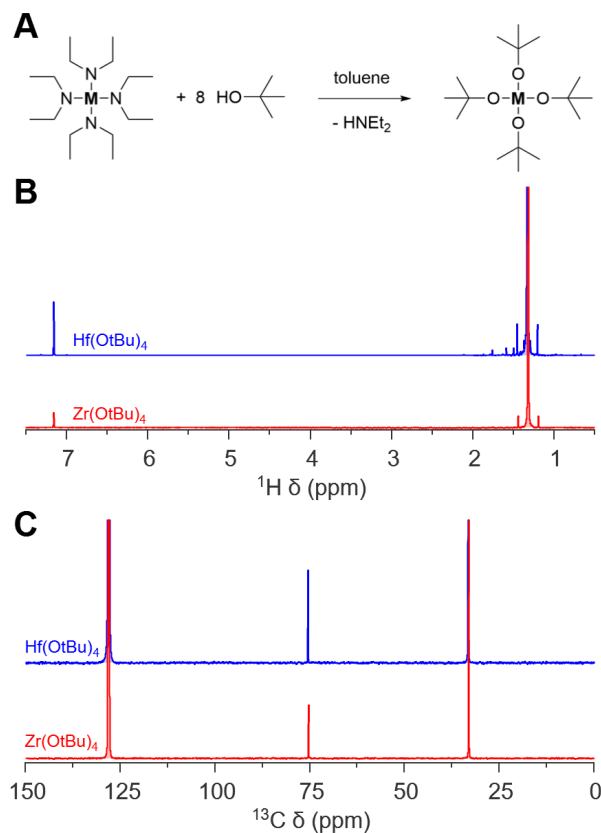
**Figure 1:** The synthesis of zirconium(IV) and hafnium(IV) isopropoxide isopropanol complex. (A) General reaction scheme, (B)  $^1\text{H}$  NMR, and (C)  $^{13}\text{C}$  NMR of zirconium(IV) (lower trace, in red) and hafnium(IV) (upper trace, in blue) isopropoxide isopropanol complex in  $\text{C}_6\text{D}_6$ .

Tetrakis(diethylamido)-zirconium and -hafnium are synthesized from its metal chloride reacting with lithium diethylamide, see Figure 2.<sup>44</sup> The formation and precipitation of lithium chloride as byproduct, which is easily removed by filtration, is the driving force of the reaction. The compound is conveniently purified by vacuum distillation and the NMR spectra as shown in Figure 2.



**Figure 2:** The synthesis of zirconium(IV) and hafnium(IV) diethylamido complex. (A) General reaction scheme, (B)  $^1\text{H}$  NMR, and (C)  $^{13}\text{C}$  NMR of zirconium(IV) (lower trace, in red) and hafnium(IV) (upper trace, in blue) diethylamido complex in  $\text{C}_6\text{D}_6$ .

Zirconium and hafnium tert-butoxides are readily synthesized from these diethylamides upon addition of the alcohol.<sup>47</sup> Also these products are vacuum distilled to purity. The NMR spectra are shown in Figure 3. Although zirconium and hafnium tert-butoxide are commercially available, they are not delivered as completely colourless and transparent liquids. In some cases, the solution is yellowish and/or a little turbid. If one chooses to buy these products commercially, one is advised to purify it by vacuum distillation before use. We have experience with hafnium oxide nanocrystals synthesis from hafnium tert-butoxide. Apart from the desired nanocrystals, we observed a second population of amorphous hafnia particles with a different morphology, when turbid precursors were used.



**Figure 3:** The synthesis of zirconium(IV) and hafnium(IV) tert-butoxide complex. (A) General reaction scheme, (B)  $^1\text{H}$  NMR, and (C)  $^{13}\text{C}$  NMR of zirconium(IV) (lower trace, in red) and hafnium(IV) (upper trace, in blue) tert-butoxide complex in  $\text{C}_6\text{D}_6$ .

## Conclusion

We identified the most convenient routes to produce zirconium and hafnium isopropoxide and tert-butoxide. We optimized, modernized and clearly described the synthesis protocols.

## Associated Content

### Supporting Information

The supporting Information is available.

## Author Information

### Corresponding Author

**Jonathan De Roo** - *Department of Chemistry, University of Basel, Mattenstrasse 22, 4058 Basel, Switzerland*

Email: Jonathan.deroo@unibas.ch

### Authors

**Evert Dhaene** - *Department of Chemistry, University of Basel, Mattenstrasse 22, 4058 Basel, Switzerland*

**Carlotta Seno** - *Department of Chemistry, University of Basel, Mattenstrasse 22, 4058 Basel, Switzerland*

### Notes

The Authors declare no competing interest.

