

From Precursor Engineering to Material Synthesis: Mixed-Ligand Al, Ga, Zr, and Hf Complexes for Chemical Vapor Deposition

An Inaugural Dissertation
to obtain a Doctoral Degree

submitted by
Billy Oktor Abdilah Fauzi
from
Bandung, Indonesia



Institute of Inorganic and Materials Chemistry
Cologne Graduate School of Chemistry
The University of Cologne

Accepted in 2026

“Growth occurs when one goes beyond one’s limit. Realizing that is also part of training.”

- *Itachi Uchiha*

Acknowledgement

First and foremost, I express my deepest gratitude to **Allah, the Almighty**, for His endless blessings, mercy, and guidance throughout my PhD journey. His strength, patience, and wisdom have enabled me to persevere through challenges and complete this dissertation.

My utmost appreciation and profound respect go to **Prof. Dr. Dr. (h.c.) Sanjay Mathur**, my first supervisor, my doctor father, for his exceptional mentorship, visionary guidance, and unwavering support throughout my doctoral studies. His profound expertise in inorganic and materials chemistry, particularly in alkoxide and single-source precursor chemistry for chemical vapor deposition, has been a constant source of inspiration. I am deeply thankful for the invaluable discussions, critical insights, and encouragement he provided, which greatly enriched both my scientific knowledge and personal growth. Working under his supervision has been an extraordinary privilege that has shaped the way I approach research with curiosity, persistence, and integrity.

I am also sincerely grateful to **Prof. Dr. Axel Klein**, my second supervisor and examiner, for his kindness, constructive feedback, and thoughtful discussions that helped refine my research and strengthen this dissertation.

I would like to express my sincere gratitude to **Prof. Dr. Prince Ravat** from the Institute of Organic Chemistry, University of Cologne, for graciously agreeing to serve as the Chair of my doctoral defense. I greatly appreciate his time, support, and willingness to undertake this responsibility.

I would like to express my sincere gratitude to the **DAAD** for providing me with the invaluable opportunity to study at the University of Cologne, fully supported financially. This generous funding not only enabled me to pursue my academic interests in an outstanding research environment but also allowed me to focus entirely on my work without the burden of financial constraints. Without this support, I would not have been able to pursue my dream of completing a doctoral degree in Germany, and for that, I remain deeply thankful.

I thank **Dr. Michael Wilhelm** for his support in preparing my DAAD scholarship proposal, which made my study in Germany possible, and for generously allowing me to use his fume hood for nearly four years. I also thank **Dr. Chijioke Kingsley Amadi** for his guidance before and after I arrived in Germany, and for introducing me to the stock line for precursor synthesis. My gratitude further extends to **Dr. Andreas Lichtenberg** for his continuous help and valuable

suggestions, **Dr. Corinna Hegemann** for her insightful advice on NMR analysis, and **Dr. Thomas Fischer** for his reliable support in both research and administrative matters.

I would like to express my sincere gratitude to **Prof. Dr. Dr. (h.c.) Anjana Devi, Dr. Harish Parala, and Mr. Marcel Schmickler** of the Leibniz Institute for Solid State and Materials Research, IFW Dresden, Germany, for generously providing the facilities and support necessary for the successful progress of my research. I would like to thank **Dr. Mattia Cattelan** of the Industrial Engineering Department, University of Padova for his help for the XPS measurement. Their assistance was instrumental in enabling me to achieve the milestones required for the completion of my PhD. Without their guidance and support, the completion of my first manuscript would not have been possible.

I am thankful to the **Thurstea group - Dr. Seulgi Ji, Jessica Kirchhartz, Nurgül Tosun, and Dirk Pullem** - for their friendship and cheerful company. Special thanks to Jessica Kirchhartz for our delightful weekly tea times, which brought warmth and laughter amidst the demands of research. I also appreciate **Dr. Andreas Lichtenberg, Dr. Ziyaad Aytuna, Jessica Kirchhartz, Tom-Jonas Schneider, Dirk Pullem, Nurgül Tosun, Lukas Rryci, and Simon Diel** for their assistance in materials characterization, including SEM-EDX, elemental analysis, TEM, TG-DSC, and thin-film XRD measurements.

I would like to extend my gratitude to the XRD team at the Institute of Inorganic and Materials Chemistry, with special appreciation to **Ms. Silke Kremer** for her invaluable assistance with the single-crystal XRD measurements and for the pleasant and engaging conversations that made the experience even more enjoyable.

I would like to express my sincere appreciation to the NMR team at the Department of Chemistry, University of Cologne, particularly **Dr. Philipp Hegemann**, for their guidance and support. I am especially grateful for his assistance with the installation and licensing of MestReNova, which became challenging as I changed laptops several times. His patience and willingness to help ensured that I could continue my work without interruption.

My gratitude also goes to all other group members besides those mentioned above for their kindness, collaboration, and support, especially **Angelika Feuerlein, Dr. Shaista Ilyas, Dr. Veronika Brune, Dr. Maria Basso, Dr. Touraj Karimpour, Dr. Anja Sutorius, Dr. Khan Le, Dr. Niusha Hesmati, Dr. Sumiya Iqbal, Dr. Benedict Witulski, Dr. David Patrun, René Weißing, Naina Goyal, Ruth Adam, Moritz Steiner**, and LabMathur members mentioned

above for creating such a welcoming and supportive atmosphere throughout my time in the group.

I also thank **Prof. Dr. Mitsuru Kondo**, my former supervisor at Shizuoka University, whose mentorship and encouragement laid the foundation for my PhD studies in Germany. I would like to extend my sincere appreciation to **all members** of the Department of Chemistry at the University of Cologne for their support, as well as to **Muhammad Ihsan Karimurrahman** for the enjoyable moments and many pleasant coffee times we shared in Cologne. I would like to thank **Adenan Yandra Nofrizal**, my junior and friend from Shizuoka University, for the mutual support and encouragement as we pursue our dreams in Europe.

My deepest love and gratitude go to my wife, **Febrianty Nurpratiwi**, for her endless love, patience, and unwavering support. Her constant belief in me gave me the strength and motivation to complete this PhD journey. I would also like to express my deepest gratitude to her for her patience, strength, and sacrifice in carrying our beloved “**Rora**” in her womb while we were apart. I am truly grateful for her unwavering love and for the precious gift she has given me. I also thank my beloved parents, **Agus Akhmad Fauzi** and **Enung Syarifah Nurhayati**, for their unconditional love and prayers; my brother **Renato Eka Sakti Fauzi**, his wife **Eka Sylvianti Rahayu**, and their son **Enzo Elmanadzir Fauzi**; as well as my beloved sister **Mediana Fauziah Ulfi**, for their constant encouragement and affection. I extend my heartfelt thanks to all my **relatives** that I cannot mention one by one, my parents-in-law **Endang Sumitra** and **Imas Liawati** and my sister-in-law **Fenia Dwi Destiani** for their understanding, prayers, and continuous support. Finally, I am deeply grateful to all my former teachers and lecturers who brought me to who I am now. I thank my friends who have befriended with me since elementary school, junior high school, senior high school (especially MXMW crew), undergraduate, master’s degree, and wherever I met for their lasting friendship, encouragement, and for always reminding me of where I came from. May God repay all the goodness that has been given.

Bapak Aki, Ema, A Hendri, this dissertation is dedicated for you. Hope you can read it from above the sky.

Abstract

In the era of rapidly advancing technologies, the demand for high-performance semiconductor thin films continues to increase, driven by applications in microelectronics, energy systems, sensing devices, and emerging quantum technologies. Ongoing device miniaturization and the need for higher efficiency require thin films with precise control over thickness, composition, crystallinity, and interface quality. Consequently, the development of scalable and reliable fabrication techniques has become a central focus in materials science and semiconductor research.

Atomic layer deposition (ALD) is widely used for thin film fabrication due to their ability to produce uniform and high-quality layers. However, ALD is inherently slow because of its sequential surface reactions. This factor can restrict throughput and increase production costs for large-scale manufacturing. Metal-organic chemical vapor deposition (MOCVD) offers a promising alternative, combining high deposition rates, compositional tunability, and compatibility with industrial-scale processes. Nevertheless, MOCVD relies on the availability of suitable precursor chemistry that remains a critical challenge.

Precursors chemically designed to match the material composition and simplified the chemical input to the thin film growth are termed as single-source precursors (SSPs). SSPs are particularly advantageous because all required film-forming elements are incorporated within a single molecular framework, enabling precise stoichiometric control and minimizing gas-phase side reactions. The rational design of metal-organic precursors is therefore essential, as their molecular structure influences volatility, thermal stability, and decomposition behavior during film growth. An effective precursor design integrates coordinative saturation of the metal center with thermal lability of ligands enabling low decomposition temperature.

This dissertation focuses on the application of novel aluminum, gallium, zirconium, and hafnium complexes in MOCVD. These precursors were developed for the deposition of technologically relevant materials, including zirconium oxynitride (ZrON), hafnium zirconium oxide ($\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$, HZO), and aluminum gallium oxide ($(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$). These materials are of significant interest due to their dielectric, ferroelectric, and ultra-wide bandgap semiconductor properties, which are relevant for next-generation memory, power electronics, and optoelectronic applications.

Both homoleptic and heteroleptic complexes based on alkoxide ($-\text{OR}^-$) and fluorinated β -ketoenamine ($-\text{N}^+\text{ORF}^-$) ligands were synthesized and structurally characterized. The presence of $-\text{CF}_3$ groups in the ligand backbone enhances volatility and thermal stability by

reducing intermolecular interactions, while the chelating β -ketoenamine framework ($N^{\wedge}O$) stabilizes the metal center and promotes controlled decomposition pathways. Importantly, the resulting complexes form solid-state compounds that can be purified efficiently by low-pressure sublimation, ensuring high purity and ease of handling.

The interplay of steric and electronic effects is evident in both main group (Al, Ga) and transition metal (Zr, Hf) compounds. Al and Ga preferentially form tetrahedral complexes, only one chelating β -ketoenamine unit could be incorporated in the coordination sphere of Al and Ga complexes. In contrast, Zr and Hf formed octahedral complexes, allowing an introduction of two β -ketoenamine ligands to form a series of stable compounds.

This dissertation reports precursor synthesis, structural characterization, thermal properties, and vapor-phase behavior, followed by evaluation of their performance in MOCVD processes. By correlating molecular design with thin film growth behavior and material properties, the study establishes structure-property relationships that guide the development of advanced SSPs.

Table of Contents

	Page
Acknowledgement	i
Abstract	iv
Table of Contents	vi
1. Motivation and Scientific Objectives	1
2. Introduction	3
2.1. Deposition of Thin Films	3
2.2. Aluminum-, Gallium-, Zirconium-, and Hafnium-based Thin Films from Chemical Vapor Deposition.....	5
2.3. Metal-Organic Precursor Concept in Chemical Vapor Deposition	7
2.4. Single-Source Precursors and Metal-Organic Chemical Vapor Deposition	10
2.4.1. Homoleptic and Heteroleptic Precursors.....	13
2.5. Advancements in Precursor Design Concept.....	16
3. Syntheses and Characterization of Fluorinated β-Ketoenamine-based Aluminum and Gallium Complexes and Their Application in Deposition of Al_2O_3, Ga_2O_3, and $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ Thin Films	21
3.1. Scientific Context.....	21
3.2. Syntheses and Characterization of $[\text{Al}(\text{TFB-}i\text{BuA})(\text{O}'\text{Bu})_2]$ and $[\text{Ga}(\text{TFB-}i\text{BuA})(\text{O}'\text{Bu})_2]$	24
3.3. Thermal Analyses of $[\text{Al}(\text{TFB-}i\text{BuA})(\text{O}'\text{Bu})_2]$ and $[\text{Ga}(\text{TFB-}$ $i\text{BuA})(\text{O}'\text{Bu})_2]$, Vapor Pressure of $[\text{Al}(\text{TFB-}i\text{BuA})(\text{O}'\text{Bu})_2]$ and $[\text{Ga}(\text{TFB-}i\text{BuA})(\text{O}'\text{Bu})_2]$ and Their Comparison to $[\text{Al}(\text{O}'\text{Bu})_3]_2$ and $[\text{Ga}(\text{O}'\text{Bu})_3]_2$	31
3.4. Deposition of Al_2O_3 and Ga_2O_3 films Using $[\text{Al}(\text{TFB-}i\text{BuA})(\text{O}'\text{Bu})_2]$, $[\text{Ga}(\text{TFB-}i\text{BuA})(\text{O}'\text{Bu})_2]$, $[\text{Al}(\text{O}'\text{Bu})_3]_2$, and $[\text{Ga}(\text{O}'\text{Bu})_3]_2$ precursors	37
3.5. Deposition of $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ Using $[\text{Al}(\text{TFB-}i\text{BuA})(\text{O}'\text{Bu})_2]$ and $[\text{Ga}(\text{TFB-}i\text{BuA})(\text{O}'\text{Bu})_2]$	52
4. Syntheses and Characterization of Fluorinated β-Ketoenamine-based Zirconium Complexes and Their Application in Deposition of Zirconium Oxynitride Thin Films	63
4.1. Scientific Context.....	63

4.2.	Syntheses and Characterization of [Zr(TFB-MEA) ₂ (NEt ₂) ₂], [Zr(TFB- <i>t</i> BuA) ₂ (NEt ₂) ₂], [Zr(TFB- <i>t</i> BuA) ₂ {η ² -(<i>i</i> PrN) ₂ CNEt ₂ } ₂], [Zr(TFB-TFEA) ₄], and [Zr(TFB- <i>t</i> BuA) ₂ (NEt ₂)(O'Bu)]	66
4.3.	Thermal Analysis of [Zr(TFB-TFEA) ₄]	96
5.	Syntheses and Characterization of Fluorinated β-Ketoenamine-based Zirconium and Hafnium Complexes and Their Application in Deposition of ZrO₂, HfO₂, and Hf_xZr_{1-x}O₂ Thin Films	99
5.1.	Scientific Context.....	99
5.2.	Syntheses, Characterization, and Thermal Analyses of [M(L) ₂ (O'Bu) ₂] (M = Zr, Hf; L = TFB- <i>t</i> BuA, TFB-TFEA)	103
5.3.	Deposition of ZrO ₂ , HfO ₂ , and Hf _x Zr _{1-x} O ₂ Thin Films Using [M(L) ₂ (O'Bu) ₂] (M = Zr, Hf; L = TFB- <i>t</i> BuA, TFB-TFEA)	120
6.	Summary and Outlook	136
6.1.	Summary	136
6.2.	Outlook.....	140
7.	Experimental Section	147
7.1.	Chemicals and Methods	147
7.2.	Characterization Techniques	147
7.3.	Syntheses of the Fluorinated β-Ketoenamine Ligands	149
7.4.	Syntheses of Metal Complexes	152
7.4.1.	Syntheses of Fluorinated β-Ketoenamine-based Aluminum and Gallium Complexes	153
7.4.2.	Syntheses of Fluorinated β-Ketoenamine-based Zirconium and Hafnium Complexes	155
7.5.	Syntheses of Metal Oxide Thin Films through MOCVD	163
7.5.1.	Syntheses of Al ₂ O ₃ , Ga ₂ O ₃ , and (Al _x Ga _{1-x}) ₂ O ₃ Thin Films through MOCVD	164
7.5.2.	Syntheses of ZrO ₂ , HfO ₂ , and Hf _x Zr _{1-x} O ₂ Thin Films through MOCVD	164
8.	References	166
9.	Abbreviation	175
10.	Appendix	177
11.	Teilpublikationen	264

1. Motivation and Scientific Objectives

The primary motivation of this research is to advance the chemistry of metal–organic complexes and functional materials derived from Group 13 metals (Al and Ga) and Group 4 transition metals (Zr and Hf). To achieve this objective, a series of novel metal–organic complexes containing aluminum, gallium, zirconium, and hafnium centers coordinated by various ligand systems have been designed, synthesized, and systematically characterized. These compounds were developed as potential precursors for metal–organic chemical vapor deposition (MOCVD) processes aimed at the fabrication of advanced oxide and oxynitride thin films. Particular emphasis is placed on the deposition of mixed-metal oxide thin films, including aluminum gallium oxide ($(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$) and hafnium zirconium oxide ($\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$), through dual-source precursor approaches, as well as zirconium oxynitride (Zr_2ON_2) thin films derived from single-source precursor systems. These materials are of considerable interest semiconductors (Figure 1.1).

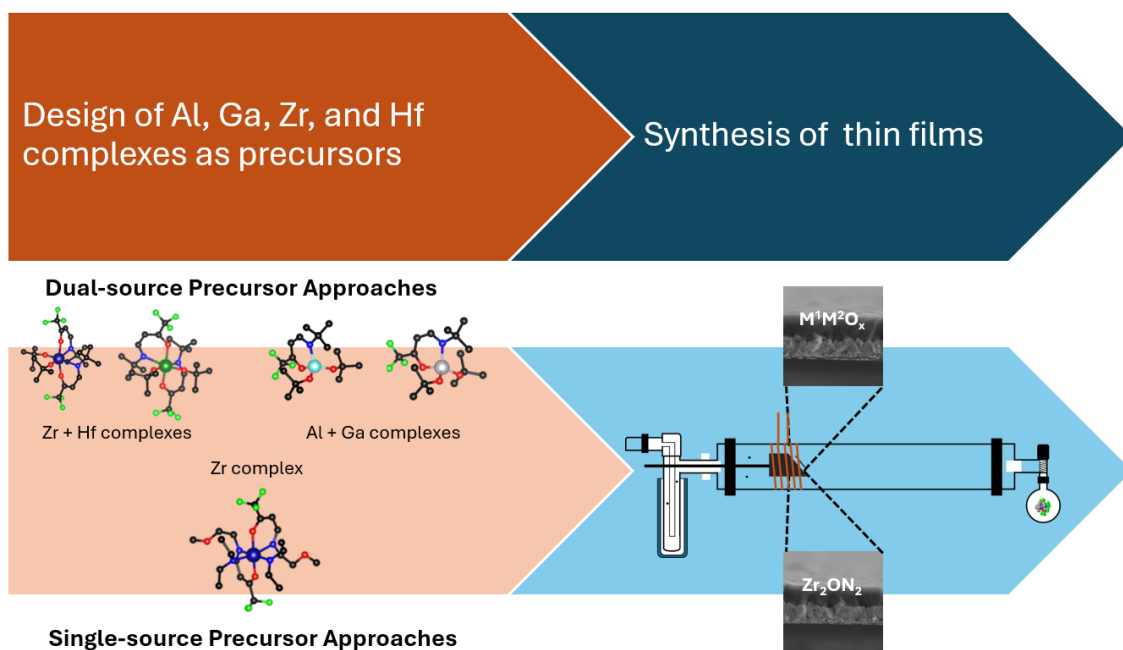


Figure 1.1. Concept for the Motivation and Scientific Objectives of this research work.

The major goals and overall structure of this dissertation can be summarized as follows:

- I. Direct synthesis of $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ and $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ thin films via MOCVD using a dual-source precursor approach based on newly developed Group 13 metals (Al and Ga) and Group 4 transition metals (Zr and Hf) complexes.

- Design, synthesis, and comprehensive characterization of volatile and thermally stable aluminum and gallium precursors suitable for MOCVD applications.
- Investigation of the relationships between precursor molecular structure, thermal properties, and thin-film growth behavior during the MOCVD deposition of $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ and $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ thin films.
- Evaluation of the influence of precursor chemistry on film composition, morphology, crystallinity, and phase formation in $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ and $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ films.

II. Conceptualization and synthesis of zirconium complexes as single-source precursors for Zr_2ON_2 thin films via MOCVD

- Design, synthesis, and structural characterization of novel zirconium complexes incorporating various fluorinated β -ketoenamine ligands.
- Investigation of the thermal stability and volatility of the synthesized zirconium complexes to assess their suitability as single-source MOCVD precursors.
- Evaluation of structure-property relationships governing precursor performance, with particular emphasis on the influence of ligand design on thermal behavior and vapor-phase transport.
- Development of molecular design strategies for zirconium-based precursors capable of delivering both oxygen and nitrogen for the deposition of Zr_2ON_2 thin films.

2. Introduction

2.1. Deposition of Thin Films

Thin films are layers of material with thicknesses ranging from a few nanometers to several micrometers that are deposited onto a substrate [1, 2]. Owing to their unique physical and chemical properties, thin films are widely used in electronic, optical, energy, and protective coating applications. Various techniques have been developed for thin-film fabrication, among which atomic layer deposition (ALD) and chemical vapor deposition (CVD) are two of the most widely employed vapor-phase deposition methods.

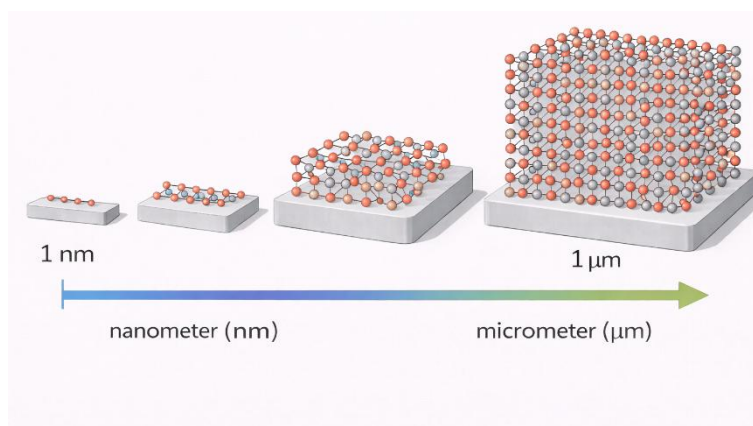


Figure 2.1. Schematic representation of thin films based on the thickness.

According to Doll *et al.* [3], ALD is a vapor-phase deposition technique based on sequential, self-limiting surface reactions between precursor molecules and an activated substrate surface. In a typical ALD cycle, the substrate surface is first exposed to precursor X (e.g., H_2O), which reacts with the surface to generate active surface species (surface-X) through a self-limiting half-reaction. Subsequently, precursor Y is introduced and reacts selectively with these activated sites, forming a new surface species (surface-XY) and depositing approximately one atomic layer of material. Excess precursor and reaction by-products are then removed before the surface is re-exposed to precursor X, regenerating reactive surface sites for the next cycle. Repetition of these alternating half-reactions enables precise layer-by-layer growth with thickness control on the Angstrom scale [3]. A schematic illustration of the ALD process is shown in Figure 2.2.

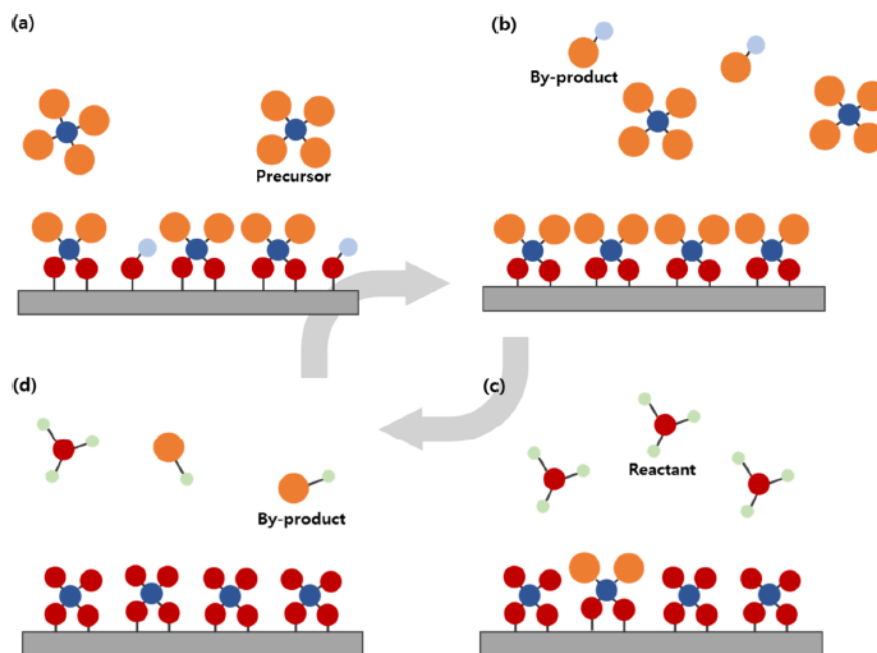


Figure 2.2. Idealized ALD process. (a) The precursor is exposed to the surface and reacts with the surface; (b) the remaining precursor and byproduct are removed by the purging; (c) the reactant is exposed and reacts with the precursor; and (d) the remaining reactant and reaction product are removed by purging. Reproduce from Choi *et al.* [4] with permission from American Chemical Society. © American Chemical Society.

Despite its excellent thickness control and conformality, ALD generally suffers from relatively slow growth rates because of the self-limiting reaction per cycle [5-8]. An alternative vapor-phase deposition technique is CVD. CVD is a thin-film deposition technique in which gaseous precursors react or decompose in an activated environment to form a solid material on a substrate surface [9]. According to Doll *et al.* [3], the CVD process involves several sequential steps: (1) vaporization and transport of the precursor into the reactor, (2) delivery of the precursor vapor to the heated substrate region, and (3) formation of reactive intermediate species. If the temperature exceeds the decomposition temperature of these intermediates, (3a) homogeneous gas-phase reactions occur, leading to powder formation and volatile by-products. Conversely, if the temperature remains below the decomposition temperature, (3b) the intermediates diffuse through the boundary layer toward the substrate surface. Subsequently, (4) adsorption of the precursor species occurs, followed by (5) surface diffusion, nucleation, and thin-film growth. Finally, (6) volatile by-products diffuse away from the surface, and (7) unreacted precursors and by-products are removed from the reactor chamber. The overall thin-film formation process by CVD is illustrated in Figure 2.3.

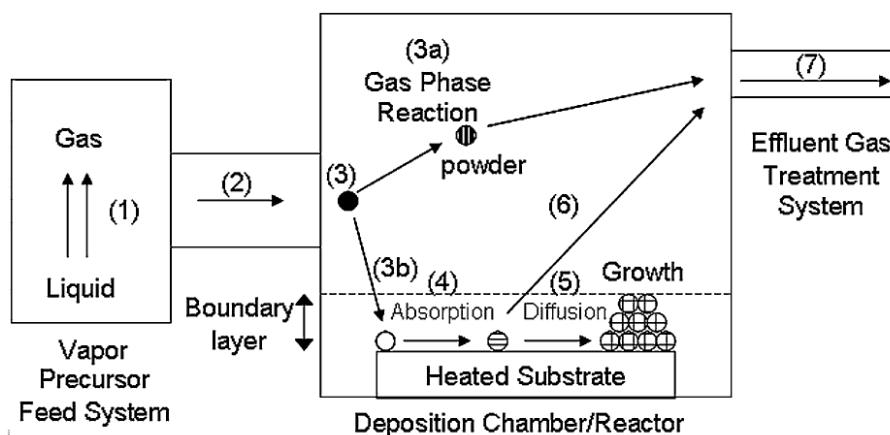


Figure 2.3. Schematic illustration of the seven key steps in a CVD process. Reproduced from Doll *et al.* [3] with permission from Springer Nature. © Springer Nature.

Choy [9] reported that the growth of thin films CVD is governed by several key process parameters, including deposition temperature, reactor pressure, reactant concentration, and gas flow rate. Among these, temperature is considered the most critical parameter, as it determines the thermodynamics and kinetics of the deposition process, thereby influencing precursor decomposition, growth rate, crystallinity, grain size, and overall film microstructure. Reactor pressure affects the transport of reactant species and the dominant growth mechanism within the reactor. At atmospheric pressure, film growth is often mass-transport limited, whereas at reduced pressures, surface chemical reactions play a more significant role, allowing improved control over film composition and uniformity. The reactant concentration, commonly expressed as the precursor partial pressure, governs the availability of reactive species at the substrate surface and consequently influences the growth rate, film thickness, and stoichiometry. Likewise, the gas flow rate controls the supply of reactants and the removal of gaseous by-products, making it an important factor for achieving uniform film growth. Furthermore, reactor geometry and substrate configuration influence reactant transport and temperature distribution within the deposition zone. Therefore, careful optimization of these process parameters is essential for obtaining thin films with uniform thickness, homogeneous composition, strong adhesion, and the desired microstructural characteristics.

2.2. Aluminum-, Gallium-, Zirconium-, and Hafnium-based Thin Films from Chemical Vapor Deposition

A fundamental requirement for CVD precursors is an ability to transform into a gas phase to enable efficient transport into the reaction chamber. Numerous precursor systems have been developed for the deposition of oxide thin films containing aluminum, gallium, zirconium, and

hafnium. One example is the work of Rупpi [10], who employed AlCl_3 together with CO_2 , Ar, H_2 , and H_2S gases to establish an $\text{AlCl}_3\text{--CO}_2\text{--Ar--H}_2\text{--H}_2\text{S}$ precursor system (Table 2.1).

Table 2.1. Process parameters used to deposit Al_2O_3 and $\text{Ti}(\text{C}, \text{N})$ layers. Reproduce from Rупpi [10] with permission from Elsevier. © Elsevier.

	Al_2O_3	$\text{Ti}(\text{C}, \text{N})$
Temperature ($^{\circ}\text{C}$)	1000	860
Time (min)	560/60	120
Pressure (mbar)	80	50
H_2 (vol%)	Balance	Balance
Ar (vol%)	10	0
N_2 (vol%)	—	18
CO_2 (vol%)	4.2	—
AlCl_3 (vol%)	4.0	—
H_2S (vol%)	0.4	—
TiCl_4 (vol%)	—	2
CH_3CN (vol%)	—	0.8
HCl (vol%)	2	1

This system is used for the deposition of Al_2O_3 coatings on $\text{Ti}(\text{C}, \text{N})$ substrates at approximately 1000 $^{\circ}\text{C}$ (Figure 2.4). In this process, AlCl_3 serves as the aluminum source, while CO_2 provides the oxygen required for oxide formation. Because AlCl_3 exhibits limited volatility and a tendency to form polymeric species, carrier gases are required to facilitate its transport into the gas phase.

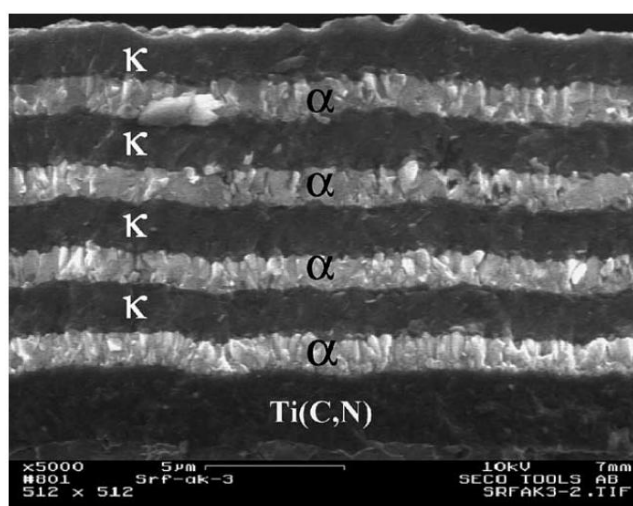
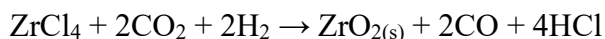
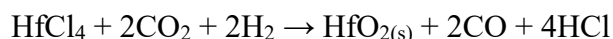
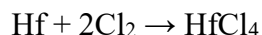


Figure 2.4. Multilayered Al_2O_3 coating composed of four alternating layers of $\kappa\text{-Al}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$, respectively. The Al_2O_3 phase is controlled by a nucleation step prior to deposition of Al_2O_3 and the $\kappa\text{-Al}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ layers were deposited using identical process data. Reproduce from Rупpi [10] with permission from Elsevier. © Elsevier.

Similar approaches have been reported for the deposition of gallium and zirconium oxide films. For example, Binions *et al.* [11] utilized a mixture of GaCl₃ and anhydrous methanol, which was transported into the reactor using heated nitrogen gas to produce Ga₂O₃ thin films. Likewise, Choi *et al.* [12] reported the deposition of ZrO₂ thin films using a precursor mixture containing ZrCl₄, H₂, and CO₂, with HCl generated as a volatile byproduct during the deposition process [12]. The corresponding reaction pathways are summarized in the reaction schemes below.



A comparable strategy has also been applied to hafnium oxide deposition. Bi *et al.* [13] generated gaseous HfCl₄ *in situ* by reacting metallic hafnium with Cl₂ at temperatures above 1200 °C. The resulting HfCl₄ vapor was subsequently introduced into the deposition chamber together with H₂ and CO₂, leading to the formation of HfO₂ thin films on molybdenum substrates [13]. The overall process is represented by the reaction equations shown below.



These examples demonstrate that conventional CVD processes often rely on multiple precursor and reactant streams, including separate metal sources, carrier gases, and oxygen-containing reactants, to achieve the desired thin-film composition. Furthermore, the precursor systems described above are largely based on Group 13 metal halides (Al and Ga) and Group 4 transition-metal halides (Zr and Hf), which tend to exist as oligomeric or polymeric species in the solid state [14, 15]. Such structural characteristics generally result in reduced volatility and make vapor-phase transport more challenging, often requiring elevated temperatures and the use of carrier gases to achieve sufficient vapor pressures for deposition. These limitations highlight the need for alternative precursor systems with lower molecular weights and improved volatility. In this regard, metal–organic compounds are particularly attractive candidates, as their molecular structures can be tailored to enhance volatility, thermal stability, and reactivity, making them well suited for CVD applications [16, 17].

2.3. Metal-Organic Precursor Concept in Chemical Vapor Deposition Process

Since metal halides (M = Al, Ga, Zr, and Hf) commonly form polymeric structures, resulting in high effective molecular weights and consequently low volatility, various strategies

have been developed to reduce their degree of aggregation. One widely employed approach involves reacting the metal halide with an organic compound capable of replacing the halide ligands and disrupting the polymeric network. Such compounds are generally referred to as ligands [18]. Among the most extensively studied ligands are alkoxides, which are formed through the deprotonation of alcohols (ROH) to generate the corresponding alkoxide anion (RO⁻) [19]. For example, the reaction of one equivalent of AlCl₃ with three equivalents of MOR (M = Na or K; R = a simple or substituted alkyl group) yields Al(OR)₃ [20]. Interestingly, Al(OR)₃ may exist as a polymer, oligomer, dimer, trimer, or monomer depending on the steric and electronic properties of the alkoxide ligand [21]. The extent of aggregation is largely governed by the ability of the ligand to prevent intermolecular metal–oxygen–metal bridging [21]. Small alkoxide ligands generally provide limited steric protection and therefore favor the formation of highly aggregated species [21]. In contrast, bulky alkoxide ligands create significant steric hindrance around the metal center, making it increasingly difficult for neighboring metal atoms to approach and form bridging alkoxide bonds [21]. Consequently, the degree of aggregation decreases, leading to lower-nuclearity species and a reduction in the effective molecular weight of the precursor [21].

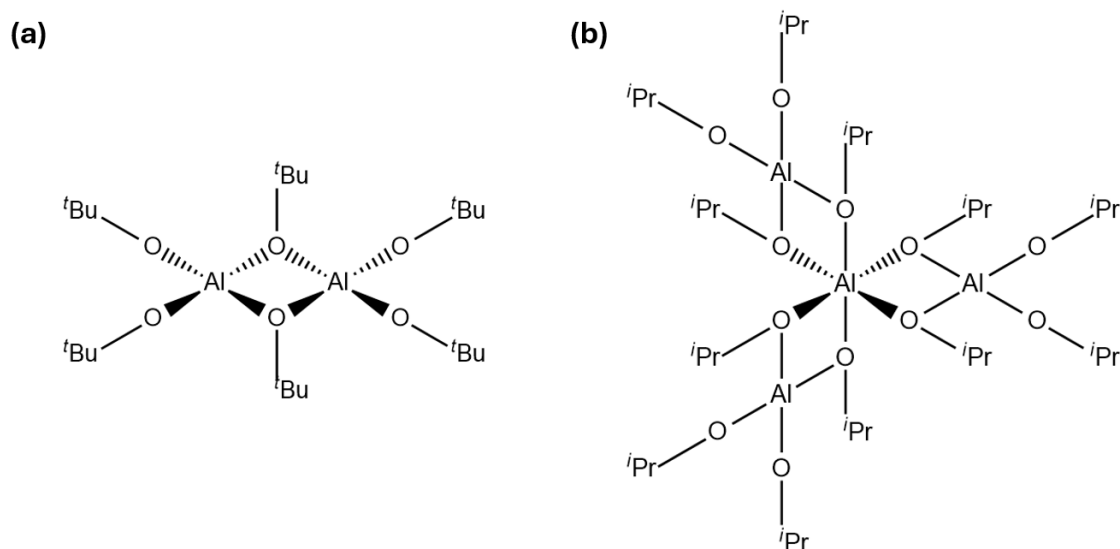


Figure 2.5. Structural representations of (a) dimer [Al(O^tBu)₃]₂ and (b) tetramer [Al(OⁱPr)₃]₄ [20].

More broadly, ligands play a central role in controlling the nuclearity and molecular weight of metal-organic compounds [21]. Bulky ligands reduce intermolecular association through steric shielding, whereas chelating ligands such as β-diketonate and β-ketoester, occupy multiple coordination sites and limit the availability of bridging positions forming chelate [21]. Schematic representation of chelating ligand with metal is presented in Figure 2.6.

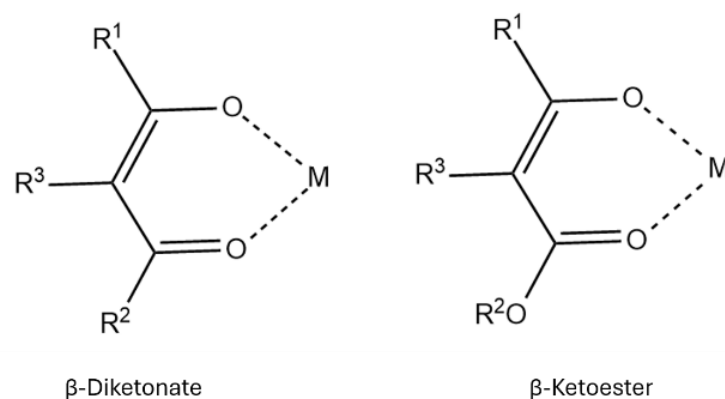


Figure 2.6. Schematic representation of β -diketonate and β -ketoester ligands forming chelates with metal center.

In addition, strong donor ligands can satisfy the coordination requirements of electron-deficient metal centers, thereby reducing the tendency toward aggregation [21]. Through these steric and electronic effects, ligands can convert highly aggregated metal halides and metal alkoxides into discrete monomeric or low-nuclearity complexes with lower molecular weights and enhanced volatility [21]. Such characteristics are highly desirable for CVD precursors, as monomeric species generally exhibit higher vapor pressures, cleaner evaporation behavior, and improved transport properties during vapor-phase deposition [21].

In the case of aluminum, Hon and Pfluger [22] reported that the coordination of aluminum with three acetylacetonate (acac) ligands yields tris(acetylacetonato)aluminum(III), $\text{Al}(\text{acac})_3$. In this complex, the aluminum center is six-coordinate, with each acac ligand binding in a bidentate fashion (Figure 2.7). The resulting saturated coordination sphere prevents the formation of Al–O–Al bridges between neighboring molecules, leading to a monomeric structure rather than the oligomeric or polymeric species commonly observed for many aluminum compounds.

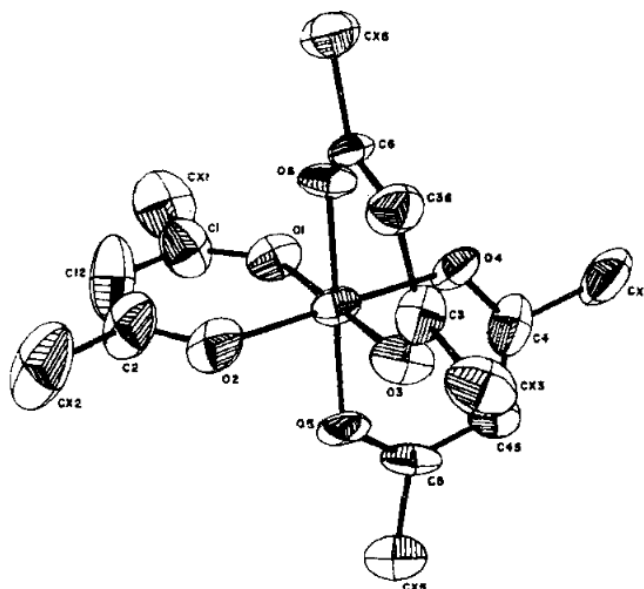


Figure 2.7. Stereodrawing of an isolated molecule of tris(acetylacetonato)Al(III). View is essentially down the c axis. Reproduced from P. K. Hon and C. E. Pfluger [22], "The Crystal and Molecular Structure of Tris(acetylacetonato)-Aluminum(III) and -Cobalt(III)", *Journal of Coordination Chemistry*, © copyright 1973, reprinted by permission of Informa UK Limited, trading as Taylor & Francis Group, <https://www.tandfonline.com>.

From this perspective, the development of monomeric aluminum, gallium, zirconium, and hafnium complexes as CVD precursors represents an important area of research. By preventing oligomerization and polymerization through appropriate ligand design, the molecular weight of the precursor can be reduced while its volatility can be enhanced. Such molecular engineering can facilitate vapor-phase transport, improve precursor delivery during deposition, and ultimately enable more efficient and controllable thin-film growth processes. Consequently, the synthesis of monomeric metal-organic compounds has attracted considerable interest for the development of next-generation CVD precursors based on Al, Ga, Zr, and Hf.

2.4. Single-Source Precursors and Metal-Organic Chemical Vapor Deposition

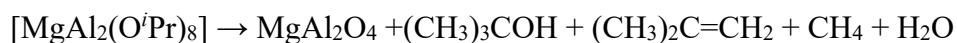
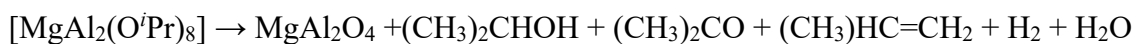
Metal-organic chemical vapor deposition (MOCVD) is a vapor-phase deposition technique widely used for the growth of thin films based on metal oxides and other functional materials. In this method, metal-organic precursors are vaporized and reacted at low pressure, resulting in thermal decomposition on the substrate surface, forming a thin film with a controlled composition. Operating at low pressure increases the mean free path of gas molecules, resulting in more efficient diffusion toward the surface and more controlled surface reactions [5, 7, 8, 23-25].

Single-source precursors (SSPs) in MOCVD are mostly molecules that contain all the elements required to form the target material within a single molecule. This means that the metal element and an anion (e.g., O^{2-} , N^{3-} , S^{2-} , or Se^{2-}) are chemically bonded within a single precursor molecular structure [26]. When this precursor undergoes thermal decomposition on the substrate surface under low pressure, it immediately forms a solid phase with a relatively favorable stoichiometry without the need for additional reactants such as oxygen (O_2), ozone (O_3), ammonia (NH_3), or nitrogen gas (N_2) as external element sources [26].

The main advantage of SSPs over conventional multi-source MOCVD is better stoichiometric control [5, 7]. In multi-source systems, film composition is highly dependent on the balance of flow rates and reactivity of each gas, which often have different decomposition kinetics [7, 8]. This can lead to compositional deviations, the formation of secondary phases, or defects due to side reactions in the gas phase [7, 8]. With SSPs, because the element ratio is "locked" within a single molecule, compositional variations due to gas flow fluctuations can be minimized, so the resulting films are more homogeneous and reproducible [5].

Furthermore, the use of SSP reduces the chemical complexity in the reactor. Without the need for oxygen, ozone, or ammonia as external oxidizers/nitrogenating agents, the risk of parasitic gas-phase reactions (premature gas-phase reactions) is minimized [7, 8, 23]. This is particularly important in MOCVD, where control of surface reaction kinetics is a dominant factor in determining crystal quality [7, 23].

For example, in the MOCVD deposition of pure oxide materials, Mathur *et al.* [27] demonstrated that the monomeric single-source precursor $[MgAl_2(OR)_8]$ ($R = ^iPr, ^tBu$) and $[MgAl_2(O^tBu)_4H_4]$ (Figure 2.8) can be readily volatilized between 20 and 125 °C without the use of a carrier gas. This precursor was successfully employed for the deposition of phase-pure $MgAl_2O_4$ thin films on Fe substrates at temperatures of 450-500 °C (Figure 2.9). The overall process can be represented by the chemical reaction shown below.



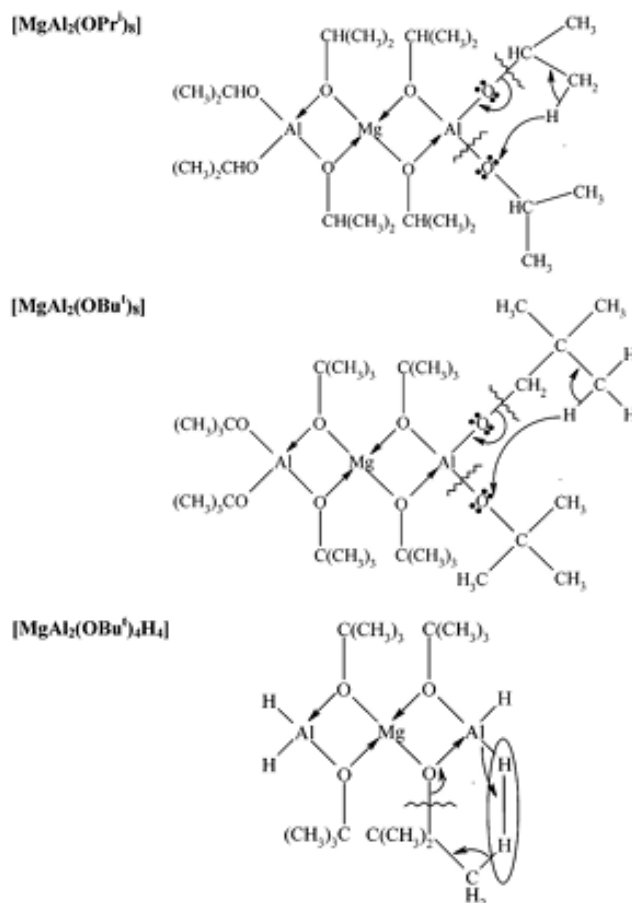


Figure 2.8. Structure of $[\text{MgAl}_2(\text{OR})_8]$ ($\text{R} = {}^i\text{Pr}, {}^t\text{Bu}$) dan $[\text{MgAl}_2(\text{O}^t\text{Bu})_4\text{H}_4]$ with possible ligand elimination mechanisms in the thermolytic decomposition of $[\text{MgAl}_2(\text{OR})_8]$ ($\text{R} = {}^i\text{Pr}, {}^t\text{Bu}$) dan $[\text{MgAl}_2(\text{O}^t\text{Bu})_4\text{H}_4]$. Reproduce from Mathur *et al.* [27] with permission from American Chemical Society. © American Chemical Society.

These results highlight the importance of molecular engineering in precursor design, as incorporating all required elements for the target material within a single molecular framework can simplify the deposition process, improve stoichiometric control, and facilitate the formation of high-purity thin films.

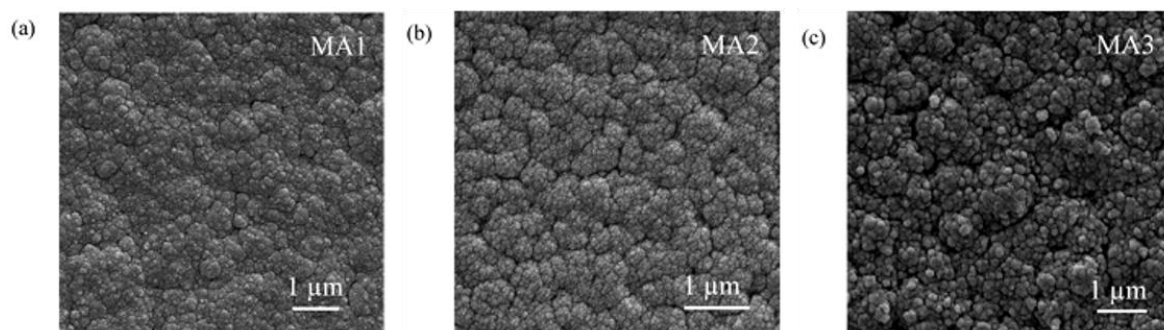


Figure 2.9. Scanning electron micrographs (a-c) of the MgAl_2O_4 films deposited on Fe at 550 °C using $[\text{MgAl}_2(\text{O}^t\text{Bu})_8]$ (MA1), $[\text{MgAl}_2(\text{O}^i\text{Pr})_8]$ (MA2), and $[\text{MgAl}_2(\text{O}^t\text{Bu})_4\text{H}_4]$ (MA3), respectively. Adapted from Mathur *et al.* [27] with permission from American Chemical Society. © American Chemical Society.

From a thin film research perspective, SSP is attractive because it enables tailored molecular design to specific material requirements [5, 28]. By engineering the chemical structure of precursors, for example, selecting ligands with clean decomposition, researchers can optimize deposition temperatures, minimize carbon residue, and improve crystal quality and film purity [28]. Therefore, SSP in MOCVD not only simplifies the process, but also opens up a molecular chemistry-based approach to control thin film growth more precisely and directed.

In SSPs systems for MOCVD, one of the key requirements is that the precursor must have sufficient volatility to be efficiently evaporated and transported to the substrate surface without premature decomposition [7, 8]. Good volatility ensures a stable precursor flow, more precise growth rate control, and reduces the risk of residue or contamination in the reactor [8]. One common strategy to increase volatility is to engineer the precursor molecular structure by using ligands containing certain groups, such as fluorinated ligands. The presence of fluorine atoms can reduce intermolecular forces and increase the vapor pressure of the compound, making the precursor more volatile and more suitable for MOCVD applications that require both thermal stability and high volatility [29].

2.4.1. Homoleptic and Heteroleptic Precursors

Molecular precursors can be designed in both homoleptic and heteroleptic configuration. Homoleptic precursors consist of a single type of ligand coordinated to the metal center, resulting in a symmetric molecular structure [30]. In contrast, heteroleptic precursors contain at least two different types of ligands [31].

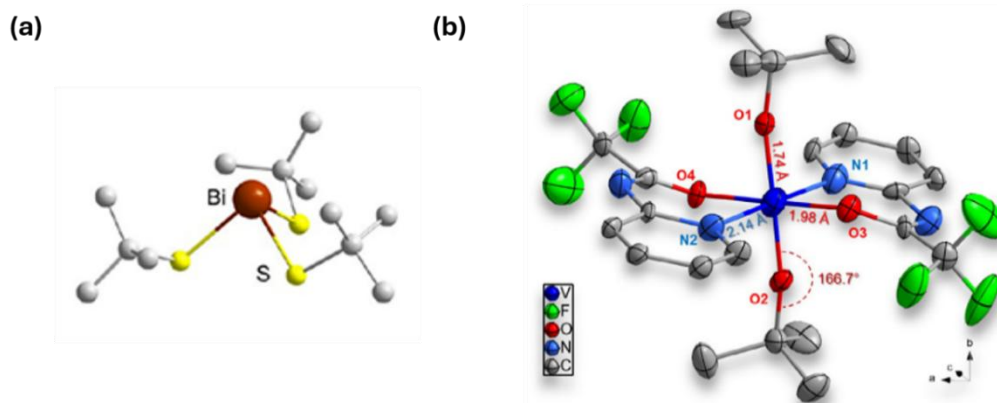


Figure 2.10. (a) Molecular structure of $\text{Bi}(\text{S}'\text{BU})_3$ as a representation of a homoleptic precursor [30] and (b) molecular structure of $[\text{V}(\text{O}'\text{BU})_2(\text{PyTFA})_2]$ as a representation of a heteroleptic precursor [31]. Adapted from Ufuk *et al.* [30] with permission from the American Chemical Society. © American Chemical Society. Adapted from Graf *et al.* [31] with permission from Elsevier. © Elsevier.

Heteroleptic precursors are of particular interest in MOCVD processes due to their structural versatility. As reported by Jürgensen *et al.* [32], the heteroleptic precursor $[(\text{COD})\text{Ir}(\text{ThTFP})]$ (COD = cyclooctadiene, ThTFP = (Z)-3,3,3-trifluoro-1-(thiazol-2-yl)prop-1-en-2-olate) (Figure 2.11a) exemplifies the so-called **“Janus-headed” precursor concept** (Figure 2.11b). In this molecular design, the two ligands fulfill distinct functions: one ligand provides thermal stability during vapor-phase transport, while the other acts as a reactive moiety that facilitates precursor decomposition and film formation at the substrate surface. Through this heteroleptic architecture, the precursor achieves a balance between stability and reactivity, two key requirements for efficient CVD processing and the deposition of high-purity materials.

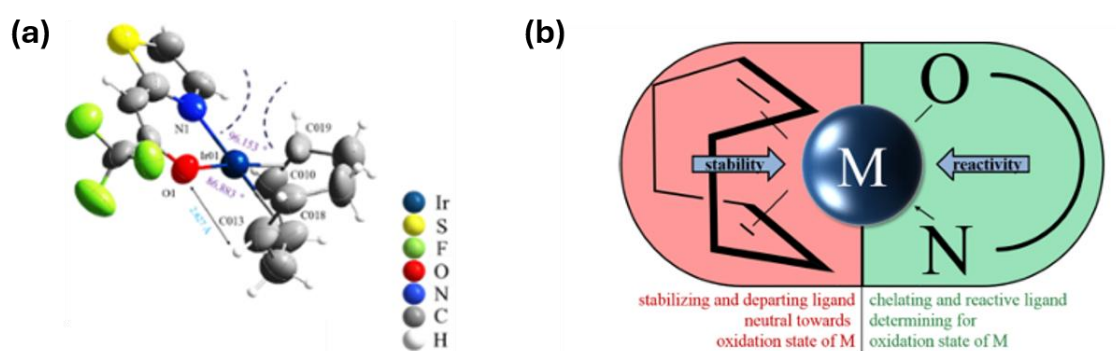


Figure 2.11. (a) Molecular structure of $[(\text{COD})\text{Ir}(\text{ThTFP})]$ and (b) **“Janus-headed” precursor concept** to combine structural stability with electronic. Adapted from Jürgensen *et al.* [32] with permission from American Chemical Society. © American Chemical Society.

Thermal analysis of $[(\text{COD})\text{Ir}(\text{ThTFP})]$ (Figure 2.12) demonstrates the effectiveness of this design strategy. The ligand ThTFP serves as the reactive component and undergoes dissociation at temperatures above approximately 200 °C, thereby promoting film formation. In contrast, the COD ligand contributes to the thermal stability of the precursor during transport to the substrate. As a result, the precursor exhibits suitable volatility and controlled decomposition behavior, enabling the deposition of metallic Ir and IrO_2 thin films with high compositional purity [32]. These findings illustrate how rational ligand design in heteroleptic complexes can be used to independently tune precursor stability and reactivity, providing an effective approach for the development of advanced CVD precursors.

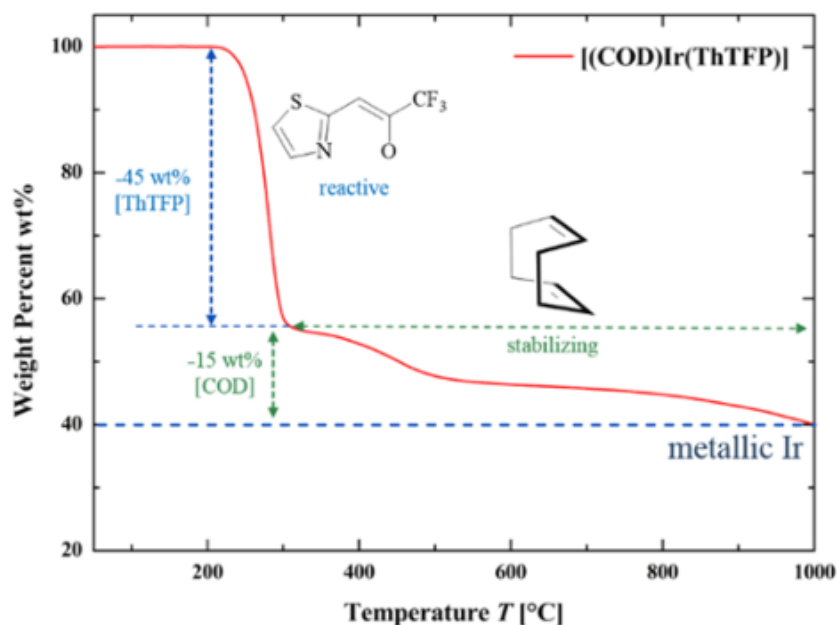


Figure 2.12. Thermogravimetric curve of $[(\text{COD})\text{Ir}(\text{ThTFP})]$ precursor. Reproduced from Jürgensen *et al.* [32] with permission from American Chemical Society. © American Chemical Society.

Graf *et al.* [31] further demonstrated the advantages of heteroleptic precursor design for CVD applications. Based on thermogravimetric analysis (Figure 2.13), the heteroleptic vanadium precursor $[\text{V}(\text{O}^i\text{Bu})_2(\text{PyTFA})_2]$ exhibited significantly greater thermal stability than its homoleptic counterpart, $[\text{V}(\text{O}^i\text{Bu})_4]$, which was developed for VO_2 thin-film deposition. Specifically, $[\text{V}(\text{O}^i\text{Bu})_2(\text{PyTFA})_2]$ remained thermally stable up to temperatures above 160 °C, whereas $[\text{V}(\text{O}^i\text{Bu})_4]$ began to decompose at temperatures above 95 °C. The enhanced thermal stability of the heteroleptic complex was attributed to the incorporation of the PyTFA ligands, which stabilize the coordination environment around the vanadium center while maintaining sufficient volatility for vapor-phase transport. These findings further highlight the importance of ligand design in tailoring precursor properties and demonstrate that heteroleptic complexes can offer a more favorable balance between volatility and thermal stability than analogous homoleptic compounds.

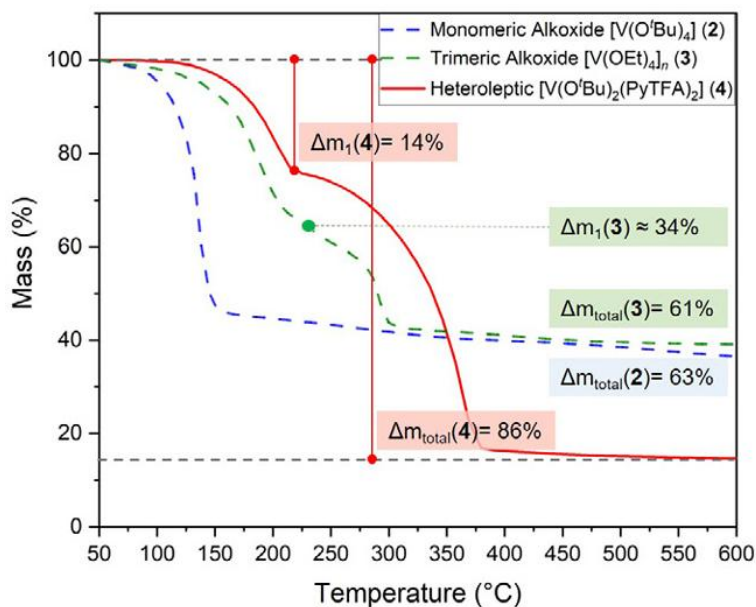


Figure 2.12. Thermogravimetric curve of $[V(O'Bu)_2(PyTFA)_2]$ (red light) and $[V(O'Bu)_4]$ (blue dash) precursors. Adapted from Graf *et al.* [31] with permission from Elsevier. © Elsevier.

2.5. Advancements in Precursor Design Concept

Introduction of perfluoroalkyl groups is a widely developed chemical strategy to improve volatility of precursors, as shown from previous findings from Graf *et al.* [31] and Jürgensen *et al.* [32]. The presence of fluorine atoms in ligands, for example, in the form of $-CF_3$ or perfluoroalkyl chains, can significantly increase volatility by reducing intermolecular forces and increasing the vapor pressure of the compound. In addition, strong C–F bonds provide good thermal stability during the evaporation process, allowing the precursor to be transported to the reaction zone without premature decomposition. Fluorination can also help achieve cleaner decomposition by reducing carbon residues in the film, thereby improving the purity and crystal quality of the formed film [29].

Brückmann *et al.* [33] demonstrated that the incorporation of perfluoroalkyl substituents can significantly influence crystal packing by increasing intermolecular distances between neighboring molecules. Furthermore, the magnitude of this effect depends on the size of the perfluoroalkyl group. This trend was observed in a series of bis(pyridylalkenolato)palladium(II) complexes, namely $Pd[PyCHC(CH_3)O]_2$, $Pd[PyCHC(CF_3)O]_2$, and $Pd[PyCHC(C_2F_5)O]_2$. Among these compounds, $Pd[PyCHC(C_2F_5)O]_2$ exhibited the largest intermolecular separation, followed by $Pd[PyCHC(CF_3)O]_2$, whereas $Pd[PyCHC(CH_3)O]_2$ showed the most compact crystal packing (Figure 2.13). The observed increase in intermolecular distance with increasing fluorination

was accompanied by enhanced volatility, indicating that perfluoroalkyl substituents weaken intermolecular interactions and reduce packing efficiency within the crystal lattice. These findings highlight the beneficial role of fluorination in the design of volatile metal–organic precursors for CVD applications [33].

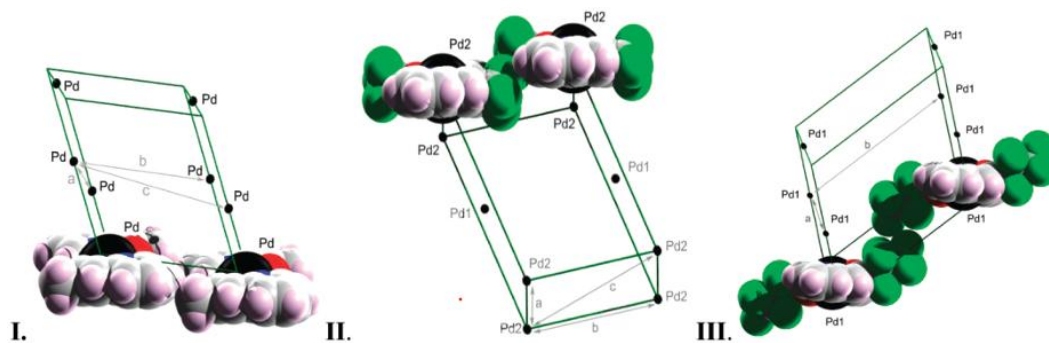


Figure 2.13. Systematic views of intermolecular packing in $\text{Pd}[\text{PyCHC}(\text{CH}_3)\text{O}]_2$ (I), $\text{Pd}[\text{PyCHC}(\text{CF}_3)\text{O}]_2$ (II), and $\text{Pd}[\text{PyCHC}(\text{C}_2\text{F}_5)\text{O}]_2$ (III). Reproduced from Brückmann *et al.* [33] with permission from American Chemical Society. © American Chemical Society.

Besides, $\text{Pd}[\text{PyCHC}(\text{C}_2\text{F}_5)\text{O}]_2$ shows higher volatility and thermal stability than its less-fluorinated analogue, $\text{Pd}[\text{PyCHC}(\text{CF}_3)\text{O}]_2$, as indicated by EI-MS and thermogravimetric analyses (TGA) shown in Figure 2.14.

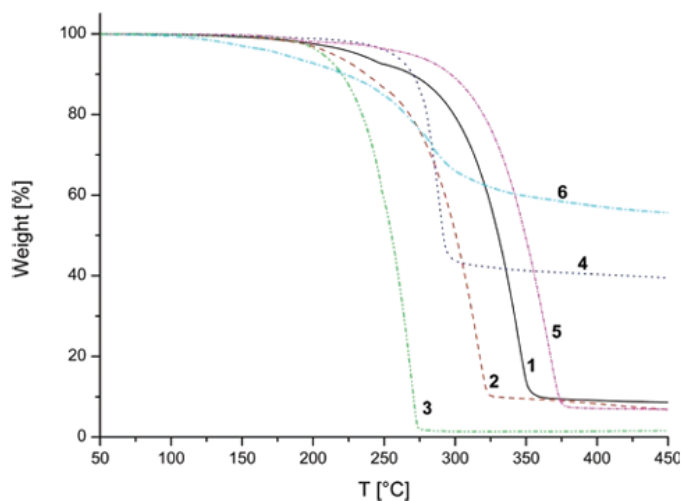


Figure 2.14. TGA profiles of complexes $\text{Pd}[\text{PyCHC}(\text{CH}_3)\text{O}]_2$ (4), $\text{Pd}[\text{PyCHC}(\text{CF}_3)\text{O}]_2$ (1), and $\text{Pd}[\text{PyCHC}(\text{C}_2\text{F}_5)\text{O}]_2$ (3). Reproduce from Brückmann *et al.* [33] with permission from American Chemical Society. © American Chemical Society.

This improvement is attributed to the steric effect of the perfluoroalkyl group, which increases intermolecular distances. EI-MS results also show that Pd–ligand bond cleavage occurs earlier in $\text{Pd}[\text{PyCHC}(\text{CH}_3)\text{O}]_2$, whereas $\text{Pd}[\text{PyCHC}(\text{CF}_3)\text{O}]_2$ first undergoes $-\text{CF}_3$ loss, with metal–

ligand bond cleavage occurring at higher energies [33]. Despite this, π - π stacking from the aromatic ligand may enhance intermolecular interactions in $\text{Pd}[\text{PyCHC}(\text{CF}_3)\text{O}]_2$ (Figure 2.15).

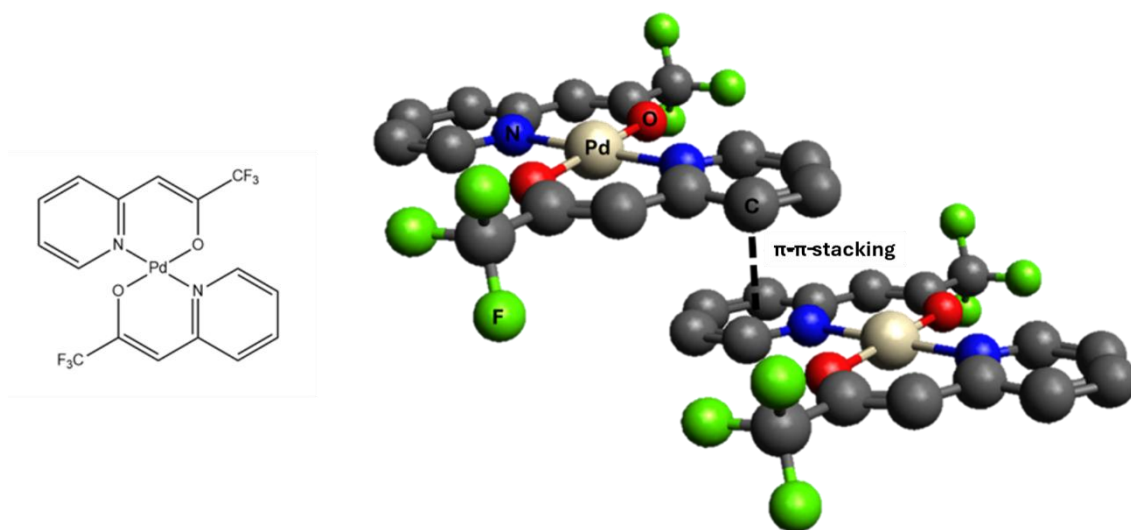


Figure 2.15. Schematic representation of possible π - π stacking between two aromatic rings in $\text{Pd}[\text{PyCHC}(\text{CF}_3)\text{O}]_2$ from Brückmann *et al.* [33].

Meanwhile, fluorinated aliphatic ligands (Figure 2.16), containing non-aromatic carbon chains with $-\text{CF}_3$ or perfluoroalkyl substituents [29, 34, 35], tend to exhibit higher volatility due to structural flexibility and reduced intermolecular forces. The choice between aromatic and aliphatic ligands depends on the need for a balance between volatility, thermal stability, and the desired decomposition mechanism to produce films with optimal purity and crystal quality.

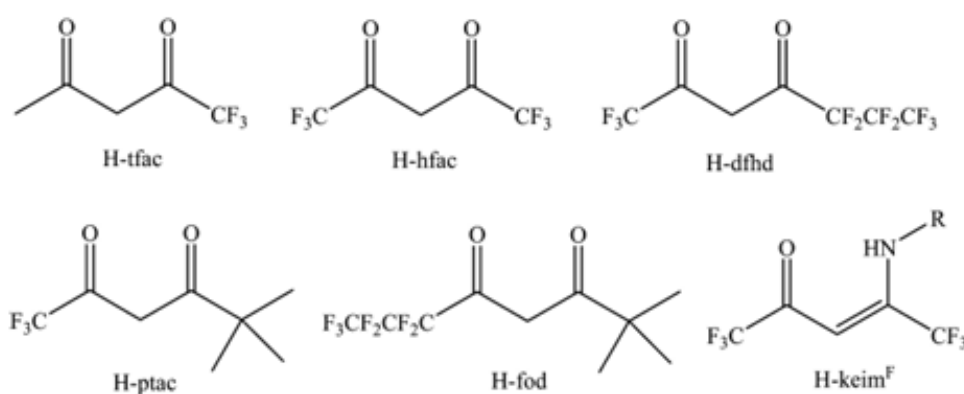


Figure 2.16. Schematic representation of fluorinated aliphatic ligands. Adapted from Mishra and Daniele [29] with permission from American Chemical Society. © American Chemical Society.

Fluorinated β -ketoenamine ligands (β -ketoenaminato ligands upon coordination to a metal center) are particularly attractive for the design of metal-organic precursors because they

possess an aliphatic backbone rather than the aromatic frameworks commonly found in related ligand systems (Figure 2.18). The absence of aromatic rings reduces the molecular weight of the resulting complexes and eliminates the possibility of π – π stacking interactions in the solid state. Consequently, intermolecular interactions are weakened, which can enhance volatility and facilitate vapor-phase transport. In addition, the reduced crystal-packing efficiency associated with these aliphatic ligands may contribute to more favorable thermal properties, making fluorinated β -ketoenaminato complexes promising candidates for MOCVD precursor applications. Heteroleptic metal complexes with fluorinated β -ketoenaminato ligands have shown to possess high thermal stability, adequate volatility, and intramolecular ligand elimination mechanisms [34, 35]. For example, the fluorinated β -ketoenamine ligand (*Z*)-1,1,1-trifluoro-4-((2,2,2-trifluoroethyl)amino)but-3-en-2-one (*H*-TFB-TFEA) has been utilized to synthesize copper- and iridium-containing heteroleptic complexes, which served as efficient low-pressure MOCVD precursors to grow CuO_x , Cu [36] and IrO_x [37] thin films.

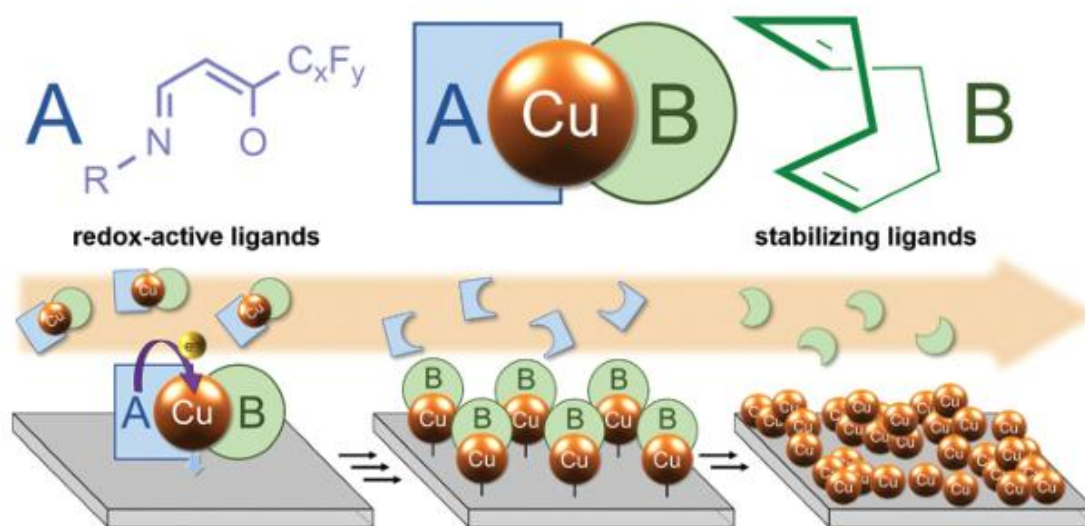


Figure 2.17. Schematic representation of Janus-headed precursor configuration for Cu deposition. Reproduced from Jürgensen *et al.* [36] with permission from Royal Society of Chemistry. © Royal Society of Chemistry.

Similarly, (*Z*)-1,1,1-trifluoro-4-((2-methoxyethyl)amino)but-3-en-2-one (*H*-TFB-MEA) has enabled the preparation of volatile thorium complexes $[\text{Th}(\text{OR})_2(\text{TFB-MEA})_2]$ ($\text{R} = \textit{i}\text{Pr}$, $\textit{t}\text{Bu}$) suitable for ThO_2 thin film deposition via low-pressure MOCVD [38]. Besides, fluorinated β -ketoenamine ligands have shown to possess the ability to act as a clean leaving agent during the thin film deposition process [34–38].

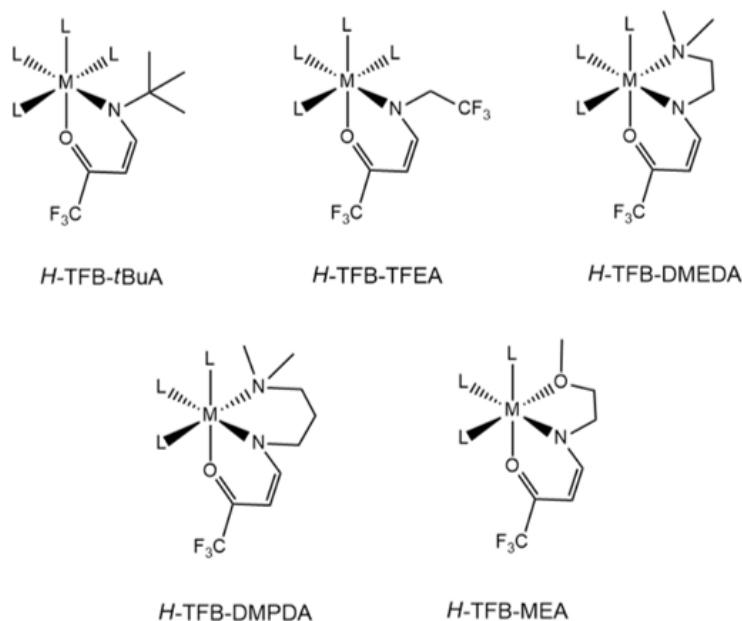


Figure 2.18. Schematic representations of general chemical structures of octahedral metal complexes containing fluorinated β -ketoenamine ligands (Z)-4-(*tert*-butylamino)-1,1,1-trifluorobut-3-en-2-one (*H*-TFB-*t*BuA) [39, 40], (Z)-1,1,1-trifluoro-4-((2,2,2-trifluoroethyl)amino)but-3-en-2-one (*H*-TFB-TFEA) [36, 37], (Z)-4-((2-(dimethylamino)ethyl)amino)-1,1,1-trifluorobut-3-en-2-one (*H*-TFB-DMEDA) [34], (Z)-4-((3-(dimethylamino)propyl)amino)-1,1,1-trifluorobut-3-en-2-one (*H*-TFB-DMPDA) [35], and (Z)-1,1,1-trifluoro-4-((2-methoxyethyl)amino)but-3-en-2-one (*H*-TFB-MEA) [38] (M = metal center). Reproduced from B. O. A. Fauzi, A. Lichtenberg, C. Hegemann, T. Fischer, M. Schmickler, H. Parala, A. Devi and S. Mathur, *RSC Applied Interfaces*, 2026, 3, 706–720 [39]. Licensed under the Creative Commons Attribution 3.0 Unported Licence (CC BY 3.0).

Notably, the fluorinated β -ketoenamine ligand (Z)-4-(*tert*-butylamino)-1,1,1-trifluorobut-3-en-2-one (*H*-TFB-*t*BuA) has previously been investigated in uranium(IV) coordination chemistry, where it afforded a seven-coordinate heteroleptic complex, $[\text{UCl}_2(\text{TFB-}t\text{BuA})_2(\text{THF})]$. However, this uranium-based complex was found to be unsuitable for low-pressure MOCVD applications due to its low volatility and air sensitivity [40].

Based on the studies discussed above, the synthesis of heteroleptic aluminum, gallium, zirconium, and hafnium complexes incorporating fluorinated β -ketoenaminato ligands represents a promising area of research. The combination of heteroleptic precursor design and ligand fluorination offers opportunities to tailor key precursor properties, including volatility, thermal stability, and decomposition behavior. Such characteristics are essential for efficient vapor-phase transport and controlled film growth during MOCVD processes. Consequently, these complexes are attractive candidates as single-source precursors for the deposition of Al-, Ga-, Zr-, and Hf-based thin films and warrant detailed investigation of their molecular structures, thermal properties, and deposition behavior.

3. Syntheses and Characterization of Fluorinated β -Ketoenamine-based Aluminum and Gallium Complexes and Their Application in Deposition of Al_2O_3 , Ga_2O_3 , and $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ Thin Films

The vapor pressure measurements were carried out in collaboration with Marcel Schmickler from the research group of Prof. Dr. Dr. (h.c.) Anjana Devi at the Leibniz Institute for Solid State and Materials Research (IFW Dresden), Dresden, Germany. The grazing-incidence X-ray diffraction (GI-XRD) were carried out in collaboration with Dr. Maria Basso of the Industrial Engineering Department, University of Padova, Padova, Italy. The X-ray photoelectron spectroscopy (XPS) were carried out in collaboration with Dr. Mattia Cattelan of the Industrial Engineering Department, University of Padova, Padova, Italy.

3.1. Scientific Context

$(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ is an ultra-wide bandgap ternary oxide semiconductor formed by alloying aluminum oxide (Al_2O_3) with gallium oxide (Ga_2O_3), most commonly based on the monoclinic β -phase of Ga_2O_3 (commonly called β - Ga_2O_3), and it has emerged as one of the most promising materials for next-generation high-power and deep-ultraviolet (DUV) electronic and optoelectronic devices due to its highly tunable physical properties and exceptional breakdown strength [41-48]. By varying the aluminum composition (x), the bandgap can be continuously engineered from approximately 4.8-4.9 eV for β - Ga_2O_3 up to values exceeding 8 eV as the composition approaches Al_2O_3 , enabling precise control of electronic band structure, conduction band offsets, and optical absorption edges [41-48]. This bandgap tunability makes $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ particularly attractive for heterostructure engineering, where it can serve as a barrier material in Modulation-Doped Field-Effect Transistors (MODFETs), High-Electron-Mobility Transistors (HEMT-like structures), and solar-blind UV photodetectors [41-48]. The material exhibits an exceptionally high theoretical critical electric field (exceeding 8 MV/cm), which translates into very high breakdown voltage capability and superior Baliga's figure of merit compared with conventional wide-bandgap semiconductors such as SiC and GaN, positioning it as a strong candidate for next-generation power electronics including Schottky barrier diodes, MOSFETs, and vertical power devices [41-49].

Additionally, the incorporation of Al increases the bandgap and modifies the dielectric constant, refractive index, and conduction band alignment, allowing the formation of effective electron confinement layers and high-quality insulating barriers [41-48]. Functionally, $(Al_xGa_{1-x})_2O_3$ plays multiple roles: it can act as an active semiconducting channel (at lower Al contents), as a wide-bandgap barrier layer for carrier confinement, as a high-resistivity buffer layer to suppress leakage current, or as a transparent conductive or semi-insulating layer in DUV optoelectronics [41-48]. Its strong absorption in the deep-UV region while remaining transparent in the visible range makes it ideal for solar-blind photodetectors used in flame sensing, missile plume detection, and environmental monitoring [41-48]. From a materials synthesis standpoint, $(Al_xGa_{1-x})_2O_3$ can be fabricated using several advanced thin-film growth techniques, including MOCVD [50, 51], Molecular-Beam Epitaxy (MBE) [41], magnetron sputtering [44, 48], and Pulsed Laser Deposition (PLD) [46]. Among these, MOCVD and MBE are particularly favored for epitaxial growth due to their precise control over composition, thickness, and interface abruptness, which are essential for high-performance heterostructures [41, 50, 51]. In MOCVD processes, metal-organic precursors such as trimethylgallium (TMGa) and trimethylaluminum (TMAI) are introduced along with oxygen sources (e.g., O_2 or H_2O vapor) under carefully controlled temperature and pressure conditions, enabling accurate adjustment of the Al mole fraction through precursor flow ratios [50, 51].

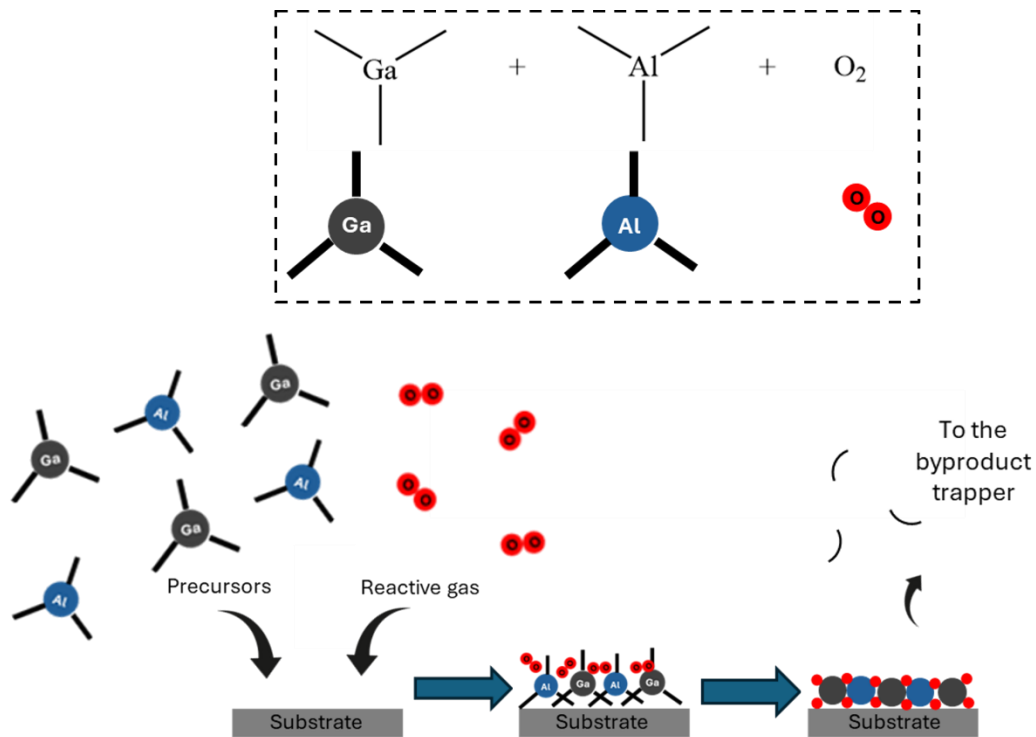


Figure 3.1. Schematic representation of $(Al_xGa_{1-x})_2O_3$ thin films synthesis via MOCVD based on experiment conducted by Bhuiyan *et al.* [51].

Bhuiyan *et al.* [51] reported that CVD deposition using this precursor system at 950 °C ($p = 60$ Torr) resulted in the formation of β -($\text{Al}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ thin films. Interestingly, as the aluminum content in the films increased, the intensity of the characteristic β -($\text{Al}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ diffraction peaks gradually decreased, indicating a reduction in crystallinity. At higher aluminum concentrations, a phase transition from the β -phase to the γ -phase was observed, leading to the formation of γ -($\text{Al}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ (Figure 3.2). These results suggest that increasing aluminum incorporation influences both the crystal structure and phase stability of aluminum gallium oxide, with higher aluminum contents favoring the formation of less-ordered or metastable phases [51].

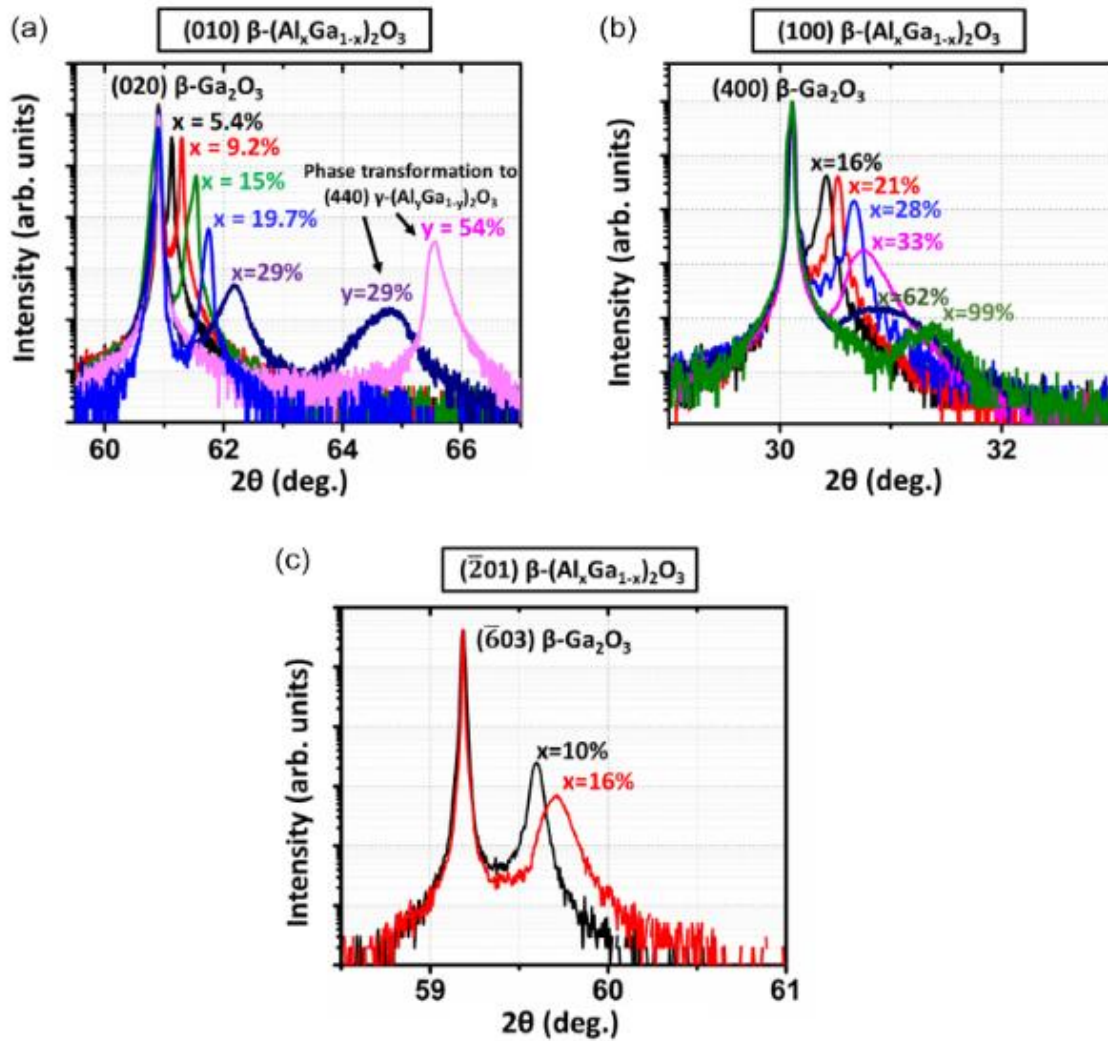


Figure 3.2. The XRD ω - 2θ scan profiles of the (a) (020), (b) (400), and (c) (-603) reflections of β -($\text{Al}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ films grown on (010), (100), and ($\bar{2}01$) β - Ga_2O_3 substrates with Al incorporations up to 29%, 99%, and 16%, respectively. Reproduced from Bhuiyan *et al.* [51] with permission from Wiley. © Wiley.

Growth temperature, oxygen partial pressure, and substrate selection (often β - Ga_2O_3 substrates, sapphire, or SiC) critically influence phase stability, crystalline quality, strain state,

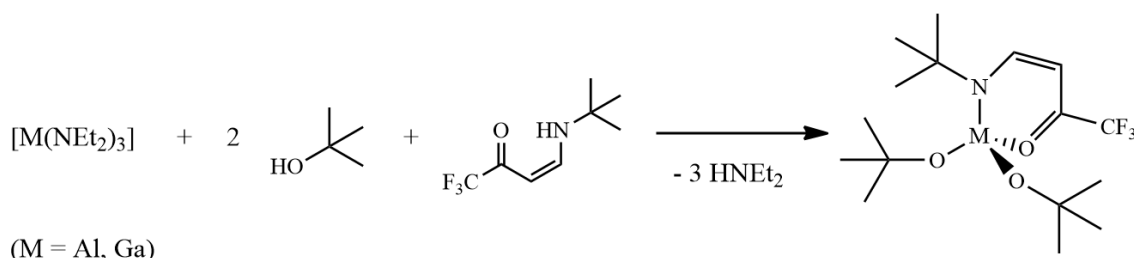
and defect density [50, 51]. However, increasing Al content can introduce challenges such as phase instability, lattice mismatch, and reduced electron mobility due to increased alloy scattering and deeper donor levels, requiring careful optimization of growth parameters [50, 51]. Overall, the combination of ultra-wide bandgap tunability, extremely high breakdown field, chemical and thermal stability, and compatibility with advanced epitaxial growth techniques makes $(Al_xGa_{1-x})_2O_3$ a highly versatile and strategically important material platform for future high-voltage electronics and deep-ultraviolet optoelectronic systems [41-48].

To date, no single-source precursor containing both aluminum and gallium has been reported for the deposition of $(Al_xGa_{1-x})_2O_3$ thin films. In contrast, the individual deposition of Al_2O_3 and Ga_2O_3 has been extensively investigated using a variety of aluminum- and gallium-containing precursors, many of which exist as dimeric species. For example, Veith *et al.* [52] employed the dimeric precursor $(tBuOAlH_2)_2$ for Al_2O_3 deposition, while Fahlman and Barron [53] reported the growth of Al_2O_3 using a precursor system consisting of $AlH_3(NMe_2Et)$ and H_2O in a 1:25 ratio. Similarly, Valet and Hoffman [54] demonstrated the deposition of Ga_2O_3 thin films using $[Ga(O^tBu)_3]_2$, with oxygen serving as both the carrier and reactant gas.

Despite these advances, the direct deposition of mixed aluminum gallium oxide remains comparatively unexplored. In particular, the use of structurally related monomeric precursors offers an attractive strategy for achieving controlled incorporation of both metals during film growth. The development of isostructural aluminum and gallium complexes with comparable coordination environments may facilitate more predictable vapor-phase transport and deposition behavior than conventional dimeric systems. Consequently, the deposition of $(Al_xGa_{1-x})_2O_3$ through the co-evaporation of monomeric aluminum and gallium precursors represents a promising and scientifically interesting approach, providing an opportunity to investigate the relationship between precursor design, vapor-phase transport, and mixed-metal oxide film formation.

3.2. Syntheses and Characterization of $[Al(TFB-tBuA)(O^tBu)_2]$ and $[Ga(TFB-tBuA)(O^tBu)_2]$

The reaction of one equivalent of $[M(NEt_2)_3]$ ($M = Al$ or Ga) with two equivalents of *tert*-butyl alcohol and one equivalents of *H*-TFB-*t*BuA ligand (Scheme 3.1) at room temperature resulted in the formation of needle-like colorless crystalline compounds, $[Al(TFB-tBuA)(O^tBu)_2]$ and $[Ga(TFB-tBuA)(O^tBu)_2]$ (Scheme 3.1), which could be purified by sublimation at 85-105 °C (Figure 3.3a and b) under 1 mbar, respectively.



Scheme 3.1. Reaction scheme for the synthesis of $[M(TFB-tBuA)(O^tBu)_2]$ (M = Al, Ga).

The diethylamido ligands in $[M(NEt_2)_3]$ (M = Al or Ga) were replaced by two *tert*-butoxo ligands via proton transfer from *tert*-butyl alcohol, releasing two equivalents of diethylamine. Subsequent addition of one equivalent of *H*-TFB-*t*BuA ligand to the intermediate mono(diethylamido)bis(*tert*-butoxo)metal complex led to further substitution of the remaining diethylamido ligands. The substitution of all three diethylamido ligands was driven by the oxygen atom from *tert*-butoxo ligand because oxygen is a stronger electron donor than nitrogen, and by the propensity to increase the coordination number of the complexes by the chelating β -ketoenamine framework ($N^{\wedge}O$) of TFB-*t*BuA, forming thermodynamically more stable complexes with strongly coordinating *tert*-butoxo and chelating TFB-*t*BuA ligands.

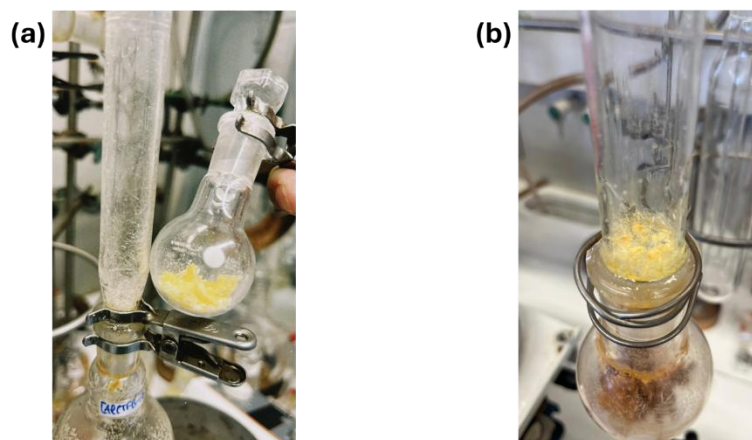


Figure 3.3. Sublimates of (a) $[Al(TFB-tBuA)(O^tBu)_2]$ and (b) $[Ga(TFB-tBuA)(O^tBu)_2]$.

While $[M(NEt_2)_3]$ (M = Al or Ga) can also be used as a precursor for aluminum oxide and gallium oxide deposition, they need a secondary oxygen source. Consequently, the use of $[M(NEt_2)_3]$ does not fully comply with the SSP concept, as the deposition of metal oxides requires an external oxygen source such as O_2 or O_3 . Therefore, mixed-ligand compounds were developed in this work.

$[Al(TFB-tBuA)(O^tBu)_2]$ and $[Ga(TFB-tBuA)(O^tBu)_2]$, both compounds are crystalline solids with sufficient volatility to allow sublimation under reduced pressure. Their solid-state nature enables accurate weighing, straightforward handling, and controlled delivery into the

deposition chamber, resulting in improved consistency and reproducibility during thin film growth. Importantly, these complexes incorporate oxygen atoms within their molecular framework, eliminating the need for an additional oxidizing co-reactant during MOCVD of metal oxides. These observations highlight that by tailoring the ligand framework, it is possible to modulate not only thermal stability and volatility but also the practical handling characteristics of the metal complexes. Consequently, rational ligand design emerges as a key strategy for developing robust, manageable, and reproducible precursors for advanced thin-film deposition processes.

The solution behavior of $[Al(TFB-tBuA)(O^tBu)_2]$ and $[Ga(TFB-tBuA)(O^tBu)_2]$ was characterized using ^1H nuclear magnetic resonance (NMR) spectroscopy (Figure 3.4). For $[Al(TFB-tBuA)(O^tBu)_2]$, a singlet (s) at 1.14 ppm, integrating for nine protons, was attributed to the three methyl groups of one TFB-*t*BuA ligand. One doublet to doublet (dd) at 5.16-5.18 ppm and one doublet (d) at 6.90-6.92 ppm were assigned to two protons at C5 and C6 of one TFB-*t*BuA ligand, respectively, with a 1:1 proton ratio. Additionally, two *tert*-butoxo ligands exhibited a singlet (s) at 1.41 ppm, corresponding to eighteen protons from their six methyl groups. The ^1H NMR spectrum of $[Ga(TFB-tBuA)(O^tBu)_2]$ showed similarities to those of $[Al(TFB-tBuA)(O^tBu)_2]$. The three methyl groups in the TFB-*t*BuA ligand were identified by a singlet (s) at 1.10 ppm, which integrated to nine protons. Two chemically differentiable doublets to doublets (dd) with a 1:1 ratio, at 5.06-5.08 ppm and 6.80-6.83 ppm, respectively, represented two protons at C5 and C6 of one TFB-*t*BuA ligand. The six methyl groups of two *tert*-butoxo ligands were also linked to a singlet (s) at 1.46 ppm, which integrated for eighteen protons.

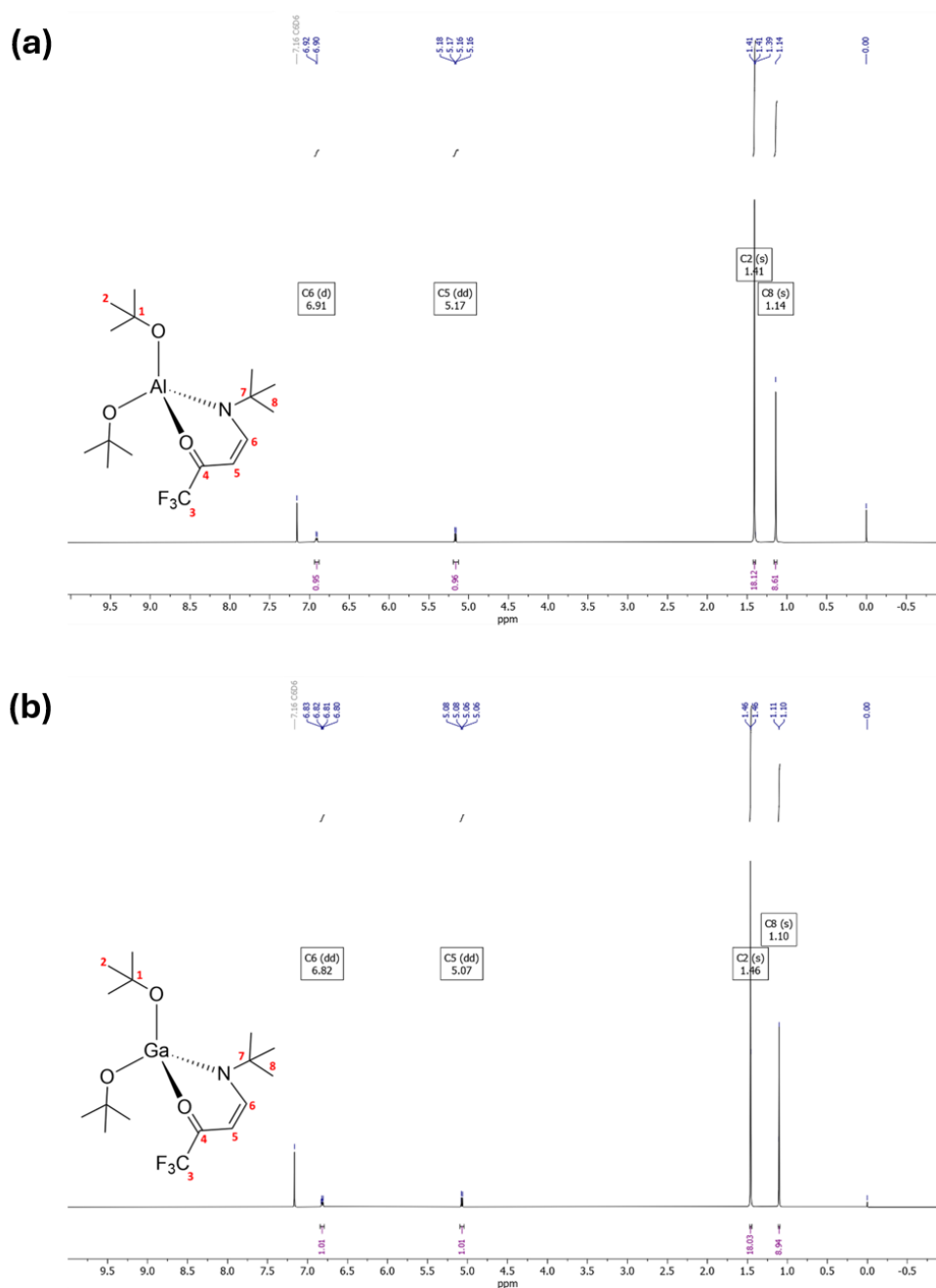


Figure 3.4. ^1H NMR spectra of (a) $[Al(TFB-tBuA)(O'Bu)_2]$ and (b) $[Ga(TFB-tBuA)(O'Bu)_2]$.

The ^{13}C $\{^1H, ^{19}F\}$ NMR spectra of $[Al(TFB-tBuA)(O'Bu)_2]$ and $[Ga(TFB-tBuA)(O'Bu)_2]$ (Figure 3.5) each exhibited eight distinct resonances, consistent with the carbon environments in the molecular structures, allowing unambiguous assignment of all carbon atoms.

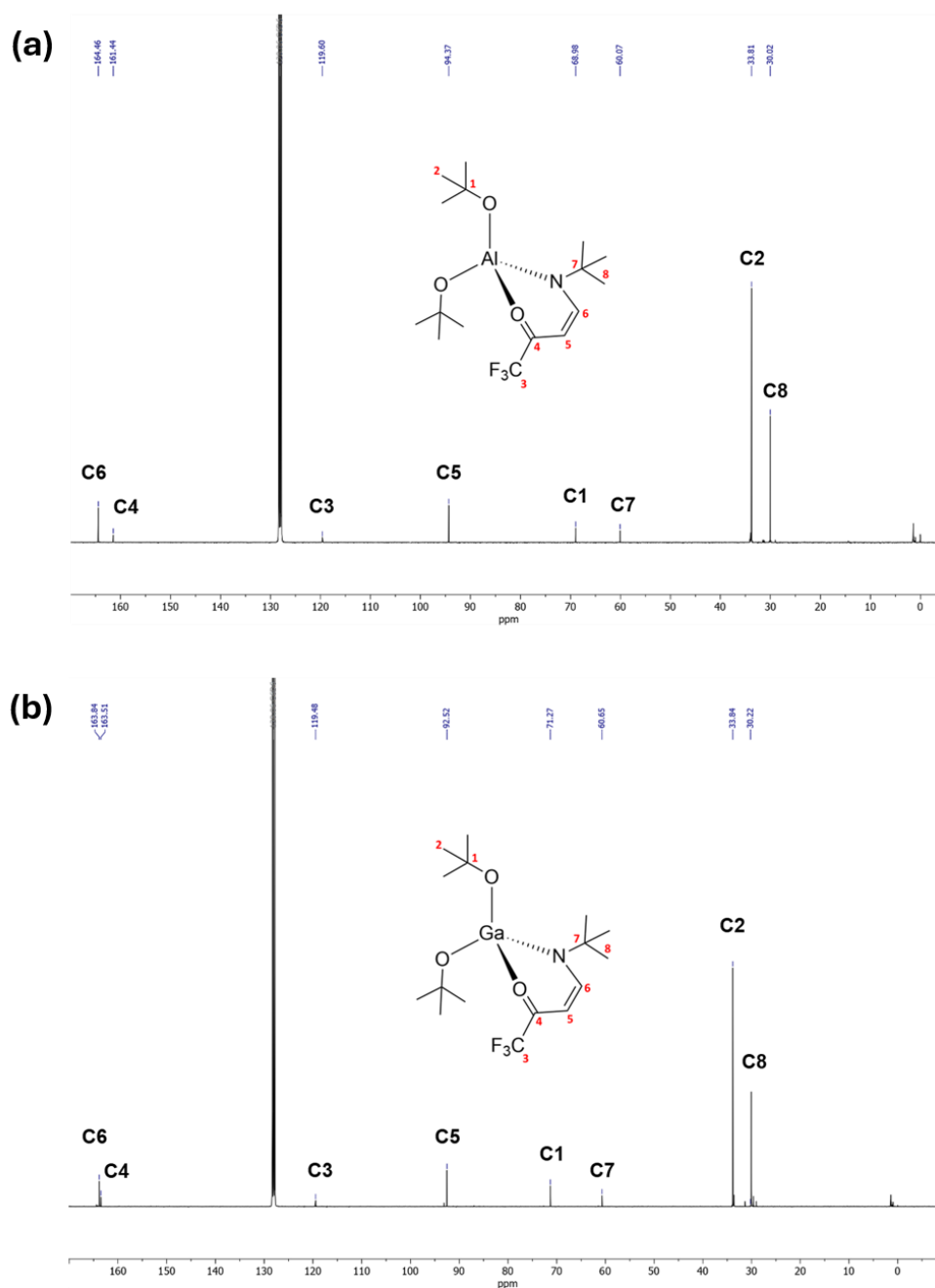


Figure 3.5. ^{13}C { ^1H , ^{19}F } NMR spectra of (a) $[Al(TFB-tBuA)(O'Bu)_2]$ and (b) $[Ga(TFB-tBuA)(O'Bu)_2]$.

The ^{19}F NMR spectra (Figure 3.6) confirmed the presence of the trifluoromethyl group, showing characteristic singlets at -74.48 ppm for $[Al(TFB-tBuA)(O'Bu)_2]$ and -74.61 ppm for $[Ga(TFB-tBuA)(O'Bu)_2]$. CHNS elemental analysis further confirmed the proposed molecular compositions, as the experimentally determined values were in good agreement with the calculated percentages derived from the respective molecular formulas. Together with the spectroscopic results, these data support the structural assignment and indicate a satisfactory level of purity for both precursors.

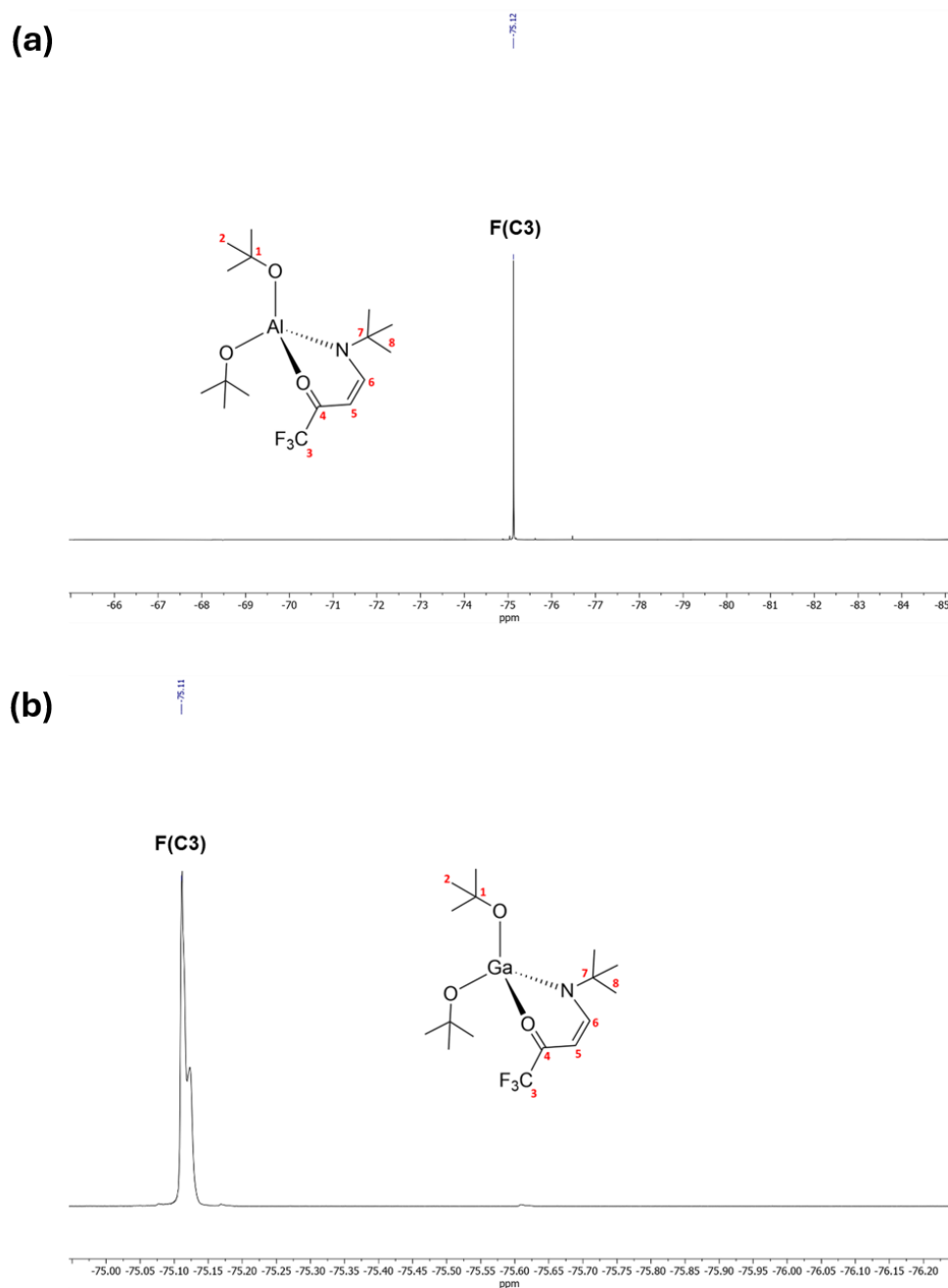


Figure 3.6. ^{19}F NMR spectra of (a) $[Al(TFB-tBuA)(O'Bu)_2]$ and (b) $[Ga(TFB-tBuA)(O'Bu)_2]$.

Single-crystal X-ray diffraction (SC-XRD) analyses revealed that $[Al(TFB-tBuA)(O'Bu)_2]$ crystallizes in the triclinic space group $P\bar{1}$, while $[Ga(TFB-tBuA)(O'Bu)_2]$ crystallizes in the monoclinic space group $P2_1/n$. The SC-XRD results show that the solid-state structure agrees well with the coordination environment predicted from the ^1H NMR data. Despite possessing different space groups, both complexes are isostructural and exhibit a similar coordination environment around the metal centers (Figure 3.7a and b). In both complexes, the metal atom adopts a distorted tetrahedral geometry.

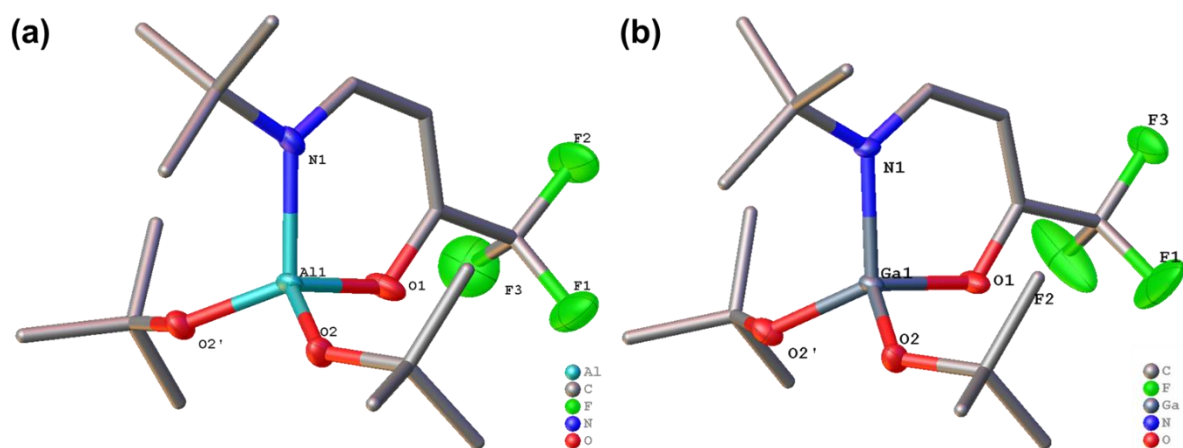


Figure 3.7. The single crystal X-ray crystal structures of (a) $[\text{Al}(\text{TFB-}t\text{BuA})(\text{O}'\text{Bu})_2]$ and (b) $[\text{Ga}(\text{TFB-}t\text{BuA})(\text{O}'\text{Bu})_2]$ possessing C_2 symmetry. Hydrogen atoms are omitted for clarity.

The Al–O and Ga–O bond lengths involving the TFB-*t*BuA ligands fall within the ranges of 1.786(7)–1.8843(19) Å (Table 3.1), while the corresponding Al–N and Ga–N bond distances lie between 1.941(8) and 1.970(2) Å. These values are consistent with those reported for related heteroleptic Group 13 metal complexes. For example, in $[(\mu\text{-OCH}_2\text{CH}_2\text{OPh})\text{Al}(\text{Bu}^i)_2]_2$, Al–O bond lengths range from 1.828(2) to 1.864(2) Å [55], whereas in $[\text{Ga}(\text{O}'\text{Bu})_3(\text{HNMe}_2)]$, the Ga–O bond length is approximately 1.81 Å [54]. Similarly, in $[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph}_2)(\text{N}'\text{Bu})]\text{MCl}_2$ (M = Al, Ga), the M–N bond lengths are 1.862(3)–1.877(3) Å for Al–N and 1.909(3)–1.941(3) Å for Ga–N [56], indicating comparable metal–ligand interactions.

The M–O bonds associated with the tert-butoxide ligands are slightly shorter, ranging from 1.699(7) to 1.7989(19) Å (Table 3.1), which can be attributed to the stronger σ -donor character of the alkoxide ligand compared to the β -ketoenaminato donor set. Overall, the molecular structures of $[\text{Al}(\text{TFB-}t\text{BuA})(\text{O}'\text{Bu})_2]$ and $[\text{Ga}(\text{TFB-}t\text{BuA})(\text{O}'\text{Bu})_2]$ are remarkably similar, exhibiting nearly identical coordination geometries and bonding parameters. This similarity is expected given the closely related chemical properties and valence electron configurations of Al^{3+} and Ga^{3+} . The observed structural equivalence suggests that substitution of aluminum by gallium has only a minor influence on the coordination environment, highlighting the robustness of this heteroleptic β -ketoenaminato/alkoxide framework across Group 13 metals.

Table 3.1. Bond lengths [$\text{\AA}$] for $[\text{Al}(\text{TFB-}i\text{BuA})(\text{O}'\text{Bu})_2]$ and $[\text{Ga}(\text{TFB-}i\text{BuA})(\text{O}'\text{Bu})_2]$.

	$[\text{Al}(\text{TFB-}i\text{BuA})(\text{O}'\text{Bu})_2]$	$[\text{Ga}(\text{TFB-}i\text{BuA})(\text{O}'\text{Bu})_2]$
M–O1 [$\text{\AA}$]	1.786(7)	1.8843(19)
M–O2 [$\text{\AA}$]	1.706(7)	1.7989(19)
M–O2' [$\text{\AA}$]	1.699(7)	1.7959(18)
M–N1 [$\text{\AA}$]	1.941(8)	1.970(2)

3.3. Thermal Analyses of $[\text{Al}(\text{TFB-}i\text{BuA})(\text{O}'\text{Bu})_2]$ and $[\text{Ga}(\text{TFB-}i\text{BuA})(\text{O}'\text{Bu})_2]$, Vapor Pressure of $[\text{Al}(\text{TFB-}i\text{BuA})(\text{O}'\text{Bu})_2]$ and $[\text{Ga}(\text{TFB-}i\text{BuA})(\text{O}'\text{Bu})_2]$ and Their Comparison to $[\text{Al}(\text{O}'\text{Bu})_3]_2$ and $[\text{Ga}(\text{O}'\text{Bu})_3]_2$

Preliminary thermal evaluation of $[\text{Al}(\text{TFB-}i\text{BuA})(\text{O}'\text{Bu})_2]$ and $[\text{Ga}(\text{TFB-}i\text{BuA})(\text{O}'\text{Bu})_2]$ was carried out by sublimation under reduced pressure ($p \approx 1$ mbar) using a Schlenk line setup described in the previous chapter. Both complexes began to sublime at temperatures above 90 °C, forming yellowish crystalline deposits on the cold finger (Figure 3.2). This behavior demonstrates sufficient volatility and thermal robustness (stable beyond 100 °C), indicating their suitability as precursors for MOCVD processes. The thermogravimetric (TG) analyses under nitrogen atmosphere were performed to assess the potential decomposition products. The TG data revealed a major decomposition stops near 250–260 °C, resulting in ~74–77% mass loss of $[\text{Al}(\text{TFB-}i\text{BuA})(\text{O}'\text{Bu})_2]$ and $[\text{Ga}(\text{TFB-}i\text{BuA})(\text{O}'\text{Bu})_2]$. Residual masses at this stage were 23.6% for $[\text{Al}(\text{TFB-}i\text{BuA})(\text{O}'\text{Bu})_2]$ (Figure 3.8a) and 25.68% for $[\text{Ga}(\text{TFB-}i\text{BuA})(\text{O}'\text{Bu})_2]$ at around 260 °C (Figure 3.8b), in reasonable agreement with theoretical oxide contents (Al_2O_3 : 13.87%; Ga_2O_3 : 22.85%), with slight deviations attributed to incomplete ligand decomposition or volatilization of metal intermediates. Final residue of $[\text{Al}(\text{TFB-}i\text{BuA})(\text{O}'\text{Bu})_2]$ at 550 °C was 15.9%, which is still reasonable for Al_2O_3 with some residue remains in the metal oxide. In contrast, the final residue of $[\text{Ga}(\text{TFB-}i\text{BuA})(\text{O}'\text{Bu})_2]$ at 550 °C was 17.4%, which is lower than the theoretical oxide yields, likely due to partial volatilization of the samples.

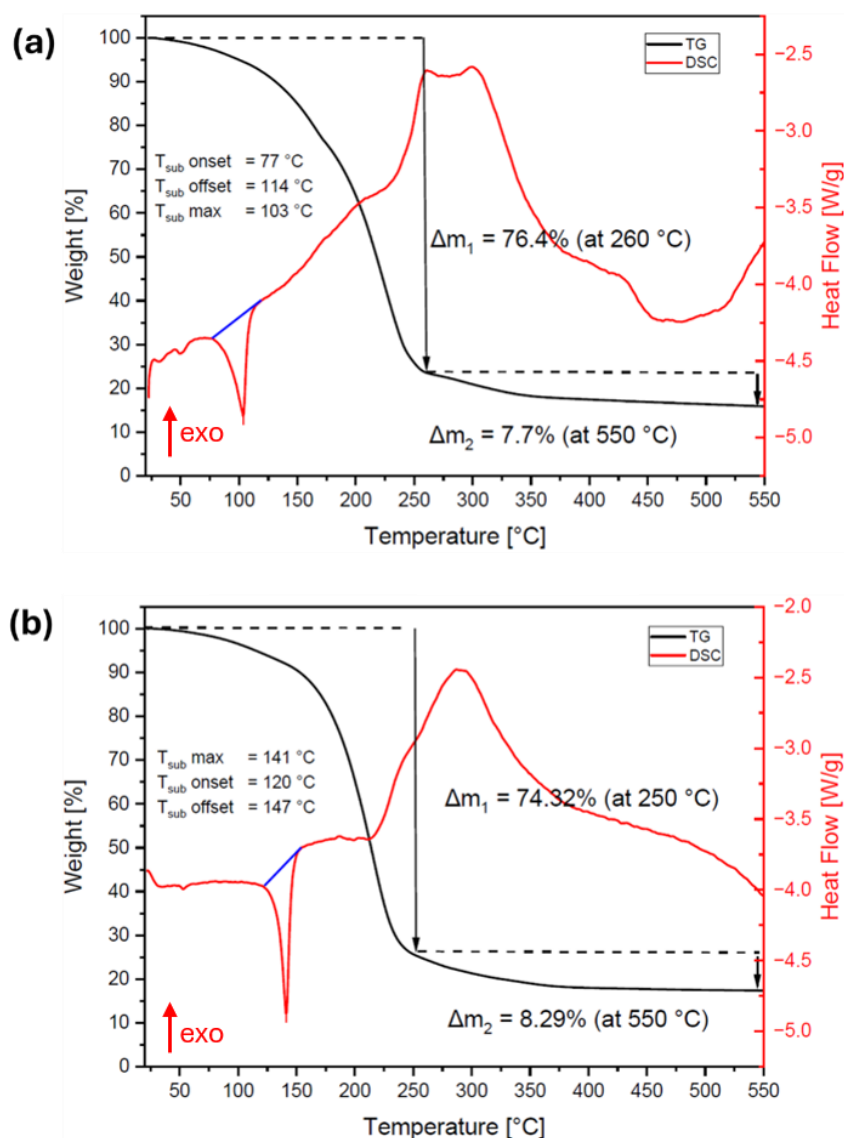


Figure 3.8. TG (black) and DSC (red) profiles of (a) $[Al(TFB-tBuA)(O'Bu)_2]$ and (b) $[Ga(TFB-tBuA)(O'Bu)_2]$ under N_2 flow at atmospheric pressure from 20-550 °C.

Differential scanning calorimetry (DSC) was used to examine the thermal behavior of the complexes and to identify thermal events associated with volatilization. For the aluminum complex $[Al(TFB-tBuA)(O'Bu)_2]$, the DSC curve shows a pronounced endothermic event with a maximum at approximately 103 °C, beginning at about 77 °C and finishing near 114 °C (Figure 3.8a). The broad endothermic signal indicates a gradual sublimation process as the vapor pressure of the compound increases with temperature. This behavior is consistent with the volatilization of a molecular solid and occurs prior to any indication of thermal decomposition. A similar endothermic event is observed for the gallium analogue $[Ga(TFB-tBuA)(O'Bu)_2]$, but it is shifted to higher temperatures. In this case, the DSC peak maximum occurs at approximately 141 °C, with the sublimation process taking place between about 120

and 147 °C (Figure 3.8b). Since the two complexes are isostructural and possess identical ligand environments, substantial differences in intermolecular interactions within the crystal lattice are unlikely. The higher sublimation temperature observed for the gallium compound is therefore most plausibly attributed to its larger molecular mass and the resulting lower volatility compared to the aluminum analogue. Consequently, the DSC data indicate that both complexes undergo endothermic sublimation, while the heavier gallium derivative requires higher temperatures to reach comparable vapor pressures. Overall, the two precursors exhibit broadly similar thermal behavior, consistent with their closely related molecular structures. Nevertheless, the relatively large difference in sublimation temperatures may present challenges for the co-deposition of $(Al_xGa_{1-x})_2O_3$ films using $[Al(TFB-tBuA)(O'Bu)_2]$ and $[Ga(TFB-tBuA)(O'Bu)_2]$ in MOCVD processes. The mismatch in volatility could lead to differences in precursor delivery rates, which may complicate precise control over the Al:Ga ratio during film growth.