## Acknowledgement

The authors thank the University of Basel and the SNF Eccellenza funding scheme (project number: 194172).

## References

- (1) Joo, J.; Yu, T.; Kim, Y. W.; Park, H. M.; Wu, F.; Zhang, J. Z.; Hyeon, T. Multigram Scale Synthesis and Characterization of Monodisperse Tetragonal Zirconia Nanocrystals. *Journal of the American Chemical Society* **2003**, *125*, 6553–6557.

- (2) De Keukeleere, K.; Coucke, S.; De Canck, E.; Van Der Voort, P.; Delpech, F.; Coppel, Y.; Hens, Z.; Van Driessche, I.; Owen, J. S.; De Roo, J. Stabilization of Colloidal Ti, Zr, and Hf Oxide Nanocrystals by Protonated Tri-n-octylphosphine Oxide (TOPO) and Its Decomposition Products. *Chemistry of Materials* **2017**, *29*, 10233–10242.
- (3) Villa, I.; Moretti, F.; Fasoli, M.; Rossi, A.; Hattendorf, B.; Dujardin, C.; Niederberger, M.; Vedda, A.; Lauria, A. The Bright X-Ray Stimulated Luminescence of HfO<sub>2</sub> Nanocrystals Activated by Ti Ions. *Advanced Optical Materials* **2020**, *8*, 1901348.
- (4) Lauria, A.; Villa, I.; Fasoli, M.; Niederberger, M.; Vedda, A. Multifunctional Role of Rare Earth Doping in Optical Materials: Nonaqueous Sol–Gel Synthesis of Stabilized Cubic HfO<sub>2</sub> Luminescent Nanoparticles. *ACS Nano* **2013**, *7*, 7041–7052.
- (5) Villa, I.; Vedda, A.; Fasoli, M.; Lorenzi, R.; Kränzlin, N.; Rechberger, F.; Ilari, G.; Primc, D.; Hattendorf, B.; Heiligtag, F. J.; Niederberger, M.; Lauria, A. Size-Dependent Luminescence in HfO<sub>2</sub> Nanocrystals: Toward White Emission from Intrinsic Surface Defects. *Chemistry of Materials* **2016**, *28*, 3245–3253.
- (6) Villa, I.; Lauria, A.; Moretti, F.; Fasoli, M.; Dujardin, C.; Niederberger, M.; Vedda, A. Radio-luminescence spectral features and fast emission in hafnium dioxide nanocrystals. *Phys. Chem. Chem. Phys.* **2018**, *20*, 15907–15915.
- (7) Buha, J.; Arčon, D.; Niederberger, M.; Djerdj, I. Solvothermal and surfactant-free synthesis of crystalline Nb<sub>2</sub>O<sub>5</sub>, Ta<sub>2</sub>O<sub>5</sub>, HfO<sub>2</sub>, and Co-doped HfO<sub>2</sub> nanoparticles. *Phys. Chem. Chem. Phys.* **2010**, *12*, 15537–15543.
- (8) Garnweitner, G.; Goldenberg, L.; Sakhno, O.; Antonietti, M.; Niederberger, M.; Stumpe, J. Large-Scale Synthesis of Organophilic Zirconia Nanoparticles and their Application in Organic–Inorganic Nanocomposites for Efficient Volume Holography. *Small* **2007**, *3*, 1626–1632.