Vapor pressure measurements of $[Al(TFB-tBuA)(O'Bu)_2]$, $[Ga(TFB-tBuA)(O'Bu)_2]$, $[Al(O'Bu)_3]_2$, and $[Ga(O'Bu)_3]_2$ were carried out to evaluate their volatility and suitability as precursors for MOCVD processes. The measurements were initiated at 40 °C, with the temperature increased stepwise by 10 °C at each stage (Table 3.2). These experiments were intended to provide a better understanding of the evaporation behavior of the precursors and their compatibility for co-deposition processes.

Table 3.2. Vapor pressure measurement results of $[Al(TFB-tBuA)(O'Bu)_2]$, $[Ga(TFB-tBuA)(O'Bu)_2]$, $[Al(O'Bu)_3]_2$, and $[Ga(O'Bu)_3]_2$.

Sample Name	Temperature [°C]	Vapor Pressure [Pa]	Mass Loss [mg min ⁻¹]	Consumption Time [min]
$[Al(TFB-tBuA)(O'Bu)_2]$	40	1.4882×10^{-1}	3.0967×10^{-4}	67
	50	6.3011×10^{-1}	1.2907×10^{-3}	63
	60	2.0552	4.1462×10^{-3}	75
	70	6.0239	1.1974×10^{-2}	60
	80	37.268	7.3026×10^{-2}	53
	90	106.96	2.0667×10^{-1}	12
$[Ga(TFB-tBuA)(O'Bu)_2]$	60	2.4385×10^{-1}	5.1979×10^{-4}	46
	70	8.5274×10^{-1}	1.7910×10^{-3}	60
	80	3.7972	7.8615×10^{-3}	117
	90	16.467	3.3619×10^{-2}	146
	100	59.076	1.1899×10^{-1}	65
$[Al(O'Bu)_3]_2$	60	8.1405×10^{-2}	1.3530×10^{-4}	41
	70	3.7787×10^{-1}	6.1883×10^{-4}	49
	80	1.5189	2.4519×10^{-3}	150
	90	5.2285	8.3234×10^{-3}	149
	100	15.454	2.4271×10^{-2}	159
	110	41.013	6.3562×10^{-2}	82
$[Ga(O'Bu)_3]_2$	50	5.6431×10^{-2}	1.0307×10^{-4}	44
	60	1.3311×10^{-1}	2.3945×10^{-4}	85
	70	3.2990×10^{-1}	5.8474×10^{-4}	77
	80	5.2122×10^{-1}	9.1067×10^{-4}	116
	90	1.8186	3.1333×10^{-3}	166
	100	5.9923	1.0185×10^{-2}	134
	110	24.981	4.1903×10^{-2}	93

Among the investigated compounds, **[Al(TFB-*t*BuA)(O'*Bu*)₂]** exhibited the highest volatility. At 70 °C, this precursor showed a vapor pressure of 6.0239 Pa (6.0239×10^{-2} mbar) together with an evaporation rate of 1.1974×10^{-2} mg min⁻¹. In contrast, **[Ga(TFB-*t*BuA)(O'*Bu*)₂]** displayed a significantly lower vapor pressure of 0.85274 Pa (8.5274×10^{-3} mbar) and a lower evaporation rate of 1.791×10^{-3} mg min⁻¹ at the same temperature. These differences clearly indicate that the aluminum precursor evaporates much more readily than the gallium analogue under identical conditions. From these results, it can be inferred that direct co-sublimation of **[Al(TFB-*t*BuA)(O'*Bu*)₂]** and **[Ga(TFB-*t*BuA)(O'*Bu*)₂]** at the same precursor temperature would likely result in the deposition of $(Al_xGa_{1-x})_2O_3$ films with a significantly higher aluminum content relative to gallium. In other words, the difference in precursor volatility may strongly influence the final film stoichiometry during co-deposition processes.

This interpretation is further supported by analysis of the vapor pressure data using the Clausius-Clapeyron equation. The calculated sublimation enthalpy for **[Al(TFB-*t*BuA)(O'*Bu*)₂]** was determined to be 124.6 kJ mol⁻¹ (Figure 3.9a), whereas **[Ga(TFB-*t*BuA)(O'*Bu*)₂]** exhibited a higher value of 143.9 kJ mol⁻¹ (Figure 3.9b). The lower sublimation enthalpy of the aluminum precursor indicates that less thermal energy is required for sublimation, explaining its substantially higher vapor pressure and evaporation rate at comparable temperatures. These observations are particularly interesting because both compounds possess very similar molecular structures and ligand environments. Nevertheless, they exhibit markedly different thermal and vaporization characteristics. This demonstrates that even subtle differences in the metal center can significantly affect intermolecular interactions, sublimation behavior, and precursor transport properties. Such differences are highly important in dual-precursor MOCVD processes, where achieving precise stoichiometric control depends strongly on matching the volatility and vapor transport characteristics of the individual precursors.

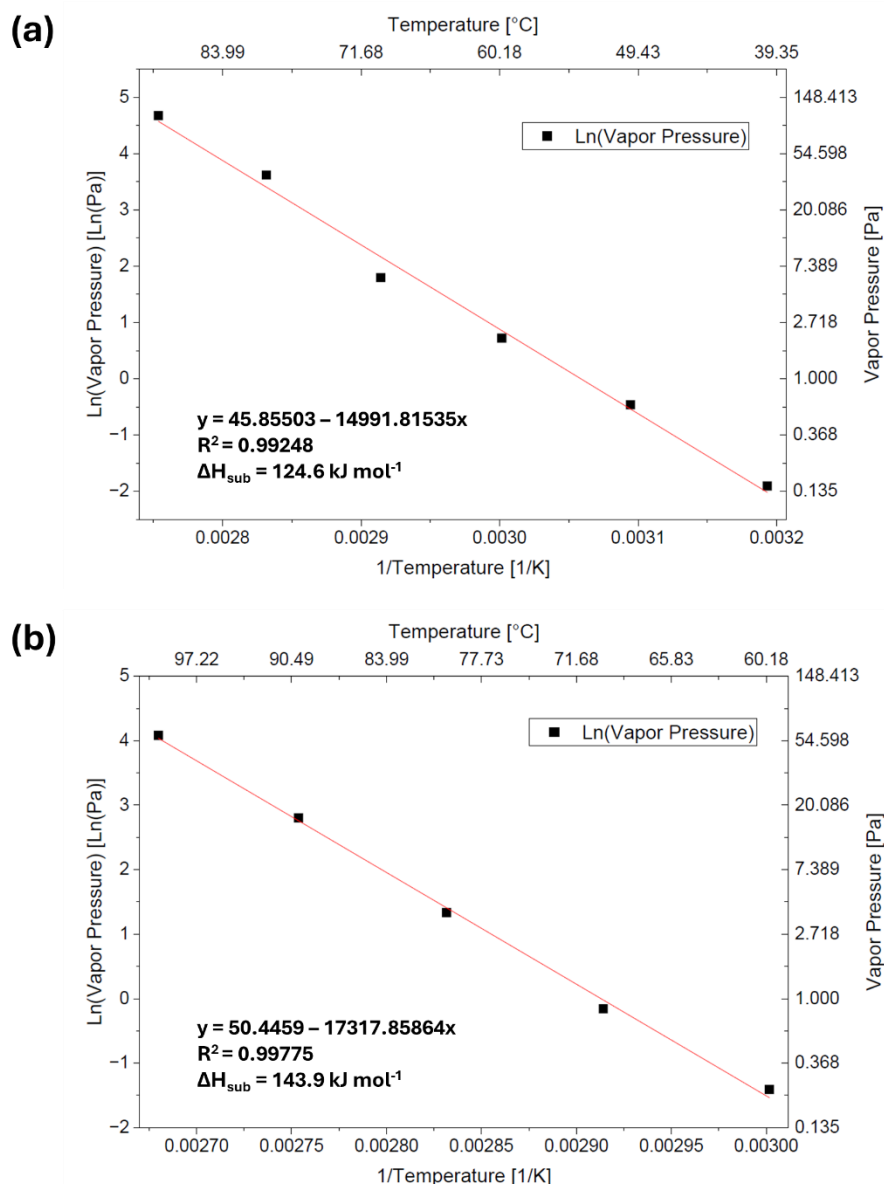


Figure 3.9. Vapor pressure integration analyses of (a) $[Al(TFB-tBuA)(O'Bu)_2]$ and (b) $[Ga(TFB-tBuA)_2(O'Bu)_2]$ based on Clausius-Clapeyron relationship, $\ln(P) = A - B/T$.

In contrast to the fluorinated β -ketoenaminato derivatives, the conventional alkoxide precursors $[Al(O'Bu)_3]_2$ and $[Ga(O'Bu)_3]_2$ exhibit relatively similar vapor pressures at 70 °C, with values of 3.7787×10^{-1} Pa and 3.2990×10^{-1} Pa, respectively. The comparable vapor pressures indicate that both compounds possess closely matched thermodynamic sublimation characteristics, which is advantageous for co-deposition processes targeting homogeneous mixed-metal oxide deposition. However, despite this apparent compatibility, both precursors display relatively low sublimation rates, only on the order of 5 to $6 \times 10^{-4} \text{ mg min}^{-1}$, indicating limited vapor flux generation under low-temperature conditions. Thermodynamic analysis based on the Clausius-Clapeyron relationship further supports these observations. The

sublimation enthalpy of $[Al(O'Bu)_3]_2$ was determined to be $132.2 \text{ kJ mol}^{-1}$ (Figure 3.10a), exceeding that of $[Al(TFB-tBuA)(O'Bu)_2]$, whereas $[Ga(O'Bu)_3]_2$ exhibits a lower sublimation enthalpy of $100.8 \text{ kJ mol}^{-1}$ (Figure 3.10b) compared to $[Ga(TFB-tBuA)(O'Bu)_2]$. These results demonstrate that incorporation of the TFB-*t*BuA ligand substantially modifies the intermolecular interactions and volatilization behavior of the parent alkoxide complexes.

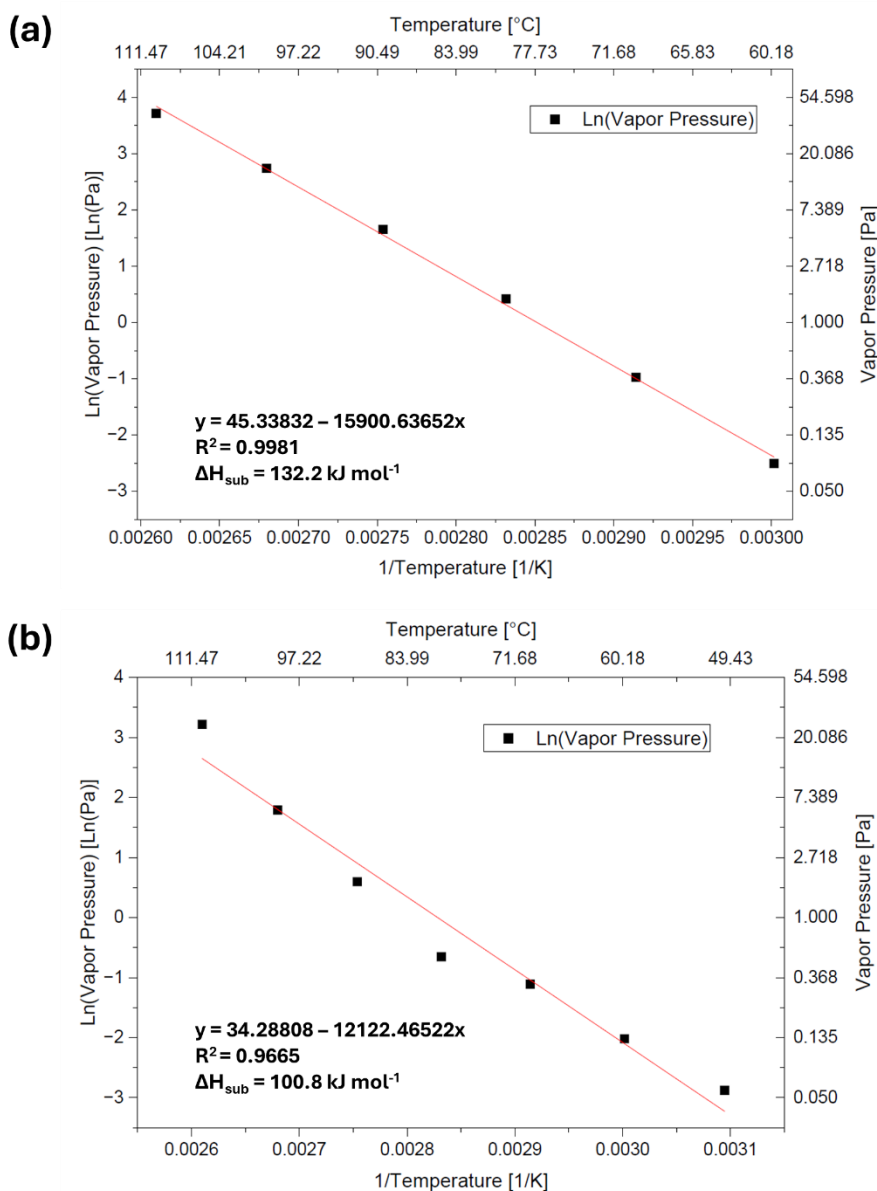


Figure 3.10. Vapor pressure integration analyses of (a) $[Al(O'Bu)_3]_2$ and (b) $[Ga(O'Bu)_3]_2$ based on Clausius-Clapeyron relationship, $\ln(P) = A - B/T$.

Low evaporation rates of $[Al(O'Bu)_3]_2$ and $[Ga(O'Bu)_3]_2$ suggest that they are less suitable for MOCVD processes operated at relatively low precursor temperatures. Efficient MOCVD requires sufficient precursor vapor flux to maintain stable mass transport and continuous film growth under reduced-pressure conditions. Therefore, limited sublimation

kinetics may restrict deposition efficiency and process controllability. The derivatization strategy employing the TFB-*t*BuA ligand successfully enhances the volatility and transport behavior of the resulting heteroleptic complexes. In particular, the TFB-*t*BuA ligand likely reduces intermolecular aggregation and modifies crystal-packing interactions, thereby facilitating sublimation at lower temperatures. Consequently, $[Al(TFB-tBuA)(O^tBu)_2]$ and $[Ga(TFB-tBuA)(O^tBu)_2]$ exhibit improved suitability as molecular precursors for MOCVD, enabling vapor-phase transport and thin film deposition under comparatively mild thermal conditions.

3.4. Deposition of Al_2O_3 and Ga_2O_3 Films Using $[Al(TFB-tBuA)(O^tBu)_2]$, $[Ga(TFB-tBuA)(O^tBu)_2]$, $[Al(O^tBu)_3]_2$, and $[Ga(O^tBu)_3]_2$ Precursors

$[Al(TFB-tBuA)(O^tBu)_2]$ and $[Ga(TFB-tBuA)(O^tBu)_2]$ were utilized as SSPs for the deposition of aluminum oxide, gallium oxide, and aluminum gallium oxide thin films via MOCVD under reduced pressure ($p \approx 10^{-2}$ mbar), without the use of an external oxidizing co-reactant such as O_2 . The precursor reservoirs were maintained at 70 °C to ensure sufficient vapor delivery. The deposition temperatures were maintained at 600 °C. Separate depositions of aluminum oxide and gallium oxide performed for 2 h resulted in precursor consumptions of 0.21 g for $[Al(TFB-tBuA)(O^tBu)_2]$ and 0.17 g for $[Ga(TFB-tBuA)(O^tBu)_2]$, respectively. For the co-deposition of $(Al_xGa_{1-x})_2O_3$, defined molar ratios of the aluminum and gallium precursors were employed to achieve targeted Al:Ga compositions in the resulting mixed-oxide films.

Aluminum oxide thin films obtained using $[Al(TFB-tBuA)(O^tBu)_2]$ showed the formation of a visible gray or blackish film (Figure 3.11b) on the initially colorless fluorine-doped thin oxide (FTO) substrate, indicating that material deposition had occurred. Based on previous studies on hafnium zirconium oxide (HZO) deposition, the observed blackish appearance is likely associated with the incorporation of impurities, particularly carbon- and fluorine-containing species originating from incomplete precursor decomposition [38]. To remove these impurities, the deposited films were subjected to calcination in air at 600 °C for 8 hours. After this treatment, the film became colorless, suggesting the effective removal of residual contaminants (Figure 3.11c). Subsequent X-ray diffraction (XRD) characterization was performed to identify the resulting crystalline phases and to confirm the formation of the desired oxide material after calcination.

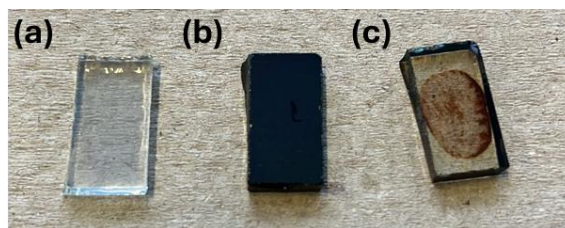


Figure 3.11. Surface appearance of (a) only FTO substrate, (b) as-deposited, and (c) calcined aluminum oxide films.

XRD patterns of both as-deposited and calcined aluminum oxide films did not show any diffraction peaks attributable to the deposited aluminum oxide films. Only peaks corresponding to SnO_2 (JCPDS no. 77-0452) from the underlying FTO substrate were observed (Figure 3.12). This suggests that the deposited films remain amorphous, even after calcination.

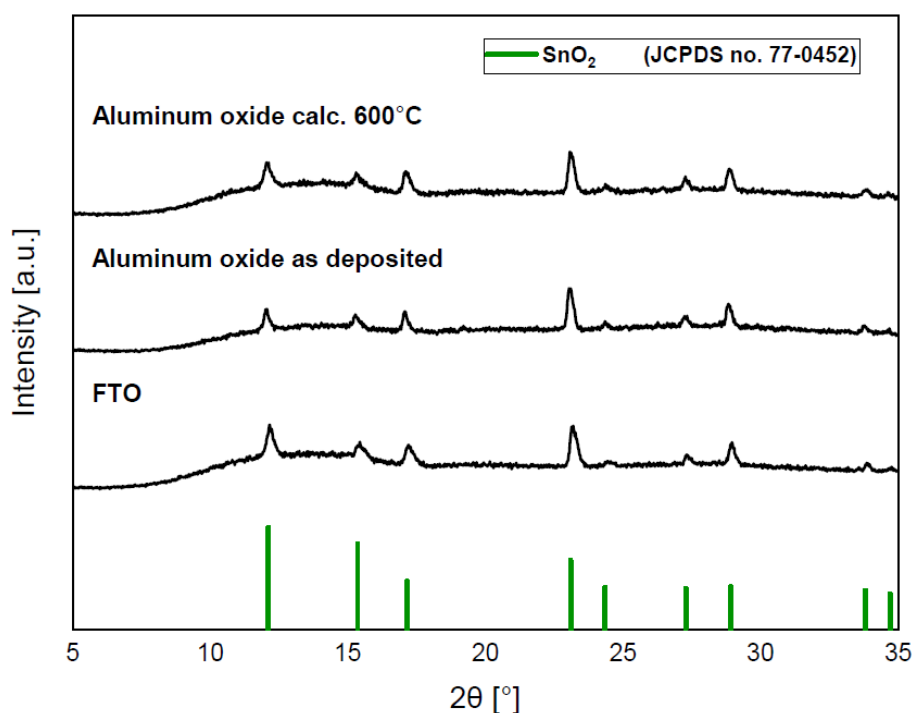


Figure 3.12. The XRD pattern of films obtained from the MOCVD of $[Al(TFB-tBuA)(O^tBu)_2]$.

Grazing-incidence X-ray diffraction (GIXRD) measurements were performed on the aluminum oxide film calcined at 600 °C using an incident angle of $\omega = 0.5^\circ$. This configuration was chosen to enhance surface sensitivity by limiting X-ray penetration depth, thereby minimizing the contribution from the underlying SnO_2 substrate and improving the detection of diffraction signals from the deposited film. Despite these optimized conditions, the GIXRD pattern (Figure 3.13) did not reveal any diffraction peaks attributable to aluminum oxide. This result indicates that the calcined film remains amorphous, even after thermal treatment at 600 °C.

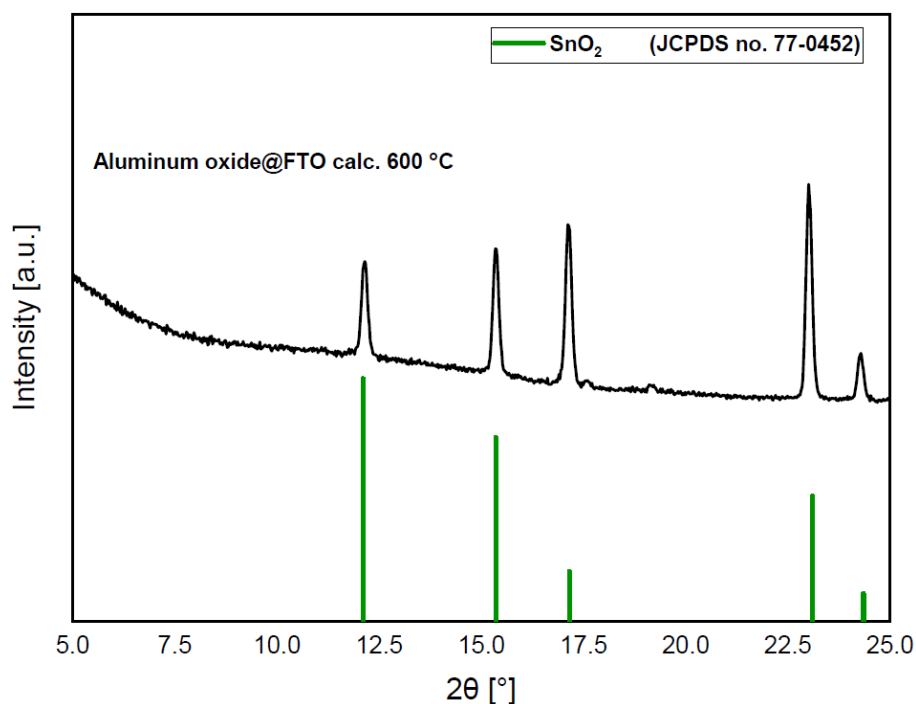


Figure 3.13. The GIXRD pattern of calcined (600 °C) aluminum oxide films obtained from the MOCVD of $[Al(TFB-tBuA)(O'Bu)_2]$.

This observation is consistent with previous reports indicating that any type of aluminum oxide typically requires temperatures above 800 °C to crystallize [57]. However, such conditions cannot be applied in this case, as the FTO substrate is thermally limited to approximately 650 °C. Therefore, to investigate the chemical composition of the films, scanning electron microscope (SEM) and energi-dispersive X-ray (EDX) analyses were performed.

SEM images confirm that the films were successfully deposited using the precursor $[Al(TFB-tBuA)(O'Bu)_2]$, as evident in the clear morphological differences between the FTO surface before (Figure 3.14a) and after deposition (Figure 3.14b). The observed morphology is consistent with typical morphology of amorphous aluminum oxide films that have been reported [58]. Furthermore, no significant changes in the film morphology were observed after calcination in air at 600 °C (Figure 3.14c), indicating that the thermal treatment did not substantially alter the surface structure of the deposited layer. Cross-sectional SEM analysis further confirms the successful deposition of the aluminum oxide films (Figure 3.14d). From the measured film thickness, the growth rate of the aluminum oxide deposited using $[Al(TFB-tBuA)(O'Bu)_2]$ was estimated to be approximately 8.67 nm min^{-1} .

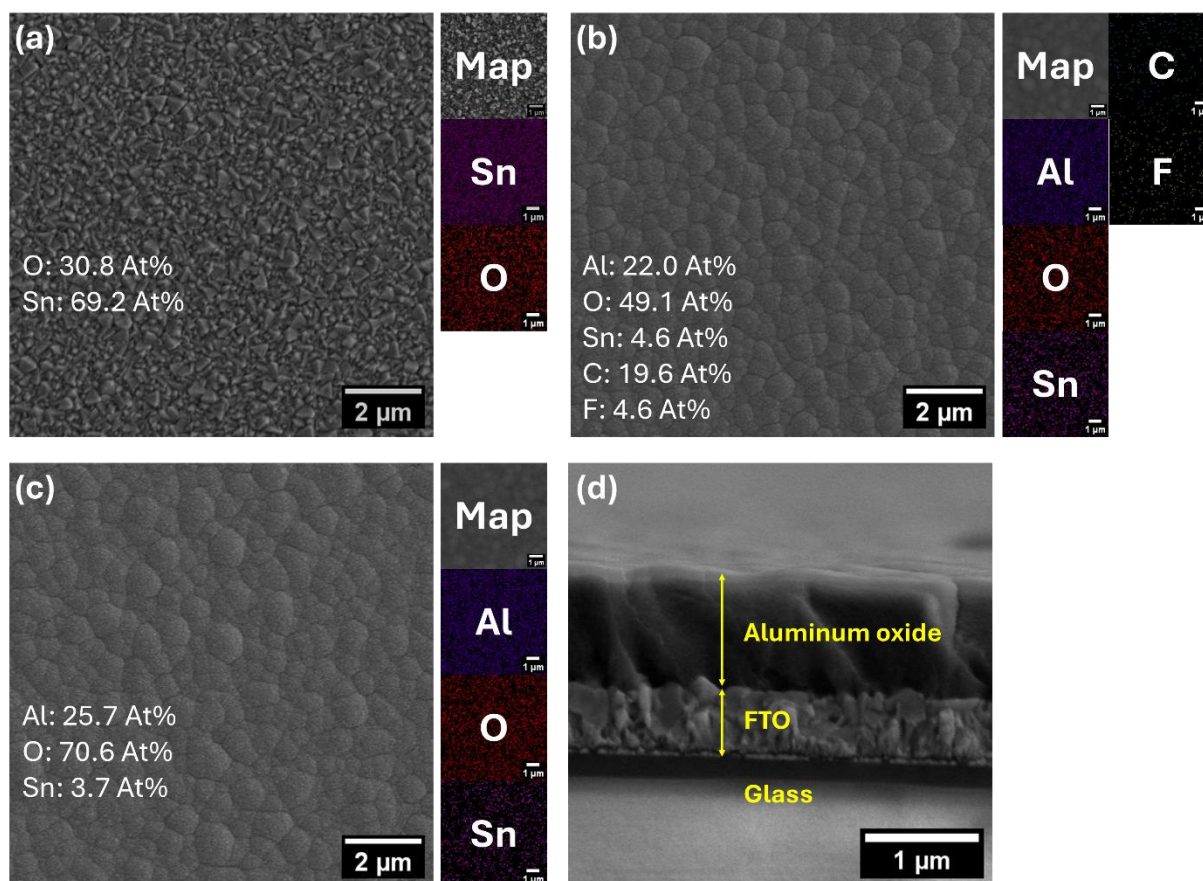


Figure 3.14. Top-view SEM images of (a) only FTO substrate, (b) as-deposited, (c) calcined aluminum oxide films ($T_{\text{calcination}} = 600\text{ }^{\circ}\text{C}$). (d) Cross-sectional SEM image of calcined aluminum oxide films ($T_{\text{calcination}} = 600\text{ }^{\circ}\text{C}$) synthesized from $[Al(TFB-tBuA)(O'Bu)_2]$ via MOCVD.

EDX analysis further indicates the presence of aluminum and oxygen in the deposited layer, along with impurities such as carbon and fluorine in the as-deposited film (Figure 3.14b). However, the measured Al:O ratio deviates from the expected stoichiometry of the most stable aluminum oxide (Al_2O_3 with Al:O = 2:3), showing an apparent excess of oxygen. This overestimation may partly arise from contributions of the underlying SnO_2 substrate, which is also detected during EDX measurements. Even after accounting for the SnO_2 contribution ($Sn:O = 1:2$), the film still exhibits a relatively high oxygen content. Therefore, the deposited film may form non-stoichiometric aluminum oxide [58-63]. It should be noted, however, that EDX provides only semi-quantitative results.

X-ray photoelectron spectroscopy (XPS) was performed on the aluminum oxide thin film after calcination at $600\text{ }^{\circ}\text{C}$ to investigate its surface composition and chemical states. The survey spectrum (Figure 3.15) confirmed the presence of aluminum and oxygen, the constituent elements of aluminum oxide, together with a detectable carbon signal. The carbon species are most likely associated with adventitious surface contamination or residual carbon-containing

fragments originating from precursor decomposition. For detailed chemical-state analysis, the spectrum were calibrated using the C 1s peak at 284.8 eV (Figure 3.15). The high-resolution Al 2p spectrum exhibited a single symmetric peak centered at 74.51 eV (Figure 3.15). This binding energy is characteristic of Al^{3+} species in Al_2O_3 and agrees well with values reported in the literature [64]. No additional peaks were observed at lower binding energies, indicating the absence of metallic aluminum (Al^0) or other reduced aluminum species within the film [65]. The O 1s spectrum displayed a dominant singlet peak at 531.63 eV (Figure 3.15), which is characteristic of O^{2-} in aluminum oxide lattices [64-66].

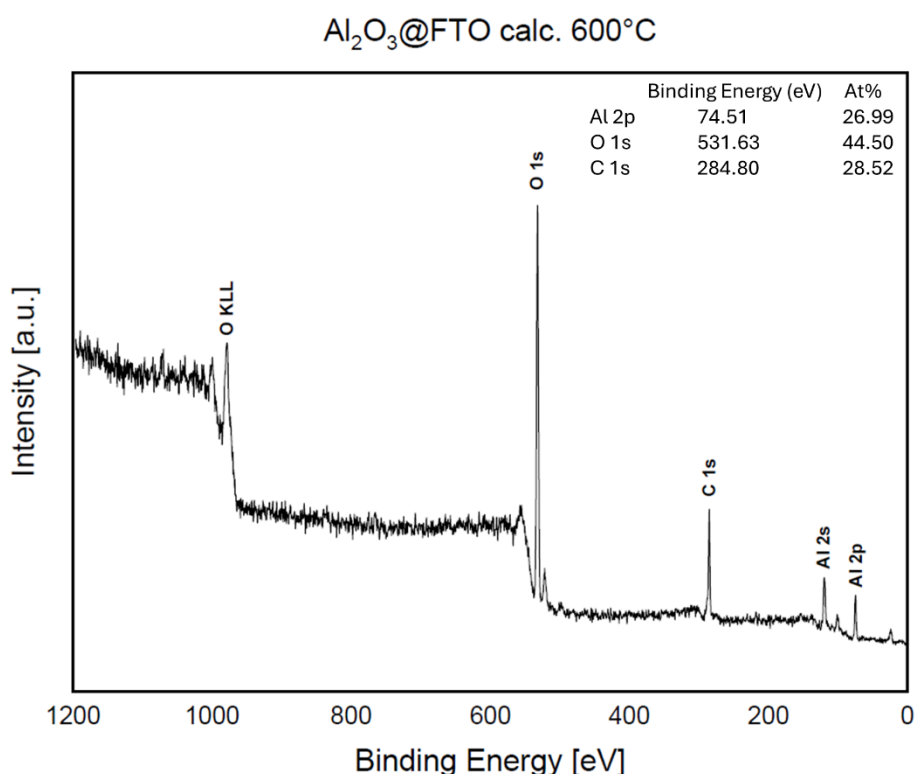


Figure 3.15. The XPS survey spectrum for calcined Al_2O_3 films obtained from $[\text{Al}(\text{TFB-}t\text{BuA})(\text{O}^i\text{Bu})_2]$.

Quantitative analysis of the XPS survey spectrum obtained from the aluminum oxide thin film calcined at 600 °C revealed aluminum and oxygen concentrations of 26.99 at.% and 44.50 at.%, respectively. Based on these values, the calculated Al:O atomic ratio is approximately 2:3.3. This ratio is reasonably close to the theoretical stoichiometry of Al_2O_3 (Al:O = 2:3), indicating that the deposited film is nearly stoichiometric aluminum oxide. The slight excess oxygen may originate from surface hydroxyl species, adsorbed oxygen-containing contaminants, or the inherent uncertainty associated with surface-sensitive XPS quantification.

Combined with the high-resolution spectrum, the XPS results provide strong evidence for the formation of stoichiometric aluminum oxide on the substrate surface. The Al 2p

spectrum confirms that aluminum is present exclusively in the Al^{3+} oxidation state, while the O 1s spectrum is characteristic of lattice oxygen (O^{2-}) in a metal oxide environment. No signals attributable to metallic aluminum or other reduced aluminum species were detected. These findings demonstrate the effective conversion of $[Al(TFB-tBuA)(O^tBu)_2]$ into an aluminum oxide thin film during the MOCVD process and subsequent calcination. Furthermore, the close agreement between the measured Al:O ratio and the theoretical stoichiometry of Al_2O_3 indicates that the resulting film is predominantly composed of near-stoichiometric aluminum oxide.

The deposition of aluminum oxide using $[Al(O^tBu)_3]_2$ was initially carried out under the same conditions employed for $[Al(TFB-tBuA)(O^tBu)_2]$, with a precursor sublimation temperature of 70 °C. Under these conditions, no visible changes were observed on the FTO substrate after deposition (Figure 3.16b) and no significant reduction in the mass of $[Al(O^tBu)_3]_2$ following the Al_2O_3 deposition process. SEM images further confirmed the absence of any significant morphological differences between the untreated (Figure 3.17a) and deposited substrates (Figure 3.16b), indicating that no appreciable film growth occurred. This conclusion is supported by EDX measurements, which showed no detectable aluminum signal on the FTO surface (Figure 3.16b). These observations suggest that the vapor flux generated by $[Al(O^tBu)_3]_2$ at 70 °C is insufficient to enable effective film deposition.

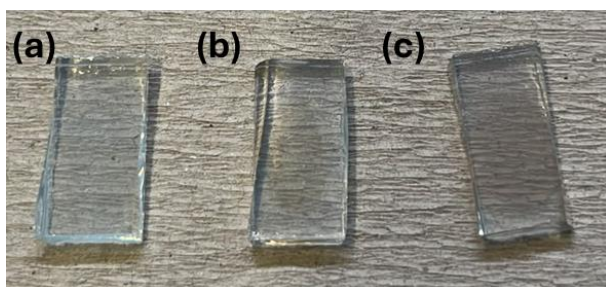


Figure 3.16. Surface appearance of (a) only FTO substrate, (b) as-deposited aluminum oxide films ($T_{\text{sublimation}} = 70$ °C), and (c) as-deposited aluminum oxide ($T_{\text{sublimation}} = 120$ °C).

To increase the precursor vapor supply, the deposition was subsequently repeated at a higher sublimation temperature of 120 °C. Although the FTO substrate remained visually unchanged after deposition (Figure 3.16c), SEM images revealed pronounced morphological differences between the pristine FTO (Figure 3.17a) and deposited surfaces (Figure 3.17c). These changes clearly indicate the formation of a deposited layer, demonstrating that $[Al(O^tBu)_3]_2$ can act as an effective precursor for aluminum oxide growth when operated at sufficiently high sublimation temperatures. Furthermore, compared with $[Al(TFB-$

$t\text{BuA})(\text{O}'\text{Bu})_2]$, the precursor $[\text{Al}(\text{O}'\text{Bu})_3]_2$ undergoes more efficient ligand elimination during deposition, resulting in as-deposited Al_2O_3 thin films with significantly lower carbon contamination and, in some cases, virtually carbon-free compositions.

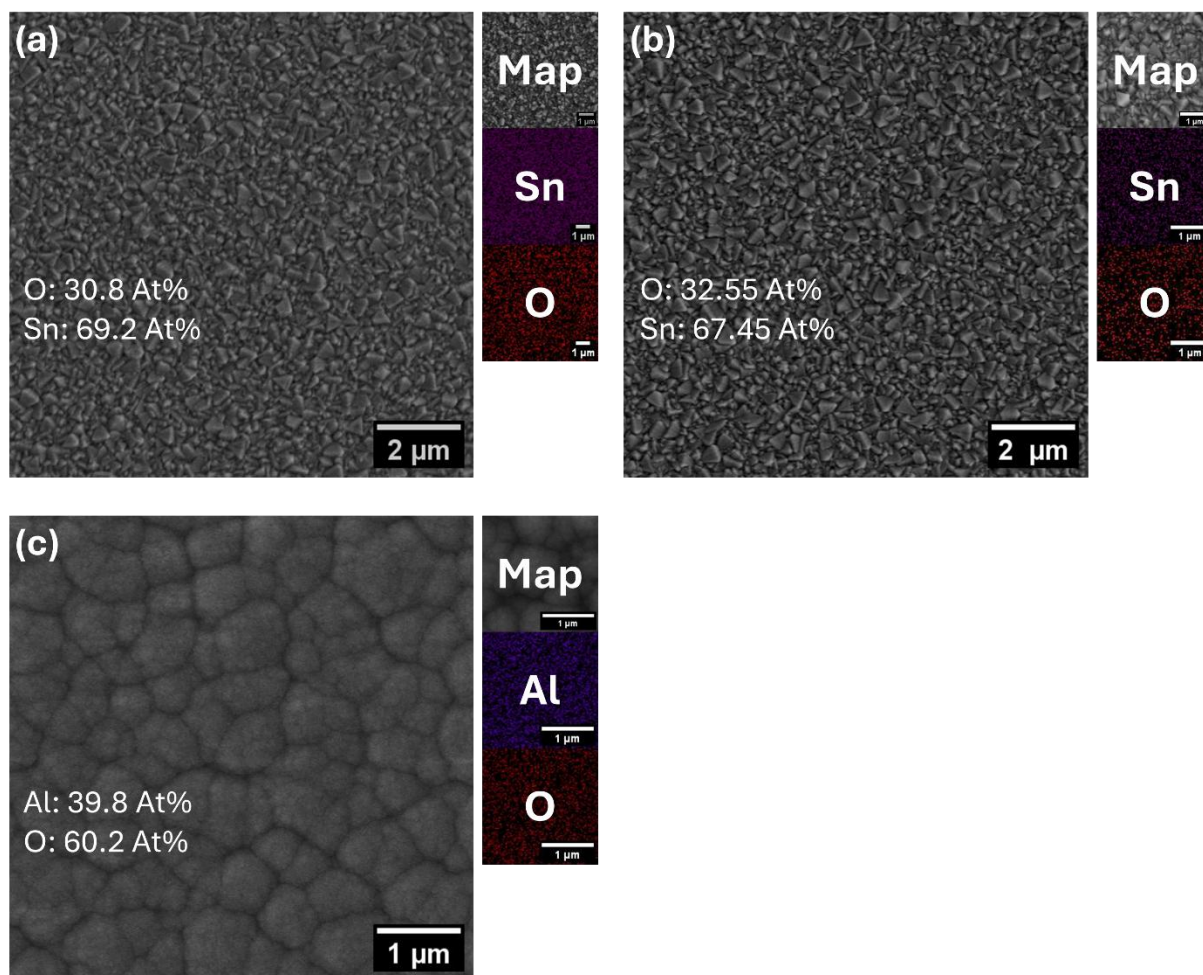


Figure 3.17. Top-view SEM images of (a) only FTO substrate, (b) as-deposited aluminum oxide films ($T_{\text{sublimation}} = 70^\circ\text{C}$), and (c) as-deposited aluminum oxide ($T_{\text{sublimation}} = 120^\circ\text{C}$).

The successful deposition was further confirmed by EDX analysis, which detected both aluminum and oxygen in the deposited layer. The measured elemental ratio was close to the expected Al:O stoichiometry of 2:3 for Al_2O_3 (Figure 3.17c). Furthermore, no significant carbon signal was detected, suggesting that the deposition process proceeds with minimal incorporation of carbonaceous impurities. This interpretation is consistent with the colorless appearance of the as-deposited film and contrasts with the impurity-containing films obtained from $[\text{Al}(\text{TFB-}t\text{BuA})(\text{O}'\text{Bu})_2]$. Collectively, these results demonstrate that $[\text{Al}(\text{O}'\text{Bu})_3]_2$ is suitable for producing relatively pure aluminum oxide films, although higher sublimation temperatures are required compared to $[\text{Al}(\text{TFB-}t\text{BuA})(\text{O}'\text{Bu})_2]$ to achieve sufficient precursor transport and film growth.

During the deposition of gallium oxide thin films using $[Ga(TFB-tBuA)(O'Bu)_2]$, a visible color change on the FTO substrate was observed after the MOCVD process, transitioning from colorless (Figure 3.18a) to blackish (Figure 3.18b). This observation indicates that a film was successfully deposited on the FTO surface. A similar phenomenon was previously observed for the deposition of aluminum oxide thin films using $[Al(TFB-tBuA)(O'Bu)_2]$. Subsequently, the deposited film was calcined in air at 600 °C to remove impurities and promote crystallization. After calcination, the film became colorless (Figure 3.18c), suggesting the oxidation of residual carbon.

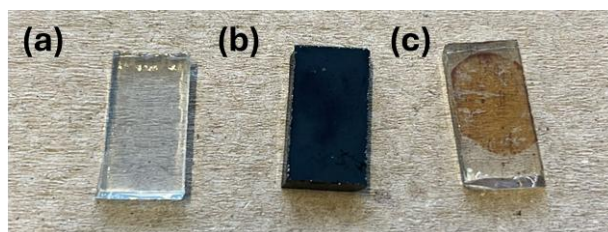


Figure 3.18. Surface appearance of (a) only FTO substrate, (b) as-deposited, and (c) calcined gallium oxide films.

XRF analysis was then performed to confirm the presence of gallium in the film. The results show that both the as-deposited and calcined films exhibit characteristic fluorescence signals of gallium (Figure 3.19), confirming its presence. However, XRF analysis alone cannot determine whether the deposited film corresponds to gallium oxide. Therefore, additional characterization techniques, such as XRD, are required to identify the phase of the deposited material obtained via MOCVD using $[Ga(TFB-tBuA)(O'Bu)_2]$.

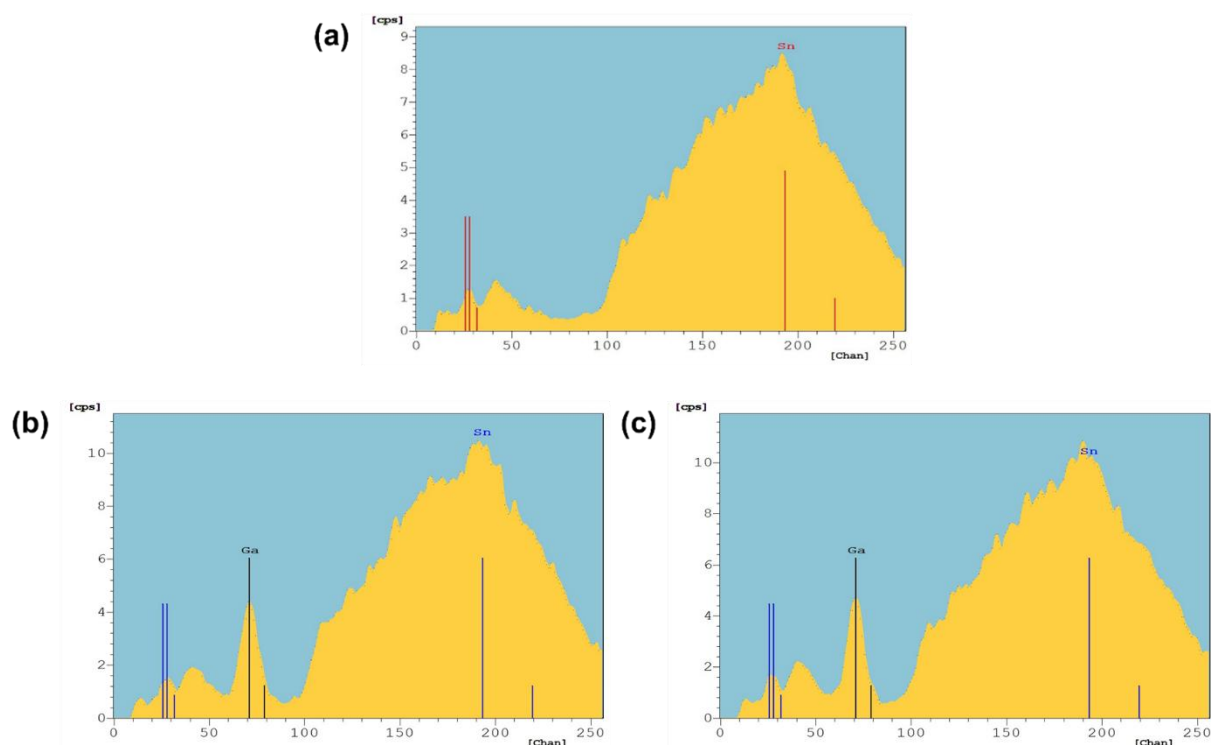


Figure 3.19. The XRF results of (a) only FTO substrate, (b) as-deposited gallium oxide thin films, and (c) gallium oxide thin films after calcination in air at 600 °C for 8 hours.

XRD patterns of both the as-deposited and calcined films do not exhibit any diffraction peaks corresponding to any type of gallium oxide. Only peaks associated with SnO_2 (JCPDS no. 77-0452) from the underlying FTO substrate are observed (Figure 3.20). This behavior is consistent with the results obtained for the previously deposited aluminum oxide thin films. These findings indicate that the deposited gallium oxide layer is amorphous and remains in an amorphous state even after calcination in air at 600 °C for 8 hours.

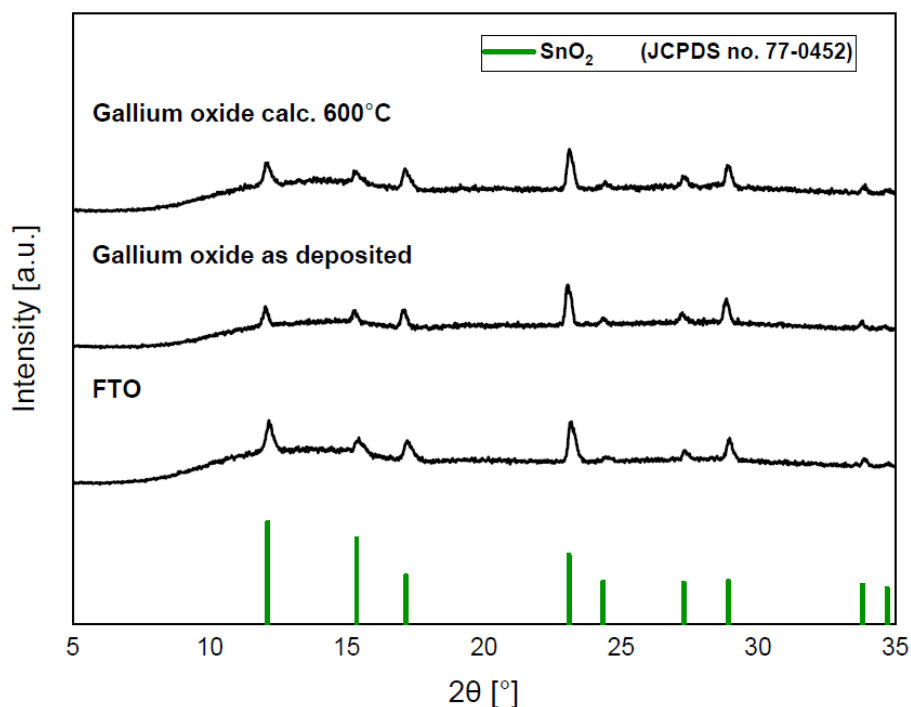


Figure 3.20. The XRD pattern of films obtained from the MOCVD of $[Ga(TFB-tBuA)(O'Bu)_2]$.

Similar to aluminum oxide, gallium oxide typically requires temperatures above 800 °C to achieve crystallization [67, 68]. However, in this case, calcination above 650 °C is not feasible, as the gallium oxide film is deposited on an FTO substrate based on soda-lime glass, which can only withstand temperatures up to approximately 650 °C. In contrast, using the same GIXRD parameters applied for the aluminum oxide film, analysis of the gallium oxide film calcined at 600 °C reveals distinct diffraction peaks corresponding to monoclinic gallium oxide (β - Ga_2O_3), consistent with JCPDS reference no. 11-0370. The (-202) reflection is observed as the most intense peak among the detected facets (Figure 3.21). These results indicate that calcination at 600 °C is sufficient to induce crystallization of the gallium oxide film.

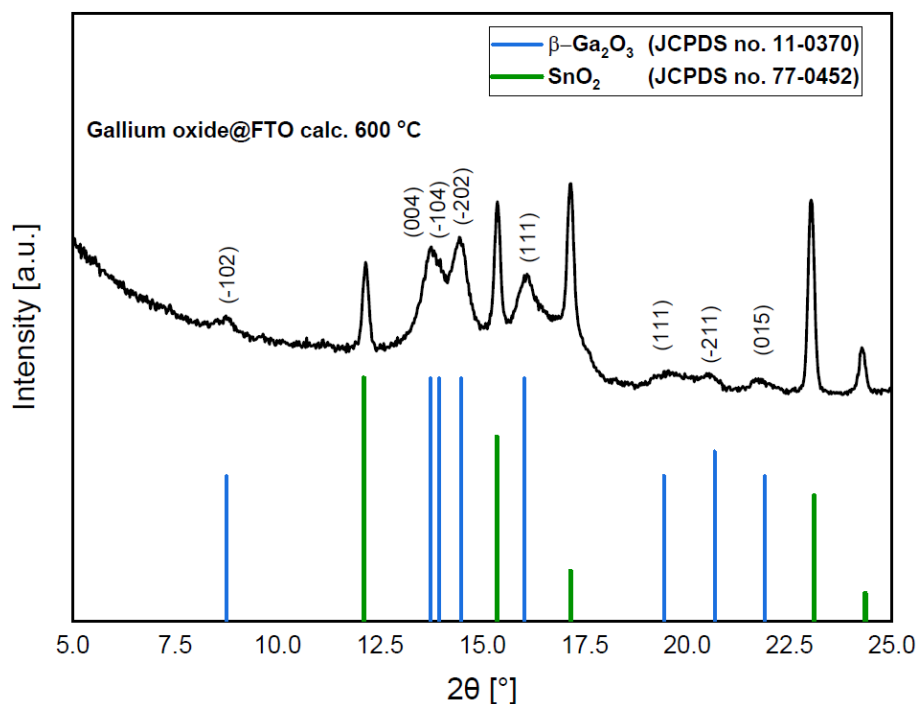


Figure 3.21. The GIXRD pattern of calcined (600 °C) gallium oxide films obtained from the MOCVD of $[Ga(TFB-tBuA)(O'Bu)_2]$.

Previous studies have shown that β - Ga_2O_3 can crystallize at temperatures as low as 550 °C [69]. In contrast, Al_2O_3 generally remains amorphous under similar thermal treatment conditions. This difference arises from the fundamentally different crystallization behaviors of the two oxides. Al_2O_3 possesses stronger Al–O bonds, lower cation diffusivity, and a higher activation energy for crystallization than Ga_2O_3 [70, 71]. As a result, atomic rearrangement into a long-range ordered crystal structure occurs much more slowly in alumina, and significantly higher annealing temperatures are typically required to induce the formation of crystalline Al_2O_3 phases. In contrast, the lower kinetic barrier for crystallization in Ga_2O_3 enables the formation of crystalline β - Ga_2O_3 at substantially lower temperatures.

SEM images confirm that a thin film was successfully deposited via MOCVD using $[Ga(TFB-tBuA)(O'Bu)_2]$ on the FTO substrate, as evidenced by the clear morphological differences between the bare FTO surface (Figure 3.22a) and the as-deposited gallium oxide film (Figure 3.22b). The observed morphology is consistent with previously reported [72]. SEM images of the calcined film show no significant morphological changes compared to the as-deposited state (Figure 3.22c), indicating that calcination at 600 °C does not substantially alter the surface structure. The successful formation of the gallium oxide layer is further verified by cross-sectional SEM, which reveals well-defined layers corresponding to the film,

FTO, and glass substrate (Figure 3.22d). The calculated growth rate from thickness measurements is approximately 2.55 nm min^{-1} .

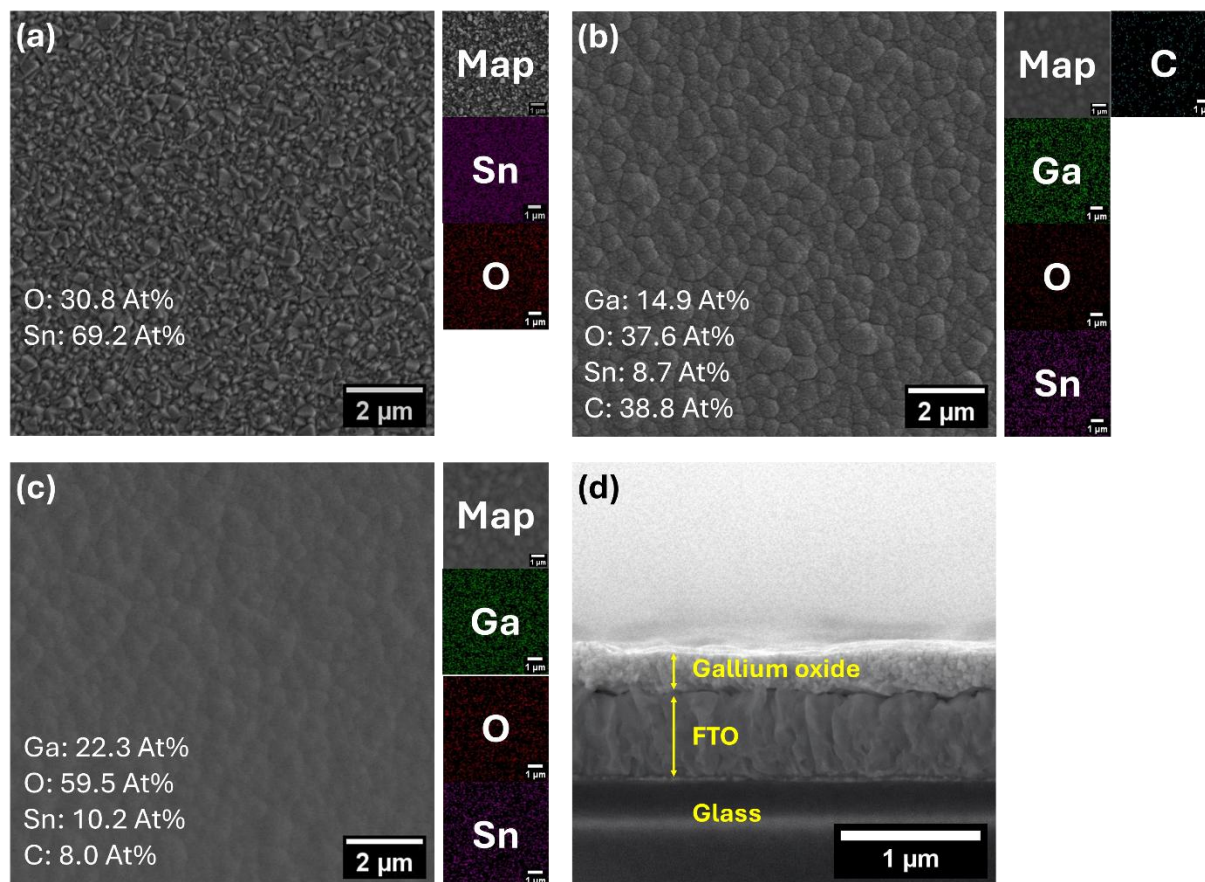


Figure 3.22. Top-view SEM images of (a) only FTO substrate, (b) as-deposited, (c) calcined gallium oxide films ($T_{\text{calcination}} = 600 \text{ }^\circ\text{C}$). (d) Cross-sectional SEM image of calcined gallium oxide films ($T_{\text{calcination}} = 600 \text{ }^\circ\text{C}$) synthesized from $[Ga(TFB-tBuA)(O'Bu)_2]$ via MOCVD.

EDX analysis of the as-deposited film confirms the presence of gallium and oxygen, which are relatively homogeneously distributed, along with impurities such as carbon. In the calcined film, carbon is still detected (Figure 3.22c), suggesting incomplete removal of residual impurities during the thermal treatment. The persistence of carbon impurities after calcination further indicates that the thermal treatment at $600 \text{ }^\circ\text{C}$ was not fully effective in removing residual contaminants under the applied conditions. Additionally, signals from SnO_2 originating from the FTO substrate are observed, making it difficult to definitively determine whether the deposited film corresponds to Ga_2O_3 . Even when accounting for the oxygen contribution from SnO_2 ($Sn:O = 1:2$), the measured $Ga:O$ ratio does not match the expected stoichiometry of Ga_2O_3 ($Ga:O = 1:1.5$). Despite the common occurrence of non-stoichiometric gallium oxide in deposited films [73, 74], the GIXRD findings in this study reveal the formation of phase-pure β - Ga_2O_3 .

To further verify the chemical composition of the deposited gallium oxide film after calcination at 600 °C, XPS measurements were performed. The survey spectrum (Figure 3.23) revealed the presence of gallium and oxygen as the major constituents of the film, together with negligible carbon contribution. When compared to analogues Al precursor, the detected carbon signal is most likely associated with surface contamination originating from atmospheric exposure or residual organic species remaining after precursor decomposition. Following calibration of the spectrum using the adventitious C 1s peak at 284.8 eV, the high-resolution Ga 2p_{3/2} spectrum was analyzed. A single peak was observed at a binding energy of 1117.61 eV (Figure 3.23), which is characteristic of Ga³⁺ in gallium oxide and is in good agreement with reported literature values for Ga₂O₃ [75]. Importantly, no peaks corresponding to metallic gallium (Ga⁰) were detected at lower binding energies, indicating that gallium is present exclusively in its oxidized form.

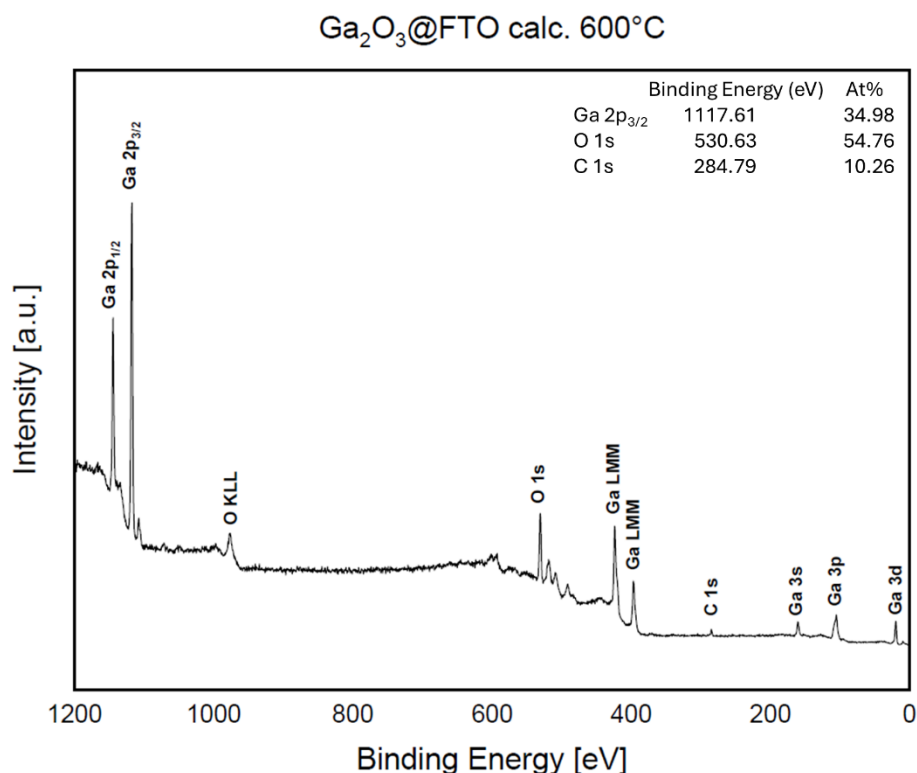


Figure 3.23. The XPS survey spectrum for calcined Ga₂O₃ films obtained from [Ga(TFB-*t*BuA)(O^{*i*}Bu)₂].

Additional information was obtained from the O 1s spectrum, which exhibited a dominant peak centered at 530.63 eV (Figure 3.23). This binding energy is characteristic of lattice oxygen (O²⁻) in Ga₂O₃ [54, 75]. The presence of a single dominant oxygen component indicates that oxygen is predominantly incorporated within the gallium oxide framework, with only minor contributions from surface adsorbates or oxygen-containing contaminants. Quantitative

analysis of the XPS survey spectrum further supports this assignment. The gallium oxide thin film calcined at 600 °C contained 34.98 at.% gallium and 54.76 at.% oxygen, corresponding to a Ga:O atomic ratio of approximately 2:3.13. This value is in excellent agreement with the theoretical stoichiometry of Ga_2O_3 (Ga:O = 2:3), indicating that the deposited film is predominantly stoichiometric gallium oxide. Together with the Ga 2p and O 1s results, these findings confirm the successful formation of Ga_2O_3 through the deposition and calcination processes. The combined XPS results clearly demonstrate the successful conversion of **[Ga(TFB-*t*BuA)(O^tBu)₂]** into gallium oxide during deposition and calcination. The observed Ga^{3+} and O^{2-} chemical states, together with the absence of metallic gallium, confirm the formation of fully oxidized gallium oxide at the film surface. These findings further support the GIXRD results, which identified the deposited material as crystalline β - Ga_2O_3 .

To evaluate the feasibility of employing conventional metal alkoxide precursors for mixed aluminum gallium oxide deposition, gallium oxide growth experiments were carried out using $[Ga(O^tBu)_3]_2$. Particular attention was given to this precursor because its aluminum analogue, $[Al(O^tBu)_3]_2$, had previously demonstrated successful Al_2O_3 deposition at a sublimation temperature of 120 °C. Therefore, the gallium precursor was investigated under identical deposition conditions to assess its suitability for future co-deposition processes targeting $(Al_xGa_{1-x})_2O_3$ thin films.

Following deposition at a precursor temperature of 120 °C, no visible changes were observed on the FTO substrate surface (Figure 3.24b). Although this initially did not exclude the possibility of film formation, since Al_2O_3 deposited from $[Al(O^tBu)_3]_2$ also remained visually indistinguishable from the bare substrate, subsequent microscopic analysis provided a different conclusion.

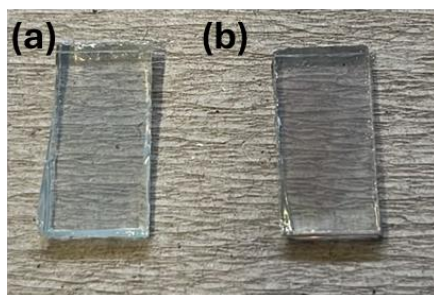


Figure 3.24. Surface appearance of (a) only FTO substrate and (b) as-deposited gallium oxide films ($T_{\text{sublimation}} = 120$ °C).

SEM images revealed no noticeable differences in surface morphology between the untreated FTO substrate and the substrate subjected to the gallium oxide deposition process

(Figure 3.25a and b). The absence of any significant surface modification suggests that little to no film growth occurred under the applied conditions. This conclusion is supported by EDX analysis, which showed no detectable gallium signal on the substrate surface. Together, these results indicate that $[Ga(O^tBu)_3]_2$ is unable to produce measurable gallium oxide deposition at a sublimation temperature of 120 °C. This behavior is markedly different from that of the analogous precursor $[Al(O^tBu)_3]_2$, despite their similar molecular structures.

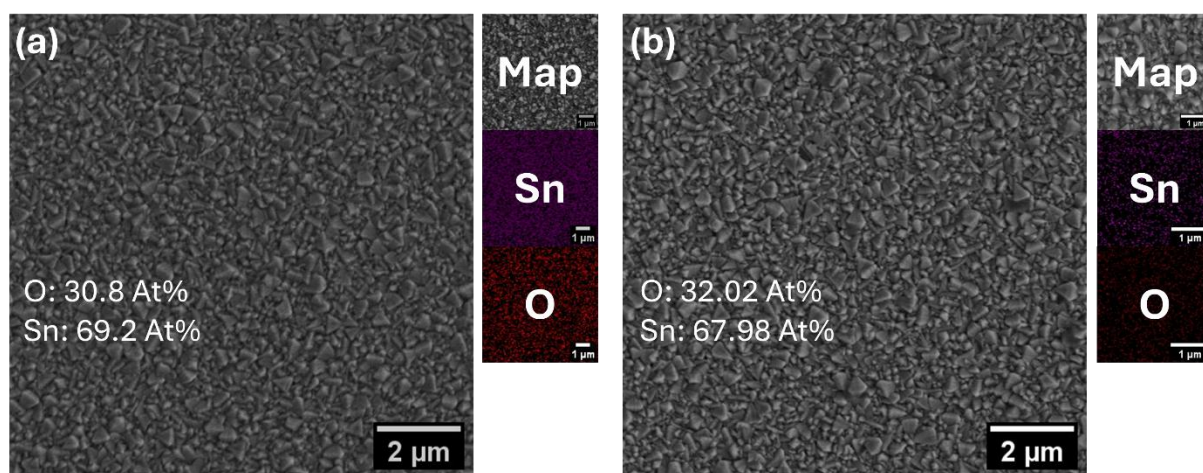


Figure 3.25. Top-view SEM images of (a) only FTO substrate and (b) as-deposited gallium oxide films ($T_{\text{sublimation}} = 120$ °C).

The absence of film growth can also be explained by the deposition chemistry of $[Ga(O^tBu)_3]_2$. Previous studies have reported successful Ga_2O_3 deposition from this precursor using O_2 as both the carrier gas and the reactive oxygen source [54]. In the present work, however, no reactive gas was employed. As a result, $[Ga(O^tBu)_3]_2$ was required to act as a single-source precursor, which appears to be insufficient for efficient gallium oxide formation under the applied MOCVD conditions. This finding highlights the advantage of the heteroleptic precursor $[Ga(TFB-tBuA)(O^tBu)_2]$, which successfully produced gallium oxide films without the need for an external oxygen source.

These findings demonstrate that the precursor mixture via co-evaporation $[Al(O^tBu)_3]_2/[Ga(O^tBu)_3]_2$ is not suitable for deposition of $(Al_xGa_{1-x})_2O_3$ under low-temperature MOCVD conditions. In contrast, the fluorinated β -ketoenaminato derivatives $[Al(TFB-tBuA)(O^tBu)_2]$ and $[Ga(TFB-tBuA)(O^tBu)_2]$ exhibit sufficient volatility and deposition activity at relatively low sublimation temperatures, making them considerably more promising candidates for the deposition of aluminum gallium oxide thin films.

3.5. Deposition of $(Al_xGa_{1-x})_2O_3$ Using $[Al(TFB-tBuA)(O'Bu)_2]$ and $[Ga(TFB-tBuA)(O'Bu)_2]$

Co-evaporation of $[Al(TFB-tBuA)(O'Bu)_2]$ and $[Ga(TFB-tBuA)(O'Bu)_2]$ to deposit aluminum gallium oxide films was carried out via MOCVD using defined precursor mole fractions of aluminum $[Al(TFB-tBuA)(O'Bu)_2]/([Al(TFB-tBuA)(O'Bu)_2] + [Ga(TFB-tBuA)(O'Bu)_2])$, expressed as (x Al), as summarized in Table 3.3. This approach was employed to obtain aluminum gallium oxide, $(Al_xGa_{1-x})_2O_3$, thin films with controlled Al:Ga compositions.

Table 3.3. Mole fraction of aluminum (x Al) during MOCVD of aluminum gallium oxide.

Sample	Mass of $[Al(TFB-tBuA)(O'Bu)_2]$ (g)	Mass of $[Ga(TFB-tBuA)(O'Bu)_2]$ (g)	Mole fraction (x Al)	Mass used during deposition (g)
1	0.03	0.20	0.144	0.12
2	0.10	0.27	0.293	0.18
3	0.13	0.20	0.420	0.21
4	0.17	0.22	0.467	0.25

Similar to the individual depositions of aluminum oxide and gallium oxide, the as-deposited $(Al_xGa_{1-x})_2O_3$ films exhibited a blackish coloration (Figure 3.26b), indicating the presence of residual impurities incorporated during deposition. The films were calcined in air at 610 °C for 8 hours to remove impurities such as carbon and fluorine. In addition, the calcination at 610 °C was carried out to promote crystallization of the thin films. After calcination, the films were transformed to colorless deposits (Figure 3.26c).

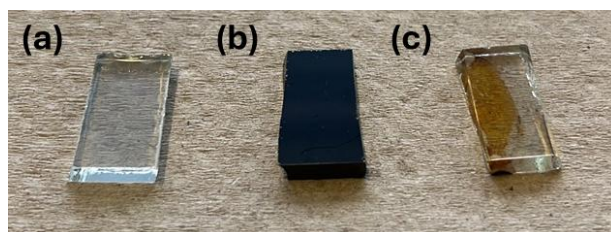


Figure 3.26. Surface appearance of (a) only FTO substrate, (b) as-deposited, and (c) calcined aluminum gallium oxide films with mole fraction of aluminum (x Al) = 0.467.

XRF analysis confirmed the presence of gallium in all calcined films (Figure 3.27), verifying that deposition had occurred. However, the presence of aluminum could not be

confirmed by XRF, as aluminum does not emit detectable fluorescence under the measurement conditions, consistent with observations from the previous aluminum oxide films.

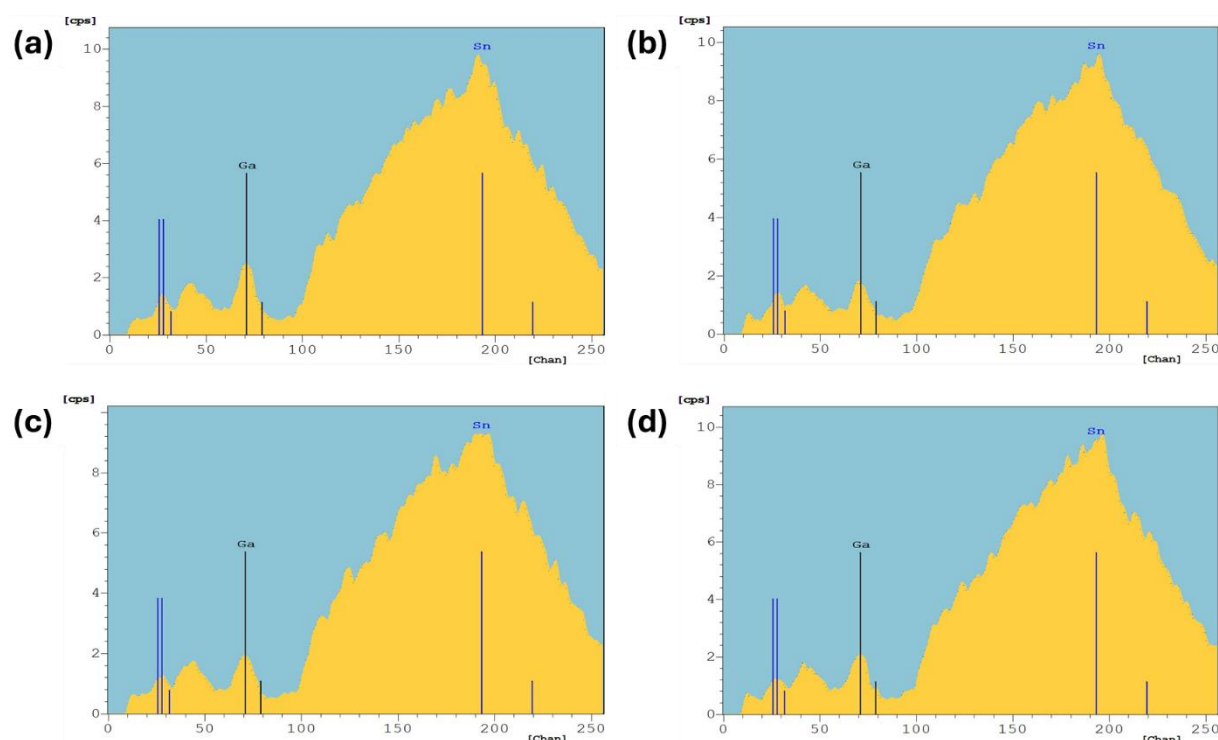


Figure 3.27. XRF results of aluminum gallium oxide thin films after calcination in air at 610 °C for 8 hours with mole fraction of aluminum (x Al) of (a) 0.144, (b) 0.293, (c) 0.420, and (d) 0.467.

XRD analysis was subsequently performed to investigate phase formation. Despite the increased calcination temperature, the XRD patterns did not show any diffraction peaks attributable to $(Al_xGa_{1-x})_2O_3$ (Figure 3.28). As observed in the individual oxide systems, the co-deposited films remained amorphous even after calcination at 610 °C, indicating that this temperature is insufficient to induce crystallization of the aluminum gallium oxide phase. As reported in previous studies [76, 77], crystallization of aluminum gallium oxide films typically requires temperatures exceeding 800 °C. These XRD results are therefore insufficient to conclusively confirm the formation of aluminum gallium oxide films.

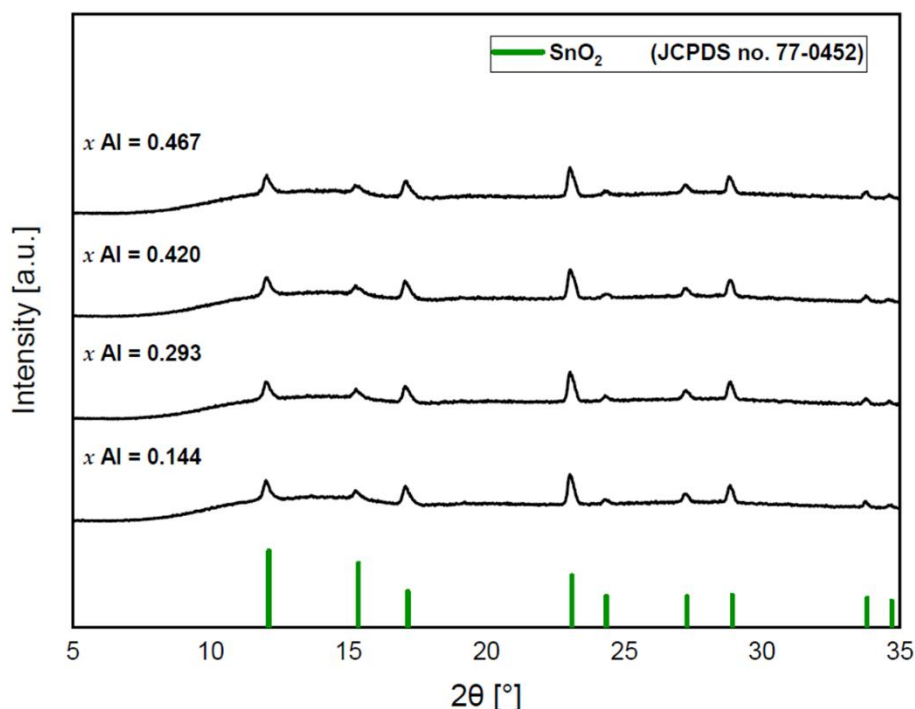


Figure 3.28. The XRD pattern of films obtained from the MOCVD of mixed $[Al(TFB-tBuA)(O'Bu)_2]$ and $[Ga(TFB-tBuA)(O'Bu)_2]$.

To obtain more surface-sensitive and reliable diffraction data, GIXRD measurements were performed using the same experimental conditions previously employed for the gallium oxide thin films. The GIXRD patterns (Figure 3.29) revealed a clear dependence of the film structure on the aluminum content. Among the four aluminum gallium oxide samples investigated, only the film prepared with an aluminum precursor fraction of $x\text{ Al} = 0.144$ exhibited distinct diffraction peaks attributable to polycrystalline β - Ga_2O_3 , in agreement with JCPDS reference no. 11-0370. Similar to the pure gallium oxide film, the (-202) reflection was the most intense diffraction peak, indicating a preferred orientation along this crystallographic plane. In contrast, the remaining three samples did not display any detectable diffraction peaks associated with crystalline aluminum gallium oxide phases, suggesting that these films remained amorphous after calcination. These observations indicate that increasing the aluminum content suppresses crystallization and promotes amorphization of the aluminum gallium oxide films. Wang *et al.* [78] reported that moderate incorporation of aluminum can improve the crystalline quality of $(Al_xGa_{1-x})_2O_3$ thin films by strengthening the metal–oxygen bonding network and stabilizing the crystal structure. However, excessive aluminum incorporation was found to introduce significant lattice strain due to the size mismatch between Al^{3+} and Ga^{3+} ions, leading to increased defect formation and a deterioration in crystalline quality.

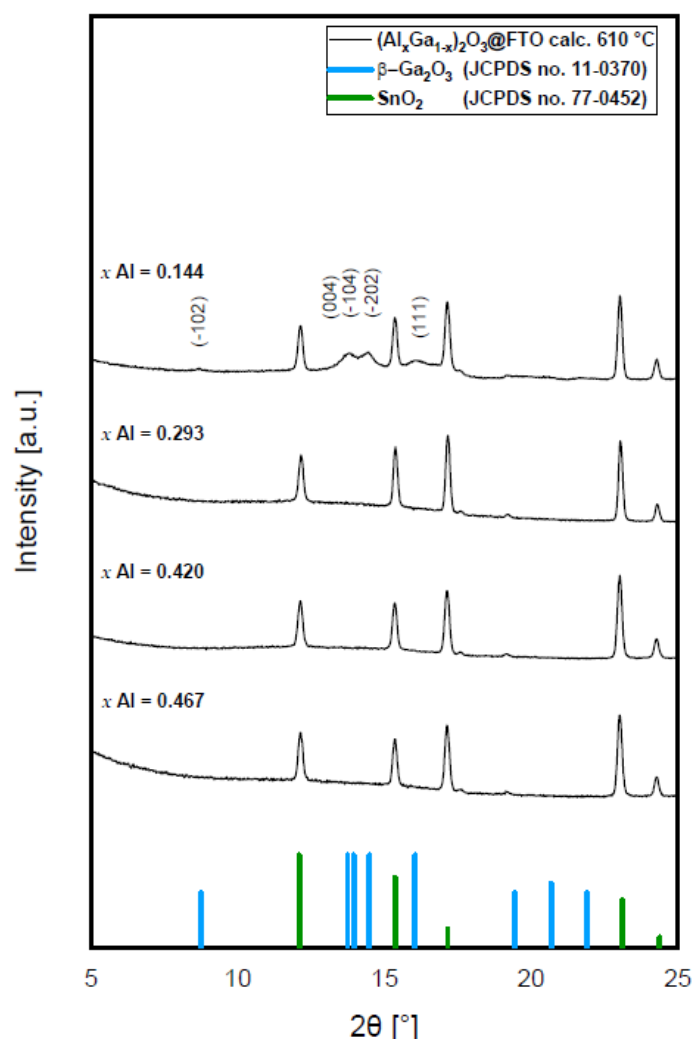


Figure 3.29. The GIXRD pattern of calcined (610 °C) aluminum gallium oxide films deposited from the MOCVD of $[Al(TFB-tBuA)(O^tBu)_2]/[Ga(TFB-tBuA)(O^tBu)_2]$ with certain ratios.

SEM images of the calcined films confirm that the co-deposition of thin films using both precursors was successfully achieved (Figure 3.30), as evidenced by the morphological features that are comparable to those observed in individually deposited aluminum and gallium oxide films. The aluminum gallium oxide films exhibit morphologies consistent with those reported in previous studies [76, 79, 80]. However, the films calcined at 610 °C exhibit the presence of fine cracks. These cracks are likely a consequence of impurity removal during thermal treatment in an oxidizing atmosphere. The associated mass loss, resulting from the elimination of residual species such as carbon- and fluorine-containing fragments, can induce stress within the film, ultimately leading to crack formation. EDX analysis further confirmed the presence of aluminum, gallium, and oxygen, which are homogeneously distributed throughout the calcined aluminum gallium oxide films (Figure 3.30). However, signals from tin originating

from the FTO substrate were also detected during the measurement. Even after accounting for the oxygen contribution from SnO_2 on the FTO substrate, the combined (Al, Ga):O ratio does not correspond to the expected stoichiometry of $(Al_xGa_{1-x})_2O_3$ (i.e., (Al, Ga):O = 2:3). Instead, the films exhibit an excess of oxygen, indicating that the deposited layers may form non-stoichiometric aluminum gallium oxide ($AlGaO_x$). Such non-stoichiometric compositions are commonly observed in thin film deposition processes and have been reported in several studies [81-84]. Based on these results, high-precision compositional analysis techniques such as XPS are expected to provide a more accurate determination of the aluminum, gallium, and oxygen contents in the deposited films.

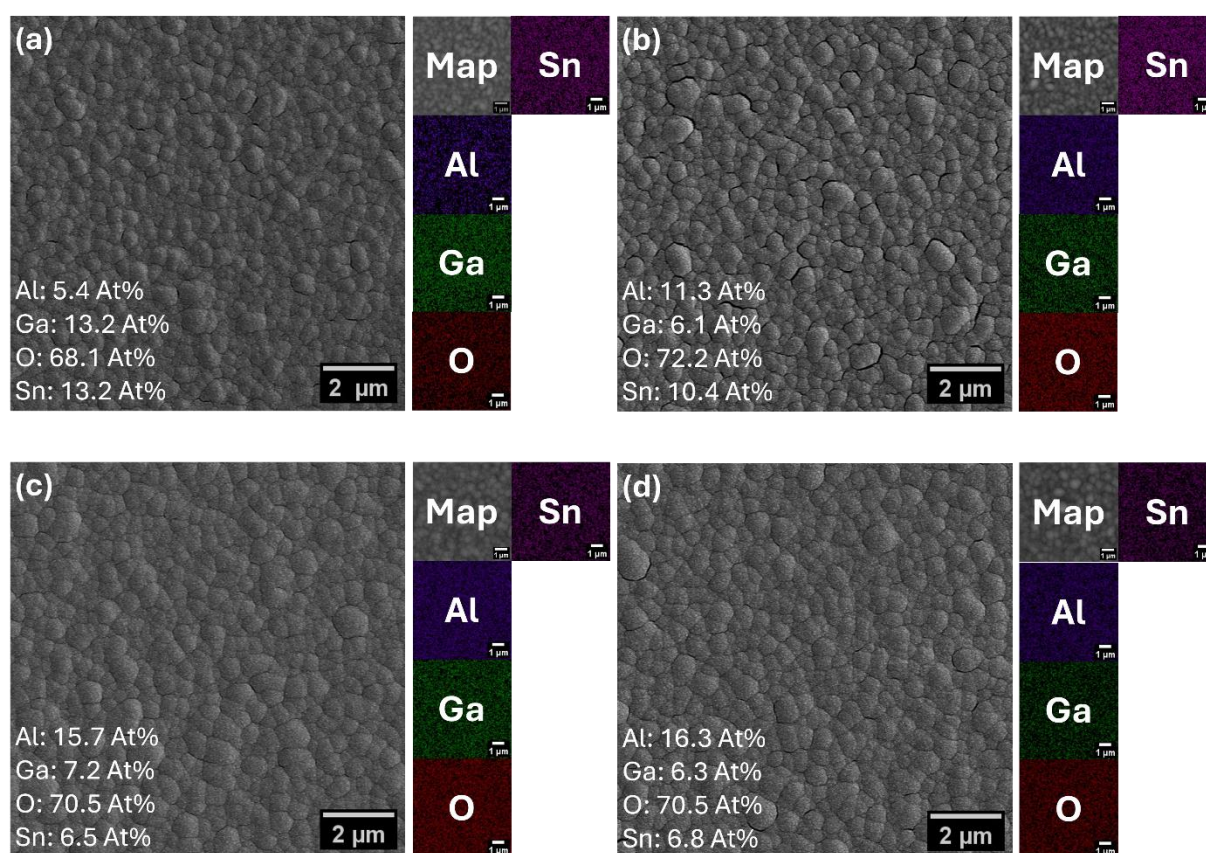


Figure 3.30. Top-view SEM images of calcined $AlGaO_x$ films ($T_{\text{calcination}} = 610\text{ }^{\circ}\text{C}$) synthesized from co-deposition of $[Al(TFB-tBuA)(O^tBu)_2]$ and $[Ga(TFB-tBuA)(O^tBu)_2]$ via MOCVD with mole fraction of aluminum (x Al) of (a) 0.144, (b) 0.293, (c) 0.420, and (d) 0.467.

XPS analysis (Figure 3.31) was subsequently carried out on the aluminum gallium oxide thin film prepared with x Al = 0.144, as this was the only sample that exhibited crystalline β - Ga_2O_3 features in the GIXRD measurements. Interestingly, no aluminum signal could be detected in the XPS spectrum. Given the substantially higher gallium content, any Al-related photoelectron signal may have been too weak to be distinguished from the spectrum

background, thereby preventing reliable identification and quantification. The high-resolution Ga $2p_{3/2}$ spectrum displayed a single peak centered at 1118.05 eV (Figure 3.31), consistent with Ga^{3+} species in gallium oxide and in agreement with the results obtained for the individually deposited Ga_2O_3 thin film. Similarly, the O 1s spectrum exhibited a dominant peak at 530.81 eV (Figure 3.31), characteristic of lattice oxygen (O^{2-}) in gallium oxide. These observations indicate that gallium is present in a fully oxidized state and that the local chemical environment of gallium closely resembles that found in β - Ga_2O_3 .

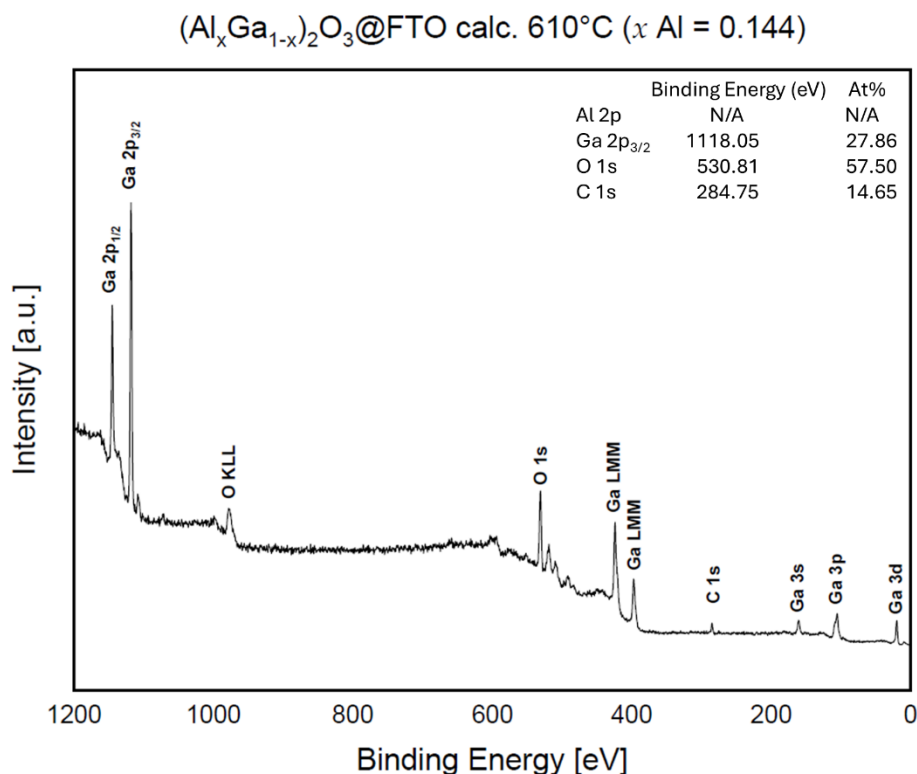


Figure 3.31. The XPS survey spectrum for calcined $(Al_xGa_{1-x})_2O_3$ film obtained from $[Al(TFB-tBuA)(O^tBu)_2]/[Ga(TFB-tBuA)(O^tBu)_2]$ (x Al = 0.144).

Quantitative analysis of the XPS survey spectrum revealed gallium and oxygen concentrations of 27.50 at.% and 57.50 at.%, respectively. These values correspond to a Ga:O atomic ratio of approximately 1:2.06. This ratio deviates significantly from the theoretical stoichiometry of Ga_2O_3 , which corresponds to a Ga:O ratio of 2:3 (or 1:1.5). The observed oxygen excess suggests that the oxygen detected by XPS cannot be attributed solely to gallium oxide. A more plausible explanation is that the oxygen signal originates from both gallium oxide and aluminum oxide phases within the film. Because aluminum could not be reliably detected, the contribution of Al–O bonds to the overall oxygen concentration cannot be directly quantified. Nevertheless, the elevated oxygen content provides indirect evidence for the

incorporation of aluminum oxide species within the deposited film, despite the absence of a measurable Al signal in the XPS spectrum.

Based on the combined GIXRD and XPS results, it can be concluded that the co-deposition process on FTO substrate does not lead to the formation of a single-phase crystalline $(Al_xGa_{1-x})_2O_3$ material under the applied deposition and calcination conditions. Instead, the deposited mixed-metal oxide film appears to consist of aluminum oxide and gallium oxide domains that coexist as composites within the same film.

This behavior can be attributed to the markedly different crystallization tendencies of the two constituent oxides. Under identical thermal treatment conditions, aluminum oxide remains amorphous, whereas gallium oxide readily crystallizes into the β - Ga_2O_3 phase. Consequently, during co-deposition and subsequent calcination, gallium-containing regions preferentially crystallize while aluminum-containing regions remain structurally disordered. As a result, the film cannot be described as phase-pure crystalline $(Al_xGa_{1-x})_2O_3$, but rather as a composite mixture of amorphous Al_2O_3 and crystalline β - Ga_2O_3 . Therefore, under the deposition conditions employed in this study, co-deposition using $[Al(TFB-tBuA)(O'Bu)_2]$ and $[Ga(TFB-tBuA)(O'Bu)_2]$ results in the formation of mixed aluminum gallium oxide films composed of amorphous Al_2O_3 and crystalline β - Ga_2O_3 rather than a single-phase crystalline $(Al_xGa_{1-x})_2O_3$ material.

To promote crystallization of the deposited material, $(Al_xGa_{1-x})_2O_3$ thin films were subsequently deposited onto Si(111) and Ti substrates, both of which can withstand the elevated temperatures required for post-deposition calcination. The deposition was carried out under the same conditions used in the previous experiments, while varying the molar ratio of $[Al(TFB-tBuA)(O'Bu)_2]$ to $[Ga(TFB-tBuA)(O'Bu)_2]$ as summarized in Table 3.4.

Table 3.4. Mole fraction of aluminum (x Al) during MOCVD of aluminum gallium oxide on Si(111) and Ti substrates.

Sample	Mass of $[Al(TFB-tBuA)(O'Bu)_2]$ (g)	Mass of $[Ga(TFB-tBuA)(O'Bu)_2]$ (g)	Mole fraction (x Al)	Mass used during deposition (g)
5	0.04	0.12	0.271	0.16

For the Si(111) substrate, a pronounced change in surface appearance was observed after deposition, as evidenced by the difference in color between the untreated substrate (Figure 3.32a) and the as-deposited sample (Figure 3.32b). Following calcination at 1000 °C for 8 h,

the film exhibited an additional change in color (Figure 3.32c), suggesting further chemical and structural transformations during the high-temperature treatment.

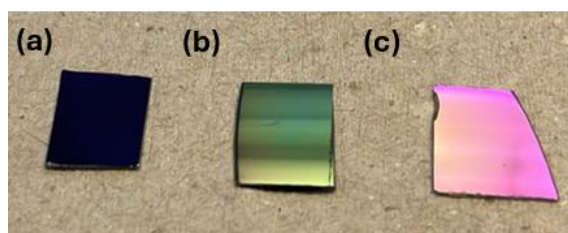


Figure 3.32. Surface appearance of (a) only Si(111) substrate, (b) as-deposited, and (c) calcined aluminum gallium oxide films with mole fraction of aluminum ($x \text{ Al}$) = 0.271.

A comparable behavior was observed for the Ti substrate. The as-deposited sample displayed a noticeable color change relative to the pristine Ti surface (Figure 3.33a and b), indicating successful film formation. Subsequent calcination at 1000 °C for 8 h resulted in a further modification of the surface appearance (Figure 3.33c), consistent with thermally induced changes in the deposited layer. These observations suggest that both substrates underwent significant surface and film changes during calcination, warranting further structural and compositional characterization to determine the nature of the resulting phases.

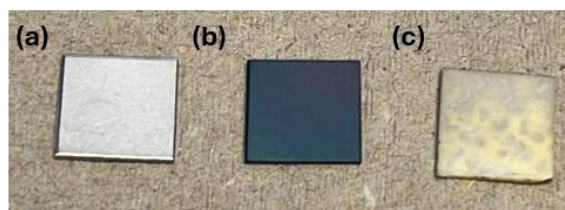


Figure 3.33. Surface appearance of (a) only Ti substrate, (b) as-deposited, and (c) calcined aluminum gallium oxide films with mole fraction of aluminum ($x \text{ Al}$) = 0.271.

XRF analysis revealed the presence of gallium on both Si(111) and Ti substrates after the $(Al_xGa_{1-x})_2O_3$ deposition process (Figure 3.34c and d), whereas no gallium signal was detected on the corresponding untreated substrates (Figure 3.34a and b). The appearance of the gallium signal following deposition provides strong evidence that an aluminum gallium oxide-containing layer was successfully formed on both substrates. After calcination, the intensity and position of the gallium peaks remained largely unchanged (Figure 3.34e and f), indicating that the deposited films remained adherent to the substrate surfaces and were not removed during the high-temperature treatment. While XRF confirms the presence of gallium-containing material, it does not provide information regarding the crystal structure of the deposited layer. Therefore, further characterization by X-ray diffraction was carried out to

verify the formation of $(Al_xGa_{1-x})_2O_3$ and to determine the crystalline phases present after calcination.

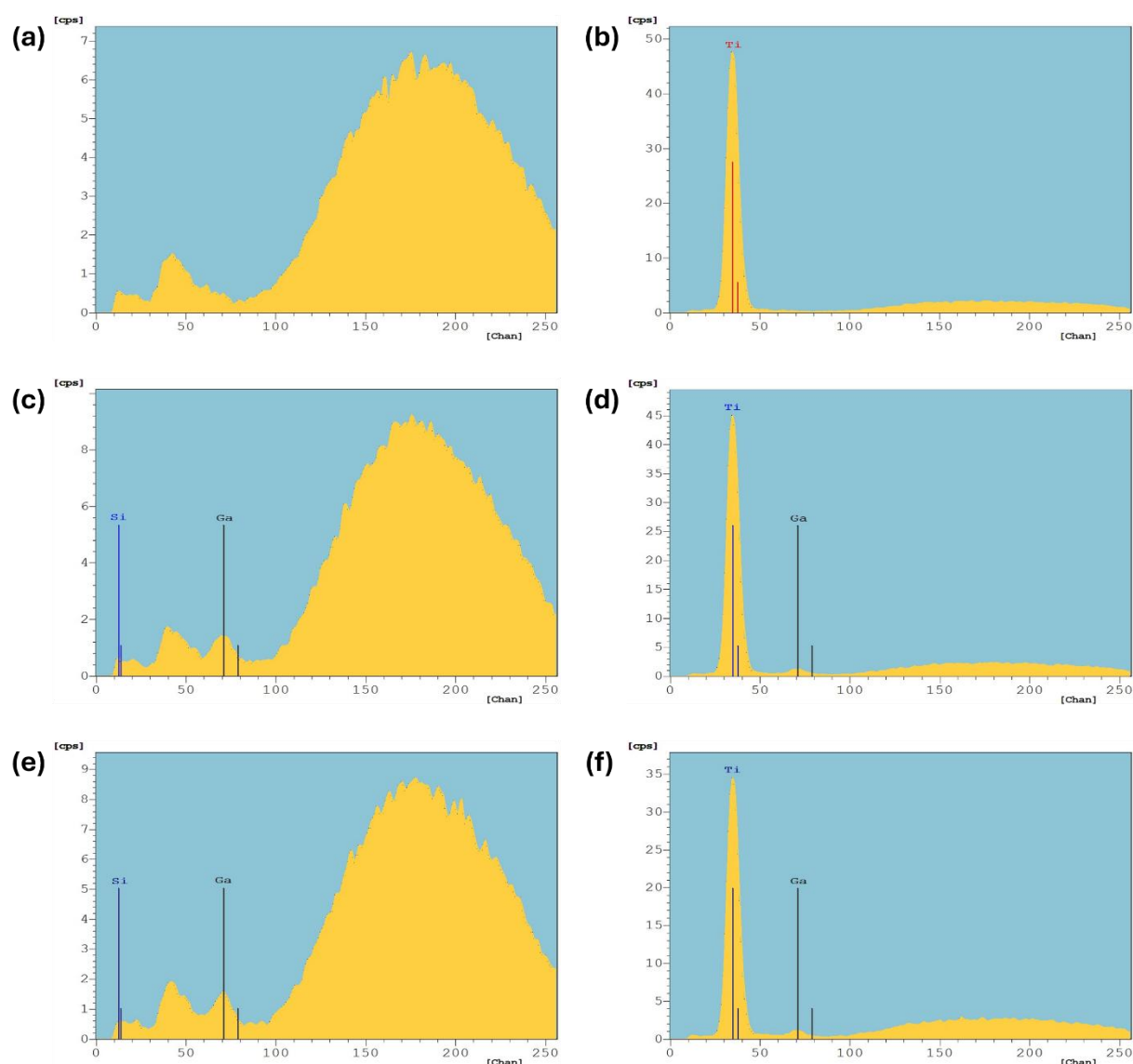


Figure 3.27. XRF results of (a) only Si(111) substrate, (b) only Ti substrate, (c) as-deposited aluminum gallium oxide thin films on Si(111), (d) as-deposited aluminum gallium oxide thin films on Ti, (e) aluminum gallium oxide thin films on Si(111) after calcination in air at 1000 °C for 8 hours, and (f) aluminum gallium oxide thin films on Ti after calcination in air at 1000 °C for 8 hours, with mole fraction of aluminum (x Al) of 0.271.

The XRD patterns of the $(Al_xGa_{1-x})_2O_3$ thin films deposited on Si(111) substrates before and after calcination are shown in Figure 3.35. No significant differences were observed between the two diffraction patterns. Moreover, no diffraction peaks attributable to β -(Al_xGa_{1-x}) $_2O_3$, represented here by the characteristic reflections of β - Ga_2O_3 , were detected. This suggests that the deposited film either remained amorphous, was present in quantities below

the detection limit of the technique, or did not crystallize into a detectable β -(Al_xGa_{1-x}) $_2O_3$ phase under the applied calcination conditions.

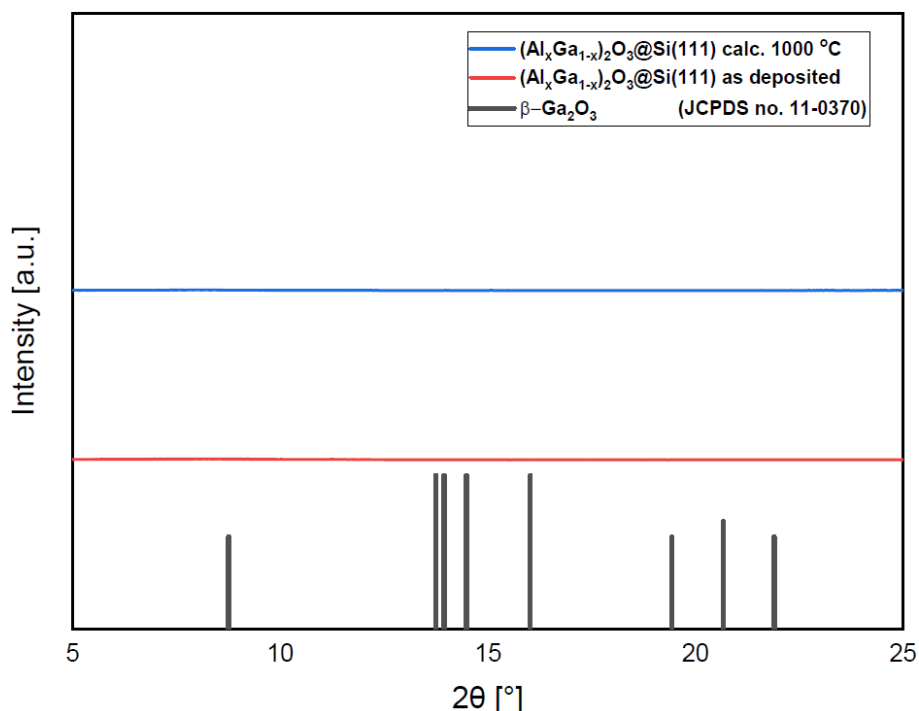


Figure 3.35. The XRD pattern of films obtained from the MOCVD of mixed $[Al(TFB-tBuA)(O'Bu)_2]$ and $[Ga(TFB-tBuA)(O'Bu)_2]$ on Si(111) substrate with mole fraction of aluminum (x Al) of 0.271.

A similar outcome was obtained for the films deposited on Ti substrates (Figure 3.36). No diffraction peaks corresponding to β -(Al_xGa_{1-x}) $_2O_3$ were observed either before or after calcination. Instead, calcination at 1000 °C in air resulted in the formation of tetragonal TiO_2 , as evidenced by reflections corresponding to t - TiO_2 (JCPDS no. 78-1510). This phase formation is attributed to oxidation of the Ti substrate (JCPDS no. 44-1294) by atmospheric oxygen during the high-temperature treatment. Consequently, the diffraction pattern was dominated by the oxide layer formed on the substrate, while no crystalline aluminum gallium oxide phase could be identified.

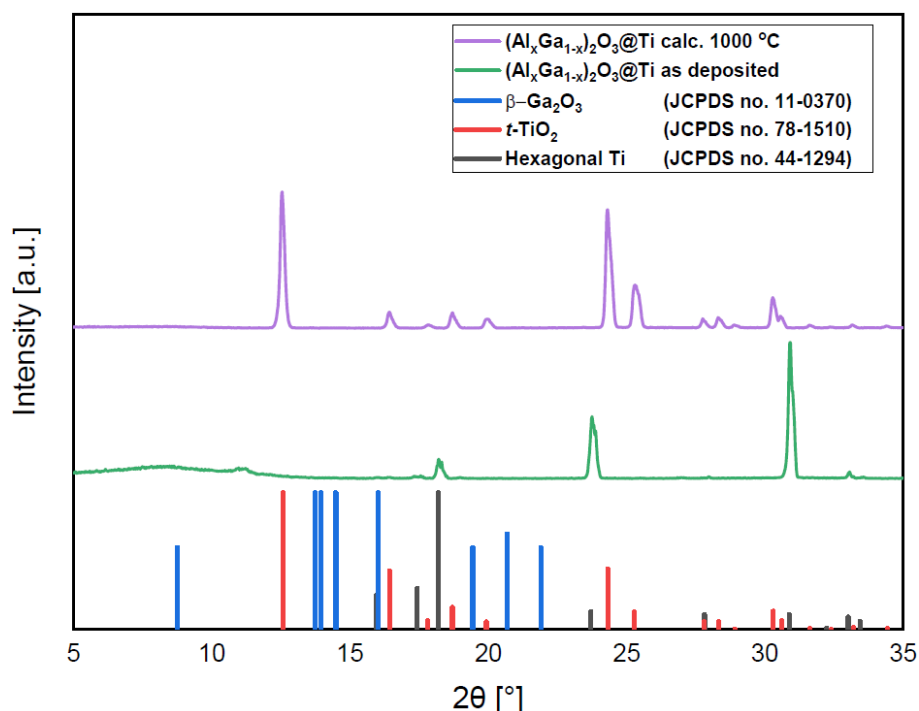


Figure 3.35. The XRD pattern of films obtained from the MOCVD of mixed $[\text{Al}(\text{TFB-}t\text{BuA})(\text{O'Bu})_2]$ and $[\text{Ga}(\text{TFB-}t\text{BuA})(\text{O'Bu})_2]$ on Ti substrate with mole fraction of aluminum (x Al) of 0.271.

Two isostructural monomeric Group 13 complexes, $[\text{M}(\text{TFB-}t\text{BuA})(\text{O'Bu})_2]$ ($\text{M} = \text{Al}$, Ga), featuring tetrahedral coordination geometries, were successfully synthesized and comprehensively characterized. Both complexes exhibited favorable thermal properties and similar decomposition behavior as determined by TG-DSC analysis. However, despite their structural similarity, significant differences in vapor pressure were observed, highlighting the important influence of the metal center on volatility and vapor-phase transport.

The synthesized complexes proved suitable as MOCVD precursors for the individual deposition of Al_2O_3 and Ga_2O_3 thin films on FTO substrates. In contrast, co-deposition using these compounds as a dual-source precursor system did not lead to the formation of phase-pure $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ under the deposition conditions investigated in this study. Instead, the results suggest that differences in precursor volatility and transport behavior hinder the controlled incorporation of aluminum and gallium into a single crystalline phase. Nevertheless, the successful deposition of aluminum- and gallium-containing oxide films demonstrates the viability of these precursors for mixed-metal oxide growth. With further optimization of precursor delivery, sublimation conditions, deposition parameters, and post-deposition treatments, these isostructural complexes remain promising candidates for the controlled synthesis of $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ thin films by MOCVD.

4. Syntheses and Characterization of Fluorinated β -Ketoenamine-based Zirconium Complexes and Their Application in Deposition of Zirconium Oxynitride Thin Films

4.1. Scientific Context

Zirconium oxynitride (abbreviated as ZrON) is an advanced ceramic material that has attracted considerable attention due to its ability to combine the beneficial characteristics of zirconium nitride (ZrN) and zirconium oxide (ZrO₂) within a single tunable compound [85-90].

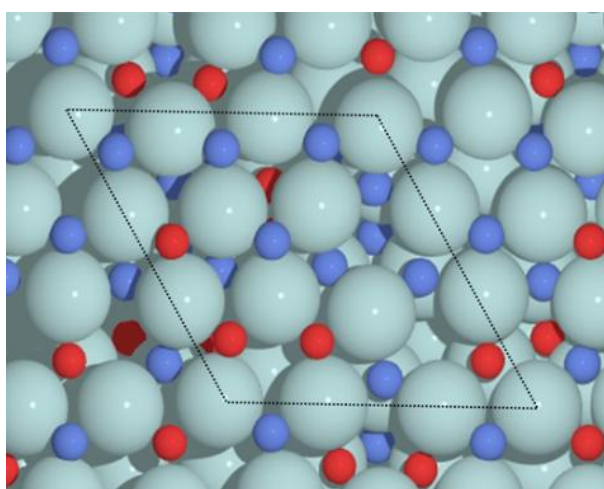


Figure 4.1. Geometry of zirconium oxynitride, Zr₂ON₂ (color code: cyan = Zr; red = O; blue = N). Adapted from Sinha *et al.* [95] licensed under CC BY.

By incorporating both oxygen and nitrogen atoms into the zirconium lattice, the material forms a solid solution whose physical, chemical, and functional properties can be precisely adjusted through control of the O/N ratio [85-90]. This compositional flexibility allows ZrON to bridge the gap between metallic-like conductive nitrides and insulating, chemically stable oxides [85-94]. As a result, ZrON exhibits a unique balance of high hardness, excellent wear resistance, improved oxidation resistance, thermal stability at elevated temperatures, and enhanced corrosion resistance in aggressive environments [85-94]. Such versatility makes ZrON highly promising for a broad range of applications, including protective hard coatings for cutting tools and mechanical components, diffusion barriers in microelectronic devices, decorative coatings with superior durability, and corrosion-resistant or biocompatible layers for biomedical and chemical processing applications [85-94]. The ability to fine-tune electrical conductivity and

optical behavior further extends its potential toward optoelectronic and energy-related technologies [90, 94-96].

To date, ZrON thin films have been predominantly synthesized using physical vapor deposition (PVD) techniques, with reactive magnetron sputtering being the most widely reported method [85, 87, 90]. In this process, a zirconium metal target is sputtered in a controlled reactive atmosphere containing argon, nitrogen, and oxygen gases, where the relative partial pressures of N_2 and O_2 govern the final stoichiometry and phase composition of the film [85, 87, 90]. Careful adjustment of deposition parameters such as substrate temperature, total pressure, target power, and substrate bias voltage strongly influences film density, crystallinity, stress state, and mechanical performance [85, 87, 90].

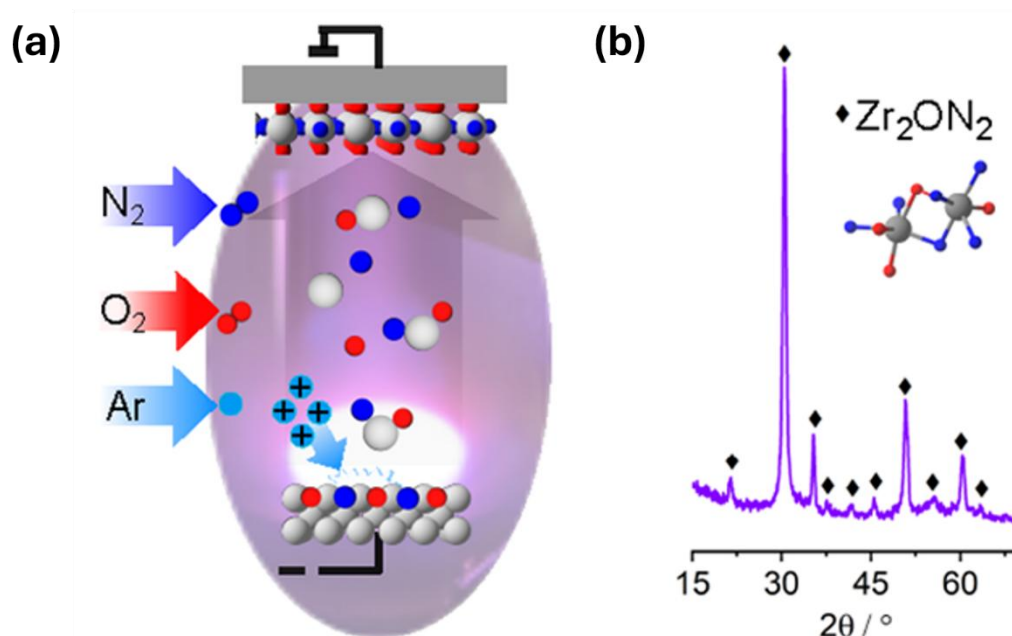


Figure 4.2. (a) Schematic representation of ZrON thin films synthesis via magnetron sputtering based on Streibel *et al.* [90], and (b) XRD pattern and chemical structure representation of Zr_2ON_2 thin films obtained by Streibel *et al.* [90]. Adapted from V. Streibel, J. L. Schönecker, L. I. Wagner, E. Sirotti, F. Munnik, M. Kuhl, C.-M. Jiang, J. Eichhorn, S. Santra and I. D. Sharp, *ACS Applied Energy Materials*, **2024**, 7, 4004-4015. Licensed under the Creative Commons Attribution 4.0 International License (CC BY 4.0).

Other PVD-based approaches, including cathodic arc evaporation, have also been explored to produce dense and adherent ZrON coatings [86]. Despite the significant body of work using these vacuum-based physical methods, there remains a clear lack of reported studies on ZrON deposition via MOCVD. This absence represents a noteworthy research gap, as MOCVD offers several intrinsic advantages. The limited investigation of ZrON growth through MOCVD therefore suggests significant untapped potential, particularly for advanced

microelectronic, energy, and coating applications where uniformity, reproducibility, and industrial scalability are critical.

One possible strategy for the deposition of zirconium oxynitride involves the development of nitrogen-rich zirconium precursors. For example, Banerjee *et al.* [97] reported the synthesis of the heteroleptic zirconium complex $[\text{Zr}\{\eta^2\text{-}(i\text{PrN})_2\text{CNMe}_2\}_2(\text{NMe}_2)_2]$ (Figure 4.3), which contains both dialkylamido and guanidinate ligands. This precursor was successfully employed for the deposition of ZrN when N_2 was used as the reactive gas, while ZrO_2 could be obtained by introducing O_2 as the oxygen source. Despite these advances, no studies have yet reported the direct deposition of ZrON thin films by MOCVD. Therefore, the design of zirconium complexes that are intrinsically rich in nitrogen while simultaneously incorporating coordinated oxygen-containing ligands represents an attractive approach toward the development of single-source precursors for ZrON deposition. Such a molecular design could provide both nitrogen and oxygen directly from the precursor itself, potentially enabling controlled formation of zirconium oxynitride films while simplifying the deposition process and reducing dependence on external reactive gases.

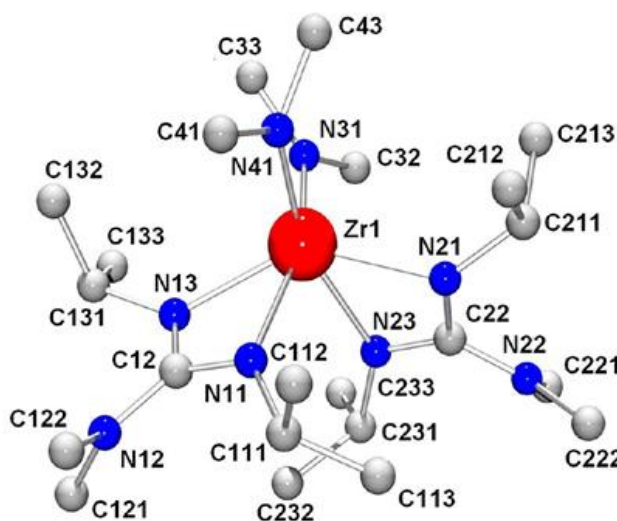
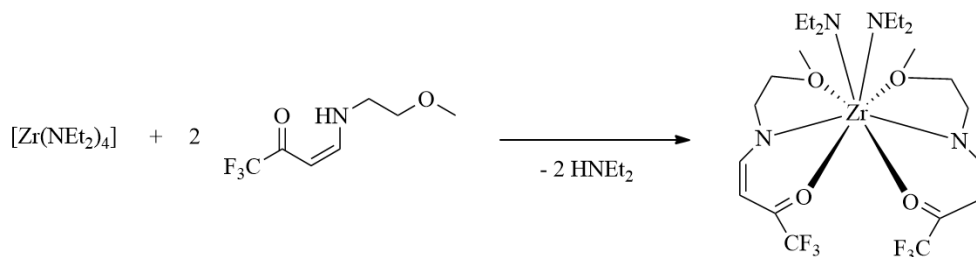


Figure 4.3. Molecular structure of $[\text{Zr}\{\eta^2\text{-}(i\text{PrN})_2\text{CNMe}_2\}_2(\text{NMe}_2)_2]$. Adapted from Banerjee *et al.* [97] with permission from American Chemical Society. © American Chemical Society.

4.2. Syntheses and Characterization of $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$, $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{NEt}_2)_2]$, $[\text{Zr}(\text{TFB-}i\text{BuA})_2\{\eta^2\text{-}(i\text{PrN})_2\text{CNEt}_2\}_2]$, $[\text{Zr}(\text{TFB-TFEA})_4]$, and $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{NEt}_2)(\text{O}^i\text{Bu})]$

The selection of the *H*-TFB-MEA ligand for the heteroleptic synthesis of zirconium complexes was motivated by an earlier finding showing that two equivalents of this ligand can

adopt a tridentate coordination mode [38]. In a reaction with one equivalent of $[\text{Th}(\text{hmds})_4]$ and two equivalents of ROH, the ligand forms the complex $[\text{Th}(\text{TFB-MEA})_2(\text{ROH})_2]$ ($\text{R} = \text{'Pr}$ or 'Bu), in which the thorium center reaches a coordination number of eight through chelation and additional coordination from the oxygen atom of methoxy group from TFB-MEA ligand [38]. This behavior demonstrates the ability of *H*-TFB-MEA to stabilize high-coordination metal centers. Based on this precedent, the reaction of one equivalent of $[\text{Zr}(\text{NEt}_2)_4]$ with two equivalents of *H*-TFB-MEA was expected to produce a zirconium complex with a similar coordination number (Scheme 4.1). Zirconium(IV), like thorium(IV), commonly favors high coordination due to its oxophilic nature and large ionic radius. A coordination number of eight would also suggest improved thermal stability, which is an essential requirement for complexes intended for solid-to-vapor transitions during heating. This made *H*-TFB-MEA a suitable candidate for the development of zirconium precursors for vapor-phase deposition.



Scheme 4.1. Reaction scheme for the synthesis of $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$.

Unlike in the synthesis of $[\text{Th}(\text{TFB-MEA})_2(\text{ROH})_2]$ (in alcohol), the reaction of one equivalent of $[\text{Zr}(\text{NEt}_2)_4]$ with two equivalents of *H*-TFB-MEA afforded a yellow powder. Based on the reaction stoichiometry, this product was tentatively assigned as $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$, formed through the substitution of two diethylamido ligands by two TFB-MEA ligands. To verify the molecular structure of the resulting complex, the crude product was recrystallized in a mixture of toluene and *n*-heptane stored at $-20\text{ }^\circ\text{C}$, yielding single crystals suitable for structural determination by Single-Crystal X-ray Diffraction (SC-XRD) analysis (Figure 4.4).



Figure 4.4. As-obtained $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$ upon recrystallization in a mixture of toluene and *n*-heptane stored at $-20\text{ }^\circ\text{C}$.

SC-XRD analysis of recrystallized $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$ revealed that the complex crystallizes in the triclinic space group *P*-1. The SC-XRD data further showed that the solid-state structure does not correspond to the coordination environment from the reaction scheme shown above. Rather than forming an eight-coordinate complex as initially expected, $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$ adopts a six-coordinate geometry. The zirconium center is arranged in a distorted octahedral environment (Figure 4.5).

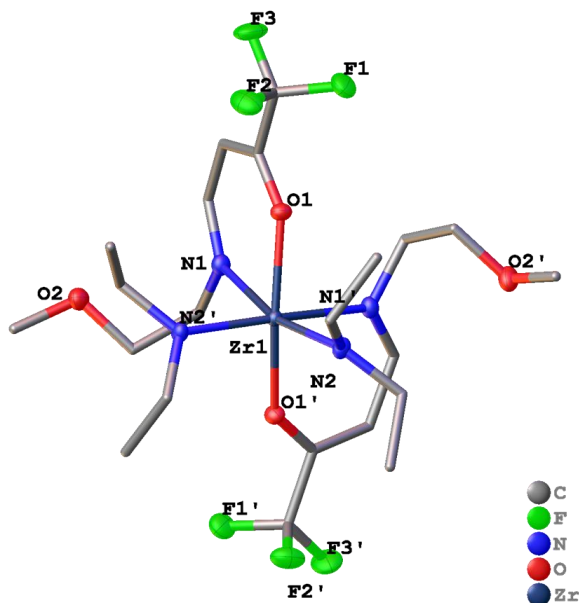


Figure 4.5. The single crystal X-ray crystal structure of $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$. Hydrogen atoms are omitted for clarity.

The Zr–O bond lengths fall within a narrow range of 2.0802(6)–2.0807(6) Å. The Zr–N distances associated with the TFB-MEA ligands are slightly longer, measured at 2.4209(7)–2.4214(7) Å, whereas the Zr–N bonds of the diethylamido ligands are shorter, lying between 2.0519(7) and 2.0533(7) Å (Table 4.1). These values are consistent with those reported for

related heteroleptic zirconium complexes in the literature, as reported by Franceschini *et al.* [98], the complex bis(4-(methylamino)pent-3-en-2-onato)bis(diethylamido)zirconium exhibits Zr–O bond lengths of approximately 2.0658(11) Å, while the Zr–N bond distances range from 2.0698(13) to 2.3896(13) Å, indicating comparable bonding characteristics and similar ligand–metal interactions [98–100].

Table 4.1. Bond lengths [Å] in [Zr(TFB-MEA)₂(NEt₂)₂].

Bond lengths [Å]	Value
Zr1–O1 [Å]	2.0807(6)
Zr1–O1' [Å]	2.0802(6)
Zr1–N2 [Å]	2.0533(7)
Zr1–N2' [Å]	2.0519(7)
Zr1–N1 [Å]	2.4214(7)
Zr1–N1' [Å]	2.4209(7)

The ¹H NMR spectrum of [Zr(TFB-MEA)₂(NEt₂)₂] (Figure 4.6) was difficult to assign unambiguously due to the presence of multiple chemically similar proton environments arising from both the coordinated TFB-MEA ligands and the diethylamido ligands. The methylene and methyl protons of these moieties resonate within a relatively narrow chemical shift range, resulting in extensive signal overlap. Furthermore, coordination to the zirconium center modifies the electronic environment of the ligands, causing shifts in resonance positions and increasing the complexity of the spectrum pattern. The presence of residual uncoordinated *H*-TFB-MEA ligand from the synthesis or purification process may also contribute additional resonances, further complicating the assignment of individual proton signals. Consequently, a complete assignment of all resonances based solely on ¹H NMR spectroscopy was not possible.