- (9) Pucci, A.; Clavel, G.; Willinger, M.-G.; Zitoun, D.; Pinna, N. Transition Metal-Doped ZrO<sub>2</sub> and HfO<sub>2</sub> Nanocrystals. *The Journal of Physical Chemistry C* **2009**, *113*, 12048–12058.
- (10) Pinna, N.; Garnweitner, G.; Antonietti, M.; Niederberger, M. Non-Aqueous Synthesis of High-Purity Metal Oxide Nanopowders Using an Ether Elimination Process. *Advanced Materials* **2004**, *16*, 2196–2200.
- (11) De Roo, J.; De Keukeleere, K.; Feys, J.; Lommens, P.; Hens, Z.; Van Driessche, I. Fast, microwave-assisted synthesis of monodisperse HfO<sub>2</sub> nanoparticles. *Journal of Nanoparticle Research* **2013**, *15*, 1778.
- (12) De Roo, J.; Van den Broeck, F.; De Keukeleere, K.; Martins, J. C.; Van Driessche, I.; Hens, Z. Unravelling the Surface Chemistry of Metal Oxide Nanocrystals, the Role of Acids and Bases. *Journal of the American Chemical Society* **2014**, *136*, 9650–9657.
- (13) De Keukeleere, K.; De Roo, J.; Lommens, P.; Martins, J. C.; Van Der Voort, P.; Van Driessche, I. Fast and Tunable Synthesis of ZrO<sub>2</sub> Nanocrystals: Mechanistic Insights into Precursor Dependence. *Inorganic Chemistry* **2015**, *54*, 3469–3476.
- (14) Shaw, S.; Yuan, B.; Tian, X.; Miller, K. J.; Cote, B. M.; Colaux, J. L.; Migliori, A.; Panthani, M. G.; Cademartiri, L. Building Materials from Colloidal Nanocrystal Arrays: Preventing Crack Formation during Ligand Removal by Controlling Structure and Solvation. *Advanced Materials* **2016**, *28*, 8892–8899.
- (15) Shaw, S.; Silva, T. F.; Bobbitt, J. M.; Naab, F.; Rodrigues, C. L.; Yuan, B.; Chang, J. J.; Tian, X.; Smith, E. A.; Cademartiri, L. Building Materials from Colloidal Nanocrystal Assemblies: Molecular Control of Solid/Solid Interfaces in Nanostructured Tetragonal ZrO<sub>2</sub>. *Chemistry of Materials* **2017**, *29*, 7888–7900.
- (16) Tian, X.; Goh, T. W.; VandenBerg, O.; VanDerslice, J.; da Silva, T. F.; Naab, F.; Hay, J. L.; Chang, J. J.; Yuan, B.; Peiris, F. C.; Huang, W.; Cademartiri, L. Self-

- Regulated Porosity and Reactivity in Mesoporous Heterogeneous Catalysts Using Colloidal Nanocrystals. *The Journal of Physical Chemistry C* **2019**, *123*, 18410–18416.
- (17) Tirosh, E.; Markovich, G. Control of Defects and Magnetic Properties in Colloidal HfO<sub>2</sub> Nanorods. *Advanced Materials* **2007**, *19*, 2608–2612.
- (18) Robinson, R. D.; Tang, J.; Steigerwald, M. L.; Brus, L. E.; Herman, I. P. Raman scattering in Hf<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> nanoparticles. *Phys. Rev. B* **2005**, *71*, 115408.
- (19) Tang, J.; Fabbri, J.; Robinson, R. D.; Zhu, Y.; Herman, I. P.; Steigerwald, M. L.; Brus, L. E. Solid-Solution Nanoparticles: Use of a Nonhydrolytic SolGel Synthesis To Prepare HfO<sub>2</sub> and Hf<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> Nanocrystals. *Chemistry of Materials* **2004**, *16*, 1336–1342.
- (20) Tang, J.; Zhang, F.; Zoogman, P.; Fabbri, J.; Chan, S.-W.; Zhu, Y.; Brus, L.; Steigerwald, M. Martensitic Phase Transformation of Isolated HfO<sub>2</sub>, ZrO<sub>2</sub>, and Hf<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> (0 < x < 1) Nanocrystals. *Advanced Functional Materials* **2005**, *15*, 1595–1602.
- (21) Omata, T.; Goto, Y.; Otsuka-Yao-Matsuo, S. Nanocrystals of zirconia- and ceria-based solid electrolytes: Syntheses and properties. *Science and Technology of Advanced Materials* **2007**, *8*, 524–530.
- (22) Luo, K.; Zhou, S.; Wu, L.; Gu, G. Dispersion and Functionalization of Nonaqueous Synthesized Zirconia Nanocrystals via Attachment of Silane Coupling Agents. *Langmuir* **2008**, *24*, 11497–11505.
- (23) Mizuno, M.; Sasaki, Y.; Lee, S.; Katakura, H. High-Yield SolGel Synthesis of Well-Dispersed, Colorless ZrO<sub>2</sub> Nanocrystals. *Langmuir* **2006**, *22*, 7137–7140.
- (24) Jerozal, R. T.; Pitt, T. A.; MacMillan, S. N.; Milner, P. J. High-Concentration Self-Assembly of Zirconium- and Hafnium-Based Metal–Organic Materials. *Journal of the American Chemical Society* **2023**, *145*, 13273–13283.



- (25) Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. P. A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability. *Journal of the American Chemical Society* **2008**, *130*, 13850–13851.
- (26) Patil, U.; Winter, M.; Becker, H.-W.; Devi, A. Synthesis and structure of mixed isopropoxide–ketoester and -ketoamide zirconium complexes: Potential precursors for MOCVD of ZrO<sub>2</sub>. *J. Mater. Chem.* **2003**, *13*, 2177–2184.
- (27) Huang, J.; Cho, Y.; Zhang, Z.; Jan, A.; Wong, K. T.; Nemani, S. D.; Yieh, E.; Kummel, A. C. Selective Pulsed Chemical Vapor Deposition of Water-Free TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> Nanolaminates on Si and SiO<sub>2</sub> in Preference to SiCOH. *ACS Applied Materials & Interfaces* **2022**, *14*, 15716–15727.
- (28) Hwang, Y.; Chobpattana, V.; Zhang, J. Y.; LeBeau, J. M.; Engel-Herbert, R.; Stemmer, S. Al-doped HfO<sub>2</sub>/In<sub>0.53</sub>Ga<sub>0.47</sub>As metal-oxide-semiconductor capacitors. *Applied Physics Letters* **2011**, *98*, 142901.
- (29) Fang, Q.; Zhang, J.-Y.; Wang, Z.; Wu, J.; O’Sullivan, B.; Hurley, P.; Leedham, T.; Davies, H.; Audier, M.; Jimenez, C.; Senateur, J.-P.; Boyd, I. W. Investigation of TiO<sub>2</sub>-doped HfO<sub>2</sub> thin films deposited by photo-CVD. *Thin Solid Films* **2003**, *428*, 263–268.
- (30) Su, C.-K.; Chuang, H.-J.; Li, C.-Y.; Yu, C.-Y.; Ko, B.-T.; Chen, J.-D.; Chen, M.-J. Oxo-Bridged Bimetallic Group 4 Complexes Bearing Amine-Bis(benzotriazole phenolate) Derivatives as Bifunctional Catalysts for Ring-Opening Polymerization of Lactide and Copolymerization of Carbon Dioxide with Cyclohexene Oxide. *Organometallics* **2014**, *33*, 7091–7100.
- (31) Huang, J.; Lian, B.; Yong, L.; Qian, Y. Syntheses of zirconium (IV) complexes with

- Schiff-base ligand and their catalytic activities for polymerization of ethylene. *Inorganic Chemistry Communications* **2001**, *4*, 392–394.
- (32) Chuang, H.-J.; Ko, B.-T. Facilely synthesized benzotriazole phenolate zirconium complexes as versatile catalysts for copolymerization of carbon dioxide with cyclohexene oxide and lactide polymerization. *Dalton Trans.* **2015**, *44*, 598–607.
- (33) Mandal, M.; Ramkumar, V.; Chakraborty, D. Salen complexes of zirconium and hafnium: synthesis, structural characterization and polymerization studies. *Polym. Chem.* **2019**, *10*, 3444–3460.
- (34) Hancock, S. L.; Mahon, M. F.; Kociok-Köhn, G.; Jones, M. D. Homopiperazine and Piperazine Complexes of ZrIV and HfIV and Their Application to the Ring-Opening Polymerisation of Lactide. *European Journal of Inorganic Chemistry* **2011**, *2011*, 4596–4602.
- (35) Nanomaterials definition matters. *Nature Nanotechnology* **2019**, *14*, 193–193.
- (36) Baek, W.; Chang, H.; Bootharaju, M. S.; Kim, J. H.; Park, S.; Hyeon, T. Recent Advances and Prospects in Colloidal Nanomaterials. *JACS Au* **2021**, *1*, 1849–1859.
- (37) Van den Eynden, D.; Pokratath, R.; De Roo, J. Nonaqueous Chemistry of Group 4 Oxo Clusters and Colloidal Metal Oxide Nanocrystals. *Chem. Rev.* **2022**, *122*, 10538–10572.
- (38) Pokratath, R.; Van den Eynden, D.; Cooper, S. R.; Mathiesen, J. K.; Waser, V.; Devereux, M.; Billinge, S. J. L.; Meuwly, M.; Jensen, K. M. O.; De Roo, J. Mechanistic Insight into the Precursor Chemistry of ZrO<sub>2</sub> and HfO<sub>2</sub> Nanocrystals; towards Size-Tunable Syntheses. *JACS Au* **2022**, *2*, 827–838.
- (39) De Roo, J. Chemical Considerations for Colloidal Nanocrystal Synthesis. *Chemistry of Materials* **2022**, *34*, 5766–5779.
- (40) Bradley, D. C.; Wardlaw, W. 62. Zirconium alkoxides. *J. Chem. Soc.* **1951**, 280–285.