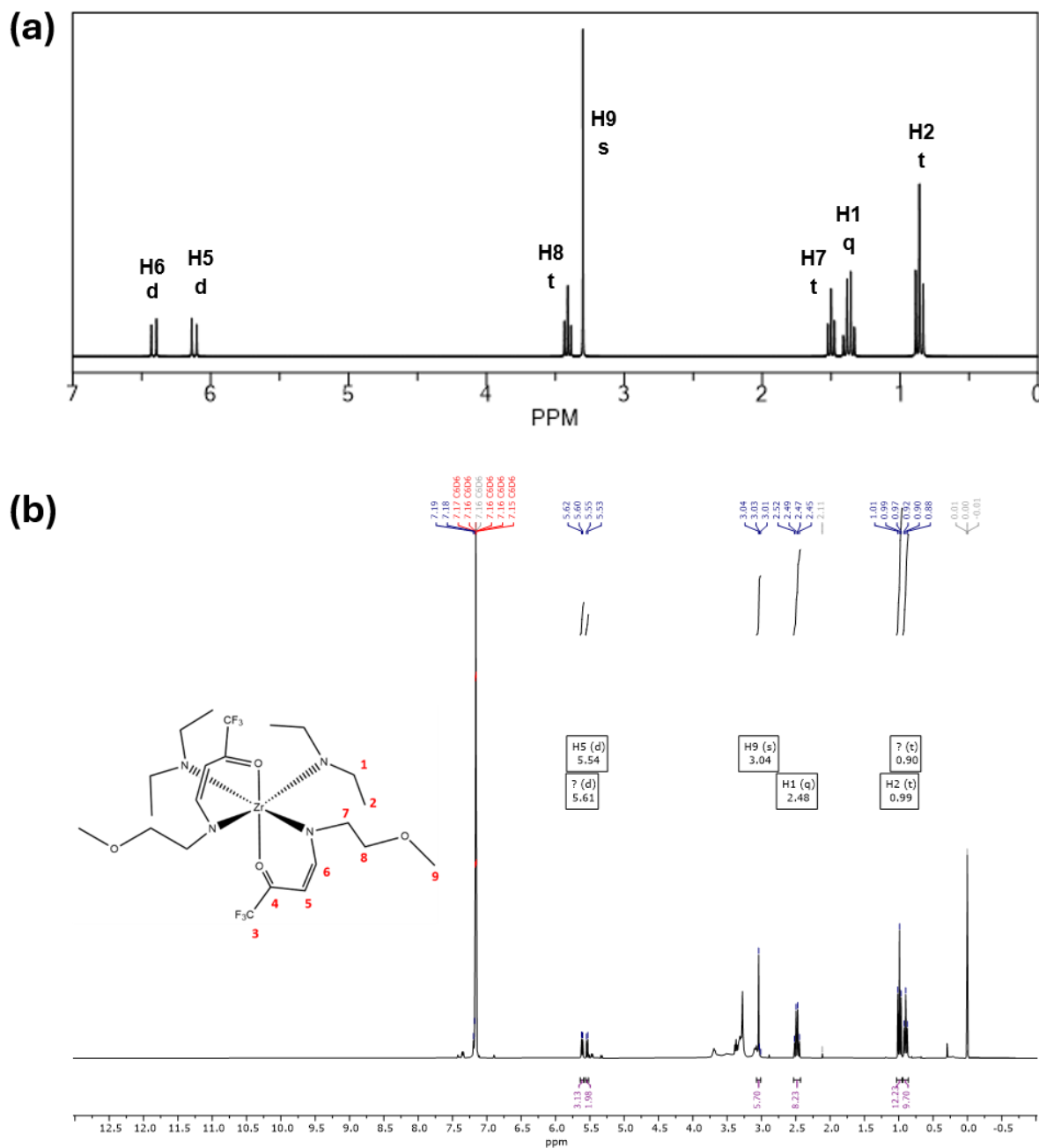


Figure 4.6. (a) Predicted ^1H NMR spectrum of $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$ (b) actual ^1H NMR spectrum of $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$.

In the $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$, the oxygen atoms of the methoxy substituents are not coordinated to the zirconium center. This structural feature contrasts clearly with the thorium analogue $[\text{Th}(\text{TFB-MEA})_2(\text{ROH})_2]$, in which the oxygen atoms of methoxy groups from the TFB-MEA ligands are able to participate in metal coordination (Figure 4.7). The absence of this interaction in the zirconium complex can be explained by the pronounced difference in ionic radii between the two metal ions. The Zr^{4+} ion (ionic radius = $0.72 \text{ \AA}$ for a coordination

number of six) is considerably smaller and more compact than the Th^{4+} ion (ionic radius = 1.05 Å for a coordination number of eight) [101].

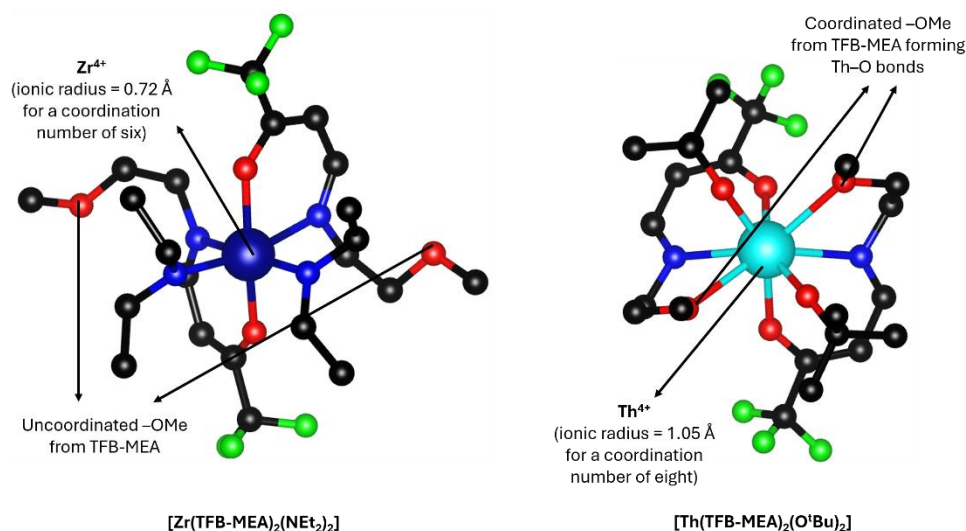


Figure 4.7. Comparison of the metal center coordination environments of Zr^{4+} in $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$ and Th^{4+} in $[\text{Th}(\text{TFB-MEA})_2(\text{O}^i\text{Bu})_2]$ from Lichtenberg *et al.* [38].

Because of the substantially reduced size of Zr^{4+} , the metal center cannot accommodate the same spatial arrangement of donor atoms as Th^{4+} . The geometry around zirconium becomes more restricted, and the oxygen atoms of methoxy groups from the TFB-MEA ligands are simply unable to reach the metal center without incurring significant geometric strain. As a result, coordination is limited to the donor atoms that can be accommodated within the steric and electronic constraints of the six-coordinate zirconium environment. This difference highlights an important metal-dependent limitation, while the TFB-MEA ligand is flexible enough to act as a tridentate donor toward larger metal ions, such as Th^{4+} , the same binding mode cannot be adopted toward smaller, more compact ions such as Zr^{4+} . Consequently, the zirconium complex forms a six-coordinate, distorted octahedral structure rather than the eight-coordinate geometry observed for its thorium counterpart.

To evaluate whether $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$ is suitable for use as a precursor in the MOCVD of ZrON thin films, sublimation was carried out. The complex was subjected to gentle heating within the temperature range of 90-150 °C ($p \approx 1$ mbar). This range was selected because it corresponds to relatively low temperatures commonly applied MOCVD processes. For the experiment, a small round-bottom flask (10-50 mL) containing the solid $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$ was connected to a cold finger that was in turn attached to the stock line under vacuum ($p \approx 1$ mbar). The flask was heated using an oil bath. Under these conditions, the cold finger acted as the deposition surface on which sublimed molecules of $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$ were deposited.

$\text{MEA})_2(\text{NEt}_2)_2]$ could condense and crystallize. This setup allowed direct observation of whether the complex is capable of undergoing a clean solid-to-vapor transition, which is a key requirement for its potential application as a MOCVD precursor.

When the temperature reached approximately 100 °C, the complex did not undergo sublimation. Instead, decomposition was observed through a pronounced color change from yellow powder to brown (Figure 4.8). No crystalline material was observed to form on the surface of the cold finger, further confirming that sublimation did not occur under these conditions.



Figure 4.8. $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$ after sublimation experiment at approximately 100 °C ($p \approx 1$ mbar).

Furthermore, Hirshfeld surface (HS) analysis of $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$ was performed to quantify and visualize intermolecular interactions. Figure 4.9a-i reveals distinct regions associated with the $-\text{CF}_3$ groups. These features indicate that the $-\text{CF}_3$ units participate in intermolecular $\text{F} \cdots \text{F}$ close contacts within the solid-state packing, contributing 2.5% to the overall HS (Figure 4.9c) [102, 103]. In addition, the fluorinated substituents are involved in numerous $\text{H} \cdots \text{F}$ contacts, which account for 34.3% of the HS area (Figure 4.9d and e). These contacts may be described as weak $\text{C-H} \cdots \text{F}$ hydrogen-bonding interactions where appropriate geometrical criteria are satisfied. The high contribution of $\text{H} \cdots \text{F}$ contacts primarily reflects the extensive fluorinated surface of the molecule and the prevalence of fluorine atoms at the crystal-packing interface. Although $-\text{CF}_3$ groups are often introduced to reduce strong intermolecular interactions and disrupt efficient crystal packing through their steric bulk and fluorinated character, the HS analysis indicates that they nevertheless participate in multiple weak intermolecular contacts in the solid state crystal packing in $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$.

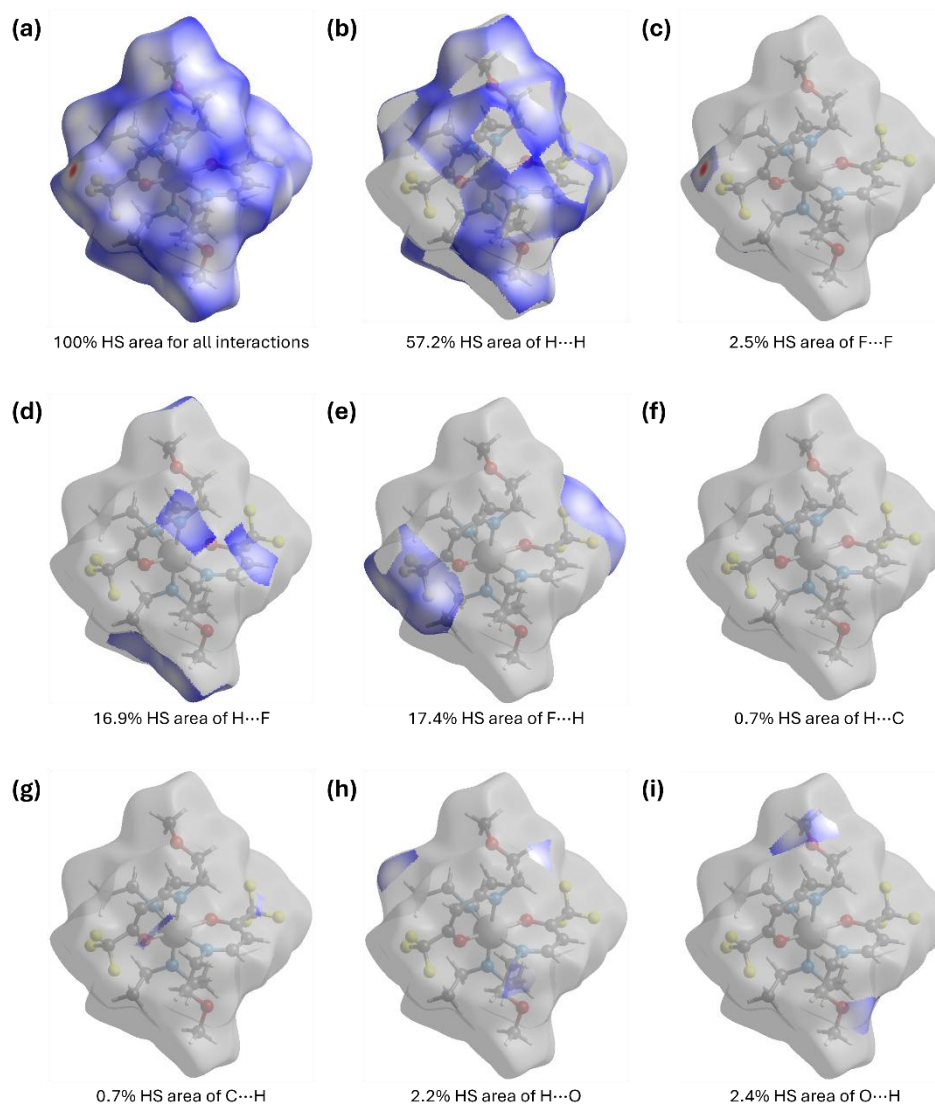
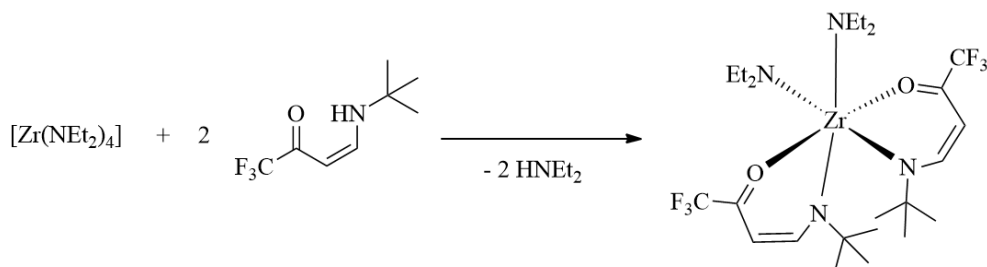


Figure 4.9. (a) Hirshfeld surface (HS) simulation of one $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$ molecule with 100% of HS area contributed to all interactions, (b) 57.2% of HS area contributed to $\text{H}\cdots\text{H}$ interaction, (c) 2.5% of HS area contributed to $\text{F}\cdots\text{F}$ interaction, (d) 16.9% of HS area contributed to $\text{H}\cdots\text{F}$ interaction, (e) 17.4% of HS area contributed to $\text{F}\cdots\text{H}$ interaction, (f) 0.7% of HS area contributed to $\text{H}\cdots\text{C}$ interaction, (g) 0.7% of HS area contributed to $\text{C}\cdots\text{H}$ interaction, (h) 2.2% of HS area contributed to $\text{H}\cdots\text{O}$ interaction, and (i) 2.4% of HS area contributed to $\text{O}\cdots\text{H}$ interaction. Color code: Gray = Zirconium; Black = Carbon; White = Hydrogen; Red = Oxygen; Cyan = Nitrogen; Yellow = Fluorine.

The oxygen atoms of the uncoordinated methoxy groups also contribute to intermolecular $\text{C-H}\cdots\text{O}$ hydrogen-bonding interactions, reflected by an additional 4.6% of the HS area (Figure 4.9h and i). While the $\text{F}\cdots\text{F}$ and $\text{H}\cdots\text{F}$ contacts are generally weak and largely dispersive in nature, the presence of $\text{C-H}\cdots\text{O}$ interactions provides additional stabilization to the crystal packing. Collectively, these intermolecular contacts contribute to the cohesion of the solid-state structure and may hinder molecular desorption during heating, thereby limiting the volatility and sublimation behavior of the complex.

These findings demonstrate that the zirconium center cannot accommodate eight coordination bonds with two equivalents of diethylamido and two equivalents of TFB-MEA ligands due to its smaller ionic radius compared to that of thorium. Instead, the reaction yields the six-coordinate complex $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$, in which the methoxy groups remain non-coordinating. The presence of these unbound methoxy groups introduces additional intermolecular $\text{C-H}\cdots\text{O}$ interactions that reinforce the crystal packing and are likely detrimental to volatility. Consequently, the development of ligand systems that do not rely on tridentate coordination and that minimize opportunities for intermolecular association while promoting steric shielding around the metal center may provide a more effective strategy for improving the volatility and sublimation behavior of zirconium complexes intended for precursor applications.

The use of bidentate *H*-TFB-*t*BuA ligand was expected to yield an octahedral zirconium complex with sufficient vapor pressure possibly due to the presence of the *tert*-butyl substituent, whose large steric bulk is anticipated to suppress intermolecular repulsion to facilitate intact vapor phase transport. The reaction of one equivalent of $[\text{Zr}(\text{NEt}_2)_4]$ with two equivalents of *H*-TFB-*t*BuA was therefore expected to produce one equivalent of the heteroleptic complex $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)_2]$ (Scheme 4.2).



Scheme 4.2. Reaction scheme for the synthesis of $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)_2]$.

$[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)_2]$ was subsequently recrystallized in a mixture of toluene and *n*-heptane stored at $-20\text{ }^\circ\text{C}$ (Figure 4.10) to obtain crystals suitable for structural analysis.



Figure 4.10. As-obtained $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)_2]$ upon recrystallization in a mixture of toluene and *n*-heptane stored at $-20\text{ }^\circ\text{C}$.

SC-XRD analysis of recrystallized $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{NEt}_2)_2]$ revealed that the complex crystallizes in the monoclinic space group $P2_1/c$. The complex adopts a six-coordinate geometry in which the zirconium center is situated in a distorted octahedral environment (Figure 4.11).

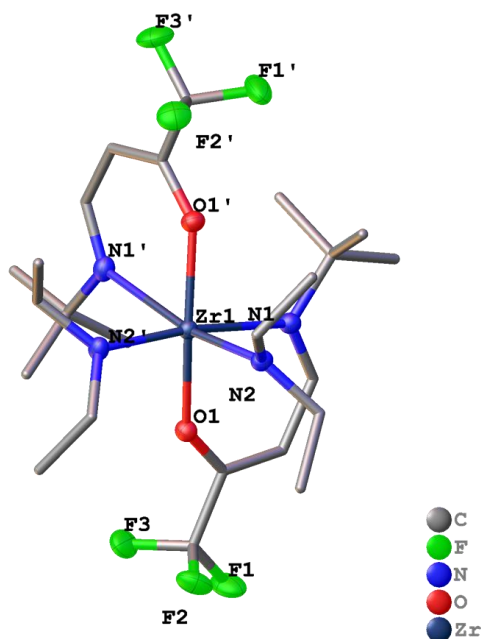


Figure 4.11. The single crystal X-ray crystal structure of $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{NEt}_2)_2]$. Hydrogen atoms are omitted for clarity.

The Zr–O bond lengths lie within a narrow range of 2.0726(18)-2.0814(17) Å, while the Zr–N distances associated with the TFB-*i*BuA ligands are slightly longer, measured at 2.551(3)-2.557(3) Å. In contrast, the Zr–N bonds of the diethylamido ligands are shorter, spanning 2.052(3)-2.053(3) Å (Table 4.2). These structural parameters closely match those observed for $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$, indicating comparable bonding interactions despite the different ligand substituents.

Table 4.2. Bond lengths [Å] in $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{NEt}_2)_2]$.

Bond lengths [Å]	Value
Zr1–O1 [Å]	2.0814(17)
Zr1–O1' [Å]	2.0725(17)
Zr1–N2 [Å]	2.052(2)
Zr1–N2' [Å]	2.053(2)
Zr1–N1 [Å]	2.551(2)
Zr1–N1' [Å]	2.557(2)

The ^1H NMR spectrum of $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{NEt}_2)_2]$ supports the formation of the desired product (Figure 4.12). A singlet (s) at 0.93 ppm, integrating to eighteen protons, corresponds to the methyl groups of the two *tert*-butyl substituents. Two doublets (d) at 5.61-5.63 ppm and 7.26-7.28 ppm were assigned to the C5 and C6 protons of the two TFB-*i*BuA ligands, respectively, each displaying the expected 2:2 proton ratio. The two diethylamido ligands gave rise to singlets (s) at 3.14 and 3.55 ppm, corresponding to the methylene protons (C1), with a combined 4:4 proton ratio, while the methyl protons (C2) appeared as a doublet of triplets (td) at 1.15-1.20 ppm, integrating for twelve protons.

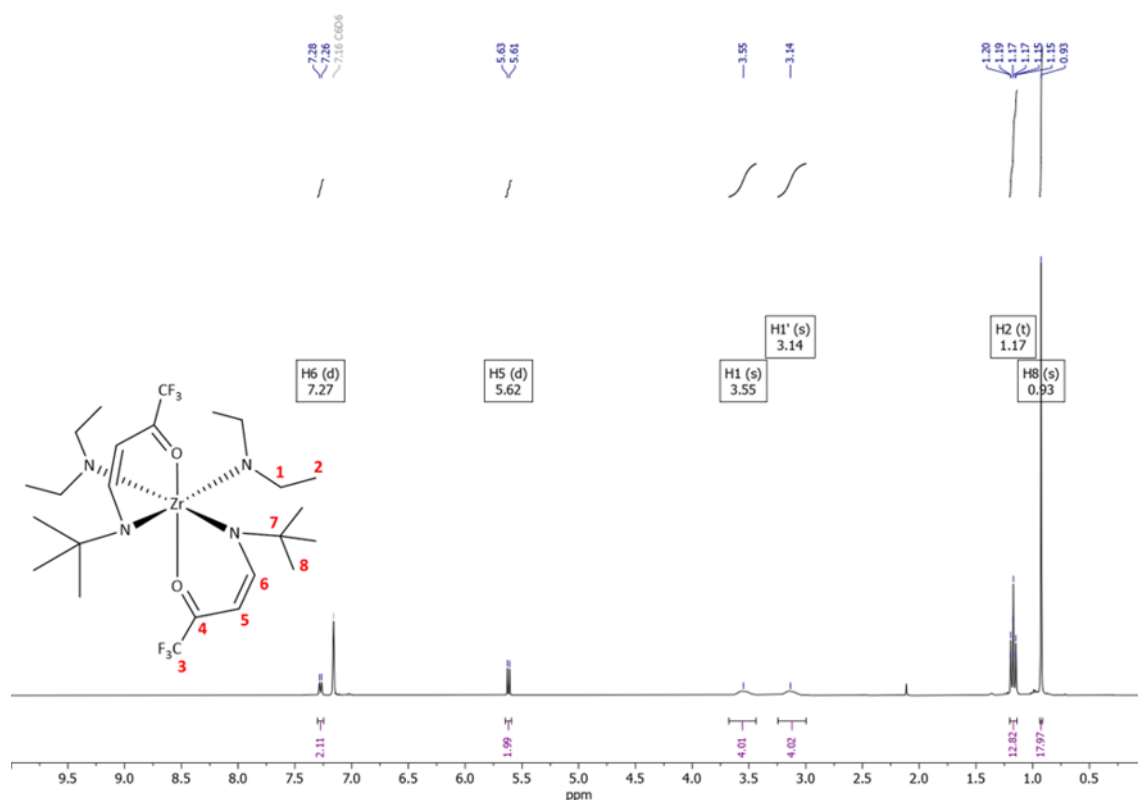


Figure 4.12. ^1H NMR spectrum of $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{NEt}_2)_2]$.

Furthermore, the ^{19}F NMR spectrum confirmed the presence of the trifluoromethyl substituent through a characteristic singlet at -73.58 ppm (Figure 4.13), consistent with the formation of $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{NEt}_2)_2]$. The NMR results show that the solid-state structure agrees well with the coordination environment predicted from the SC-XRD data.

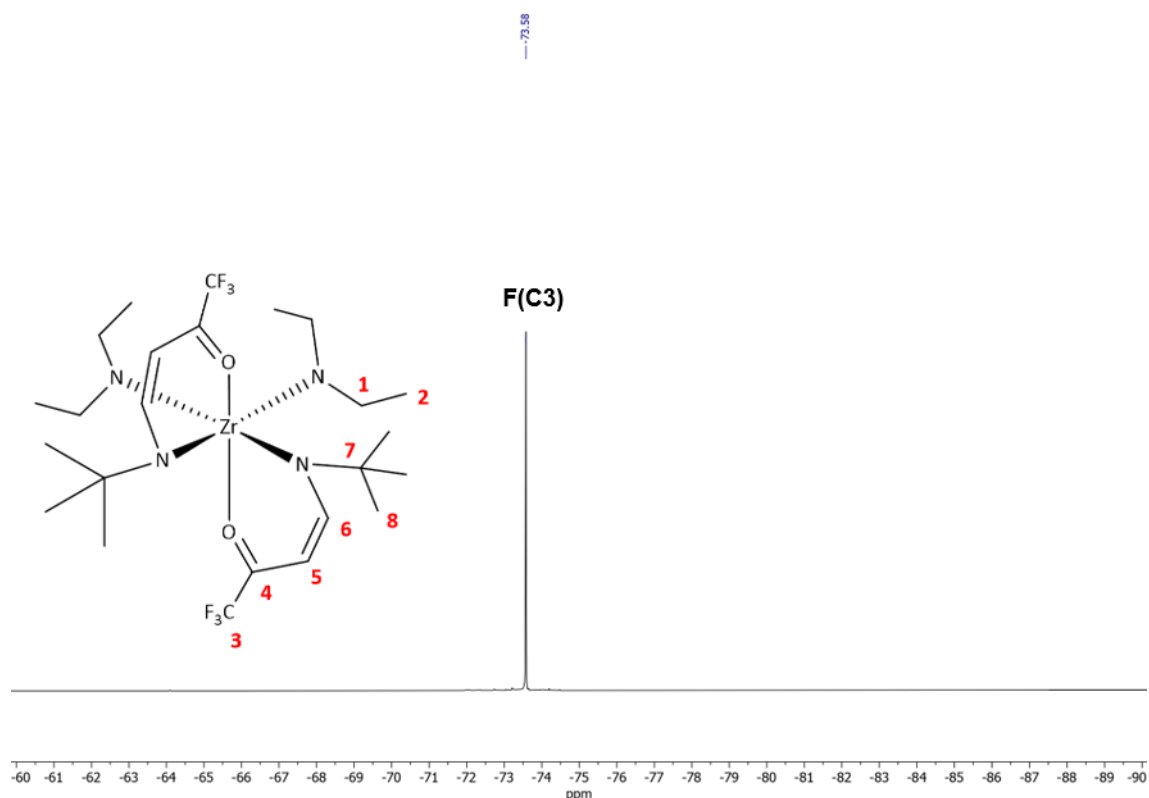


Figure 4.13. ^{19}F NMR spectrum of $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)_2]$.

A sublimation test performed for $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)_2]$ using the same procedure as described for TFB-MEA-based analogue $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$ gave no evidence of sublimation. Instead, the complex underwent thermal decomposition, resulting in the formation of a blackish-brown solid residue at the bottom of the flask (Figure 4.14). The observation suggests that, despite the introduction of the sterically bulky *tert*-butyl groups, $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)_2]$ still lacks sufficient volatility. The decomposition observed under mild heating conditions indicates that the solid-state interactions within the complex remain strong enough to prevent clean volatilization. These results demonstrate that the substitution of the TFB-MEA ligand with the TFB-*t*BuA does not overcome the limitations previously observed for the $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$.



Figure 4.14. [Zr(TFB-*t*BuA)₂(NEt₂)₂] after sublimation attempt approximately 100 °C ($p \approx 1$ mbar).

HS analysis of [Zr(TFB-*t*BuA)₂(NEt₂)₂] (Figure 4.15a-g) revealed pronounced red regions associated with the $-\text{CF}_3$ groups. These regions indicate the presence of intermolecular $\text{F} \cdots \text{F}$ close contacts [102, 103], which contribute 4.1% to the total HS area (Figure 4.15c). The analysis also showed a significant contribution from $\text{H} \cdots \text{F}$ contacts involving the fluorinated substituents and hydrogen atoms of neighboring diethylamido ligands, accounting for 31.1% of the HS area (Figure 4.15d and e). Where supported by the contact geometry, these interactions may be described as weak $\text{C}-\text{H} \cdots \text{F}$ hydrogen-bonding interactions.

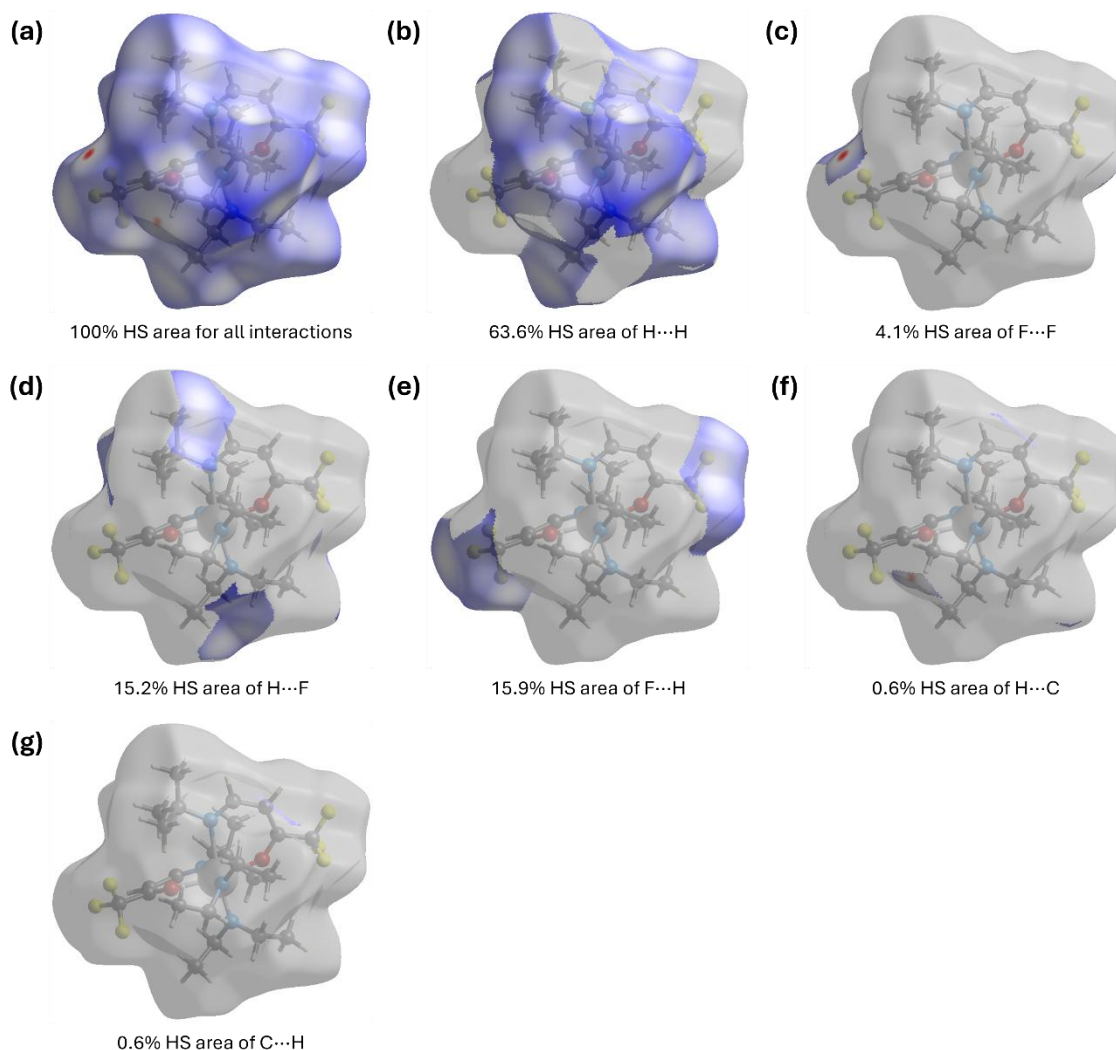
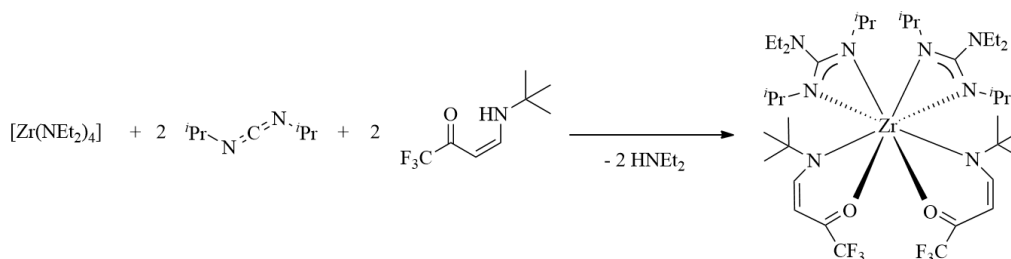


Figure 4.15. (a) Hirshfeld surface (HS) simulation of one $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)_2]$ molecule with 100% of HS area contributed to all interactions, (b) 63.6% of HS area contributed to H...H interaction, (c) 4.1% of HS area contributed to F...F interaction, (d) 15.2% of HS area contributed to H...F interaction, (e) 15.9% of HS area contributed to F...H interaction, (f) 0.6% of HS area contributed to H...C interaction, and (g) 0.6% of HS area contributed to C...H interaction. Color code: Gray = Zirconium; Black = Carbon; White = Hydrogen; Red = Oxygen; Cyan = Nitrogen; Yellow = Fluorine.

The predominance of H...F contacts reflects the extensive fluorinated surface of the complex and the participation of the $-\text{CF}_3$ groups in the crystal-packing arrangement. However, both F...F and C-H...F interactions are generally weak in nature and are best regarded as contributing to the overall intermolecular contact network rather than as strong directional forces. In contrast to $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$, no additional acceptor groups capable of forming intermolecular C-H...O interactions are present. Nevertheless, the cumulative effect of the intermolecular contacts observed in the crystal structure appears sufficient to maintain a stable solid-state packing arrangement. Consistent with this behavior, $[\text{Zr}(\text{TFB-}$

$t\text{BuA})_2(\text{NEt}_2)_2]$ did not exhibit appreciable volatility under low-pressure heating conditions, rendering the complex unsuitable as a precursor for MOCVD applications.

The observation that the monodentate diethylamido ligands in $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)_2]$ engage in intermolecular hydrogen bonding with the $-\text{CF}_3$ groups highlights a significant challenge for designing nitrogen-rich zirconium complexes. Such interactions promote solid-state stabilization and hinder sublimation, making further development of similar systems problematic. Therefore, a different ligand strategy is required, one that retains nitrogen coordination to zirconium but avoids the intermolecular interactions observed for diethylamido ligands. A promising alternative has been demonstrated by Banerjee et al. [97], who reported that the reaction of N,N' -diisopropylcarbodiimide with $[\text{Zr}(\text{NR}_1\text{R}_2)_4]$ ($\text{R}_1, \text{R}_2 = \text{methyl and/or ethyl}$) converts the dialkylamido ligands into nitrogen-rich “guanidinate” ligands, which bind through both nitrogen atoms in a bidentate fashion. In addition to providing a higher nitrogen content, the chelating nature of the guanidinate framework enhances the Zr-N bond strength. Such properties make guanidinate ligands attractive candidates for producing zirconium complexes with improved thermal behavior, particularly those capable of sublimating cleanly under low-pressure heating conditions. Motivated by these considerations, a reaction was carried out using one equivalent of $[\text{Zr}(\text{NEt}_2)_4]$, two equivalents of N,N' -diisopropylcarbodiimide, and two equivalents of $H\text{-TFB-}t\text{BuA}$, with the aim of forming an eight-coordinate zirconium complex of the type $[\text{Zr}(\text{TFB-}t\text{BuA})_2\{\eta^2\text{-(}i\text{PrN)}_2\text{CNEt}_2\}_2]$ (Scheme 4.3).



Scheme 4.3. Reaction scheme for the synthesis of $[\text{Zr}(\text{TFB-}t\text{BuA})_2\{\eta^2\text{-(}i\text{PrN)}_2\text{CNEt}_2\}_2]$.

To enable structural characterization, $[\text{Zr}(\text{TFB-}t\text{BuA})_2\{\eta^2\text{-(}i\text{PrN)}_2\text{CNEt}_2\}_2]$ was recrystallized in a mixture of toluene and n -heptane stored at $-20\text{ }^\circ\text{C}$ to produce suitably high-quality single crystals. These crystals were subsequently analyzed with SC-XRD, allowing precise elucidation of the complex's molecular structure and coordination environment. SC-XRD analysis of recrystallized $[\text{Zr}(\text{TFB-}t\text{BuA})_2\{\eta^2\text{-(}i\text{PrN)}_2\text{CNEt}_2\}_2]$ showed that the complex crystallizes in the monoclinic space group $P2_1/c$. Instead of forming the expected

eight-coordinate species, the complex adopts a six-coordinate arrangement. The zirconium center is situated in a distorted octahedral environment (Figure 4.16).

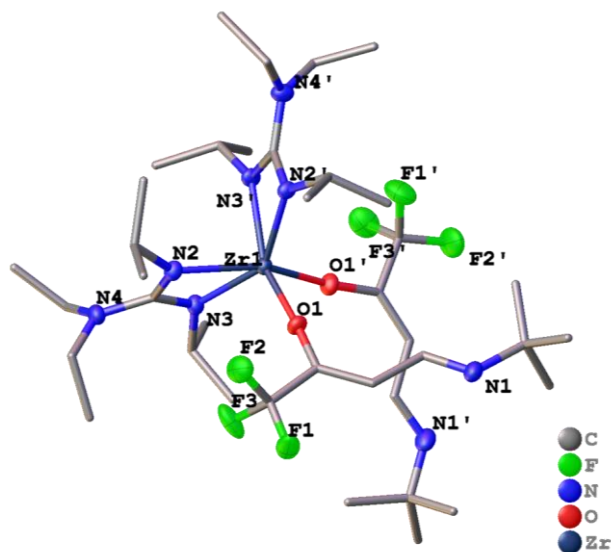


Figure 4.16. The single crystal X-ray crystal structure of $[\text{Zr}(\text{TFB-}t\text{BuA})_2\{\eta^2\text{-(}i\text{PrN)}_2\text{CNEt}_2\}_2]$. Hydrogen atoms are omitted for clarity.

The Zr–O bond lengths lie within a narrow range of 2.017(4)-2.026(4) Å, while the Zr–N distances to the guanidinate ligands are measured at 2.197(5)-2.248(5) Å (Table 4.3). Notably, the nitrogen atoms of the TFB-*t*BuA ligands are not coordinated to the zirconium center. Instead, coordination occurs exclusively through the oxygen atoms of the TFB-*t*BuA ligands. This preference can be attributed to the stronger donor ability of oxygen relative to nitrogen, together with the pronounced oxophilic character of zirconium, which favors the formation of Zr–O bonds. Consequently, the TFB-*t*BuA ligands adopt a monodentate coordination mode rather than the expected O[^]N-chelating mode. The absence of chelation is likely a result of steric hindrance imposed by the bulky *tert*-butyl substituents, which restrict the spatial accessibility required for simultaneous coordination of both donor atoms to the zirconium center.

Table 4.3. Bond lengths [Å] in $[\text{Zr}(\text{TFB-}t\text{BuA})_2\{\eta^2\text{-(}i\text{PrN)}_2\text{CNEt}_2\}_2]$.

Bond lengths [Å] and Angles [°]	Value
Zr1–O1 [Å]	2.017(4)
Zr1–O1' [Å]	2.026(4)
Zr1–N2 [Å]	2.248(4)
Zr1–N2' [Å]	2.200(4)
Zr1–N3 [Å]	2.197(4)
Zr1–N3' [Å]	2.233(4)

The ^1H NMR spectrum of $[\text{Zr}(\text{TFB-}i\text{BuA})_2\{\eta^2\text{-(}^i\text{PrN)}_2\text{CNEt}_2\}_2]$ confirms the formation of the intended complex (Figure 4.17). A singlet (s) at 1.36 ppm, integrating for eighteen protons, corresponds to the methyl groups of the two *tert*-butyl substituents. Two doublets (d) at 6.37-6.39 ppm and 8.64-8.66 ppm are assigned to the C8 and C9 protons of the TFB-*t*BuA ligands, each showing the expected 2:2 proton ratio. A heptet (hept) at 3.41-3.54 ppm accounts for the four C1 methine protons of the isopropyl groups, while a doublet (d) at 1.26-1.28 ppm, integrating for twenty-four protons, corresponds to the C2 methyl groups of the same isopropyl substituents. Additionally, a triplet (t) at 0.79-0.84 ppm represents twelve protons assigned to the C5 methyl groups of the guanidinate ligands. Finally, a quartet (q) at 2.80-2.87 ppm, integrating for eight protons, is attributed to the C4 methylene groups within the guanidinate framework.

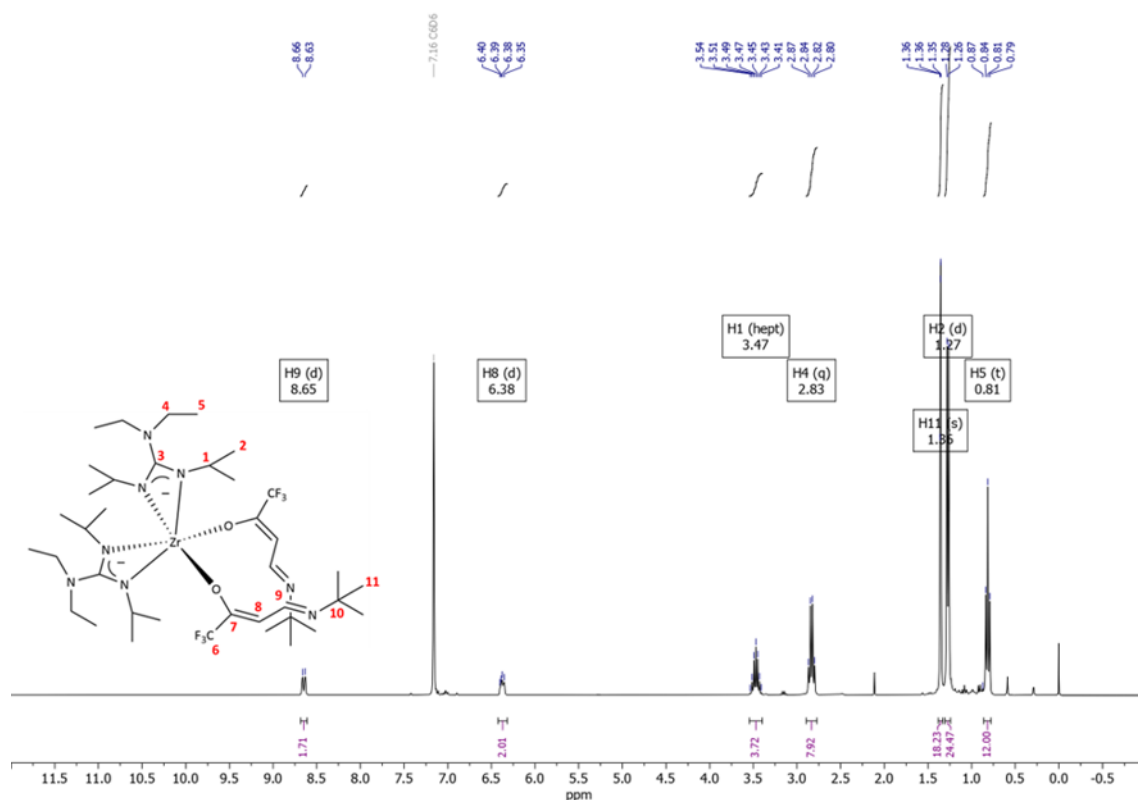


Figure 4.17. ^1H NMR spectrum of $[\text{Zr}(\text{TFB-}i\text{BuA})_2\{\eta^2\text{-(}^i\text{PrN)}_2\text{CNEt}_2\}_2]$.

The ^{19}F NMR spectrum also confirmed the presence of the trifluoromethyl substituent through a characteristic singlet at -70.81 ppm (Figure 4.18), consistent with the formation of $[\text{Zr}(\text{TFB-}i\text{BuA})_2\{\eta^2\text{-(}^i\text{PrN)}_2\text{CNEt}_2\}_2]$. Based on these results, ^1H NMR spectroscopy provides valuable information regarding the presence and chemical environment of ligands coordinated to the metal center. However, its structural resolution is limited, and it cannot unambiguously

determine the molecular geometry or coordination mode of the complex with the same level of certainty and precision as SC-XRD.

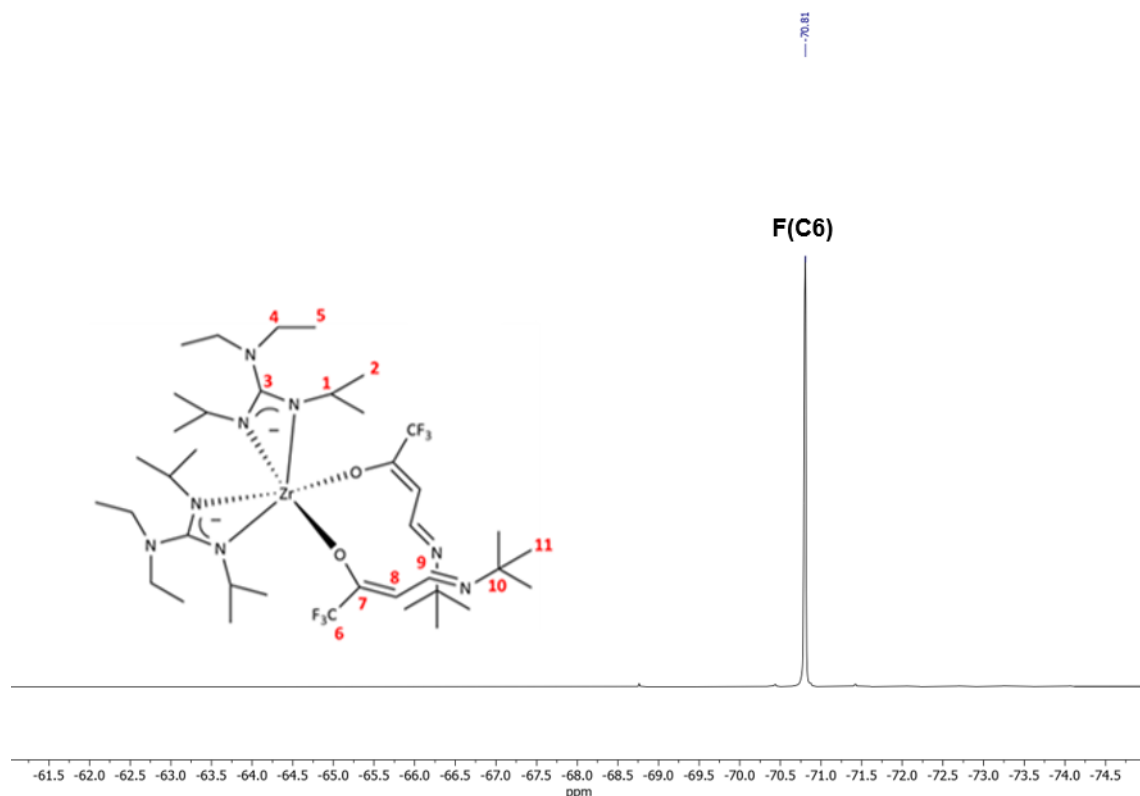


Figure 4.18. ^1H NMR spectrum of $[\text{Zr}(\text{TFB-}t\text{BuA})_2\{\eta^2\text{-(}i\text{PrN)}_2\text{CNEt}_2\}_2]$.

Sublimation tests were also carried out for $[\text{Zr}(\text{TFB-}t\text{BuA})_2\{\eta^2\text{-(}i\text{PrN)}_2\text{CNEt}_2\}_2]$ using the same procedure employed for $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$ and $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)_2]$. As the temperature approached 100 °C, no signs of sublimation were detected. Instead, the complex underwent thermal decomposition, producing a black residue on the wall of the round-bottom flask (Figure 4.19). The result indicates that introduction of guanidinato ligands in $[\text{Zr}(\text{TFB-}t\text{BuA})_2\{\eta^2\text{-(}i\text{PrN)}_2\text{CNEt}_2\}_2]$ did not impact the volatility. The thermal decomposition observed under relatively mild heating conditions suggests that strong intermolecular interactions in the solid state continue to inhibit clean volatilization. These findings show that replacing the diethylamido ligands with guanidinate ligands does not resolve the limitations previously observed for the diethylamido-containing complexes, underscoring the broader difficulty of achieving favorable sublimation behavior in zirconium β -ketoenamine systems. It is further proposed that the lack of volatility may be linked to the two nitrogen atoms of the TFB-*t*BuA ligands that remain uncoordinated to the zirconium center. These unbound nitrogen atoms are capable of forming intermolecular hydrogen-bonding interactions,

which likely reinforce the solid-state packing and contribute to the inability of the complex to sublime under low-pressure heating.



Figure 4.19. $[\text{Zr}(\text{TFB-}t\text{BuA})_2\{\eta^2\text{-(}i\text{PrN)}_2\text{CNEt}_2\}_2]$ after sublimation attempt at approximately 100 °C ($p \approx 1$ mbar).

HS analysis of $[\text{Zr}(\text{TFB-}t\text{BuA})_2\{\eta^2\text{-(}i\text{PrN)}_2\text{CNEt}_2\}_2]$ (Figure 4.20a-i) reveals distinct regions located around the nitrogen atoms of the TFB- t BuA ligands that are not coordinated to the zirconium center, indicating the presence of significant intermolecular close contacts in these regions. The HS analysis further shows that approximately 2.0% of the total surface is associated with $\text{H}\cdots\text{N}$ contacts (Figure 4.20h and i). These contacts correspond to with weak $\text{C-H}\cdots\text{N}$ hydrogen-bonding interactions between the uncoordinated nitrogen atoms and hydrogen atoms of neighboring guanidinate ligands, provided that the corresponding geometrical criteria for hydrogen bonding are satisfied. The appearance of localized red regions around the non-coordinated nitrogen atoms suggests that these sites act as intermolecular interaction centers within the crystal packing arrangement.

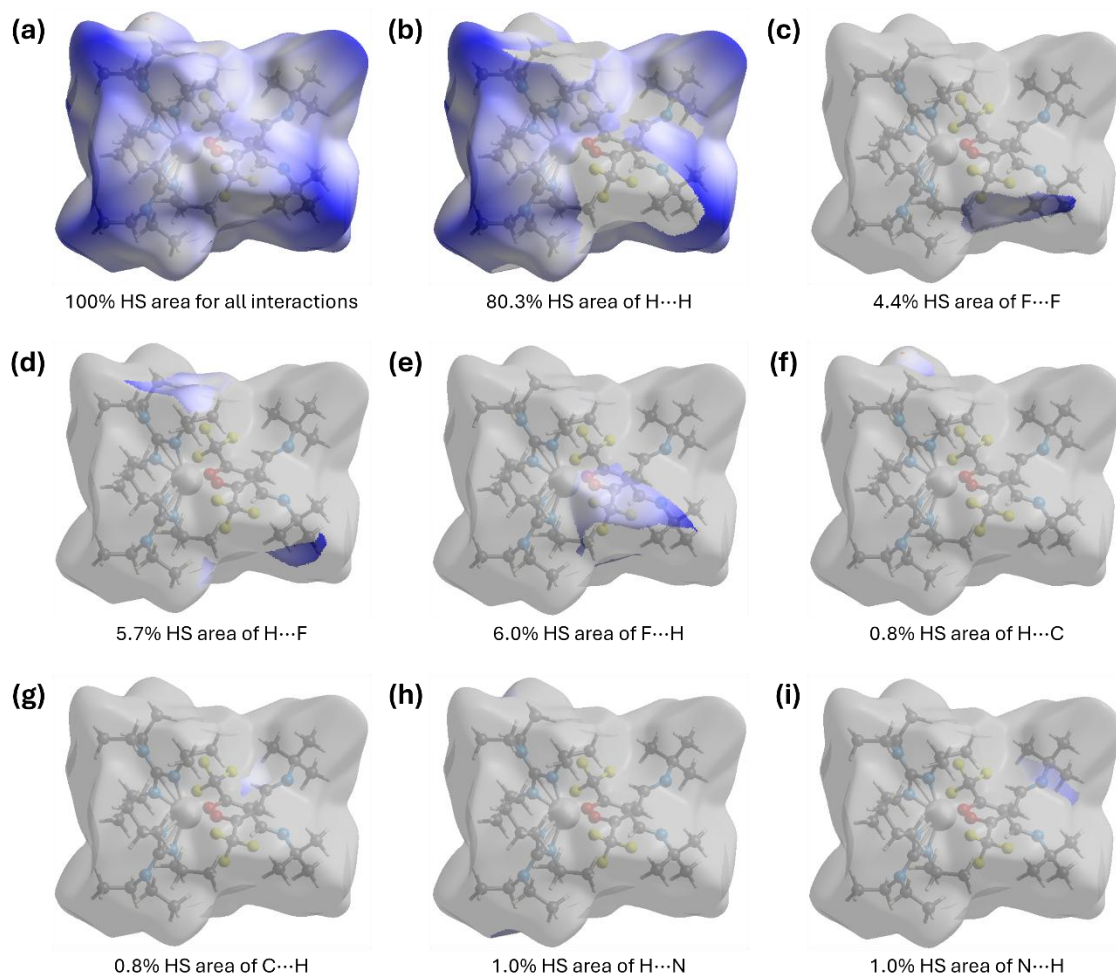
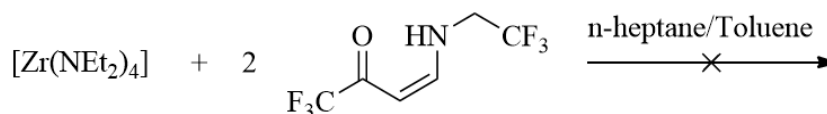


Figure 4.20. (a) Hirshfeld surface (HS) simulation of one $[\text{Zr}(\text{TFB-}t\text{BuA})_2\{\eta^2\text{-(}^i\text{PrN)}_2\text{CNEt}_2\}_2]$ molecule with 100% of HS area contributed to all interactions, (b) 80.3% of HS area contributed to H...H interaction, (c) 4.4% of HS area contributed to F...F interaction, (d) 5.7% of HS area contributed to H...F interaction, (e) 6.0% of HS area contributed to F...H interaction, (f) 0.8% of HS area contributed to H...C interaction, (g) 0.8% of HS area contributed to C...H interaction, (h) 1.0% of HS area contributed to H...N interaction, and (i) 1.0% of HS area contributed to N...H interaction. Color code: Gray = Zirconium; Black = Carbon; White = Hydrogen; Red = Oxygen; Cyan = Nitrogen; Yellow = Fluorine.

Among the three newly synthesized complexes, none were able to undergo sublimation under low-pressure heating conditions, rendering them unsuitable as precursors for MOCVD applications. This outcome underscores the inherent difficulty in developing nitrogen-rich zirconium complexes with adequate volatility. These results indicate that further exploration of alternative fluorinated β -ketoenamine ligands is necessary. In this context, the *H*-TFB-TFEA ligand, which contains two $-\text{CF}_3$ groups positioned symmetrically on the ligand backbone, represents a promising candidate. The presence of two electron-rich trifluoromethyl substituents is expected to generate substantial intermolecular repulsion, thereby reducing solid-state stabilization and potentially enabling sublimation at relatively low temperatures and

pressures. Notably, this ligand has been reported to form heteroleptic copper and iridium complexes that have demonstrated suitable volatility for MOCVD, enabling the deposition of copper oxide [36] and iridium oxide [37] thin films. Based on these precedents, the reaction of one equivalent of $[\text{Zr}(\text{NEt}_2)_4]$ with two equivalents of *H*-TFB-TFEA is anticipated to yield a nitrogen-rich heteroleptic zirconium complex with improved volatility, making it a promising candidate for further evaluation as an MOCVD precursor.

Unfortunately, the reaction illustrated in Scheme 4.4 did not yield any isolable product that could be recrystallized or characterized by ^1H NMR spectroscopy.



Scheme 4.4. Reaction scheme for attempted synthesis of $[\text{Zr}(\text{TFB-TFEA})_2(\text{NEt}_2)_2]$.

To explore an alternative approach, the reaction was repeated using *n*-heptane as the sole solvent. Under these conditions, a yellow solid was formed. The yellow solid was separated from the reaction mixture, collected, and dried under vacuum. Sublimation tests were then carried out on this material using the same experimental setup employed for the previously synthesized zirconium complexes. Remarkably, the yellow solid sublimed at 115–120 °C ($p \approx 1$ mbar), producing colorless crystals on the cold finger (Figure 4.21). The material obtained from sublimation was subsequently analyzed by solution-phase NMR spectroscopy. In addition, the sublimate was recrystallized to afford crystals of sufficient quality for structural determination by SC-XRD.



Figure 4.21. Sublimate obtained from a reaction between one equivalent of $[\text{Zr}(\text{NEt}_2)_4]$ and two equivalents of *H*-TFB-TFEA in *n*-heptane.

SC-XRD analysis of recrystallized sublimate revealed that the complex crystallizes in the triclinic space group $P\bar{1}$ with zirconium center adopting a distorted square antiprism geometry, with four TFB-TFEA ligands coordinating through their oxygen and nitrogen donor atoms (Figure 4.22). The Zr–O bond lengths fall within a narrow range of 2.114(2)–2.122(2) Å, whereas the Zr–N bond distances are slightly longer, ranging from 2.409(3) to 2.424(3) Å (Table 4.4).

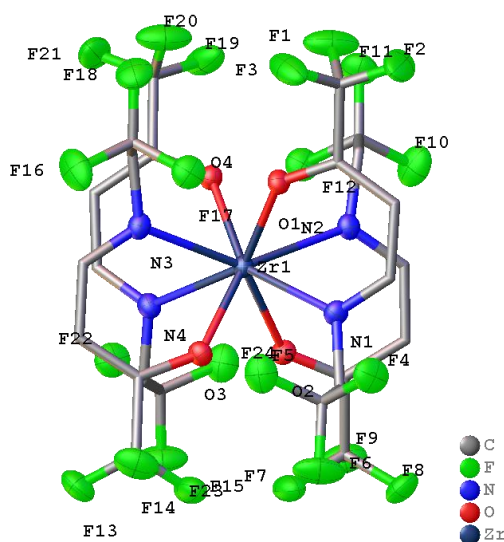


Figure 4.22. The single crystal X-ray crystal structure of $[\text{Zr}(\text{TFB-TFEA})_4]$. Hydrogen atoms are omitted for clarity.

The crystal structure clearly demonstrates that the reaction of $[\text{Zr}(\text{NEt}_2)_4]$ with H -TFB-TFEA does not afford the targeted heteroleptic complex $[\text{Zr}(\text{TFB-TFEA})_2(\text{NEt}_2)_2]$. Instead, complete substitution of all diethylamido ligands occurs, resulting in the formation of the homoleptic species $[\text{Zr}(\text{TFB-TFEA})_4]$, while excess $[\text{Zr}(\text{NEt}_2)_4]$ remains unreacted. This finding highlights the strong preference of the H -TFB-TFEA ligand for coordination to the zirconium center under the applied reaction conditions.

Table 4.4. Bond lengths [Å] for $[\text{Zr}(\text{TFB-TFEA})_4]$.

Bond lengths [Å]	Value
Zr1–O4 [Å]	2.122(2)
Zr1–O1 [Å]	2.122(2)
Zr1–O3 [Å]	2.114(2)
Zr1–O2 [Å]	2.116(2)
Zr1–N3 [Å]	2.410(3)
Zr1–N2 [Å]	2.409(3)
Zr1–N1 [Å]	2.423(2)
Zr1–N4 [Å]	2.424(3)

The formation of $[\text{Zr}(\text{TFB-TFEA})_4]$ was further confirmed by multinuclear NMR spectroscopy. The ^1H NMR spectrum of the isolated sublimate showed spectrum features fully consistent with the homoleptic structure determined by SC-XRD (Figure 4.23). A quartet (q) at 4.00-4.07 ppm, integrating to eight protons, was assigned to the methylene groups of the four TFB-TFEA ligands. Two doublets of doublets (dd) at 5.23-5.25 ppm and 6.86-6.87 ppm correspond to the C3 and C4 vinyl protons of the coordinated ligands, respectively, with the expected proton ratio of 4:4.

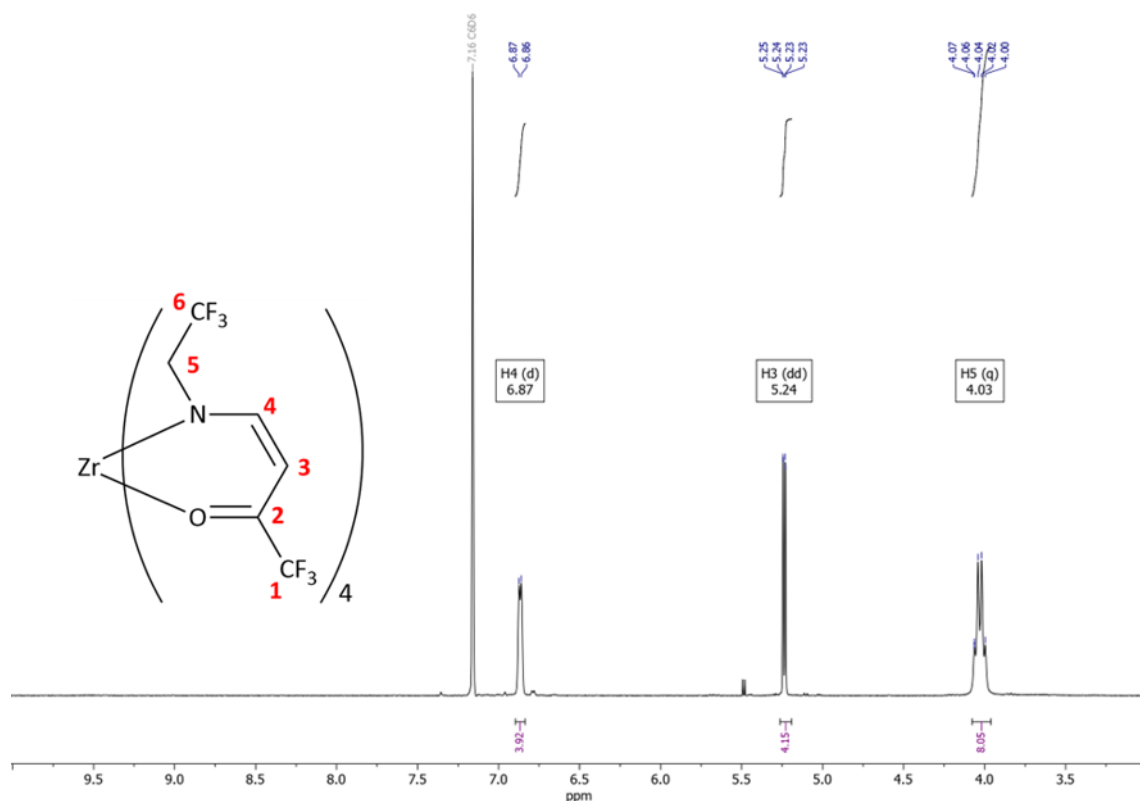
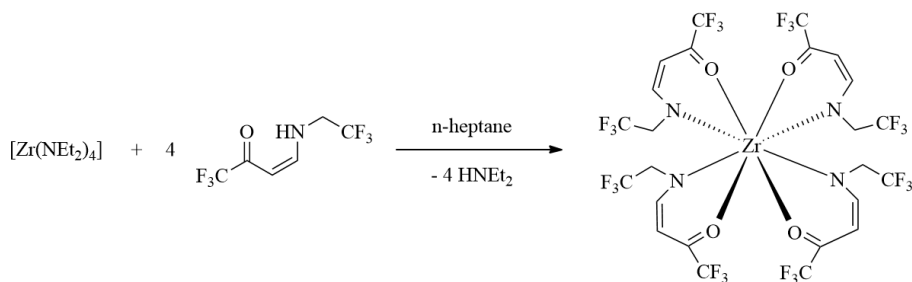


Figure 4.23. ^1H NMR spectrum of $[\text{Zr}(\text{TFB-TFEA})_4]$.