- (41) Seisenbaeva, G. A.; Gohil, S.; Kessler, V. G. Influence of heteroligands on the composition, structure and properties of homo- and heterometallic zirconium alkoxides. Decisive role of thermodynamic factors in their self-assembly. *J. Mater. Chem.* **2004**, *14*, 3177–3190.
- (42) Vaartstra, B. A.; Huffman, J. C.; Gradeff, P. S.; Hubert-Pfalzgraf, L. G.; Daran, J. C.; Parraud, S.; Yunlu, K.; Caulton, K. G. Alcohol adducts of alkoxides: intramolecular hydrogen bonding as a general structural feature. *Inorganic Chemistry* **1990**, *29*, 3126–3131.
- (43) Veith, M.; Mathur, S.; Mathur, C.; Huch, V. Synthesis, reactivity and structures of hafnium-containing homo- and hetero- (bi- and tri-) metallic alkoxides based on edge- and face-sharing bioctahedral alkoxometalate ligands. *J. Chem. Soc., Dalton Trans.* **1997**, 2101–2108.
- (44) Diamond, G. M.; Rodewald, S.; Jordan, R. F. Efficient Synthesis of rac-(Ethylenebis(indenyl))ZrX<sub>2</sub> Complexes via Amine Elimination. *Organometallics* **1995**, *14*, 5–7.
- (45) Kim, K.; Lee, W. S.; Kim, H. J.; Cho, S. H.; Girolami, G. S.; Gorlin, P. A.; Suslick, K. S. Synthesis and structure of transition-metal bis(porphyrinato) complexes. Characterization of Zr(TPP)<sub>2</sub> and Zr(OEP)<sub>2</sub>. *Inorganic Chemistry* **1991**, *30*, 2652–2656.
- (46) Bradley, D. C.; Thomas, I. M. 765. Metallo-organic compounds containing metal–nitrogen bonds. Part I. Some dialkylamino-derivatives of titanium and zirconium. *J. Chem. Soc.* **1960**, 3857–3861.
- (47) Thomas, I. M. The Preparation of Alkoxides and Triethylsilanolates of Ti, Zr, V, Nb, Ta, and Sn from the Dialkylamides. *Canadian Journal of Chemistry* **1961**, *39*, 1386–1388.

- (48) Shreider, V.; Turevskaya, E.; Koslova, N.; Turova, N. Direct electrochemical synthesis of metal alkoxides. *Inorganica Chimica Acta* **1981**, *53*, L73–L76.
- (49) Bradley, D. C.; Abd-El Halim, F. M.; Wardlaw, W. 676. The chloride ethoxides of zirconium. *J. Chem. Soc.* **1950**, 3450–3454.
- (50) WARDLAW, W.; BRADLEY, D. C. Zirconium Esters. *Nature* **1950**, *165*, 75–76.
- (51) Bradley, D. C.; Mehrotra, R. C.; Wardlaw, W. 330. Hafnium alkoxides. *J. Chem. Soc.* **1953**, 1634–1636.
- (52) Bradley, D. C.; Halim, F. M. A.-E.; Sadek, E. A.; Wardlaw, W. 377. The preparation of zirconium alkoxides. *J. Chem. Soc.* **1952**, 2032–2035.
- (53) Bradley, D. C.; Mehrotra, R. C.; Wardlaw, W. 376. Structural chemistry of the alkoxides. Part I. Alkoxides of silicon, titanium, and zirconium. *J. Chem. Soc.* **1952**, 2027–2032.
- (54) Bradley, D. C.; Mehrotra, R. C.; Wardlaw, W. 809. Structural chemistry of the alkoxides. Part II. Tertiary alkoxides of silicon, titanium, zirconium, and hafnium. *J. Chem. Soc.* **1952**, 4204–4209.
- (55) BRADLEY, D. C.; FAKTOR, M. M. Volatile Methoxides of Aluminium and Zirconium. *Nature* **1959**, *184*, 55–56.
- (56) Mehrotra, R. C. The Reaction of the Alkoxides of Titanium, Zirconium and Hafnium with Esters. *Journal of the American Chemical Society* **1954**, *76*, 2266–2267.