Importantly, no resonances attributable to coordinated diethylamido ligands were observed, providing additional evidence against the formation of the anticipated heteroleptic complex shown in Scheme 4.5.



Scheme 4.5. Reaction scheme for the synthesis of $[\text{Zr}(\text{TFB-TFEA})_4]$.

Further support was obtained from the $^{13}\text{C}\{^1\text{H}, ^{19}\text{F}\}$ NMR spectrum, which exhibited six distinct resonances corresponding to the six unique carbon environments present in the coordinated TFB-TFEA ligand framework (Figure 4.24).

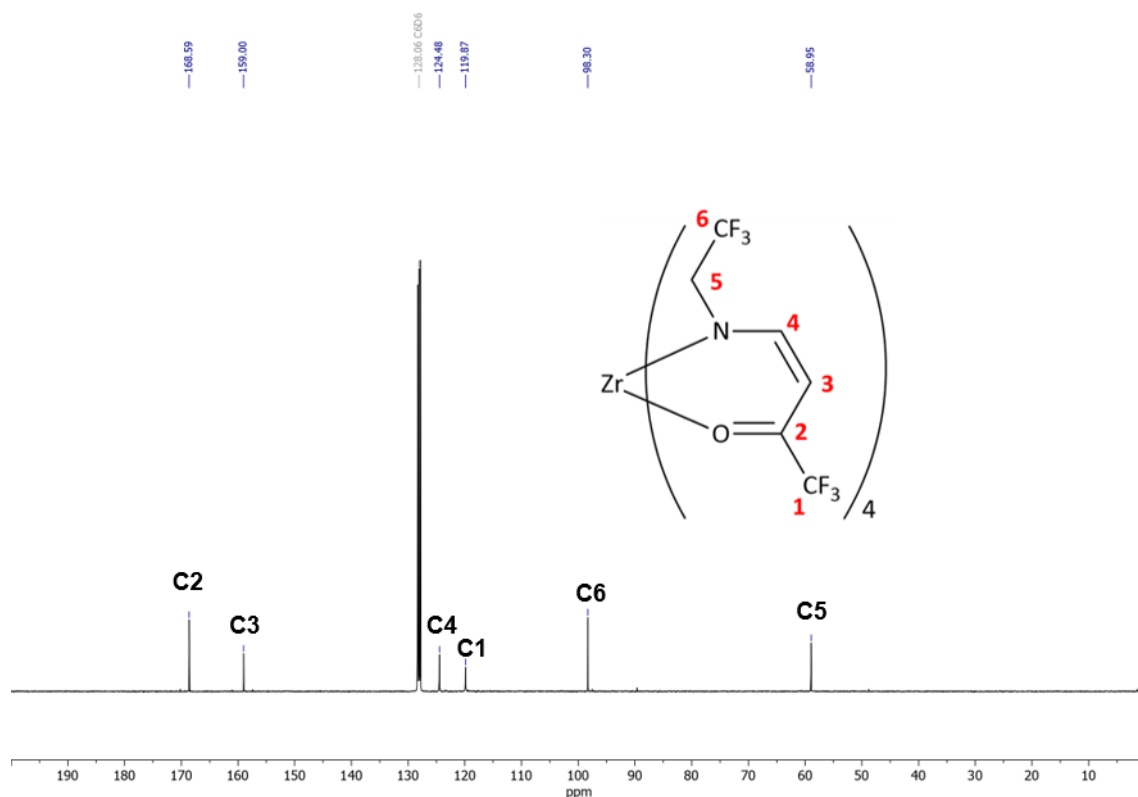


Figure 4.24. $^{13}\text{C}\{^1\text{H}, ^{19}\text{F}\}$ NMR spectrum of $[\text{Zr}(\text{TFB-TFEA})_4]$.

The ^{19}F NMR spectrum displayed two characteristic singlets at -70.61 ppm and -73.19 ppm, assigned to the trifluoromethyl groups located at the C1 and C6 positions, respectively (Figure 4.25). The excellent agreement between the SC-XRD and NMR data confirms that the isolated product is the homoleptic complex $[\text{Zr}(\text{TFB-TFEA})_4]$, rather than the initially targeted heteroleptic species $[\text{Zr}(\text{TFB-TFEA})_2(\text{NEt}_2)_2]$. Thus, both solid-state and solution-phase characterization consistently demonstrate complete ligand substitution around the zirconium center.

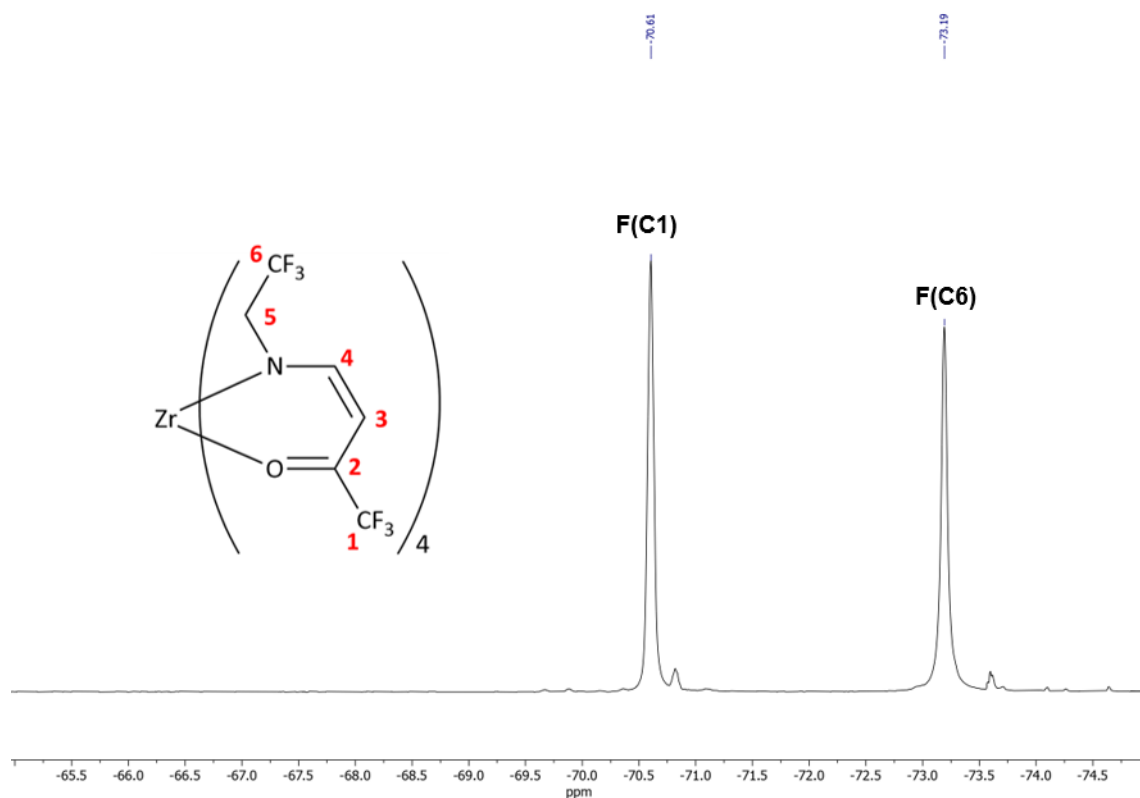


Figure 4.25. ^{19}F NMR spectrum of $[\text{Zr}(\text{TFB-TFEA})_4]$.

HS analysis of $[\text{Zr}(\text{TFB-TFEA})_4]$ (Figure 4.26a-g) revealed that $\text{F}\cdots\text{F}$ contacts account for 41.6% of the total surface area (Figure 4.26c), while $\text{H}\cdots\text{F}$ contacts represent the largest contribution at 52.2% (Figure 4.26d and e). These results indicate that the intermolecular packing of the complex is dominated by contacts involving the fluorinated substituents. The high proportion of $\text{H}\cdots\text{F}$ contacts reflects the extensive fluorinated surface of the molecule and the prevalence of fluorine atoms at the crystal-packing interface. Although some of these contacts may correspond to weak $\text{C-H}\cdots\text{F}$ hydrogen-bonding interactions, both $\text{H}\cdots\text{F}$ and $\text{F}\cdots\text{F}$ contacts are generally weak in nature and contribute primarily through van der Waals and weak electrostatic interactions.

Notably, despite the substantial contribution of $\text{H}\cdots\text{F}$ contacts, $[\text{Zr}(\text{TFB-TFEA})_4]$ remains sufficiently volatile to undergo sublimation at 115-120 $^{\circ}\text{C}$ under reduced pressure ($p \approx 1$ mbar). This behavior indicates that the predominance of fluorine-based intermolecular contacts does not significantly impede volatilization and that the crystal packing remains sufficiently weak to permit efficient sublimation. Consequently, the thermal behavior of $[\text{Zr}(\text{TFB-TFEA})_4]$ demonstrates that a high proportion of $\text{H}\cdots\text{F}$ contacts alone is not necessarily detrimental to precursor volatility. Instead, the overall strength and nature of the

intermolecular interactions, rather than their HS contribution alone, appear to be the more important factors governing sublimation behavior.

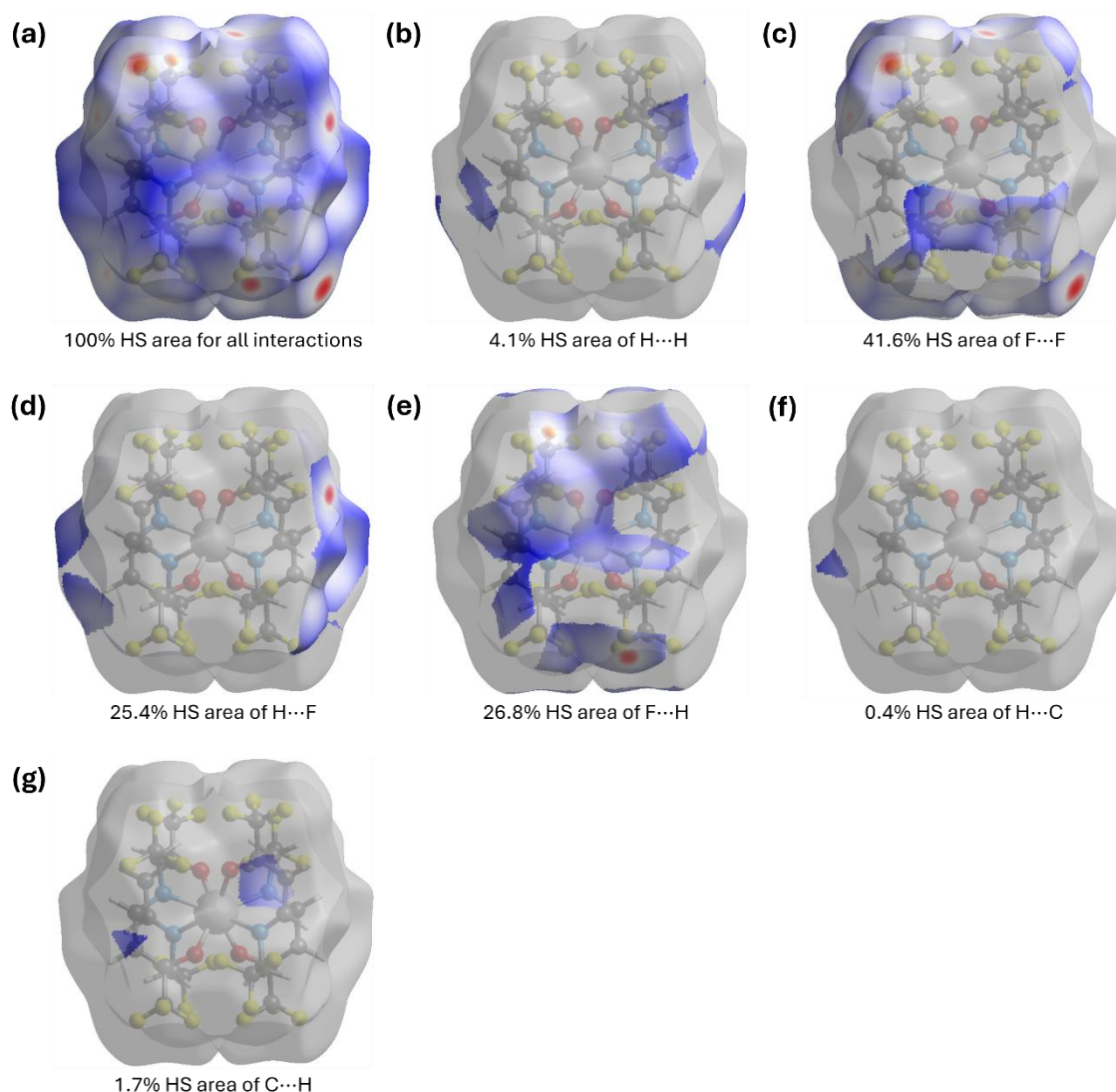
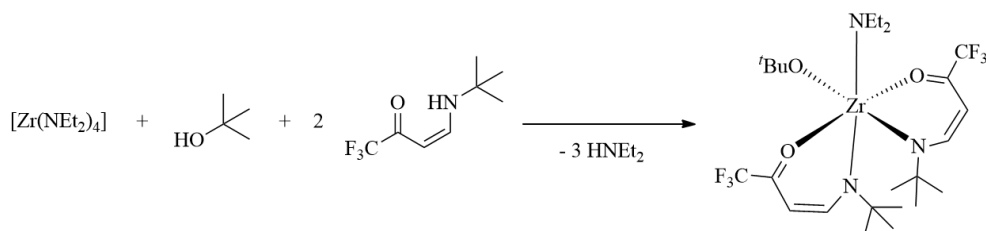


Figure 4.26. (a) Hirshfeld surface (HS) simulation of one $[\text{Zr}(\text{TFB-TFEA})_4]$ molecule with 100% of HS area contributed to all interactions, (b) 4.1% of HS area contributed to H...H interaction, (c) 41.6% of HS area contributed to F...F interaction, (d) 25.4% of HS area contributed to H...F interaction, (e) 26.8% of HS area contributed to F...H interaction, (f) 0.4% of HS area contributed to H...C interaction, and (g) 1.7% of HS area contributed to C...H interaction. Color code: Gray = Zirconium; Black = Carbon; White = Hydrogen; Red = Oxygen; Cyan = Nitrogen; Yellow = Fluorine.

The synthesis of volatile zirconium heteroleptic complexes was found to be challenging, as the attempted syntheses did not yield the desired outcomes. To address this, the incorporation of a new ligand, such as *tert*-butoxo, into the zirconium coordination sphere was considered. The *tert*-butoxo ligand is expected to enhance the thermal stability of the resulting heteroleptic complex, since zirconium is highly oxophilic and an increased number of Zr–O

bonds generally improve resistance to decomposition during heating. Moreover, the bulky *tert*-butyl substituent should introduce significant steric hindrance, increase intermolecular repulsion and thereby promote volatility and sublimation under relatively low temperature ($p \approx 1$ mbar).

The reaction of one equivalent of $[\text{Zr}(\text{NEt}_2)_4]$ with one equivalent of *tert*-butyl alcohol and two equivalents of *H*-TFB-*t*BuA was carried out to produce one equivalent of the heteroleptic complex $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)(\text{O}^t\text{Bu})]$ (Scheme 4.6).



Scheme 4.6. Reaction scheme for the synthesis of $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)(\text{O}^t\text{Bu})]$.

The reaction produced a yellow solution, which was subsequently dried under vacuum to yield yellow powder. Sublimation test was then performed on this powder using the same setup applied to the previously prepared zirconium complexes. Notably, the yellow powder sublimed at 105-110 °C ($p \approx 1$ mbar), depositing a yellow solid on the cold finger (Figure 4.29). The sublimate was then recrystallized to obtain crystals of suitable quality for structural characterization by SC-XRD.



Figure 4.29. Sublimate obtained from a reaction between one equivalent of $[\text{Zr}(\text{NEt}_2)_4]$, one equivalent of HO^tBu , and two equivalents of *H*-TFB-*t*BuA.

SC-XRD analysis of recrystallized $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)(\text{O}^t\text{Bu})]$ revealed that the complex crystallizes in the monoclinic space group $P2_1/n$. The complex displays a six-coordinate arrangement in which the zirconium center resides in a distorted octahedral geometry (Figure 4.30).

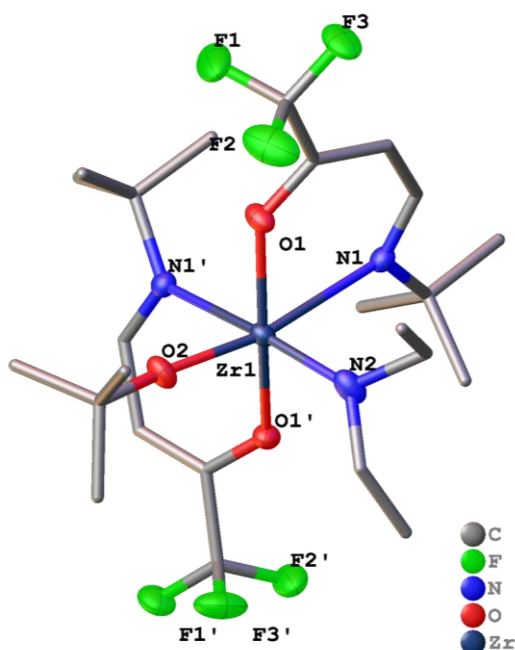


Figure 4.30. The single crystal X-ray crystal structure of $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)(\text{O}'\text{Bu})]$. Hydrogen atoms are omitted for clarity.

Within the equatorial plane, coordination is provided by three nitrogen donors arising from two TFB-*t*BuA ligands and one diethylamido ligand, together with one oxygen donor from the *tert*-butoxo ligand. The Zr–O bond lengths associated with the TFB-*t*BuA ligands fall within the range of 2.083(3)–2.098(3) Å, while the Zr–N bonds to the TFB-*t*BuA ligands are slightly longer, measuring 2.495(2)–2.527(3) Å. In comparison, the Zr–N bond to the diethylamido ligand is notably shorter at 1.982(3) Å. The Zr–O bond involving the *tert*-butoxo ligand is also shorter than the Zr–O distances to the TFB-*t*BuA ligands, with a value of 1.914(2) Å (Table 4.5).

Table 4.5. Bond lengths [Å] in $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)(\text{O}'\text{Bu})]$.

Bond lengths [Å] and Angles [°]	Value
Zr1–O1 [Å]	2.083(2)
Zr1–O1' [Å]	2.098(2)
Zr1–N2 [Å]	1.982(3)
Zr1–O2 [Å]	1.914(2)
Zr1–N1 [Å]	2.495(2)
Zr1–N1' [Å]	2.527(3)

The ^1H NMR spectrum of $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)(\text{O}'\text{Bu})]$ likewise presents considerable challenges for signal assignment (Figure 4.31). The spectrum contains numerous resonances arising from chemically similar proton environments associated with the

coordinated TFB-*t*BuA ligands, as well as the diethylamido and *tert*-butoxo ligands, leading to substantial signal overlap. In addition, coordination of the ligands to the zirconium center influences their electronic environments, resulting in variations in chemical shifts and further increasing spectral complexity. The possibility of residual uncoordinated *H*-TFB-*t*BuA ligand remaining from the synthesis or purification procedure cannot be excluded and may contribute additional resonances to the spectrum. As a result, the complete and unequivocal assignment of all proton resonances is not feasible using ^1H NMR spectroscopy.

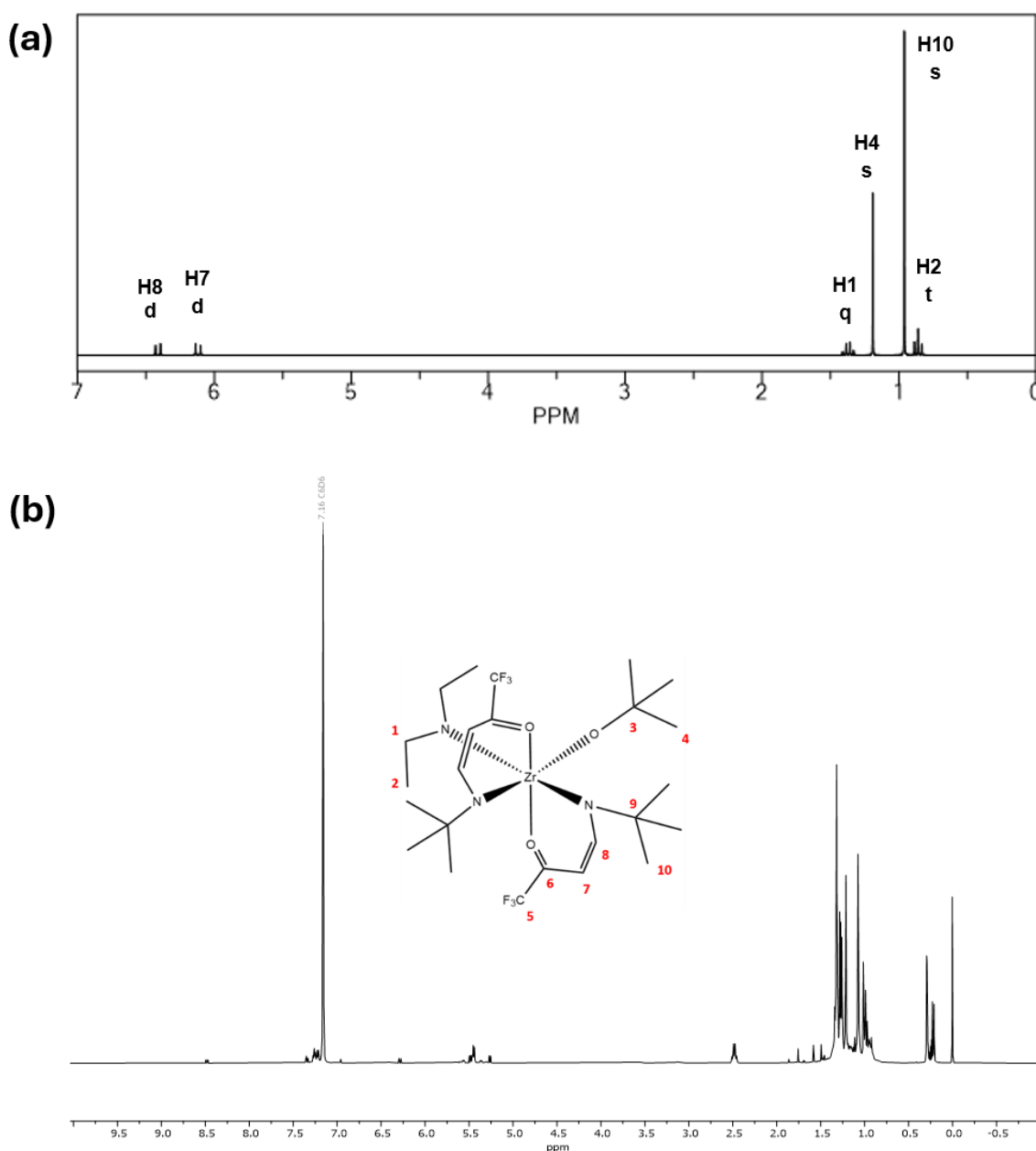


Figure 4.31. (a) ^1H NMR spectrum prediction of $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)(\text{O}^t\text{Bu})]$ (b) actual ^1H NMR spectrum of $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)(\text{O}^t\text{Bu})]$.

HS analysis of $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)(\text{O}^t\text{Bu})]$ (Figure 4.32a-h) revealed that $\text{H}\cdots\text{H}$ contacts account for 61.6% of the total HS area (Figure 4.32b), while $\text{H}\cdots\text{F}$ contacts contribute 36.8% (Figure 4.32c and d). These results indicate that the crystal packing is dominated by weak van der Waals interactions between hydrogen atoms and weak $\text{C-H}\cdots\text{F}$ contacts. Despite the presence of nitrogen and oxygen atoms from the diethylamido and *tert*-butoxo ligands, no significant $\text{C-H}\cdots\text{N}$ or $\text{C-H}\cdots\text{O}$ interactions were observed.

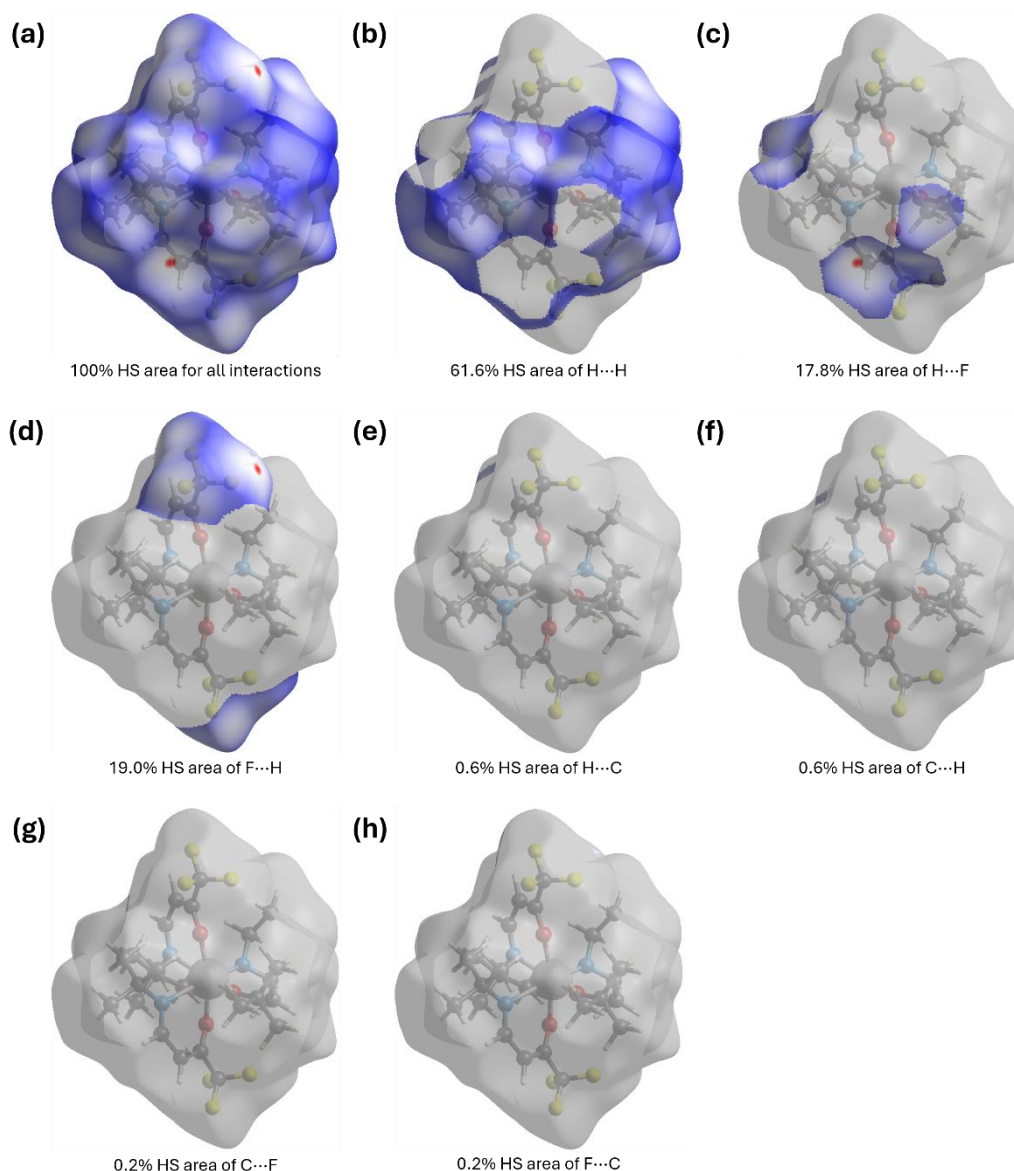


Figure 4.32. (a) Hirshfeld surface (HS) simulation of one $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)(\text{O}^t\text{Bu})]$ molecule with 100% of HS area contributed to all interactions, (b) 61.6% of HS area contributed to $\text{H}\cdots\text{H}$ interaction, (c) 17.8% of HS area contributed to $\text{H}\cdots\text{F}$ interaction, (d) 19.0% of HS area contributed to $\text{F}\cdots\text{H}$ interaction, (e) 0.6% of HS area contributed to $\text{H}\cdots\text{C}$ interaction, (f) 0.6% of HS area contributed to $\text{C}\cdots\text{H}$ interaction, (g) 0.2% of HS area contributed to $\text{C}\cdots\text{F}$ interaction, and (h) 0.2% of HS area contributed to $\text{F}\cdots\text{C}$ interaction. Color code: Gray = Zirconium; Black = Carbon; White = Hydrogen; Red = Oxygen; Cyan = Nitrogen; Yellow = Fluorine.

Interestingly, replacing one diethylamido ligand with a *tert*-butoxo ligand affords $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)(\text{O}^t\text{Bu})]$, which is capable of sublimation under reduced pressure ($p \approx 1$ mbar), whereas the related bis(diethylamido) complexes $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$ and $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)_2]$ undergo decomposition before sublimation. This behavior suggests that intermolecular interactions are not the primary factor governing volatility. Instead, the thermal stability of the metal–ligand bonds appears to be more important.

Previous studies have reported a substantial difference in bond dissociation energies between Zr–N and Zr–O bonds. The dissociation energy of the Zr–N bond is approximately 339 kJ mol^{-1} , whereas that of the Zr–O bond is significantly higher at 776 kJ mol^{-1} [104]. Consequently, Zr–N bonds are more susceptible to thermal cleavage, leading to decomposition before sufficient vapor pressure can be generated for sublimation. In contrast, the stronger Zr–O bond introduced by the *tert*-butoxo ligand enhances the thermal robustness of the coordination sphere, allowing $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)(\text{O}^t\text{Bu})]$ to survive the heating process and undergo sublimation. This interpretation is also supported by the shorter Zr–O bond distance compared with the Zr–N bond distance observed in the crystal structure.

The syntheses and thermal evaluations of $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$ and $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)_2]$ demonstrate that these nitrogen-rich heteroleptic complexes are unsuitable as MOCVD precursors. The presence of diethylamido ligands results in limited volatility and a tendency toward thermal decomposition at relatively low temperatures, which can be attributed to the relatively weak Zr–N bonds associated with the diethylamido groups. Attempts to improve precursor performance by replacing the diethylamido ligands with bidentate N[^]N-guanidinato ligands did not result in enhanced volatility, despite the increased coordination strength expected from the chelating ligand. In contrast, partial substitution of a diethylamido ligand with a *tert*-butoxo ligand afforded $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)(\text{O}^t\text{Bu})]$, which exhibited measurable sublimation under reduced pressure. This behavior highlights the beneficial effect of incorporating stronger Zr–O bonds into the coordination sphere, thereby enhancing thermal stability while preserving volatility. However, the low recovery of sublimed material (<15%) indicates that the compound still lacks the reproducibility and precursor efficiency required for practical MOCVD applications. Taken together, these findings demonstrate that the thermal behavior of these zirconium complexes is governed primarily by the stability of the metal–ligand bonds rather than by intermolecular interactions. More importantly, they establish the replacement of thermally labile diethylamido ligands with oxygen-donor ligands as a promising strategy for precursor design, providing a clear direction for the development of

more thermally robust and volatile zirconium complexes for MOCVD-based ZrON thin-film deposition.

4.3. Thermal Analysis of $[\text{Zr}(\text{TFB-TFEA})_4]$

Thermal evaluation of $[\text{Zr}(\text{TFB-TFEA})_4]$ carried out by sublimation under reduced pressure ($p \approx 1$ mbar) using a Schlenk line showed a good volatility. The complex began to sublime at temperatures above 110°C , forming colorless crystalline deposits on the cold finger, suggesting its potential suitability as a precursor for MOCVD processes. Thermogravimetric (TG) analysis under a nitrogen atmosphere was performed to investigate the decomposition behavior. The TG profile shows a major decomposition event occurring near 130°C , accompanied by a mass loss of approximately 71.6%. The remaining mass at this stage ($\sim 28.4\%$ at around 134°C ; Figure 4.33) is in reasonable agreement with the theoretical value for zirconium oxynitride (Zr_2ON_2 , 25.16%), with slight deviations likely due to incomplete ligand decomposition or partial volatilization of intermediate species. Upon further heating to 350°C , the final residue decreases to 16.4%, which is closer to the theoretical value for ZrO_2 (12.68% in $[\text{Zr}(\text{TFB-TFEA})_4]$), indicating that higher-temperature decomposition predominantly yields zirconium oxide rather than oxynitride.

Differential Scanning Calorimetry (DSC) was employed to further examine the thermal behavior and identify phase transitions. The DSC curve exhibits a broad endothermic event with a maximum at approximately 112°C , beginning at around 87°C and ending near 129°C (Figure 4.33). This signal is attributed to a gradual sublimation process, reflecting the increasing vapor pressure of the compound with temperature. The absence of overlapping exothermic features in this range suggests that sublimation occurs prior to significant thermal decomposition.

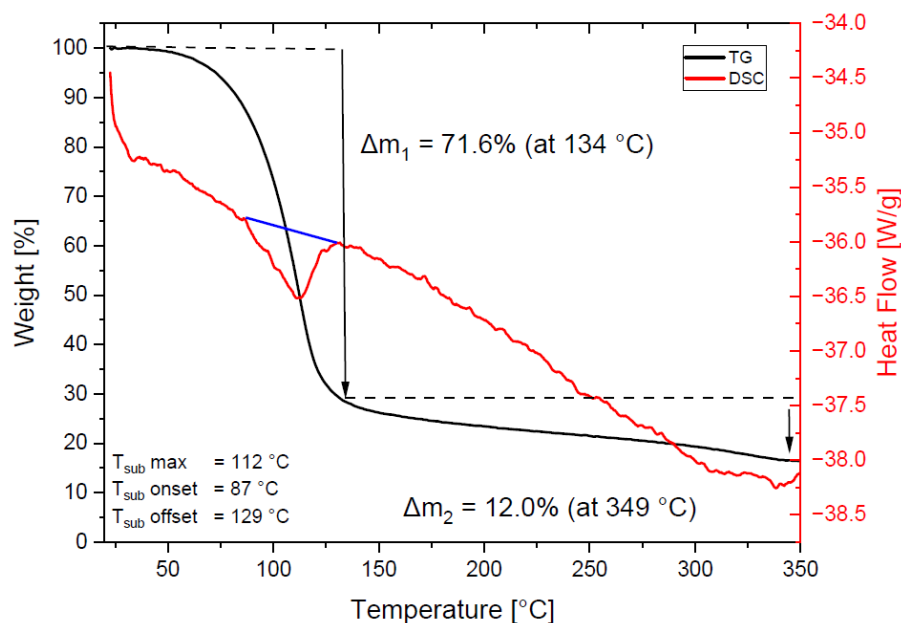


Figure 4.33. TG (black) and DSC (red) profiles of $[\text{Zr}(\text{TFB-TFEA})_4]$ under N_2 flow at atmospheric pressure from 20-350 °C.

Powder X-ray diffraction (PXRD) analysis was subsequently performed on the residue obtained after TG-DSC analysis of $[\text{Zr}(\text{TFB-TFEA})_4]$. The diffraction pattern was assigned to monoclinic ZrO_2 (JCPDS no. 37-1484), with the (-111) and (111) reflections appearing as the most intense peaks (Figure 4.34). These results confirm that thermal decomposition of $[\text{Zr}(\text{TFB-TFEA})_4]$ at temperatures above 550 °C ultimately leads to the formation of crystalline monoclinic zirconia rather than zirconium oxynitride. This observation is consistent with the TG data, which showed a residual mass at elevated temperatures that closely matches the theoretical ZrO_2 content. Therefore, although oxynitride species may be formed as intermediate decomposition products at lower temperatures, the final decomposition product under the applied thermal conditions is monoclinic ZrO_2 .

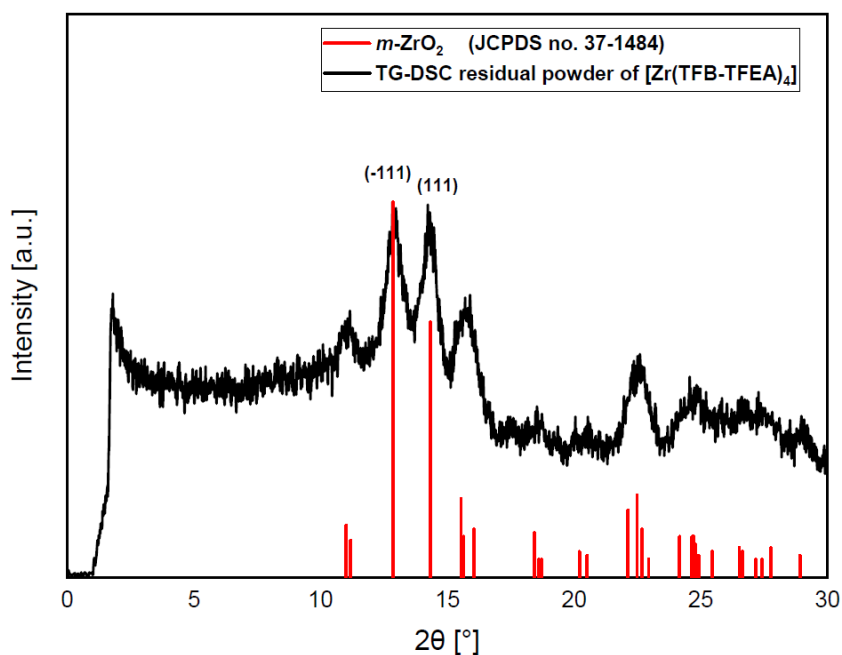


Figure 4.34. The XRD pattern of residual powder obtained from the TG-DSC of $[\text{Zr}(\text{TFB-TFEA})_4]$

Although $[\text{Zr}(\text{TFB-TFEA})_4]$ demonstrates adequate volatility under reduced pressure, its decomposition behavior is not well suited for the controlled formation of Zr_2ON_2 thin films. The competing decomposition pathways, leading ultimately to ZrO_2 at higher temperatures, make it difficult to selectively obtain the desired oxynitride phase. Therefore, despite its favorable volatility, $[\text{Zr}(\text{TFB-TFEA})_4]$ is not considered a suitable precursor for MOCVD applications targeting Zr_2ON_2 thin film deposition.

5. Syntheses and Characterization of Fluorinated β -Ketoenamine-based Zirconium and Hafnium Complexes and Their Application in Deposition of ZrO_2 , HfO_2 , and $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ Thin Films

This work was carried out in collaboration with the research group of Prof. Dr. Dr. (h.c.) Anjana Devi at the Leibniz Institute for Solid State and Materials Research (IFW Dresden), Dresden, Germany. Major parts of this chapter have been published as a peer-reviewed article with the author as first author. © The Authors, 2026.

[39] Billy Oktora Abdilah, Andreas Lichtenberg, Corinna Hegemann, Thomas Fischer, Marcel Schmickler, Harish Parala, Anjana Devi, and Sanjay Mathur. " **$\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ thin films from chemical vapor deposition of fluorinated β -ketoenamine precursors.**" *RSC Applied Interfaces*, **3**(3), (2026), p706-720.

Licensed under the Creative Commons Attribution 3.0 Unported Licence (CC BY 3.0).

[<https://doi.org/10.1039/d51f00360a>]

5.1. Scientific Context

Hafnium zirconium oxide, $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ (with $x = 0 > x > 1$), has emerged as an important material for semiconductor technologies due to its robust ferroelectric properties, high dielectric constant, and excellent thermal stability [105, 106]. In contrast to conventional ferroelectrics, HZO is fully compatible with standard Complementary Metal-Oxide-Semiconductor (CMOS) fabrication processes, making it particularly attractive for integration into advanced CMOS devices [107]. The distinctive combination of its switchable polarization and scalability supports a wide range of applications, including low-power non-volatile memories, Ferroelectric Field-Effect Transistors (FeFETs), and next-generation logic and neuromorphic computing devices [108, 109]. The electrical properties of HZO can be finely tuned through compositional variations and processing parameters, further enhancing its versatility as an important electronic material. Achieving high-quality HZO thin films with precise control over both composition and thickness often relies on ALD [6].

ALD of ZrO_2 and HfO_2 thin films is commonly performed using metal-organic precursors such as tetrakis(dimethylamido)zirconium (TDMAZr) [110], tetrakis(ethylmethylamido)zirconium (TEMAZr) [111-113], $\text{Zr}[\text{Cp}(\text{NMe}_2)_3]$ [114, 115], and

their hafnium analogues TDMAHf [116], TEMA(Hf) [117], and $\text{Hf}[\text{Cp}(\text{NMe}_2)_3]$ [118], in combination with oxidizing co-reactants including O_2 , O_3 , or H_2O .

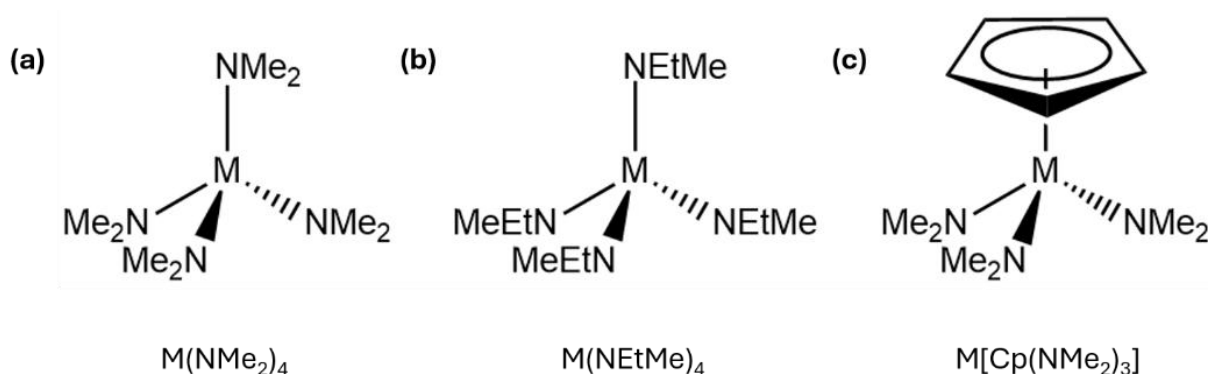


Figure 5.1. Molecular structure representations of (a) TDMA(M), (b) TEMA(M), and (c) $\text{M}[\text{Cp}(\text{NMe}_2)_3]$ ($\text{M} = \text{Zr}, \text{Hf}$).

These precursor//co-reactant systems enable sequential, self-limiting surface reactions, providing precise control over growth rate, film composition, density, and interfacial quality, as well as excellent conformality on complex substrates. Consequently, ALD has been widely employed to produce high-quality ZrO_2 and HfO_2 thin films for nanoelectronics and gate dielectric applications. However, most ALD studies to date have focused on the individual deposition of ZrO_2 and HfO_2 , while reports on the direct ALD growth of mixed HZO thin films remain limited.

More recently, Nishida *et al.* [119] reported the development of a novel liquid ALD precursor system composed of an equimolar mixture of $\text{Hf}(\text{dmap})_4$ and $\text{Zr}(\text{dmap})_4$, used together with O_3 as the oxidizing co-reactant, for the deposition of high-quality HZO thin films targeted for ferroelectric memory applications (Figure 5.2). This mixed-precursor approach exhibits enhanced thermal stability, with decomposition temperatures reaching approximately 371°C , as well as closely matched vapor pressures for the hafnium and zirconium components. These characteristics enable improved compositional control and uniform incorporation of Hf and Zr during the ALD process, resulting in films with superior structural integrity and functional performance [119].

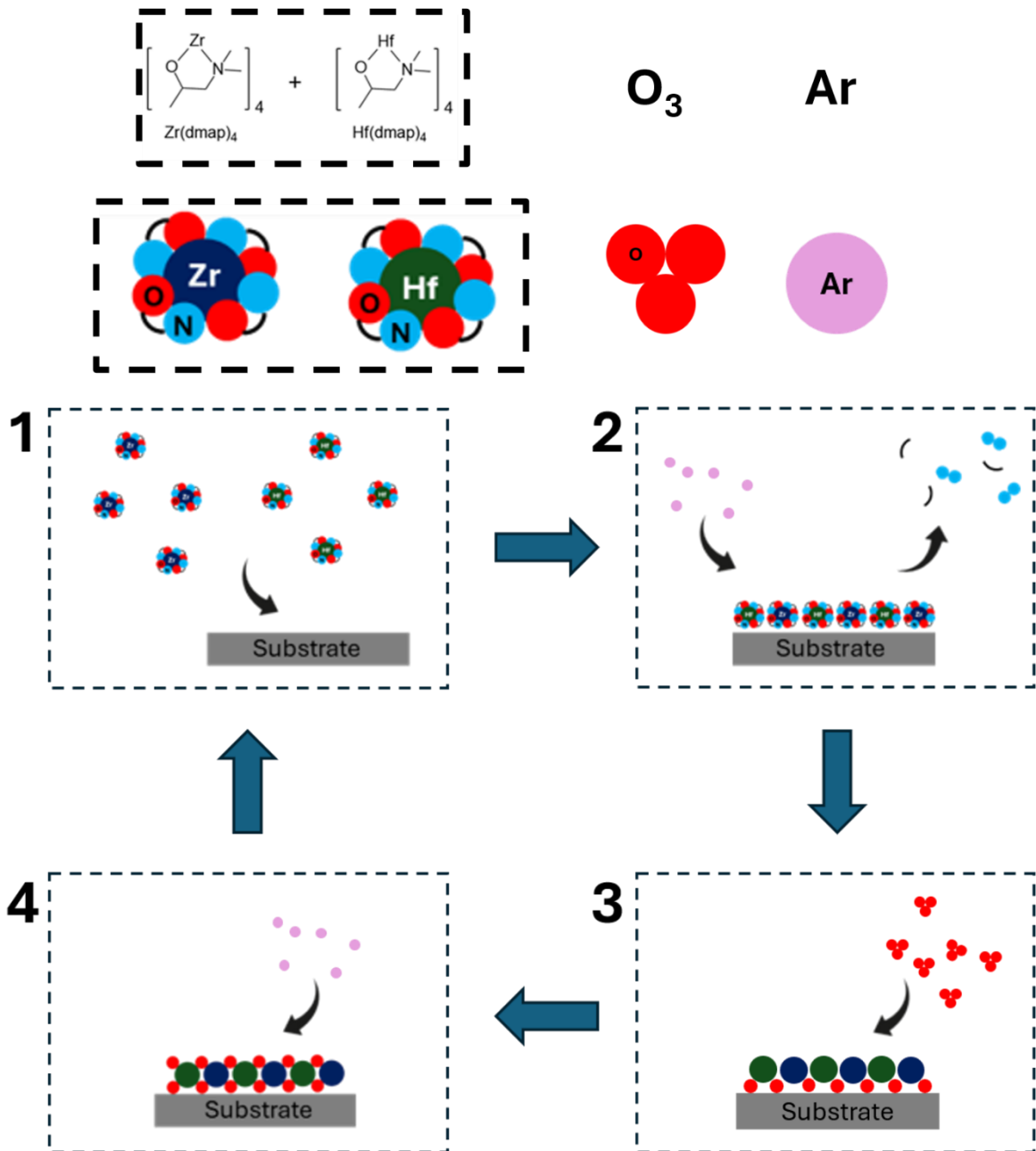


Figure 5.2. Schematic representation of HZO thin films synthesis via ALD based on experiment conducted by Nishida *et al.* [119].

Despite the demonstrated advantages of ALD in achieving excellent thickness uniformity, conformality, and reproducibility in HZO thin films, the technique remains subject to several inherent limitations. In particular, relatively low growth rates, high capital and operational costs associated with ALD equipment, and stringent requirements on precursor volatility, thermal stability, and reactivity can pose significant challenges for process throughput and scalability. These factors may ultimately constrain the adoption of ALD for large-area or high-volume manufacturing of ferroelectric HZO-based devices [120, 121].

To date, no monomeric complex containing both hafnium and zirconium has been reported as a single-source precursor for the CVD deposition of $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ thin films. In contrast, the deposition of individual ZrO_2 and HfO_2 thin films from structurally analogous precursors has been extensively investigated. For example, Williams *et al.* [122] reported the synthesis of the isostructural complexes $[\text{M}(\text{O}^i\text{Bu})_2(\text{mmp})_2]$ ($\text{M} = \text{Zr}, \text{Hf}$; $\text{mmp} = 1\text{-methoxy-2-methyl-2-propanolate}$), which were successfully employed for the deposition of ZrO_2 and HfO_2 thin films by liquid-injection MOCVD after dissolution in toluene.

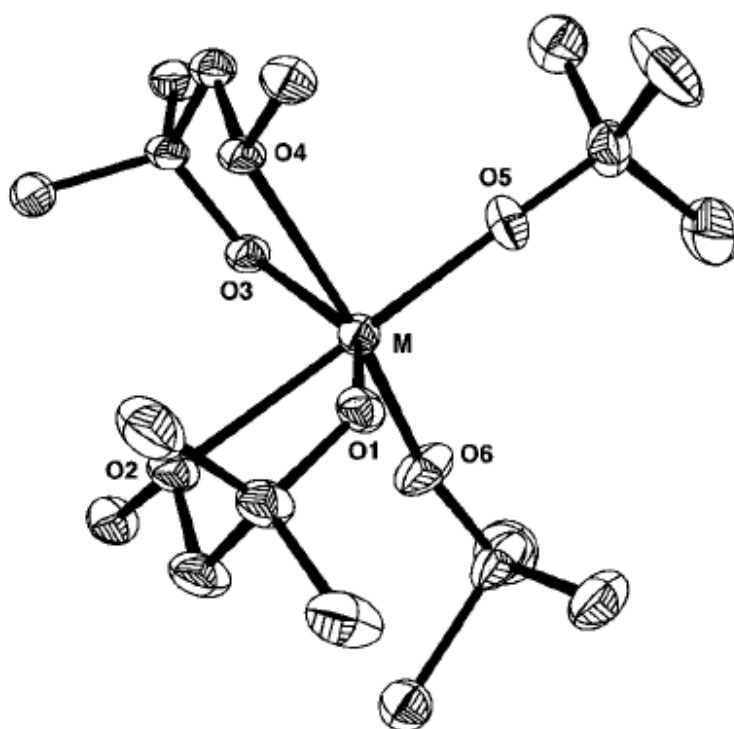
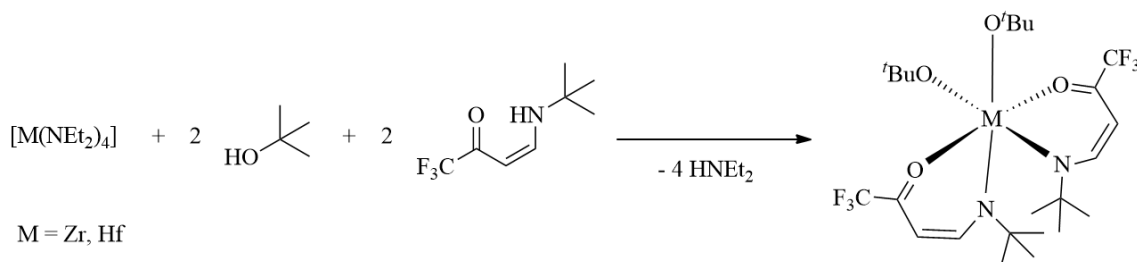


Figure 5.3. Molecular structure of $[\text{M}(\text{O}^i\text{Bu})_2(\text{mmp})_2]$ ($\text{M} = \text{Zr}, \text{Hf}$; $\text{mmp} = 1\text{-methoxy-2-methyl-2-propanolate}$). Reproduced from Williams *et al.* [122] with permission from Wiley. © Wiley.

Building upon these findings, it is of considerable interest to explore the deposition of $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ using a dual-source approach based on two highly volatile and isostructural precursors. Such a strategy could enable simultaneous delivery of zirconium- and hafnium-containing species while avoiding the complexity associated with liquid-injection systems. Moreover, the use of structurally similar precursors with comparable thermal properties may facilitate better control over precursor transport and film composition, providing a promising route toward the synthesis of $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ thin films by MOCVD.

5.2. Syntheses, Characterization, and Thermal Analyses of $[\text{M}(\text{L})_2(\text{O}^t\text{Bu})_2]$ ($\text{M} = \text{Zr}, \text{Hf}$; $\text{L} = \text{TFB-}t\text{BuA}, \text{TFB-TFEA}$)

The reaction of one equivalent of $[\text{M}(\text{NEt}_2)_4]$ ($\text{M} = \text{Zr}$ or Hf) with two equivalents each of *tert*-butyl alcohol and the *H*-TFB-*t*BuA ligand at room temperature resulted in the formation of yellowish powders, $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{O}^t\text{Bu})_2]$ and $[\text{Hf}(\text{TFB-}t\text{BuA})_2(\text{O}^t\text{Bu})_2]$ (Scheme 5.1), which could be purified by sublimation at 130–135 °C (Figure 5.4a) and 135–139 °C (Figure 5.4b) under 1 mbar, respectively. The sublimation experiments resulted in the formation of colorless crystalline compounds.



Scheme 5.1. Reaction scheme for the synthesis of $[\text{M}(\text{TFB-}t\text{BuA})_2(\text{O}^t\text{Bu})_2]$ ($\text{M} = \text{Zr}, \text{Hf}$).

Although $[\text{M}(\text{NEt}_2)_4]$ ($\text{M} = \text{Zr}$ or Hf) can serve as precursors for zirconium oxide and hafnium oxide in MOCVD, these compounds are liquids at room temperature, which makes handling difficult, particularly for accurate mass measurement, and leads to material losses during sample preparation. In contrast, $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{O}^t\text{Bu})_2]$ and $[\text{Hf}(\text{TFB-}t\text{BuA})_2(\text{O}^t\text{Bu})_2]$ are solid, crystalline materials with sufficient volatility to allow sublimation, enabling accurate weighing, convenient handling, and reproducible deposition. In addition, the objective of this reaction is to fabricate thin films using the single-source precursor concept, which requires the presence of predefined metal–oxygen bonds that are absent in the initial starting materials. Overall, the designed precursors demonstrate that rational ligand modification can produce thermally robust, easy-to-handle metal complexes suitable for controlled thin-film deposition.

The diethylamido ligands of $[\text{M}(\text{NEt}_2)_4]$ ($\text{M} = \text{Zr}$ or Hf) were replaced with *tert*-butoxo ligands via proton transfer from *tert*-butyl alcohol, releasing four equivalents of diethylamine. Subsequent addition of two equivalents of *H*-TFB-*t*BuA ligands to the intermediate bis(diethylamido)bis(*tert*-butoxo)metal complex led to further substitution of the remaining diethylamido ligands. The substitution of all four diethylamido ligands was driven by the strong oxophilicity of zirconium and hafnium and their propensity to increase the coordination number, forming thermodynamically more stable complexes with strongly coordinating *tert*-butoxo and chelating TFB-*t*BuA ligands.

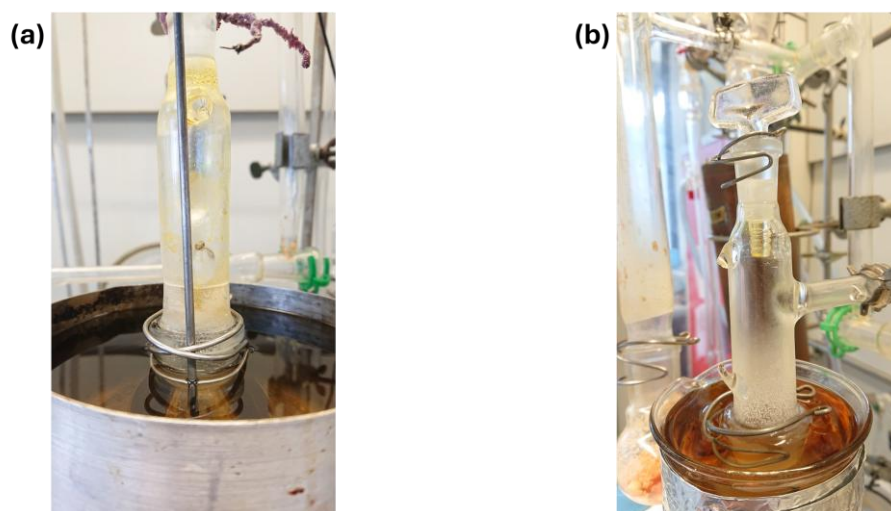


Figure 5.4. Sublimates of (a) $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ and (b) $[\text{Hf}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$.

The solution behavior of $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ and $[\text{Hf}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ was characterized using ^1H NMR spectroscopy. For $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$, a singlet (s) at 1.08 ppm, integrating for eighteen protons, was attributed to the six methyl groups of two TFB-*t*BuA ligands. Two doublets (d) at 5.44-5.46 ppm and 7.22-7.24 ppm were assigned to four protons at C5 and C6 of two TFB-*t*BuA ligands, respectively, with a 2:2 proton ratio. Additionally, two *tert*-butoxo ligands exhibited a singlet (s) at 1.31 ppm, corresponding to eighteen protons from their six methyl groups (Figure 5.5a). The ^1H NMR spectra of $[\text{Hf}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ showed similarities to those of $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$. The six methyl groups in the TFB-*t*BuA ligands were identified by a singlet (s) at 1.07 ppm, which integrated to eighteen protons. Two different doublets (d) with a 2:2 ratio, at 5.42-5.43 ppm and 7.21-7.22 ppm, respectively, represented four protons at C5 and C6 of two TFB-*t*BuA ligands. The six methyl groups of two *tert*-butoxo ligands were also linked to a singlet (s) at 1.33 ppm, which integrated for eighteen protons (Figure 5.5b). Although complexes of this type may, in principle, exist as enantiomeric or diastereoisomeric forms depending on ligand arrangement around the metal center, the observation of single, well-defined resonances for each ligand environment indicates that any such stereoisomers are either NMR-equivalent or undergo rapid interconversion on the NMR timescale. Likewise, potential fluxional processes involving ligand rearrangement appear to be fast at room temperature, resulting in time-averaged NMR signals. Consequently, the spectra are consistent with an effective C_2 -symmetric solution structure, in agreement with the predicted molecular symmetry.

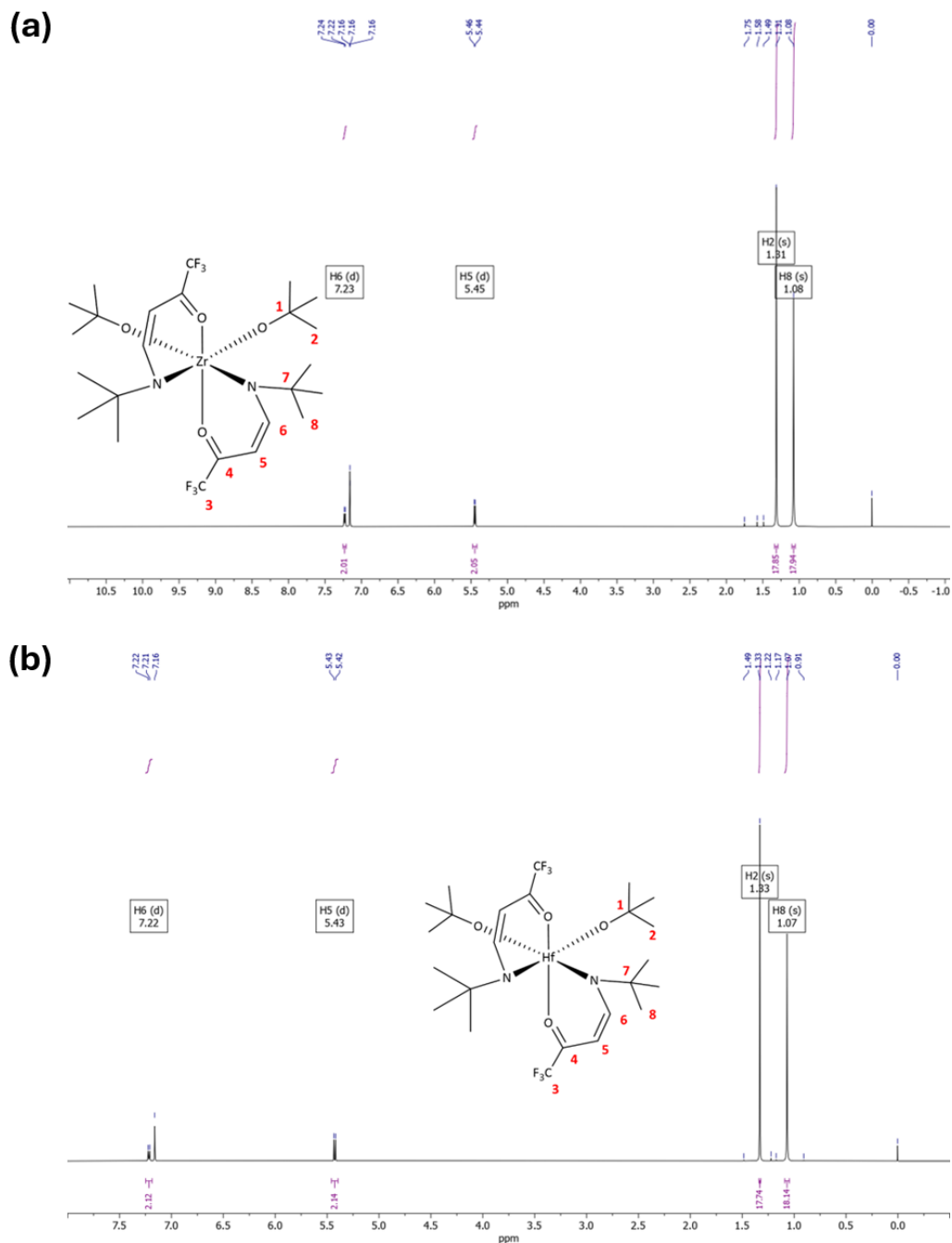


Figure 5.5. ^1H NMR spectra of (a) $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{O'Bu})_2]$ and (b) $[\text{Hf}(\text{TFB-}t\text{BuA})_2(\text{O'Bu})_2]$.

The ^{13}C $\{^1\text{H}, ^{19}\text{F}\}$ NMR spectra of $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{O'Bu})_2]$ and $[\text{Hf}(\text{TFB-}t\text{BuA})_2(\text{O'Bu})_2]$ each exhibited eight distinct resonances, consistent with the carbon environments in the molecular structures, allowing unambiguous assignment of all carbon atoms (Figure 5.6).

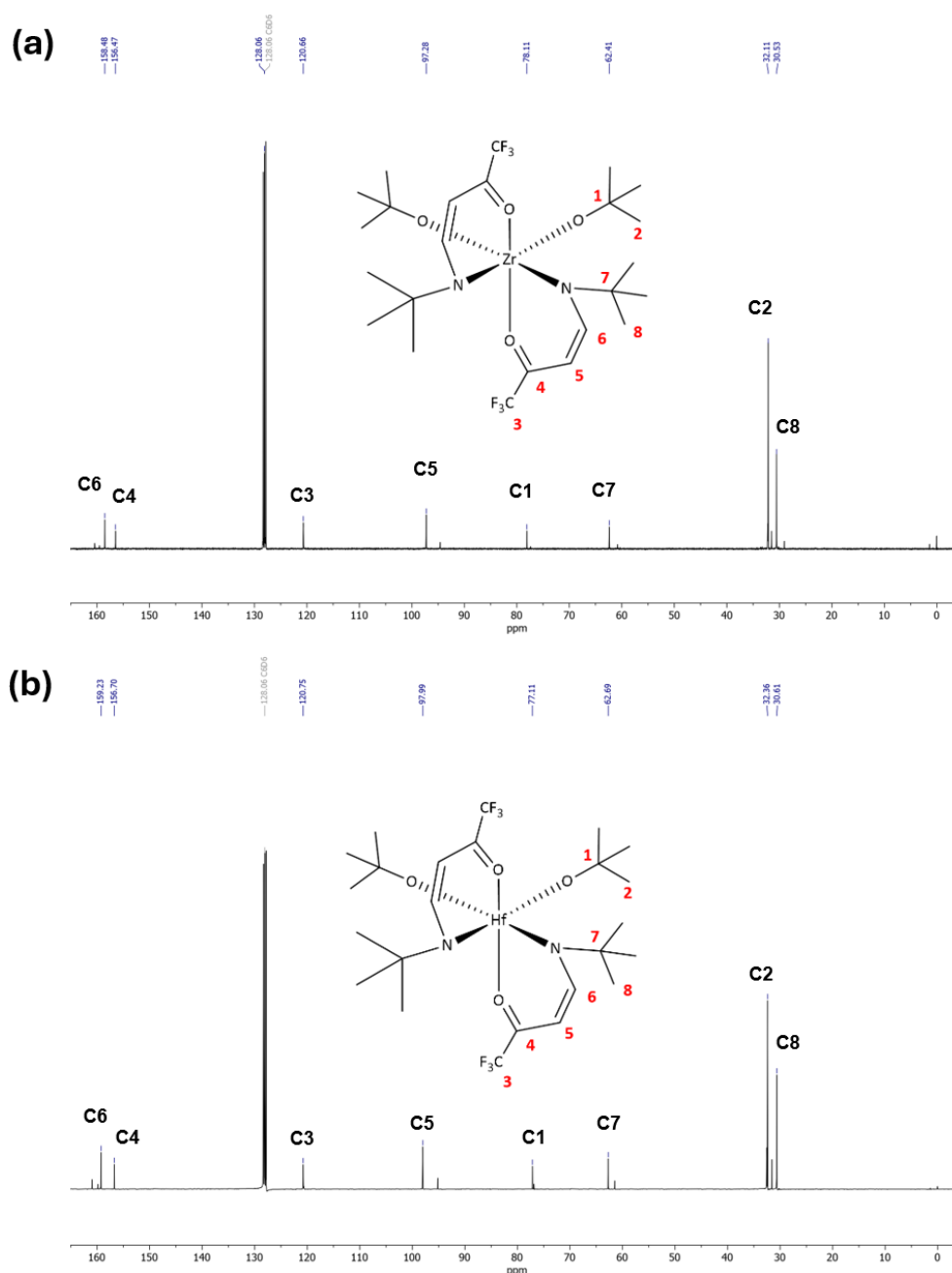


Figure 5.6. ^{13}C { ^1H , ^{19}F } NMR spectra of (a) $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{O'Bu})_2]$ and (b) $[\text{Hf}(\text{TFB-}t\text{BuA})_2(\text{O'Bu})_2]$.

The ^{19}F NMR spectra confirmed the presence of the trifluoromethyl group, showing characteristic singlets at -74.48 ppm for $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{O'Bu})_2]$ (Figure 5.7a) and -74.61 ppm for $[\text{Hf}(\text{TFB-}t\text{BuA})_2(\text{O'Bu})_2]$ (Figure 5.7b). CHNS elemental analysis further corroborated the molecular compositions, with experimental values closely matching theoretical calculations based on the molecular formulas. These combined spectroscopic and elemental data validate the structural integrity and purity of both precursors.

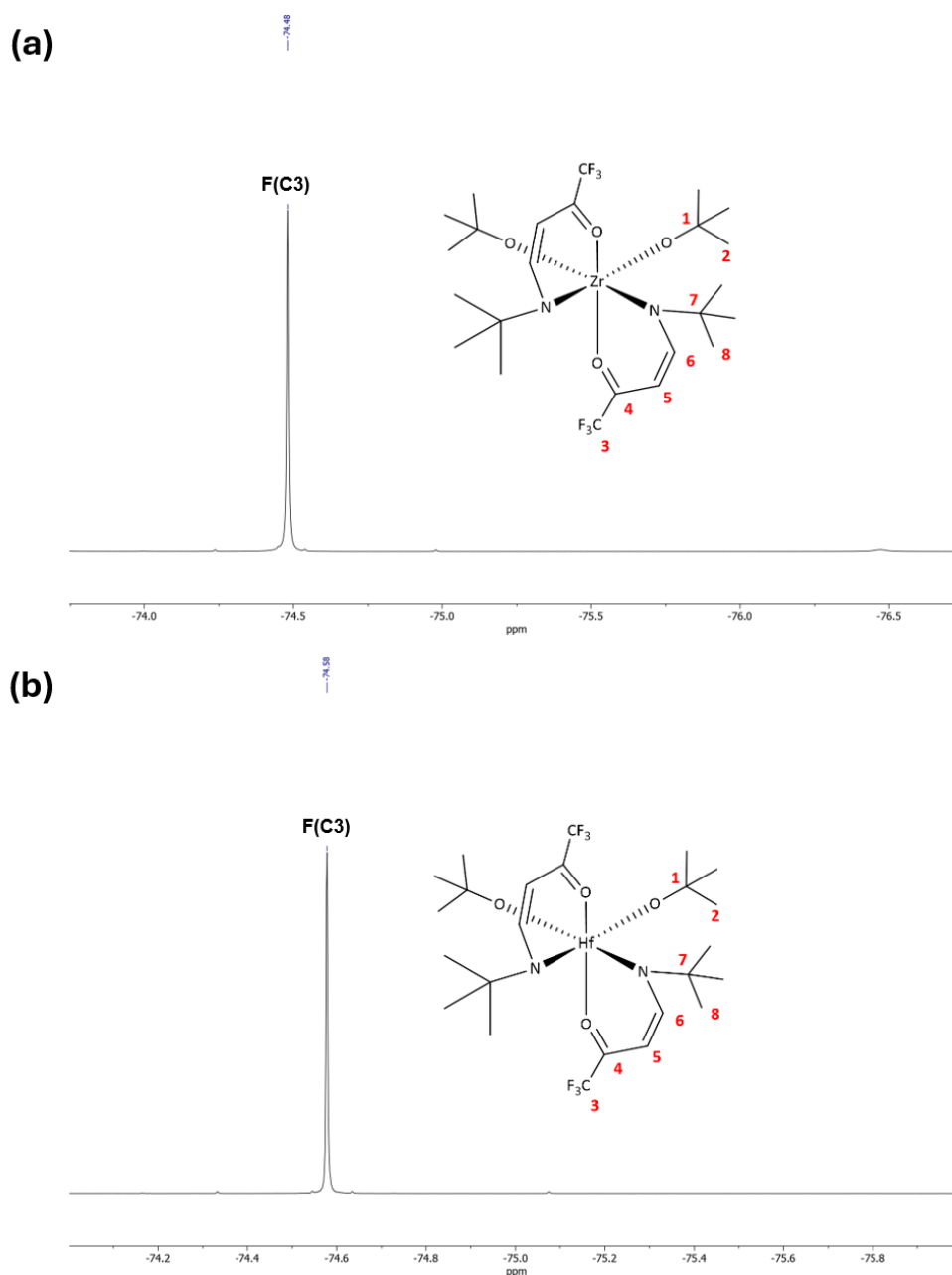


Figure 5.7. ^{19}F NMR spectra of (a) $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{O}^t\text{Bu})_2]$ and (b) $[\text{Hf}(\text{TFB-}t\text{BuA})_2(\text{O}^t\text{Bu})_2]$.

SC-XRD analyses revealed that both $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{O}^t\text{Bu})_2]$ and $[\text{Hf}(\text{TFB-}t\text{BuA})_2(\text{O}^t\text{Bu})_2]$ crystallize in the monoclinic space group $P2_1/n$, confirming that they are isostructural and exhibit a similar coordination environment around the metal centers adopting a distorted octahedral geometry (Figure 5.8a and b). The SC-XRD results show that the solid-state structure agrees well with the coordination environment predicted from the ^1H NMR spectra.

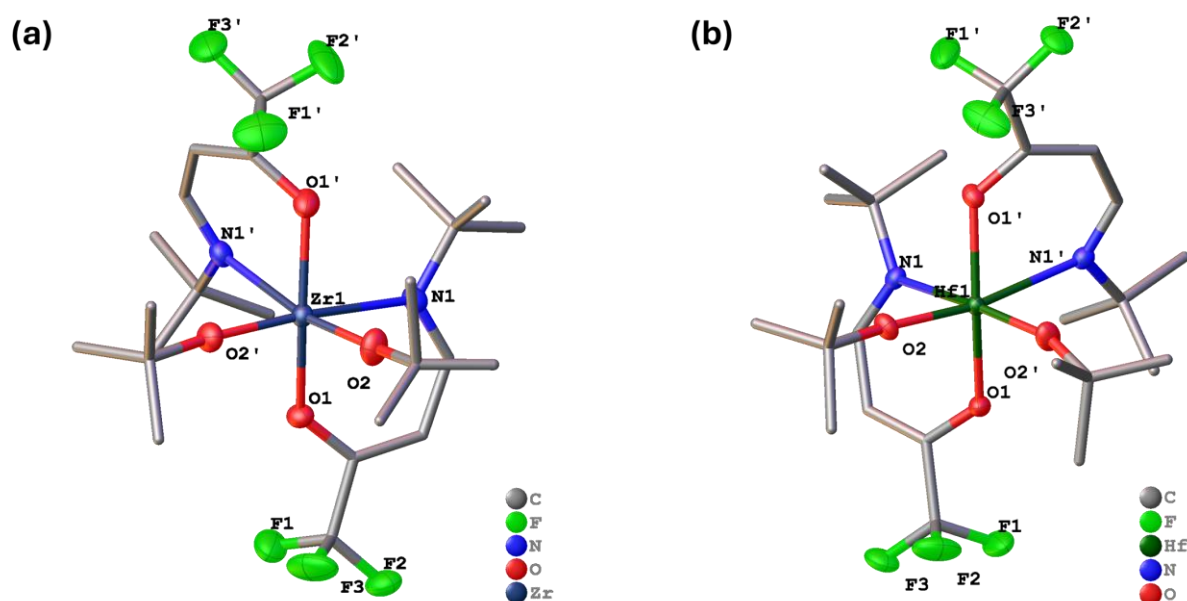


Figure 5.8. The single crystal X-ray crystal structures of (a) $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ and (b) $[\text{Hf}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$. Hydrogen atoms are omitted for clarity.

The Zr–O and Hf–O bond lengths involving the TFB-*t*BuA ligands fall within the ranges of 2.0728(17)–2.098(2) Å, while the corresponding Zr–N and Hf–N bond distances are between 2.460(2) and 2.496(4) Å. In addition, the M–O bonds associated with the *tert*-butoxo ligands are slightly shorter, ranging from 1.9022(17) to 1.913(2) Å (Table 5.1), reflecting the stronger σ -donor nature of the alkoxide group. The close structural resemblance between $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ and $[\text{Hf}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ demonstrates that the replacement of Zr by Hf does not significantly alter the overall geometry or bonding environment, which is expected to be given the nearly identical ionic radii and electronic configurations of the two metals. This structural equivalence highlights the stability and predictability of such heteroleptic architectures across the group 4 transition metal series.

Table 5.1. Bond lengths [Å] in $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ and $[\text{Hf}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$.

	$[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$	$[\text{Hf}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$
M–O1 [Å]	2.091(2)	2.0816(17)
M–O1' [Å]	2.098(2)	2.0728(17)
M–O2 [Å]	1.913(2)	1.9022(17)
M–O2' [Å]	1.910(2)	1.9069(18)
M–N1 [Å]	2.499(3)	2.460(2)
M–N1' [Å]	2.489(3)	2.465(2)

Preliminary thermal analyses of $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ and $[\text{Hf}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ were performed via sublimation under reduced pressure ($p \approx 1$ mbar) using a Schlenk line as described in the previous chapter. Both precursors sublimed above 130°C , depositing colorless crystalline material on the cold finger (Figure 5.4a and b), which confirmed adequate thermal stability ($> 100^\circ\text{C}$) and volatility for MOCVD. TG analyses under nitrogen atmosphere were performed to assess the potential decomposition products. The TG data (Figure 5.9) revealed a multistep decomposition process, with initial weight losses at $\sim 115^\circ\text{C}$ for $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ and $\sim 118^\circ\text{C}$ for $[\text{Hf}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$. A major decomposition occurred near 250°C , resulting in $\sim 66\%$ mass loss, accompanied by pronounced endothermic peaks in Differential Thermal Analysis (DTA), consistent with ligand breakdown and volatilization (Figure 5.9). Residual masses at this stage were 23% for $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ and 28% for $[\text{Hf}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$, in reasonable agreement with theoretical oxide contents (ZrO_2 : 19.68%; HfO_2 : 29.52%), with slight deviations attributed to incomplete ligand degradation or volatilization of metal intermediates. Final residues at 547.5°C were 17.7% ($[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$) and 24.4% ($[\text{Hf}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$), which are lower than the theoretical oxide yields, likely due to partial volatilization of the samples. These results confirm that both $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ and $[\text{Hf}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ exhibit sufficient thermal stability and volatility for MOCVD deposition of ZrO_2 and HfO_2 films. Their analogous decomposition behavior and structural similarity further support the use of equimolar mixtures for co-deposition of $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ films, offering a reliable route to engineer mixed-metal oxide films with controlled composition and microstructure.

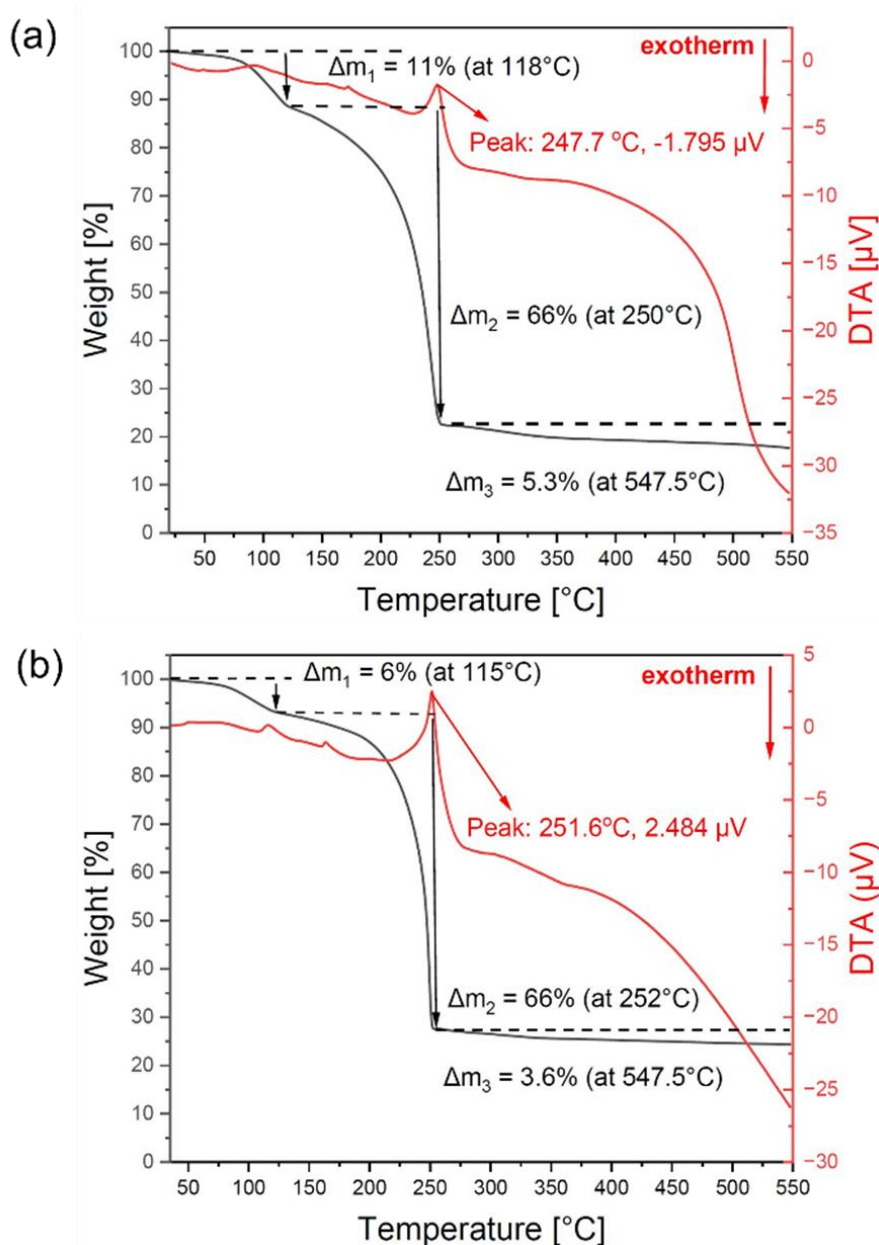


Figure 5.9. TG (black) and DTA (red) profiles of (a) $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{O'Bu})_2]$ and (b) $[\text{Hf}(\text{TFB-}t\text{BuA})_2(\text{O'Bu})_2]$ under N_2 flow at atmospheric pressure from 20–550 $^{\circ}\text{C}$.

Considering that $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{O'Bu})_2]$ and $[\text{Hf}(\text{TFB-}t\text{BuA})_2(\text{O'Bu})_2]$ exhibit different sublimation onset temperatures ($p \approx 1$ mbar) despite their closely related molecular structures, detailed vapor pressure analyses were carried out to better understand the sublimation and transport behavior of the two precursors. Vapor pressure measurements for both $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{O'Bu})_2]$ and $[\text{Hf}(\text{TFB-}t\text{BuA})_2(\text{O'Bu})_2]$ were performed starting from 80 $^{\circ}\text{C}$, with temperature increments of 10 $^{\circ}\text{C}$ for each measurement step. As summarized in Table 5.2, the results clearly show that at the same temperature, $[\text{Hf}(\text{TFB-}t\text{BuA})_2(\text{O'Bu})_2]$ consistently exhibits a higher vapor pressure than $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{O'Bu})_2]$ over the entire

investigated temperature range. This observation is directly supported by the mass loss rate data, which show systematically higher mass loss values for $[Hf(TFB-tBuA)_2(O'Bu)_2]$ compared to $[Zr(TFB-tBuA)_2(O'Bu)_2]$ at equivalent temperatures, indicating that a larger amount of $[Hf(TFB-tBuA)_2(O'Bu)_2]$ is transferred into the gas phase once sublimation is active.

Table 5.2. Vapor pressure measurement results of $[Zr(TFB-tBuA)_2(O'Bu)_2]$ and $[Hf(TFB-tBuA)_2(O'Bu)_2]$.

Temperature [°C]	Vapor Pressure [Pa]		Mass Loss [mg min ⁻¹]		Consumption Time [min]	
	$[Zr(TFB-tBuA)_2(O'Bu)_2]$	$[Hf(TFB-tBuA)_2(O'Bu)_2]$	$[Zr(TFB-tBuA)_2(O'Bu)_2]$	$[Hf(TFB-tBuA)_2(O'Bu)_2]$	$[Zr(TFB-tBuA)_2(O'Bu)_2]$	$[Hf(TFB-tBuA)_2(O'Bu)_2]$
80	-	0.3877	-	6.6021×10^{-4}	-	80
90	0.82787	1.2419	1.3024×10^{-3}	2.0855×10^{-3}	50	110
100	2.2948	4.2623	3.5614×10^{-3}	7.0611×10^{-3}	80	120
110	6.0932	11.043	9.3322×10^{-3}	1.8054×10^{-2}	70	90
120	15.072	24.955	2.2789×10^{-2}	4.0276×10^{-2}	70	50
130	35.145	-	5.2475×10^{-2}	-	60	-

However, further insight is obtained by analyzing the vapor pressure data using the Clausius-Clapeyron relationship, $\ln(P) = A - B/T$, as shown in Figure 5.10. From the slopes of the $\ln(P)$ versus $1/T$ plots, the sublimation enthalpy of $[Hf(TFB-tBuA)_2(O'Bu)_2]$ ($\Delta H_{\text{sublimation}} = 121.607$ kJ mol⁻¹) is found to be significantly higher than that of $[Zr(TFB-tBuA)_2(O'Bu)_2]$ ($\Delta H_{\text{sublimation}} = 114.237$ kJ mol⁻¹), indicating stronger solid-state interactions and a greater energetic barrier for molecular desorption in the case of $[Hf(TFB-tBuA)_2(O'Bu)_2]$. As a consequence, although $[Hf(TFB-tBuA)_2(O'Bu)_2]$ exhibits higher equilibrium vapor pressure and higher mass loss rates at a given temperature once sublimation is established, a higher thermal energy input is required to initiate efficient sublimation of $[Hf(TFB-tBuA)_2(O'Bu)_2]$ under practical conditions. This explains the experimentally observed higher sublimation onset temperature of $[Hf(TFB-tBuA)_2(O'Bu)_2]$ compared to $[Zr(TFB-tBuA)_2(O'Bu)_2]$ at around 1 mbar and demonstrates that precursor sublimation behavior cannot be described by vapor pressure alone, but rather results from the combined effects of equilibrium volatility, sublimation enthalpy, and surface desorption kinetics.

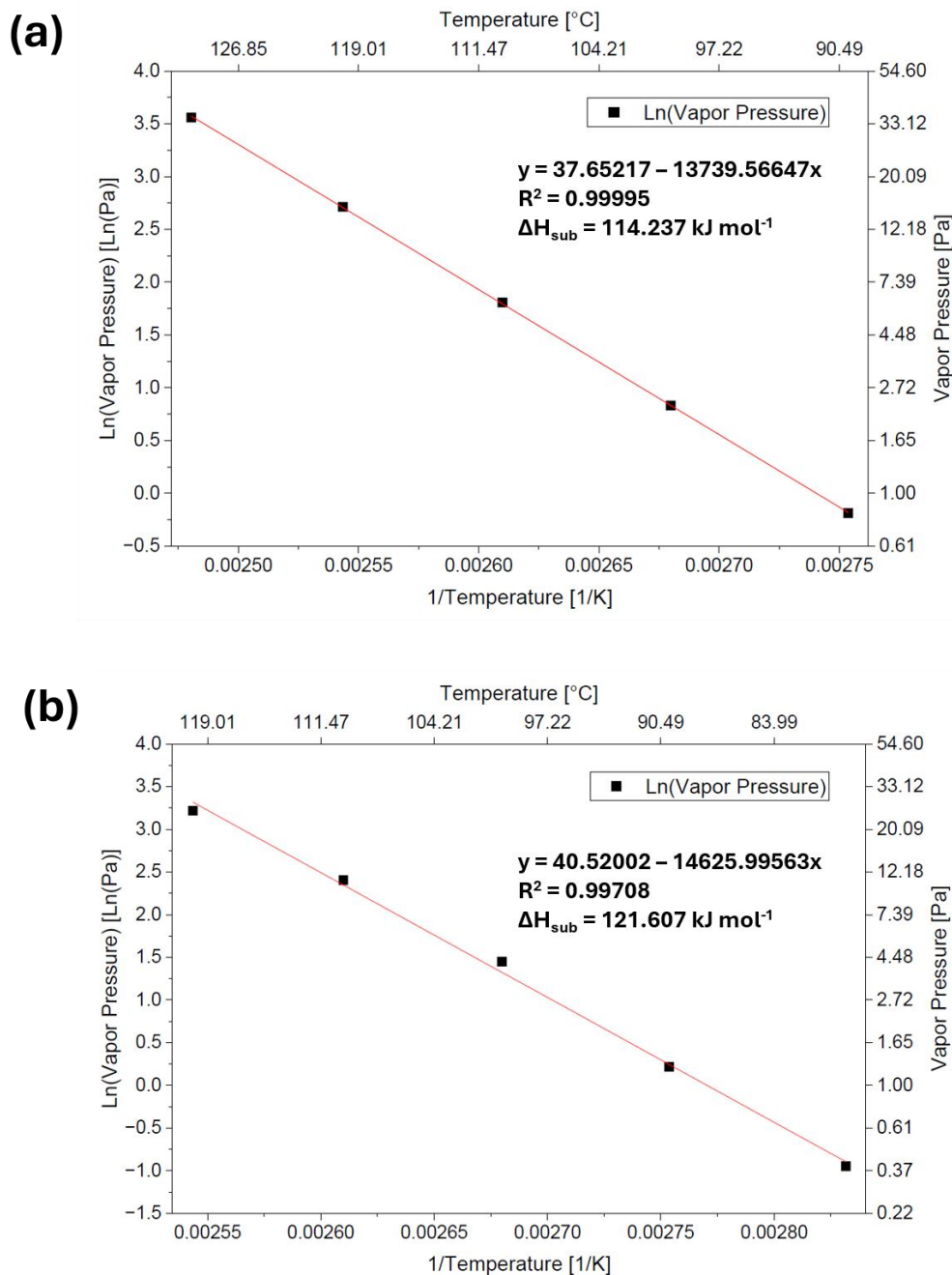
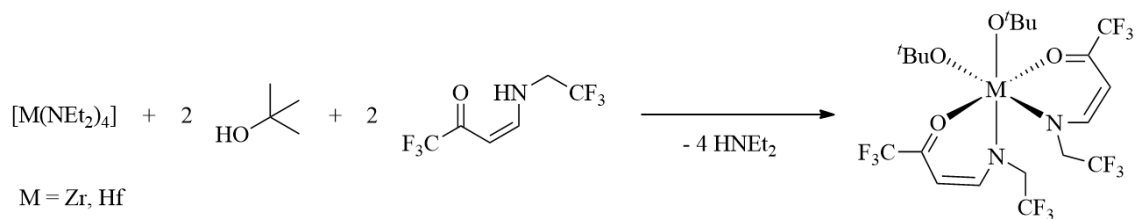


Figure 5.10. Vapor pressure integration analyses of (a) $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{O'Bu})_2]$ and (b) $[\text{Hf}(\text{TFB-}t\text{BuA})_2(\text{O'Bu})_2]$ based on Clausius-Clapeyron relationship, $\ln(P) = A - B/T$.

Using the same synthetic strategy employed for the preparation of $[\text{M}(\text{TFB-}t\text{BuA})_2(\text{O'Bu})_2]$ ($\text{M} = \text{Zr}$ or Hf), the ligand *H*-TFB-TFEA was applied to the synthesis of $[\text{M}(\text{TFB-TFEA})_2(\text{O'Bu})_2]$ ($\text{M} = \text{Zr}$ or Hf). In this approach, one equivalent of $[\text{M}(\text{NEt}_2)_4]$ ($\text{M} = \text{Zr}$ or Hf) was reacted with two equivalents of *tert*-butyl alcohol and two equivalents of the *H*-TFB-TFEA ligand at room temperature, resulting in the formation of $[\text{Zr}(\text{TFB-TFEA})_2(\text{O'Bu})_2]$ and $[\text{Hf}(\text{TFB-TFEA})_2(\text{O'Bu})_2]$, respectively (Scheme 5.2).



Scheme 5.2. Reaction scheme for the synthesis of $[\text{M}(\text{TFB-TFEA})_2(\text{O}^t\text{Bu})_2]$ ($\text{M} = \text{Zr, Hf}$).

Similar to $[\text{M}(\text{TFB-}i\text{tBuA})_2(\text{O}^t\text{Bu})_2]$, the strong M–O bonds provided by the *tert*-butoxo ligands enable $[\text{M}(\text{TFB-TFEA})_2(\text{O}^t\text{Bu})_2]$ to sublime under reduced pressure upon heating ($p \approx 1$ mbar). Under these conditions, $[\text{Zr}(\text{TFB-TFEA})_2(\text{O}^t\text{Bu})_2]$ and $[\text{Hf}(\text{TFB-TFEA})_2(\text{O}^t\text{Bu})_2]$ were observed to sublime at 93–102 °C (Figure 5.11a) and 87–95 °C (Figure 5.11b), respectively.

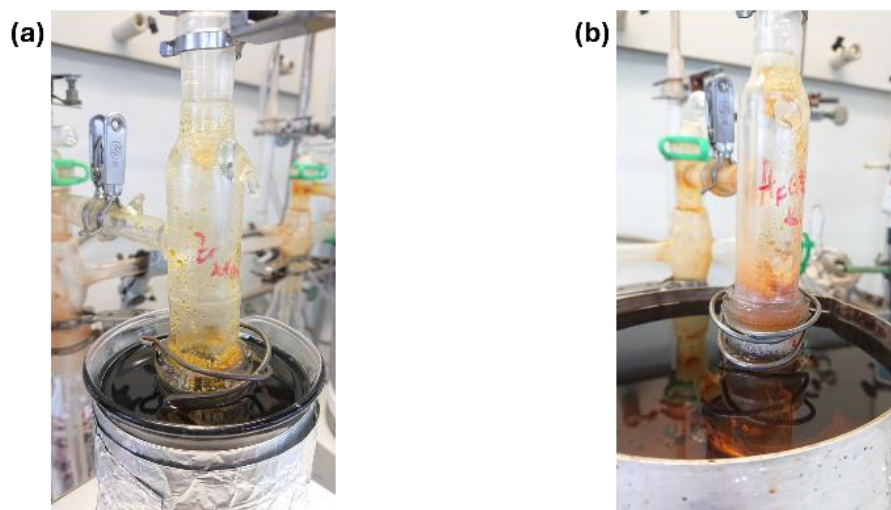


Figure 5.11. Sublimates of (a) $[\text{Zr}(\text{TFB-TFEA})_2(\text{O}^t\text{Bu})_2]$ and (b) $[\text{Hf}(\text{TFB-TFEA})_2(\text{O}^t\text{Bu})_2]$.

The solution-state behavior of $[\text{Zr}(\text{TFB-TFEA})_2(\text{O}^t\text{Bu})_2]$ and $[\text{Hf}(\text{TFB-TFEA})_2(\text{O}^t\text{Bu})_2]$ was examined by ^1H NMR spectroscopy. For $[\text{Zr}(\text{TFB-TFEA})_2(\text{O}^t\text{Bu})_2]$, two singlets (s) at 3.01 and 4.19 ppm were assigned to the four methylene protons at C7 of the two TFB-TFEA ligands. Two doublets (d) observed at 5.32–5.34 ppm and 6.73–6.74 ppm correspond to four protons at the C5 and C6 positions of the TFB-TFEA ligands, respectively, exhibiting the expected 2:2 proton ratio. In addition, the two *tert*-butoxo ligands give rise to a singlet (s) at 1.18 ppm, integrating for eighteen protons associated with their six methyl groups (Figure 5.12a). The ^1H NMR spectrum of $[\text{Hf}(\text{TFB-TFEA})_2(\text{O}^t\text{Bu})_2]$ shows closely analogous features. The methylene protons of the TFB-TFEA ligands appear as two singlets (s) at 2.87 and 4.27 ppm, together integrating for four protons. A distinct triplet to doublets (td) at 5.29–5.31 ppm and a singlet (s) at 6.71 ppm, again in a 2:2 ratio, are attributed to four protons at C5

and C6 of the TFB-TFEA ligands. The six methyl groups of the two *tert*-butoxo ligands are observed as a singlet (s) at 1.20 ppm, integrating for eighteen protons (Figure 5.12b).

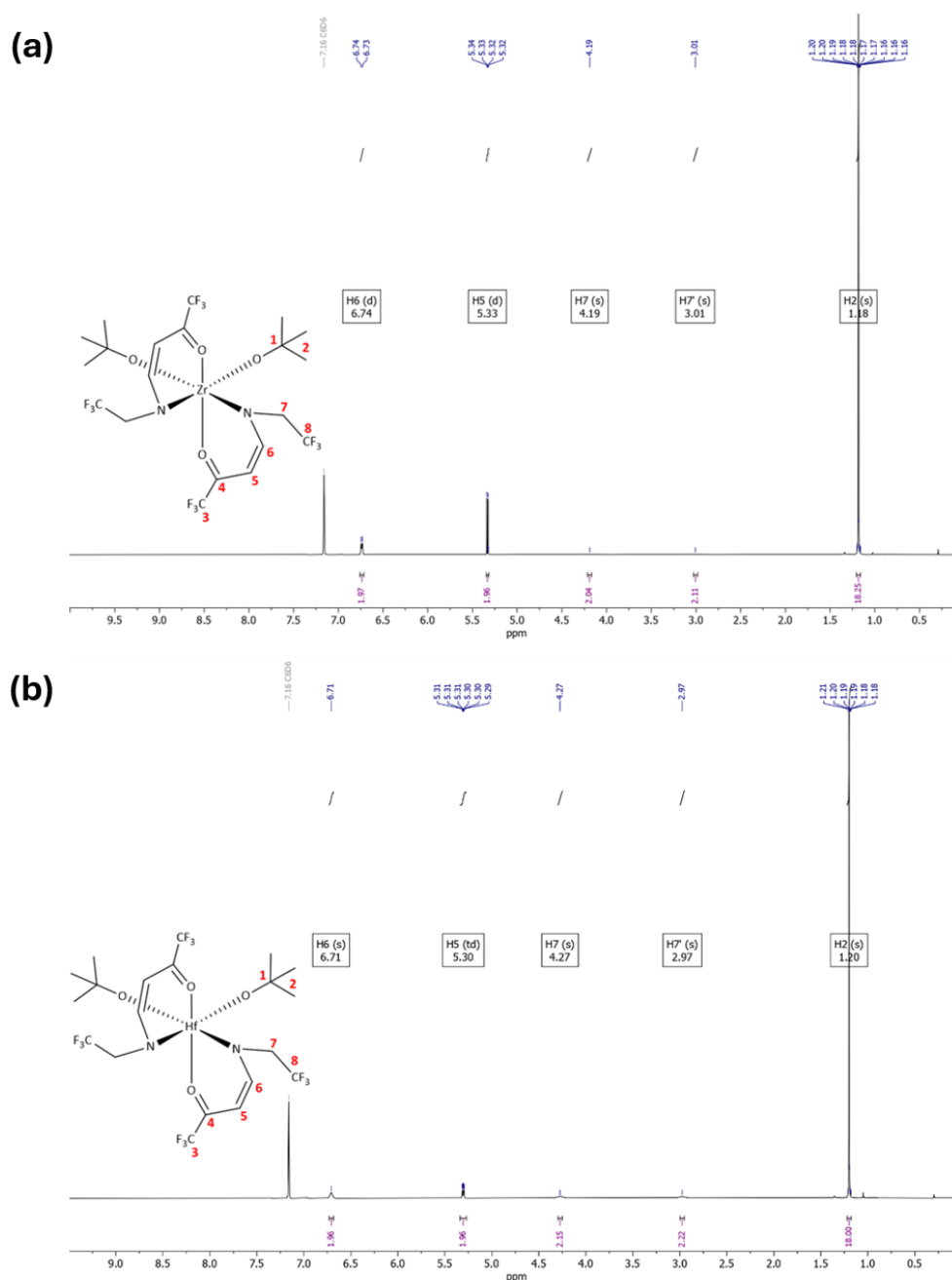


Figure 5.12. ^1H NMR spectra of (a) $[\text{Zr}(\text{TFB-TFEA})_2(\text{O'Bu})_2]$ and (b) $[\text{Hf}(\text{TFB-TFEA})_2(\text{O'Bu})_2]$.

The $^{13}\text{C}\{^1\text{H}, ^{19}\text{F}\}$ NMR spectra of both $[\text{Zr}(\text{TFB-TFEA})_2(\text{O'Bu})_2]$ and $[\text{Hf}(\text{TFB-TFEA})_2(\text{O'Bu})_2]$ exhibit eight distinct resonances, in agreement with the number of unique carbon environments present in their molecular structures. This enabled the unambiguous assignment of all carbon atoms (Figure 5.13).

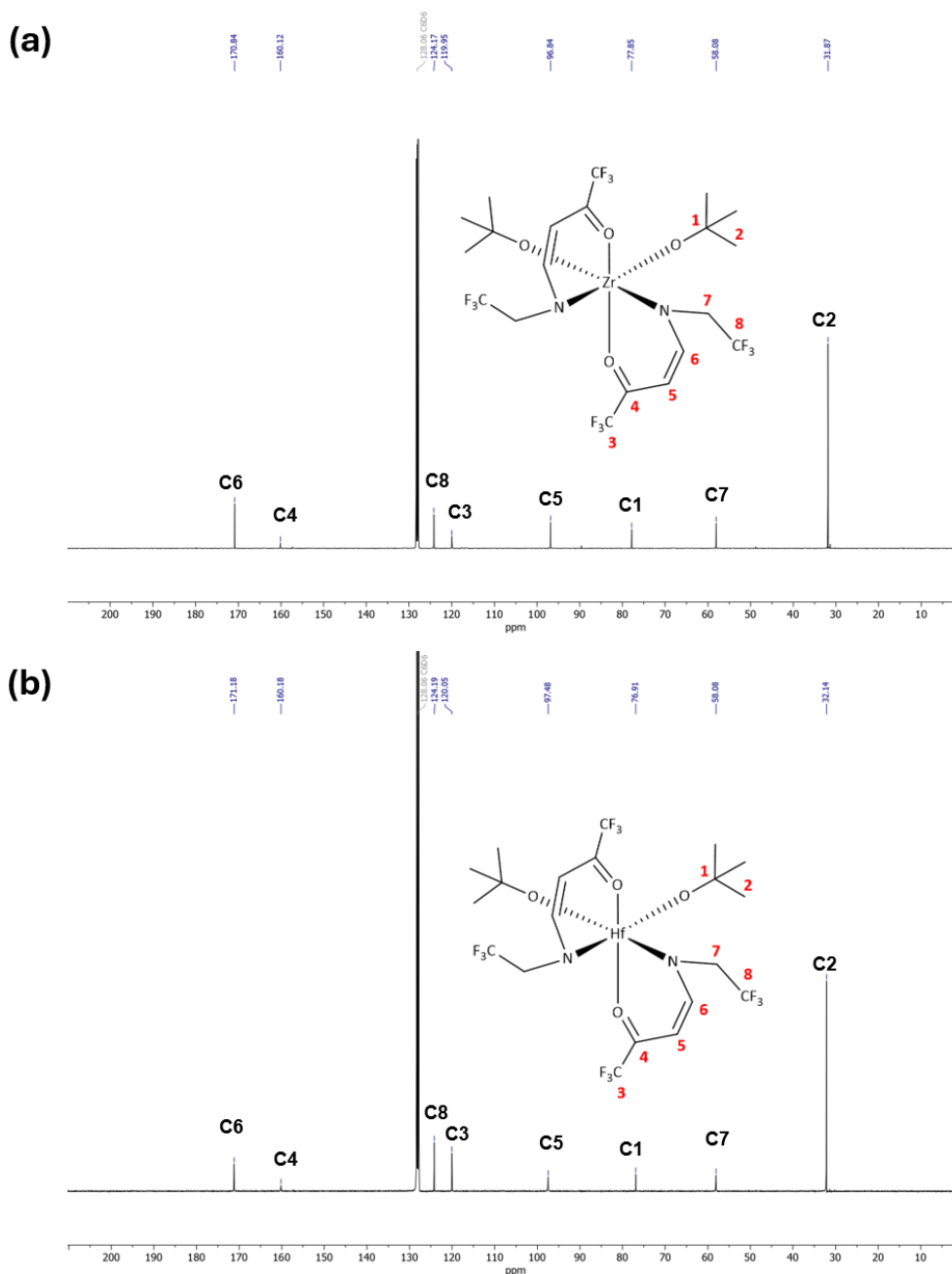


Figure 5.13. ^{13}C $\{^1\text{H}, ^{19}\text{F}\}$ NMR spectra of (a) $[\text{Zr}(\text{TFB-TFEA})_2(\text{O'Bu})_2]$ and (b) $[\text{Hf}(\text{TFB-TFEA})_2(\text{O'Bu})_2]$.

The ^{19}F NMR spectra further confirm the presence of the two trifluoromethyl groups of the TFB-TFEA ligands, showing two characteristic singlets at -70.83 ppm (CF_3 at C8) and -75.13 ppm (CF_3 at C3) for $[\text{Zr}(\text{TFB-TFEA})_2(\text{O'Bu})_2]$ (Figure 5.14a), and at -70.89 ppm (CF_3 at C8) and -75.26 ppm (CF_3 at C3) for $[\text{Hf}(\text{TFB-TFEA})_2(\text{O'Bu})_2]$ (Figure 5.14b). CHNS elemental analysis provided additional confirmation of the molecular compositions, with the experimentally determined values closely matching those calculated from the corresponding molecular formulas. Taken together, the spectroscopic and elemental analyses confirm the

structural integrity and high purity of both zirconium and hafnium complexes, supporting their suitability for further evaluation as MOCVD precursors.

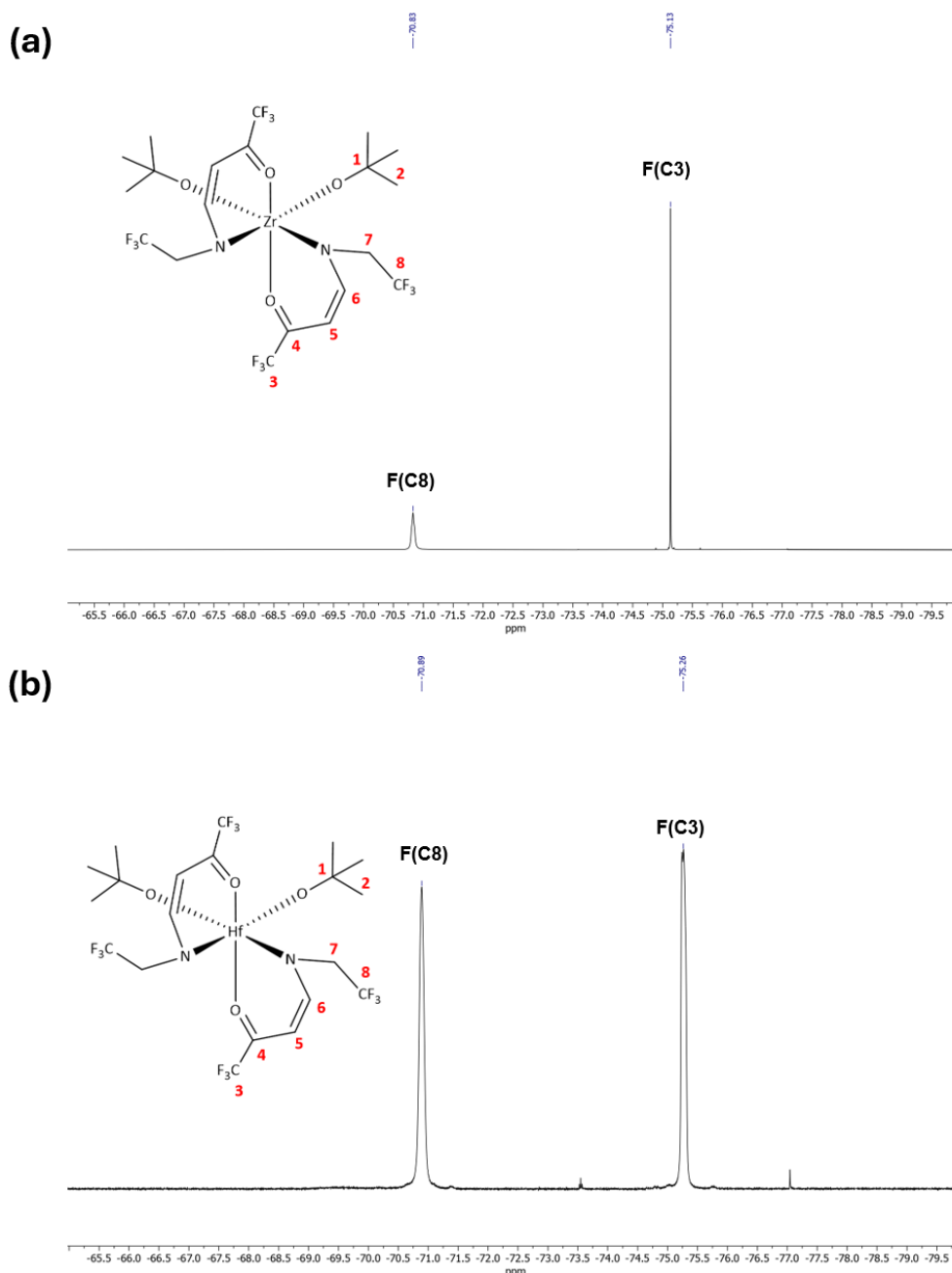


Figure 5.14. ^{19}F NMR spectra of (a) $[\text{Zr}(\text{TFB-TFEA})_2(\text{O'Bu})_2]$ and (b) $[\text{Hf}(\text{TFB-TFEA})_2(\text{O'Bu})_2]$.

SC-XRD analyses revealed that both $[\text{Zr}(\text{TFB-TFEA})_2(\text{O'Bu})_2]$ and $[\text{Hf}(\text{TFB-TFEA})_2(\text{O'Bu})_2]$ crystallize in the triclinic space group $P\bar{1}$. This finding confirms that the two complexes are isostructural and possess closely comparable coordination environments around their respective metal centers adopting a distorted octahedral geometry (Figure 5.15a and b). The SC-XRD results show that the solid-state structure agrees well with the coordination environment predicted from the ^1H NMR data.

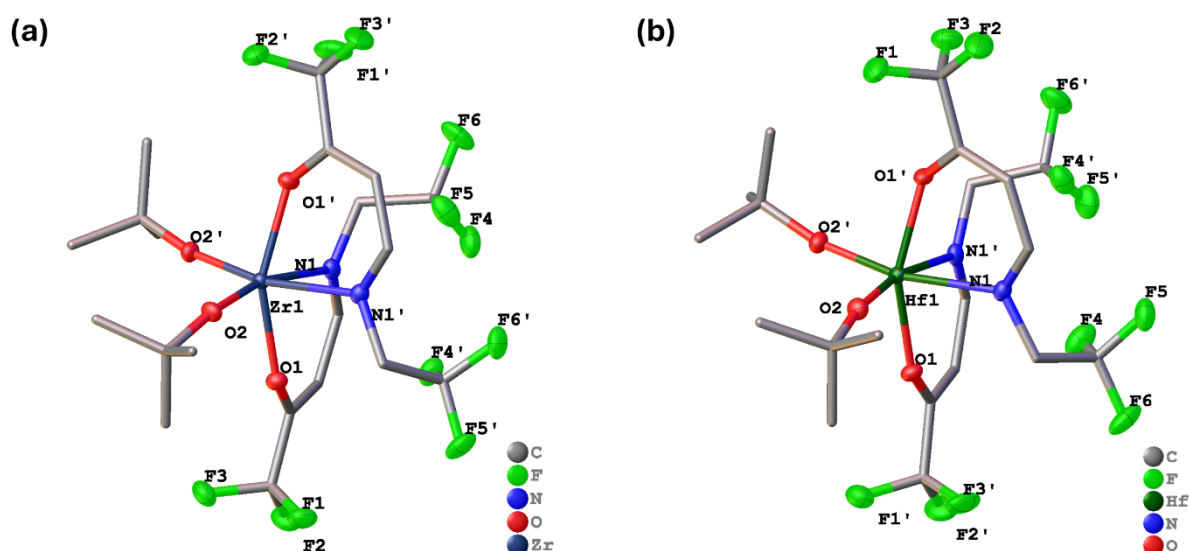


Figure 5.15. The single crystal X-ray crystal structures of (a) $[\text{Zr}(\text{TFB-TFEA})_2(\text{O'Bu})_2]$ and (b) $[\text{Hf}(\text{TFB-TFEA})_2(\text{O'Bu})_2]$. Hydrogen atoms are omitted for clarity.

The Zr–O and Hf–O bond lengths involving the TFB-TFEA ligands fall within the ranges of 2.076(2)–2.0974(11) Å, while the corresponding Zr–N and Hf–N bond distances are between 2.389(3) and 2.4211(14) Å. In addition, the M–O bonds associated with the *tert*-butoxo ligands are slightly shorter, ranging from 1.9059(11) to 1.924(3) Å (Table 5.3), reflecting the stronger σ -donor nature of the alkoxide group. The close structural resemblance between $[\text{Zr}(\text{TFB-TFEA})_2(\text{O'Bu})_2]$ and $[\text{Hf}(\text{TFB-TFEA})_2(\text{O'Bu})_2]$ demonstrates that the replacement of Zr by Hf does not significantly alter the overall geometry or bonding environment, which is expected to be given the nearly identical ionic radii and electronic configurations of the two metals, similar to $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{O'Bu})_2]$ and $[\text{Hf}(\text{TFB-}i\text{BuA})_2(\text{O'Bu})_2]$.

Table 5.3. Bond lengths [Å] in $[\text{Zr}(\text{TFB-TFEA})_2(\text{O'Bu})_2]$ and $[\text{Hf}(\text{TFB-TFEA})_2(\text{O'Bu})_2]$.

	$[\text{Zr}(\text{TFB-TFEA})_2(\text{O'Bu})_2]$	$[\text{Hf}(\text{TFB-TFEA})_2(\text{O'Bu})_2]$
M–O1 [Å]	2.0890(11)	2.077(3)
M–O1' [Å]	2.0974(11)	2.076(2)
M–O2 [Å]	1.9214(11)	1.906(3)
M–O2' [Å]	1.9059(11)	1.924(3)
M–N1 [Å]	2.4211(14)	2.389(3)
M–N1' [Å]	2.4204(14)	2.392(3)

Preliminary thermal behavior of $[\text{Zr}(\text{TFB-TFEA})_2(\text{O'Bu})_2]$ and $[\text{Hf}(\text{TFB-TFEA})_2(\text{O'Bu})_2]$ was also evaluated through sublimation experiments conducted under

reduced pressure ($p \approx 1$ mbar). Both complexes were found to sublime at temperatures above 80°C , depositing colorless crystalline material on the cold finger (Figure 5.11a and b). This behavior indicates sufficient thermal stability and volatility within a temperature range relevant for MOCVD applications. TG analyses performed under a nitrogen atmosphere revealed that both compounds undergo significant thermal decomposition at approximately 220°C . This process was accompanied by a mass loss of around 84% and pronounced endothermic signals in the DTA curves, consistent with ligand decomposition and volatilization. At this stage, the residual masses were 16.50% for $[\text{Zr}(\text{TFB-TFEA})_2(\text{O}^t\text{Bu})_2]$ (Figure 5.16a) and 15.53% for $[\text{Hf}(\text{TFB-TFEA})_2(\text{O}^t\text{Bu})_2]$ (Figure 5.16b). These values deviate notably from the calculated oxide residues (ZrO_2 : 18.2%; HfO_2 : 27.5%), suggesting incomplete ligand degradation and possible volatilization of zirconium or hafnium-containing intermediates. Upon further heating to 547.5°C , the remaining residues decreased to 7.65% for the zirconium complex and 19.39% for the hafnium complex. These values are substantially lower than the theoretical oxide yields and may reflect partial volatilization of the metal species during decomposition. While the formation of metallic residues cannot be excluded, the observed masses are also lower than the calculated metal contents (Zr: 13.5%; Hf: 23.3%), indicating complex decomposition pathways under the applied conditions.

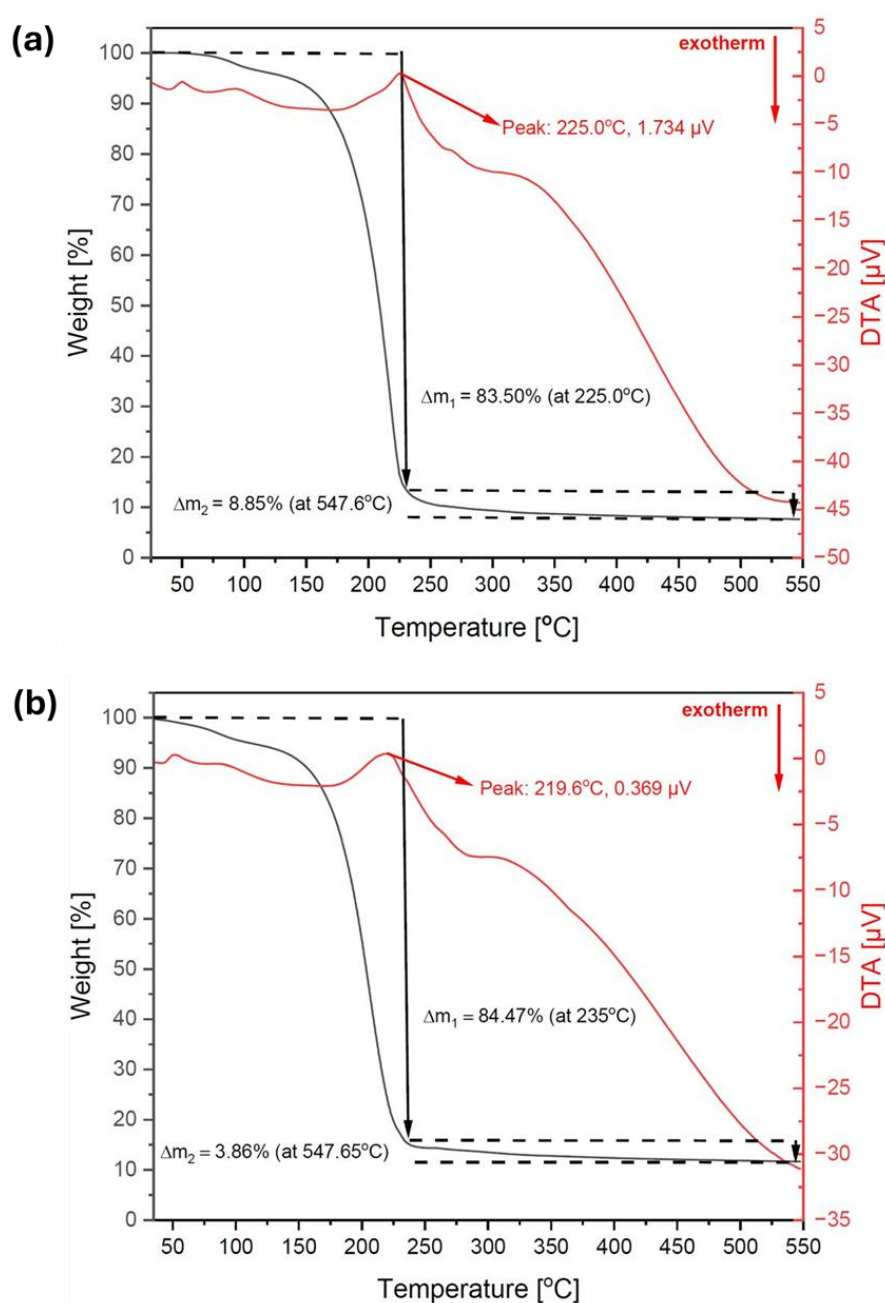


Figure 5.16. TG (black) and DTA (red) profiles of (a) $[\text{Zr}(\text{TFB-TFEA})_2(\text{O'Bu})_2]$ and (b) $[\text{Hf}(\text{TFB-TFEA})_2(\text{O'Bu})_2]$ under N_2 flow at atmospheric pressure from 20–550 $^{\circ}\text{C}$.

The combined sublimation and thermogravimetric results indicate that $[\text{Zr}(\text{TFB-TFEA})_2(\text{O'Bu})_2]$ and $[\text{Hf}(\text{TFB-TFEA})_2(\text{O'Bu})_2]$ possess a favorable balance between volatility and thermal stability required for MOCVD. Both complexes sublime cleanly above 80 $^{\circ}\text{C}$ under reduced pressure, demonstrating adequate volatility within a practical temperature window for vapor-phase delivery. At higher temperatures, significant mass loss accompanied by endothermic events reflects ligand decomposition and volatilization, which is desirable for film growth processes. The deviation of the residual masses from the calculated oxide and

metal contents suggests partial volatilization of metal-containing species, a behavior commonly observed for metal-organic precursors under inert conditions. Overall, these results support the potential of both complexes as viable MOCVD precursors, while also highlighting the need for further evaluation under actual deposition conditions to fully assess their decomposition pathways and film-forming behavior.

5.3 Deposition of ZrO_2 , HfO_2 , and $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ Thin Films Using $[\text{M}(\text{L})_2(\text{O}^i\text{Bu})_2]$ ($\text{M} = \text{Zr, Hf}$; $\text{L} = \text{TFB-}i\text{BuA, TFB-TFEA}$)

$[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ and $[\text{Hf}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ (without co-reactant gas such as O_2) were employed as precursors for the deposition of zirconium oxide, hafnium oxide, and hafnium zirconium oxide (HZO) films by MOCVD ($p \approx 1.4 \times 10^{-2}$ mbar) with the precursor reservoirs maintained at 125 °C. Individual depositions of zirconium oxide and hafnium oxide conducted for 2 h resulted in precursor consumptions of 0.80 g for $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ and 0.66 g for $[\text{Hf}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$, respectively. For the co-deposition of HZO, an equimolar mixture of $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ and $[\text{Hf}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ was used to target a composition of $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$, with a total precursor consumption of approximately 0.88 g, indicating comparable volatility and efficient co-delivery of both precursors under identical conditions.

MOCVD of $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ at a substrate temperature of 600 °C yielded films, analyzed by X-ray Fluorescence (XRF) spectroscopy, which confirmed the presence of zirconium through characteristic signals (Figure 5.17b).

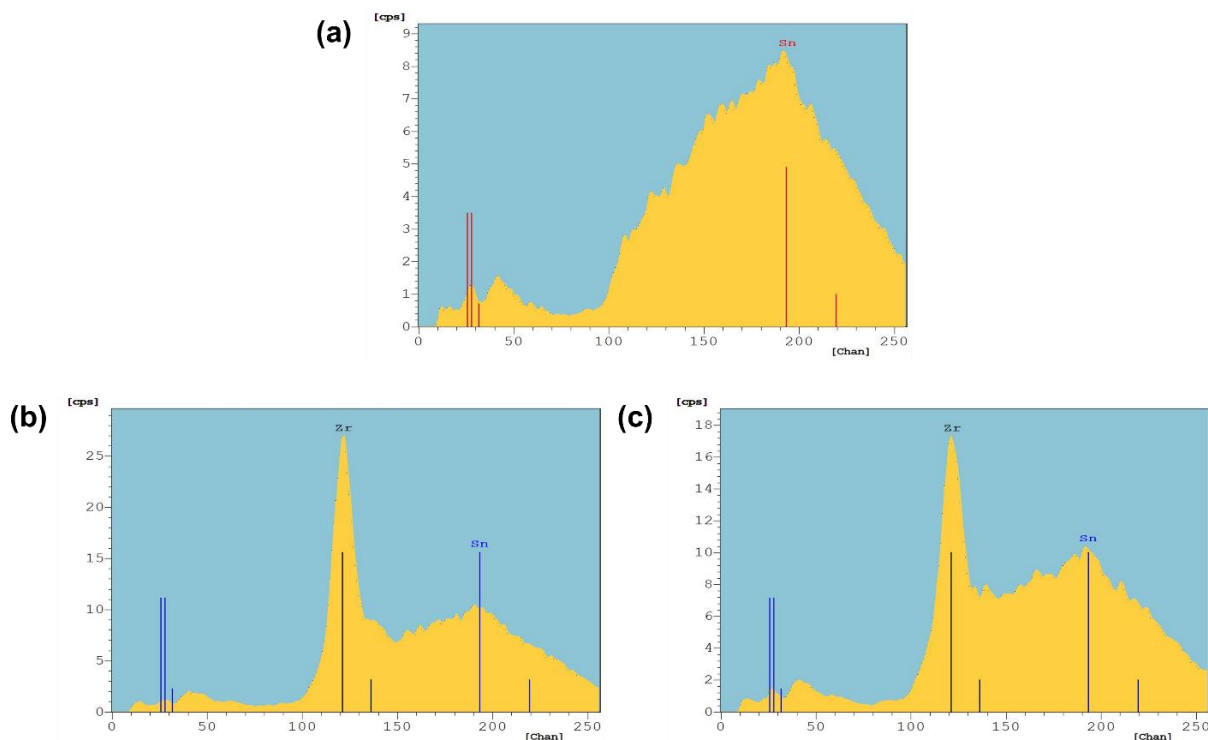


Figure 5.17. The XRF results of (a) only FTO substrate, (b) as-deposited zirconium oxide thin films, and (c) zirconium oxide thin films after calcination in air at 600 °C for 8 hours.

The thin-film XRD pattern of as-deposited films showed no peaks (Figure 5.18), indicating amorphous or poorly crystalline CVD deposits. Zirconium oxide films were calcined and annealed in air at 450, 550, and 600 °C for 8 h to improve crystallinity, inducing a visual color change from black to colorless (Figure 5.19).

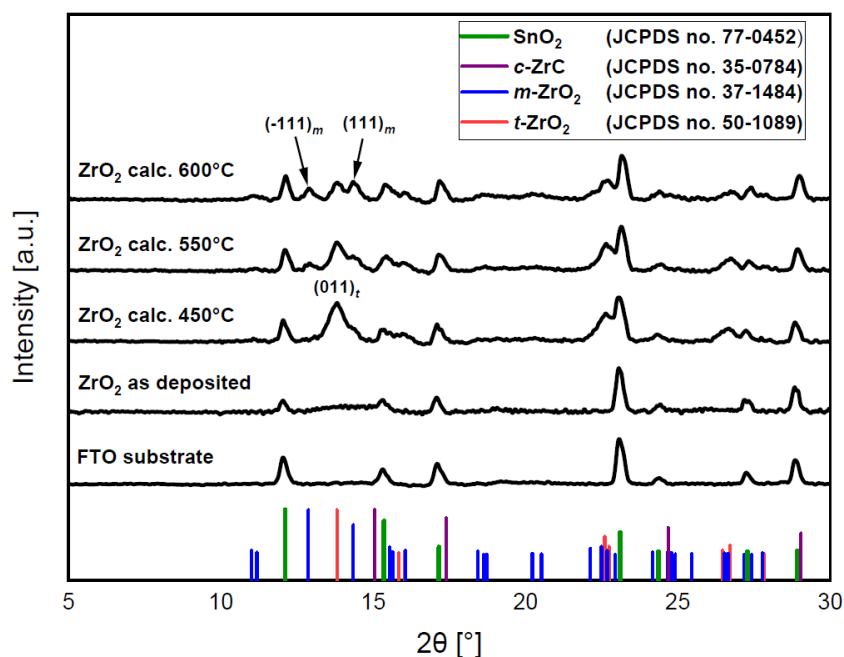


Figure 5.18. The XRD patterns of ZrO_2 thin films obtained from the MOCVD of $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$.

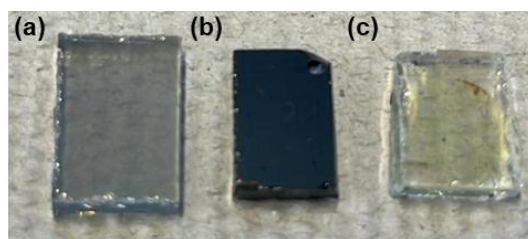


Figure 5.19. Surface appearance of (a) only FTO substrate, (b) as-deposited ZrO_2 thin films, and (c) ZrO_2 thin films after calcination in air at 600 °C for 8 hours.

XRD analysis showed that films calcined at 450 °C crystallized in the tetragonal ZrO_2 phase (JCPDS no. 50-1089), dominated by the (011) facet, whereas those treated at 550-600 °C exhibited phase transition to tetragonal and monoclinic modifications (JCPDS no. 37-1484) with prominent XRD peaks corresponding to (-111) and (111) facets (Figure 5.18). This evolution reflects the tetragonal-to-monoclinic transition typical of ZrO_2 , where nanoscale grains stabilize the tetragonal phase at lower temperatures. In comparison, grain growth at higher temperatures favors the thermodynamically stable monoclinic phase [123-128].

Scanned electron microscope (SEM) images and Energy-Dispersive X-ray (EDX) analyses (Figure 5.20) revealed that as-deposited films consisted primarily of Zr and O in an approximate 1:2 ratio, consistent with ZrO_2 , along with minor C and F impurities originating from undecomposed precursor residues.

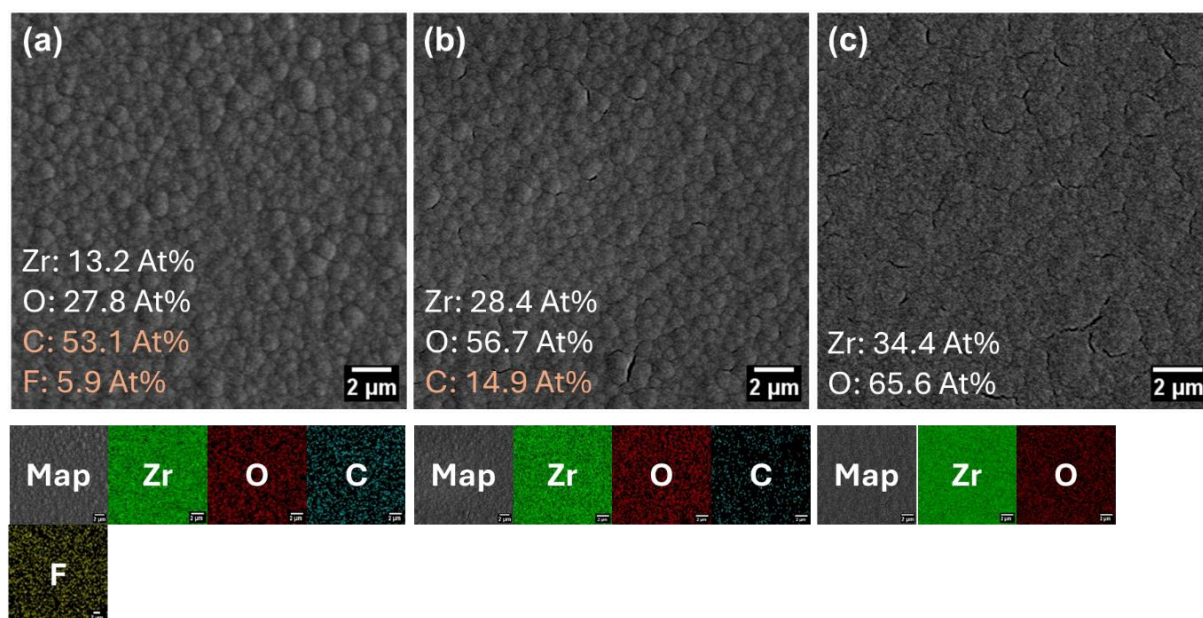


Figure 5.20. Top-view SEM and EDX images of (a) as-deposited, (b) calcined ($T_{\text{calcination}} = 550$ °C), and (c) calcined ZrO_2 films ($T_{\text{calcination}} = 600$ °C) synthesized from $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{O}'\text{Bu})_2]$ via MOCVD.

Post-annealing at 550 °C preserved the overall morphology but induced small surface cracks. Importantly, EDX confirmed the complete removal of F and a substantial reduction of C, while

maintaining the expected Zr:O stoichiometry. The residual carbon impurities observed in the films were attributed to amorphous carbon originating from incomplete decomposition of the organic ligands in the $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ precursor, rather than from the formation of carbonized phases such as zirconium carbide. This finding was supported by XRD analysis, which showed no diffraction features corresponding to zirconium carbide ($c\text{-ZrC}$, JCPDS no. 35-0784) in the deposited films (Figure 5.18). In addition, Fourier Transform Infrared (FTIR) spectroscopy further confirmed the absence of Zr–C bonding, as no characteristic Zr–C vibrational modes, typically observed in the range of 1010 and 1383 cm^{-1} [129, 130], were detected in the spectra (Figure 5.21).

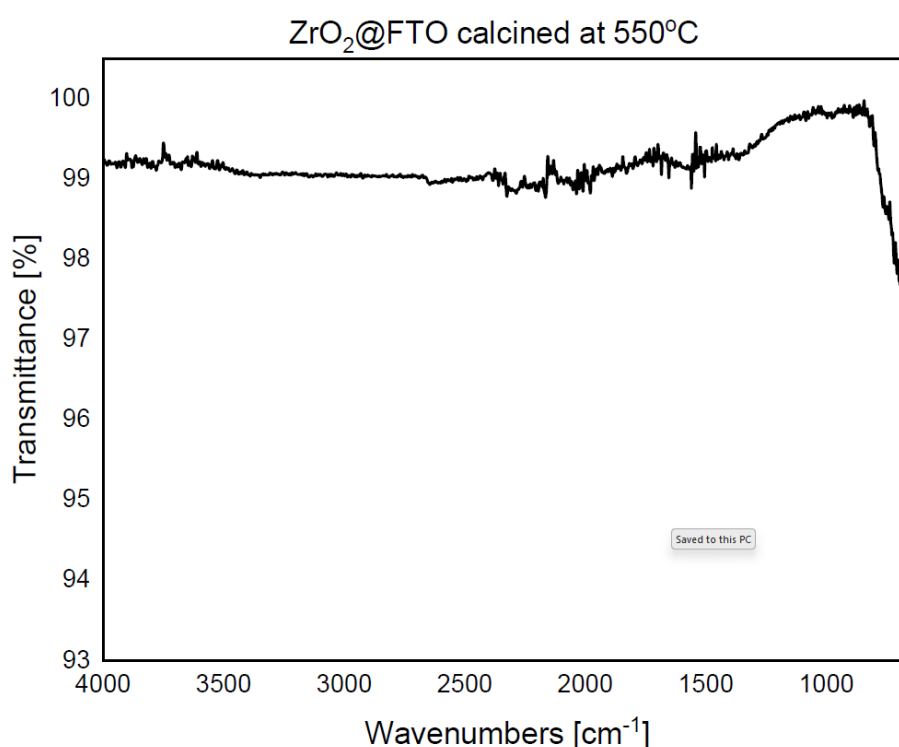


Figure 5.21. The FTIR result of ZrO_2 thin films after calcination in air at 550 °C for 8 hours.

ZrO_2 films calcined at 600 °C (Figure 5.20c) exhibited surface features similar to films treated at 550 °C, while showing a flatter and more consolidated morphology compared to both the as-deposited film and the film calcined at 550 °C. This increased surface smoothness was likely associated with enhanced atomic diffusion and structural rearrangement at elevated temperatures. In comparison with the as-deposited film, the film calcined at 600 °C displayed a higher density of surface cracks, which were attributed to the removal and oxidation of residual organic species during the calcination and annealing processes. The resulting film densification, volume shrinkage, and associated thermal and mechanical stresses are considered the primary factors responsible for crack formation at higher calcination

temperatures. EDX analyses confirmed complete removal of organic contaminants following calcination and annealing, demonstrating thorough purification of the films. These observations are consistent with previous reports [127, 128] and highlight the effectiveness of thermal treatment in eliminating residual impurities from MOCVD-derived metal oxide films [38].

The films deposited via MOCVD from $[\text{Hf}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ were confirmed to contain hafnium by XRF spectroscopy (Figure 5.22b).

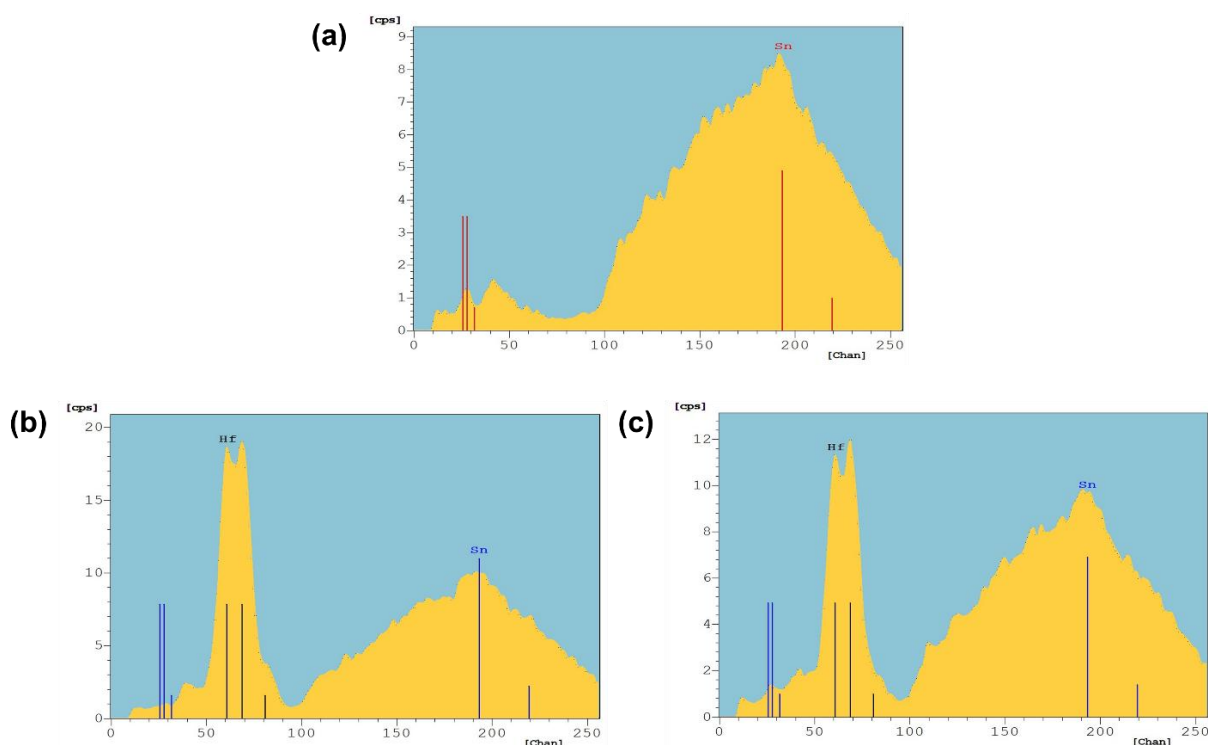


Figure 5.22. The XRF results of (a) only FTO substrate, (b) as-deposited hafnium oxide thin films, and (c) hafnium oxide thin films after calcination in air at 600 °C for 8 hours.

As-deposited films were poorly crystalline or amorphous according to XRD analysis. Calcination and annealing in air at 450, 550, and 600 °C for 8 h induced a visual color change from black to colorless and improved crystallinity (Figure 5.23).

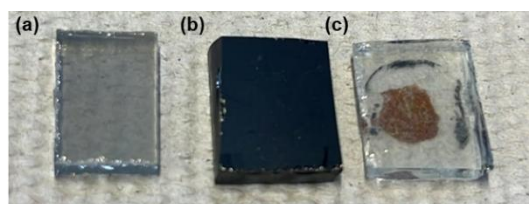


Figure 5.23. Surface appearance of (a) only FTO substrate, (b) as-deposited HfO_2 thin films, and (c) HfO_2 thin films after calcination in air at 600 °C for 8 hours.

XRF confirmed hafnium retention (Figure 5.22c), while XRD revealed the formation of monoclinic HfO_2 (JCPDS no. 43-1017), with the (111) facet as the preferred orientation (Figure 5.24).

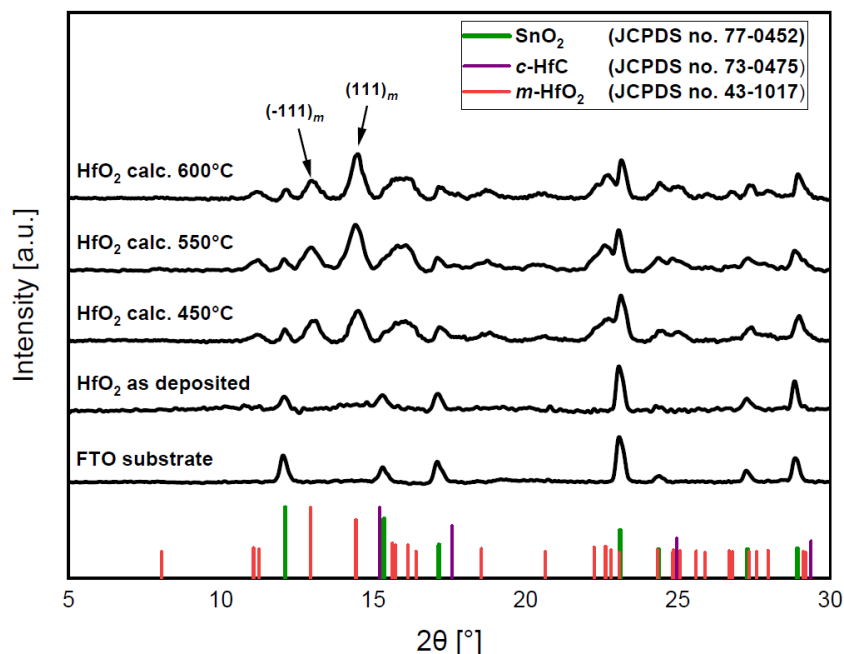


Figure 5.24. The XRD pattern of HfO_2 thin films obtained from the MOCVD $[\text{Hf}(\text{TfB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$.

SEM image showed that HfO_2 films deposited via MOCVD from $[\text{Hf}(\text{TfB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ were uniformly distributed on the Fluorine-Doped Tin Oxide (FTO) substrate. EDX analysis confirmed an Hf:O atomic ratio of approximately 1:2, consistent with HfO_2 stoichiometry, with residual C, F, and N from incomplete precursor decomposition in the as-deposited films (Figure 5.25a).

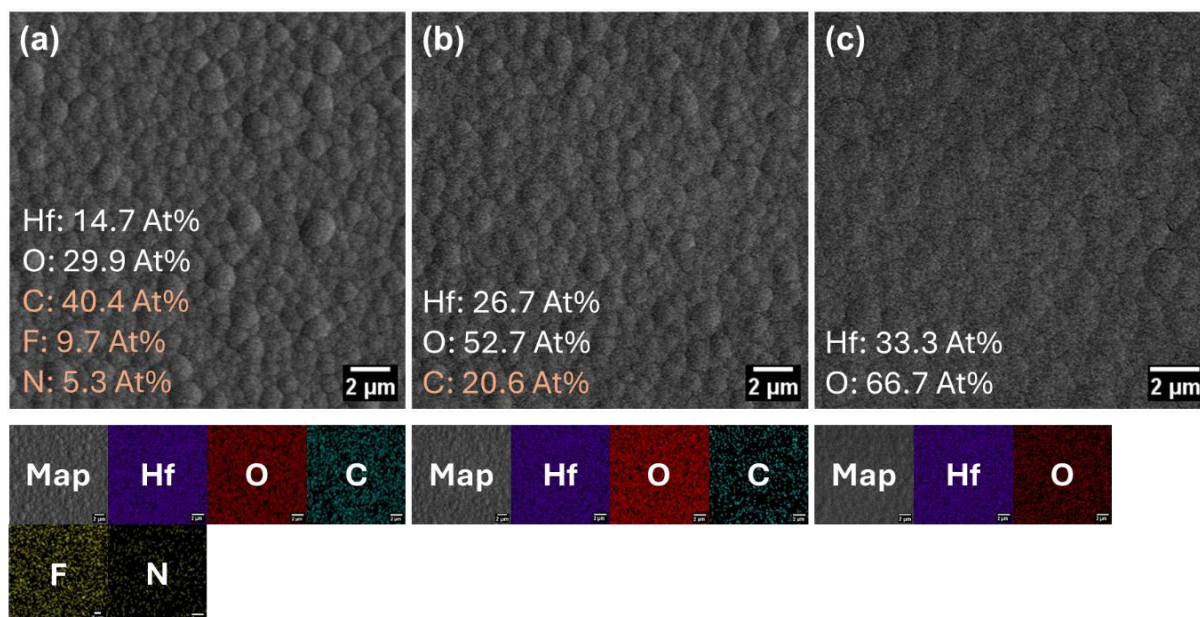


Figure 5.25. Top-view SEM images of (a) as-deposited, (b) calcined ($T_{\text{calcination}} = 550\text{ }^{\circ}\text{C}$), and (c) calcined HfO_2 films ($T_{\text{calcination}} = 600\text{ }^{\circ}\text{C}$) synthesized from $[\text{Hf}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ via MOCVD.

After calcination and annealing at $550\text{ }^{\circ}\text{C}$, the overall morphology remained largely unchanged, though the surface appeared slightly rougher. EDX revealed complete removal of F and a significant reduction of C (Figure 5.25b), demonstrating effective elimination of ligand-derived impurities during thermal treatment. In the case of the HfO_2 films, the detected carbon residues are most reasonably assigned to amorphous carbon produced by partial decomposition of the organic ligands associated with the $[\text{Hf}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ precursor, rather than to the formation of carbide phases such as hafnium carbide. This conclusion was supported by XRD measurements, which did not show any reflections attributable to hafnium carbide ($c\text{-HfC}$, JCPDS no. 73-0475) in the deposited films (Figure 5.24). To date, there are no reported infrared spectral assignments for Hf–C bonding. The FTIR spectrum of the HfO_2 film calcined at $550\text{ }^{\circ}\text{C}$ (Figure 5.26) exhibited features that closely resemble those observed for the ZrO_2 film treated under the same conditions. This similarity, together with the absence of any additional absorption bands that could be attributed to metal–carbon interactions, indicates that hafnium carbide is not present in the calcined HfO_2 film.

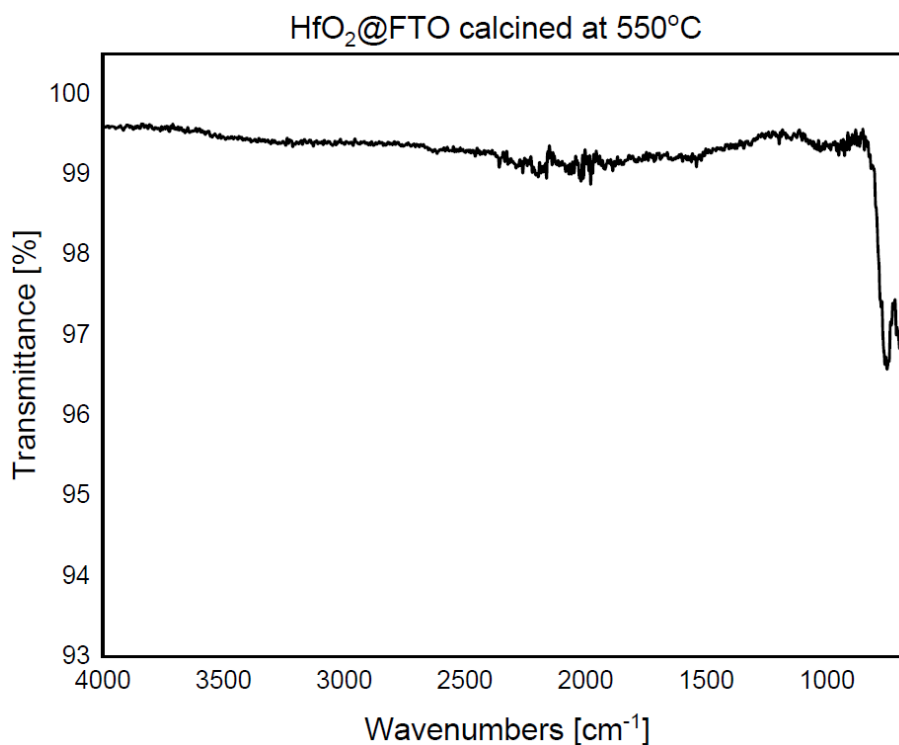


Figure 5.26. The FTIR result of HfO_2 thin films after calcination in air at 550 °C for 8 hours.

Upon calcination at 600 °C (Figure 5.25c), the HfO_2 films developed a surface morphology closely resembling that of films treated at 550 °C, consistent with trends observed for ZrO_2 . However, the surface appeared noticeably smoother and more compact than in the as-deposited or calcined films at 550 °C. The improved uniformity was likely the result of enhanced atomic diffusion and structural reorganization during high-temperature treatment. Additionally, the 600 °C calcined films displayed an increased number of surface cracks compared with the as-deposited material, which can be attributed to densification and the buildup of thermal stresses as residual organic species were removed and oxidized. EDX analysis confirmed that all organic contaminants were removed after calcination and annealing, yielding fully purified films. The observed monoclinic HfO_2 morphology agrees with previously reported results [131, 132].

XRF analysis of as-deposited films from the thermal decomposition of mixed $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{O}^i\text{Bu})_2]$ and $[\text{Hf}(\text{TFB-}t\text{BuA})_2(\text{O}^i\text{Bu})_2]$ precursors confirmed the presence of both zirconium and hafnium (Figure 5.27b), verifying successful deposition of HZO via MOCVD.

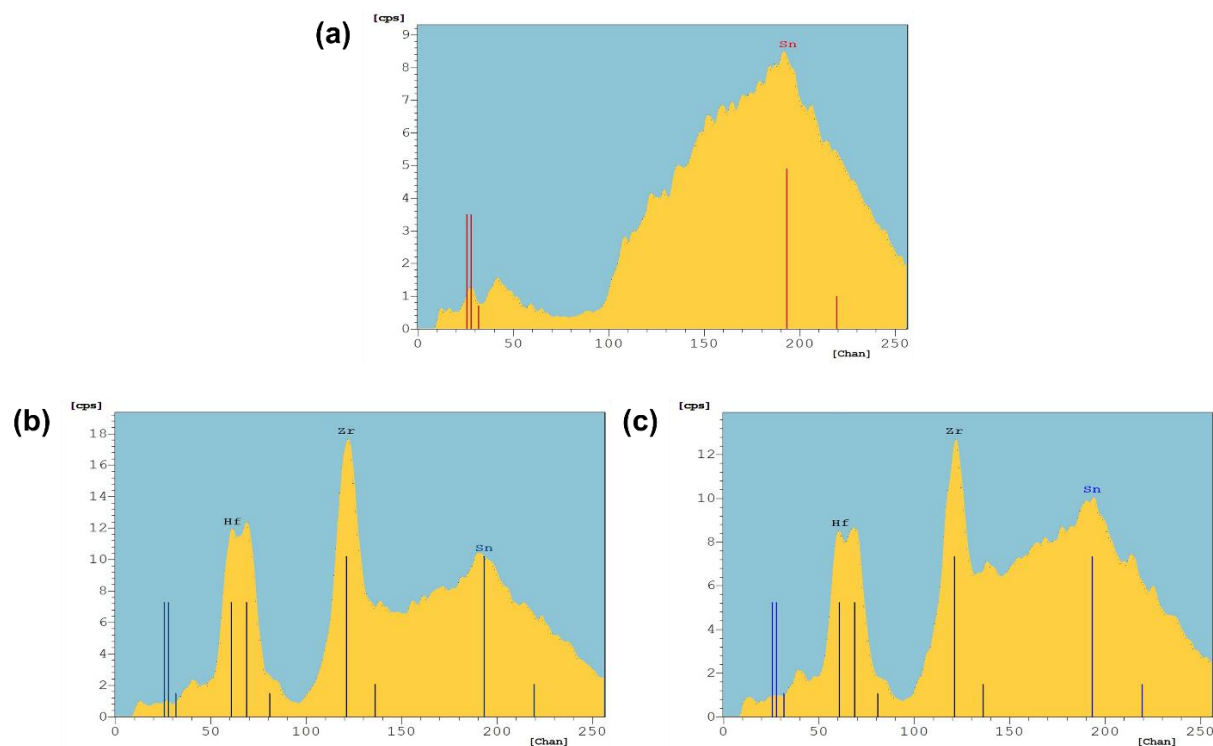


Figure 5.27. The XRF results of (a) only FTO substrate, (b) as-deposited HZO thin films, and (c) HZO thin films after calcination in air at 600 °C for 8 hours.

XRD showed that the as-deposited films were amorphous (Figure 5.28). Following calcination and annealing at 450, 550, and 600 °C, XRF confirmed retention of both elements (Figure 5.27c), while XRD analysis revealed the formation of a single-phase monoclinic structure closely matching $m\text{-HfO}_2$ (JCPDS no. 43-1017), rather than $t\text{-ZrO}_2$. This indicates that Zr and Hf were incorporated into a homogeneous monoclinic lattice, consistent with their chemical similarity and nearly identical ionic radii, allowing formation of a solid solution.

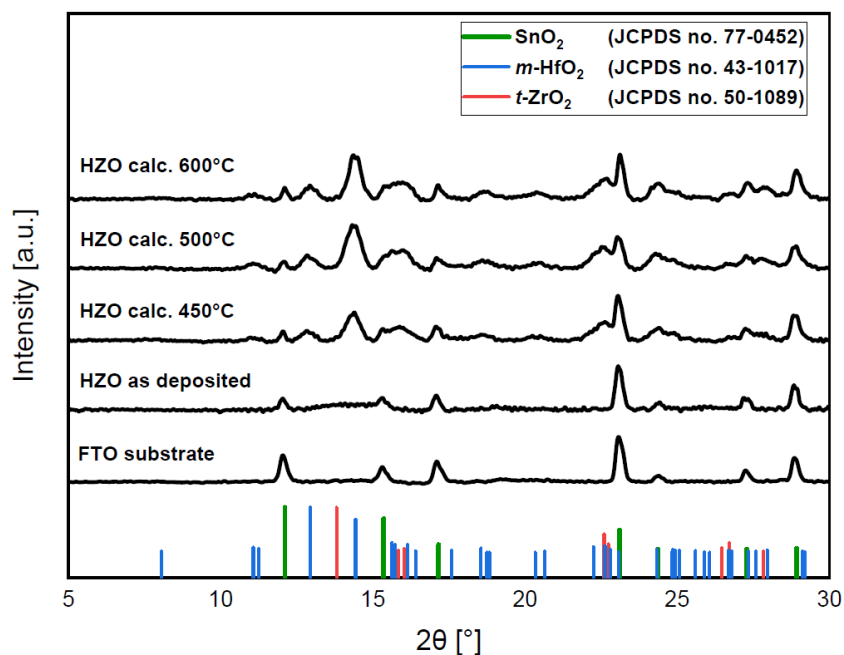


Figure 5.28. The XRD pattern of HZO thin films obtained from the MOCVD $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ and $[\text{Hf}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ with a 1:1 mole ratio.

The appearance of HZO films has also altered from black to colorless after calcination (Figure 5.29).

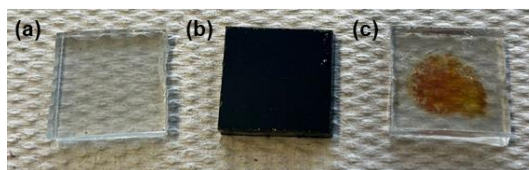


Figure 5.29. Surface appearance of (a) only FTO substrate, (b) as-deposited HZO thin films, and (c) HZO thin films after calcination in air at 600 °C for 8 hours.

SEM images and EDX analyses of ZrO_2 and HfO_2 films confirmed that calcination and annealing at 600 °C effectively removed all organic impurities. Accordingly, only as-deposited and 600 °C-calcined HZO films were characterized. SEM images showed similar morphology for both, although cracks were visible in the calcined films (Figure 5.30a). EDX confirmed complete impurity removal and an (Hf, Zr):O atomic ratio of approximately 1:2, with an Hf:Zr ratio of approximately 0.63:0.37. Importantly, EDX elemental mapping demonstrates a uniform spatial distribution of Hf, Zr, and O across the film surface, indicating homogeneous incorporation of both metal species within the HZO lattice and the formation of a single-phase solid solution rather than phase-segregated domains (Figure 5.30a). Furthermore, the cross-sectional SEM image of the HZO films indicated a uniform film thickness of approximately

1.6 μm (Figure 5.30b), with a film growth rate is approximately 13 nm/min, demonstrating good film continuity and adhesion to the substrate.

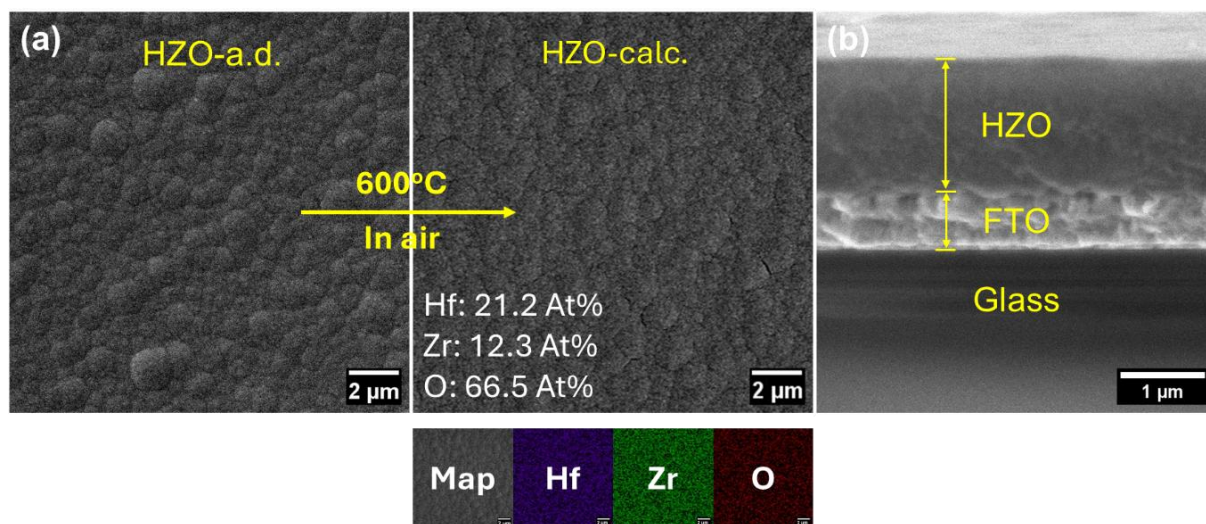


Figure 5.30. (a) Top-view SEM images of as-deposited (left) and calcined HZO films with EDX analysis (right), synthesized from a mixed $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{O}'\text{Bu})_2]$ and $[\text{Hf}(\text{TFB-}i\text{BuA})_2(\text{O}'\text{Bu})_2]$ with a 1:1 mole ratio via MOCVD, (b) Cross-section SEM image of HZO films.

Although $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{O}'\text{Bu})_2]$ and $[\text{Hf}(\text{TFB-}i\text{BuA})_2(\text{O}'\text{Bu})_2]$ were introduced in a 1:1 mole ratio and exhibit comparable volatility under reduced pressure, the resulting HZO films display a slightly Hf-rich composition ($\text{Hf}:\text{Zr} \approx 0.63:0.37$). This deviation can be partly attributed to differences in vapor pressures between the two precursors. After achieving sublimation, $[\text{Hf}(\text{TFB-}i\text{BuA})_2(\text{O}'\text{Bu})_2]$ evaporates at approximately twice the rate of $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{O}'\text{Bu})_2]$ at the same temperature, favoring its incorporation into the growing film. However, vapor-phase transport alone cannot fully account for the observed composition. Surface reaction kinetics and adsorption behavior also play a significant role in determining the final Hf/Zr ratio [133]. Hafnium species typically form stronger M–O bonds [134] and may possess higher sticking coefficients on oxide surfaces, leading to preferential incorporation during deposition. In addition, subtle differences in precursor decomposition pathways, ligand dissociation rates, and surface diffusion dynamics can further influence incorporation efficiency. Such effects are well documented in dual-source MOCVD processes and highlight the critical importance of surface chemistry, beyond simple volatility considerations, in controlling film composition. Taken together, these factors explain why Hf is consistently enriched in the HZO films, even under conditions intended to produce a 1:1 Hf:Zr ratio. Understanding these mechanisms provides valuable guidance for tuning precursor delivery,

substrate temperature, and deposition conditions to achieve precise compositional control in multicomponent oxide films.

A detailed examination of XRD patterns of ZrO_2 , HfO_2 , and HZO thin films calcined at 600 °C revealed a distinct shift in the monoclinic (111) diffraction peak, as shown in Figure 5.31. The HZO thin film exhibited a 2θ value of 14.434°, which lies between those of pure HfO_2 (14.479°) and pure ZrO_2 (14.314°), indicating the formation of a homogeneous solid solution incorporating both Hf^{4+} and Zr^{4+} cations within a single-phase lattice. This intermediate peak position provides strong evidence for successful cation intermixing at the atomic scale. The observed peak shift toward lower angles can be attributed to the partial substitution of larger Zr^{4+} ions (ionic radius = 0.72 Å for sixfold coordination) for smaller Hf^{4+} ions (ionic radius = 0.71 Å for sixfold coordination) within the HfO_2 crystal lattice. This slight size mismatch, originating from the lanthanide contraction that causes 5d elements such as Hf to exhibit nearly the same ionic size as their 4d analogues [101], leads to a measurable lattice expansion. According to Vegard's Law [135], such substitutional alloying results in a linear variation of lattice parameters with composition, which in turn increases the interplanar spacing (d) and shifts the diffraction peak to lower 2θ values, as observed in the HZO film.

Calculating $d_{(111)}$ from 2θ (Mo $K\alpha$ $\lambda = 0.70930$ Å)

All FTO peaks observed are at 12.109°

HfO_2 measured 2θ max = 14.479° $\rightarrow d_{(111)}(\text{HfO}_2) = 2.815$ Å

ZrO_2 measured 2θ max = 14.314° $\rightarrow d_{(111)}(\text{ZrO}_2) = 2.849$ Å

HZO measured 2θ max = 14.434° $\rightarrow d_{(111)}(\text{HZO, measured}) = 2.822$ Å

Vegard interpolation for HZO thin films (with ratio of Hf:Zr in HZO = 0.63:0.37)

$$\begin{aligned} d_{(111)}(\text{HZO, Vegard}) &= \{0.63 \times d_{(111)}(\text{HfO}_2)\} + \{0.37 \times d_{(111)}(\text{ZrO}_2)\} \\ &= (0.63 \times 2.815 \text{ Å}) + (0.37 \times 2.849 \text{ Å}) \\ &= 2.828 \text{ Å} \rightarrow \text{HZO Vegard } 2\theta = 14.416^\circ \end{aligned}$$

Strain relative to Vegard

$$\begin{aligned} \epsilon &= \{d_{(111)}(\text{HZO, measured}) - d_{(111)}(\text{HZO, Vegard})\} / d_{(111)}(\text{HZO, Vegard}) \\ &= (2.822 \text{ Å} - 2.828 \text{ Å}) / 2.828 \text{ Å} \\ &= -0.00212 \equiv -0.212\% \text{ (HZO measured } 2\theta \text{ is practically identical with HZO Vegard } 2\theta) \end{aligned}$$

The negative strain ($\epsilon = -0.21\%$) indicates a slight lattice contraction relative to the Vegard's law prediction, leading to a subtle shift of the $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ diffraction peak toward higher 2θ

angles in accordance with Bragg's law. This compressive strain suggests a minor lattice distortion arising from cation substitution and local structural relaxation within the $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ solid solution.

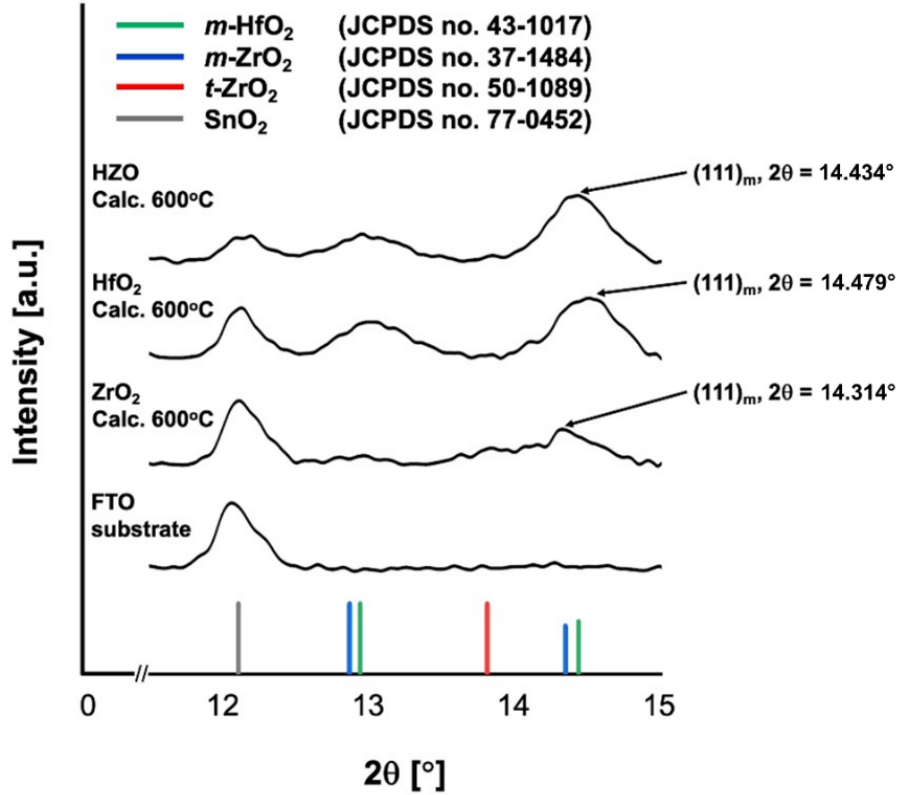


Figure 5.31. The XRD patterns of ZrO_2 , HfO_2 , and HZO thin films specific for the monoclinic (111) facet.

Analysis of HZO films calcined and annealed at 600°C revealed a dense polycrystalline microstructure composed of closely packed, randomly oriented grains averaging just over 10 nm (Figure 5.32a). High-resolution transmission electron microscope (TEM) showed (111) lattice spacings of $0.281\text{--}0.287\text{ nm}$, and Selected Area Electron Diffraction (SAED) patterns confirmed the monoclinic (111) facet (Figure 5.32b), consistent with reported parameters for $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ thin films [136-139]. These results indicate that thermal treatment promotes uniform nucleation and crystallite growth while preserving nanoscale dimensions. The dense, randomly oriented grains suggest minimal porosity and high structural homogeneity, features critical for optimizing the dielectric and ferroelectric performance of HZO films.

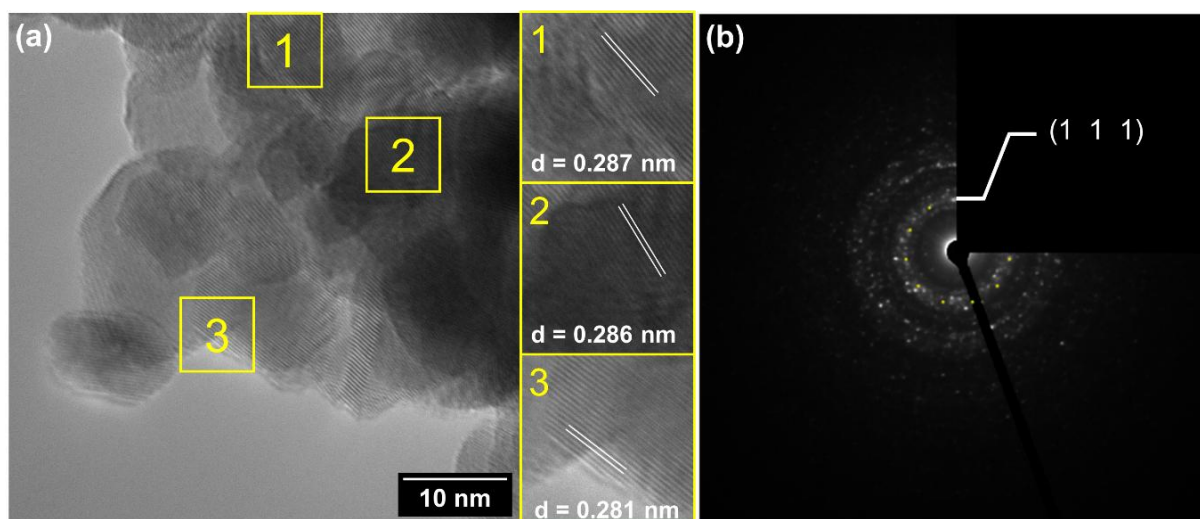


Figure 5.32. TEM analysis of HZO films deposited via MOCVD on FTO at 600 °C from a 1:1 mole ratio mixture of $[\text{Zr}(\text{TfB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ and $[\text{Hf}(\text{TfB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$, followed by calcination and annealing at 600 °C for 8 h. (a) High-magnification TEM image showing well-defined lattice planes of $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ with spacings of 0.281–0.287 nm corresponding to the monoclinic (111) facet. (b) SAED pattern confirming the polycrystalline nature and indexing to the monoclinic (111) facet (compared to ICSD PDF no. 01-090-5786 of $\text{Hf}_{0.567}\text{Zr}_{0.432}\text{O}_2$ monoclinic (111) facet).

X-ray Photoelectron Spectroscopy (XPS) was employed to examine the chemical states and elemental composition of the HZO film. The Zr 3d core-level spectrum exhibits a single, well-defined spin–orbit doublet with the Zr 3d_{5/2} peak located at approximately 182 eV and a splitting of ~2.4 eV, which is characteristic of Zr^{4+} in zirconium oxide environments (Figure 5.33c). Similarly, the Hf 4f spectrum shows a corresponding spin–orbit doublet with the Hf 4f_{7/2} peak centered at ~17 eV and a splitting of ~1.7 eV, indicative of Hf^{4+} (Figure 5.33a). The observed binding energies and line shapes of both Zr 3d and Hf 4f spectra are consistent with previously reported values for HZO thin films, confirming the fully oxidized states of both cations [119, 136, 138, 140–142]. No additional components associated with metallic Hf or Zr, or reduced suboxide species, are detected within the sensitivity of the measurement. The oxidation state of hafnium is further corroborated by the Hf 4d core-level spectrum, which displays a well-defined spin–orbit doublet at binding energies of ~213–215 eV and ~224–226 eV (Figure 5.33b), in good agreement with reported values for stoichiometric HfO_2 films and providing additional confirmation of the Hf^{4+} chemical state [143]. The O 1s spectrum consists of a single broad peak centered at approximately 532 eV (Figure 5.33d), which is attributed to overlapping contributions from lattice oxygen and surface-related oxygen species, such as hydroxyl groups or adsorbed oxygen, as commonly observed in HZO and related oxide thin films [119, 136, 138, 140–142]. Taken together, the XPS results indicate the formation of a

chemically homogeneous HZO mixed oxide with both Hf and Zr present exclusively in the +4-oxidation state and no evidence of metallic phases or oxygen-deficient suboxides.

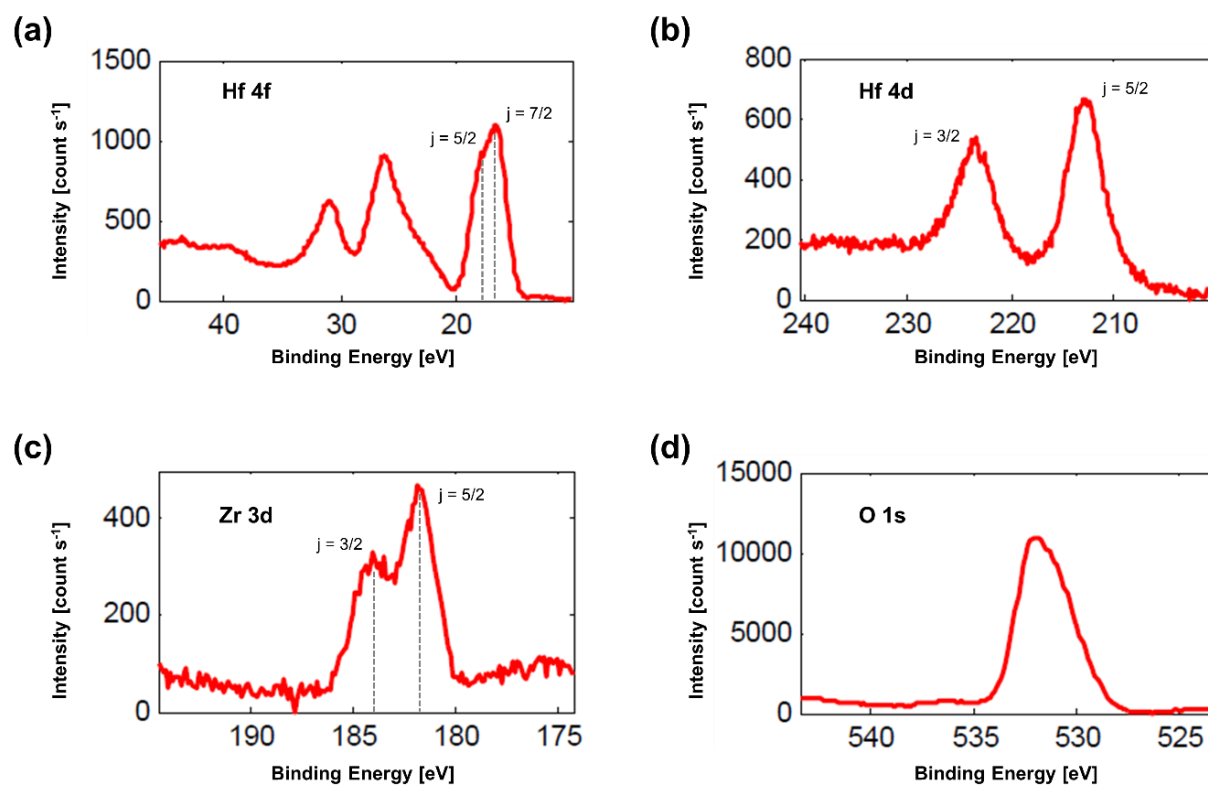


Figure 5.33. The X-ray photoelectron spectroscopy (XPS) spectra of (a) Hf 4f, (b) Hf 4d, (c) Zr 3d, and (d) O 1s for calcined HZO films.

Elemental concentrations estimated from sensitivity-factor-corrected XPS peak areas confirm oxygen as the dominant element and indicate a Hf-rich mixed oxide composition, with an approximate cation ratio of $\text{Hf}:\text{Zr} \approx 0.7:0.3$ as derived from the Hf 4f and Zr 3d core levels. Minor variations between concentrations obtained from different core levels are attributed to differences in photoionization cross sections, inelastic mean free paths, and surface sensitivity inherent to XPS analysis. Despite these variations, the overall compositional trends are consistent across the analyzed regions. Taken together with the chemical-state analysis, the XPS results confirm the formation of a chemically homogeneous $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ solid solution, in which both cations are present exclusively in the +4-oxidation state and no evidence of metallic phases or oxygen-deficient suboxides is observed.

Comparable deposition experiments for ZrO_2 , HfO_2 , and $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ (HZO) thin films were performed using the single-source precursors $[\text{Zr}(\text{TFB-TFEA})_2(\text{O}^t\text{Bu})_2]$ and $[\text{Hf}(\text{TFB-TFEA})_2(\text{O}^t\text{Bu})_2]$, respectively, without the use of an external co-reactant gas (e.g., O_2). Film growth was carried out by MOCVD at $p \approx 1.4 \times 10^{-2}$ mbar, with the precursor reservoirs

maintained at 70 °C. Individual depositions conducted for 2 h resulted in precursor consumptions of 0.63 g for the $[Zr(TFB-TFEA)_2(O'Bu)_2]$ and 0.71 g for the $[Hf(TFB-TFEA)_2(O'Bu)_2]$.

Zirconium oxide deposition using the $[Zr(TFB-TFEA)_2(O'Bu)_2]$ precursor results in a film with non-uniform coverage. In particular, no film growth is observed in regions where silver paste was applied beneath the FTO substrate to secure it to the substrate holder and facilitate thermal transfer (Figure 5.34). This localized absence of deposition is attributed to non-uniform heat distribution across the substrate surface, which affects precursor decomposition and film growth kinetics.

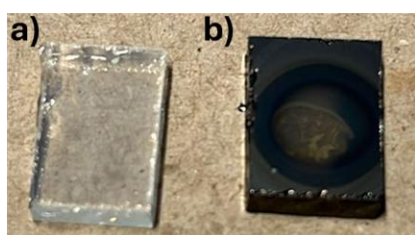


Figure 5.34. Surface appearance of (a) only FTO substrate, (b) as-deposited zirconium oxide thin films from $[Zr(TFB-TFEA)_2(O'Bu)_2]$.

A similar behavior was observed during hafnium oxide deposition using the $[Hf(TFB-TFEA)_2(O'Bu)_2]$ precursor. No film growth occurred in regions where silver paste was present beneath the substrate (Figure 5.35), indicating again the influence of localized thermal variations. This observation is particularly noteworthy because the primary structural difference between $[M(TFB-tBuA)_2(O'Bu)_2]$ and $[M(TFB-TFEA)_2(O'Bu)_2]$ ($M = Zr, Hf$) lies in the fluorinated β -ketoenamine ligands. The consistent deposition behavior suggests that the ligand environment plays a significant role in precursor decomposition and metal oxide film formation. Consequently, both ligand systems appear to critically influence the growth mechanism and thermal sensitivity of the deposition process.

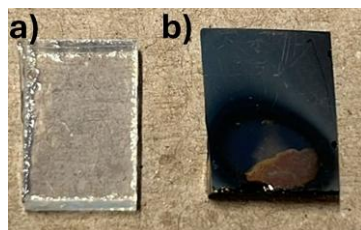


Figure 5.35. Surface appearance of (a) only FTO substrate, (b) as-deposited hafnium oxide thin films from $[Hf(TFB-TFEA)_2(O'Bu)_2]$.

Based on the results obtained, further deposition experiments of zirconium oxide and hafnium oxide using the precursors $[Zr(TFB-TFEA)_2(O'Bu)_2]$ and $[Hf(TFB-TFEA)_2(O'Bu)_2]$ were not pursued further.

6. Summary and Outlook

6.1. Summary

The transformation of molecular precursors into thin films via MOCVD has attracted considerable attention due to its simplicity, scalability, and ability to produce uniform, high-quality films suitable for semiconductor applications. A key requirement of this process is the availability of precursors with both high thermal stability and sufficient volatility, as film growth proceeds through gas-phase transport and decomposition. Precursors lacking these properties often result in uncontrolled decomposition, poor coverage, or inhomogeneous films.

In general, Group 13 metals such as aluminum and gallium predominantly exist in the +3-oxidation state and readily coordinate three monoanionic ligands to form ML_3 species. Owing to the size and electronic properties of the metal center, however, an additional donor atom can often be accommodated, resulting in a coordination number of four and a preferred tetrahedral geometry. This behavior is exemplified by the dimeric alkoxide complexes $[M(O^tBu)_3]_2$ ($M = Al, Ga$), in which two *tert*-butoxo ligands bridge adjacent $M(O^tBu)_2$ units. These bridging interactions allow each metal center to achieve a four-coordinate tetrahedral environment, which represents the most favorable coordination geometry for these trivalent metal ions.

An effective strategy for preventing such oligomerization involves the use of bulky monoanionic bidentate ligands, such as fluorinated β -ketoenamine ligands as described in the Chapter 3. Upon coordination, these ligands occupy two coordination sites while simultaneously introducing steric hindrance around the metal center, thereby reducing the likelihood of intermolecular bridging and promoting the formation of discrete monomeric complexes. As a result, tetrahedral monomeric species can be obtained while maintaining the preferred coordination environment of the metal. A similar approach was demonstrated by Prashanth and Singh [56], who reported the synthesis of monomeric Group 13 complexes, $[(2,6\text{-}^iPr_2C_6H_3N)P(Ph_2)(N^tBu)]MCl_2$ ($M = Al, Ga$), using a sterically demanding iminophosphonamide ligand (Figures 6.1a and b). Their work illustrates how appropriate ligand design can effectively suppress aggregation and stabilize monomeric aluminum and gallium complexes, a strategy that is directly relevant to the development of volatile metal-organic precursors for MOCVD applications.

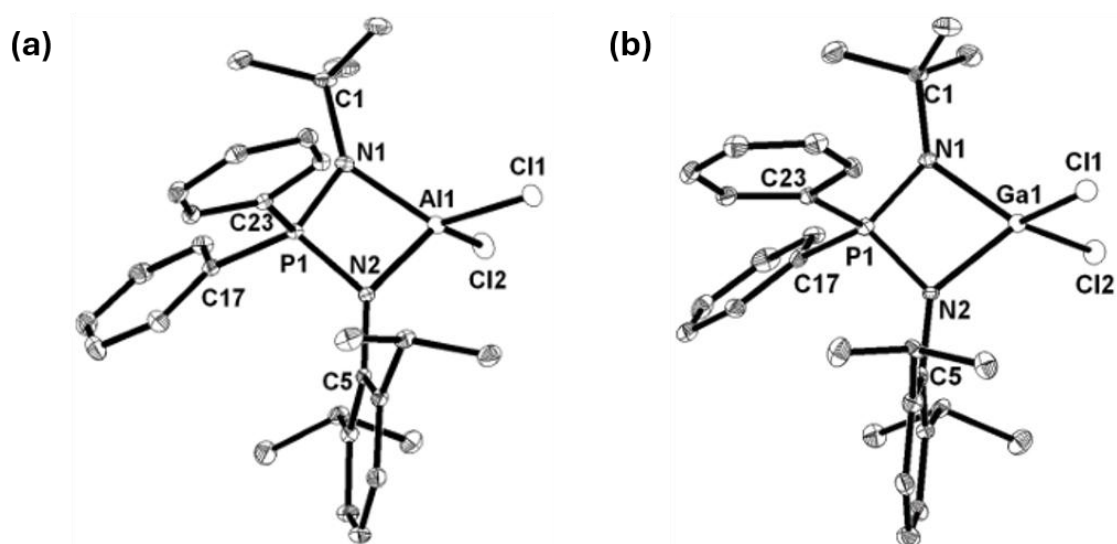


Figure 6.1. Molecular structures of (a) $[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph}_2)(\text{N}^t\text{Bu})]\text{AlCl}_2$ and (b) $[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph}_2)(\text{N}^t\text{Bu})]\text{GaCl}_2$. Adapted from Prashanth dan Singh [56] with permission from Royal Society of Chemistry. © Royal Society of Chemistry.

However, a drawback of employing bulky bidentate chelating ligands is the increase in molecular weight of the resulting complexes, which can reduce volatility and thereby limit their suitability as MOCVD precursors.

The formation of four-coordinate Group 13 complexes can be rationalized using the classical concept of orbital hybridization. Aluminum and gallium possess the electronic configurations $1s^2 2s^2 2p^6 3s^2 3p^1$ and $[\text{Ar}] 4s^2 3d^{10} 4p^1$, respectively. Upon formation of the M^{3+} ion, the valence electrons are removed, leaving vacant s and p orbitals available for coordination. These orbitals can hybridize to generate four equivalent sp^3 orbitals directed toward the corners of a tetrahedron. The resulting hybrid orbitals are capable of accepting electron pairs from ligand donor atoms, leading to the formation of four-coordinate tetrahedral complexes (Figure 6.2).

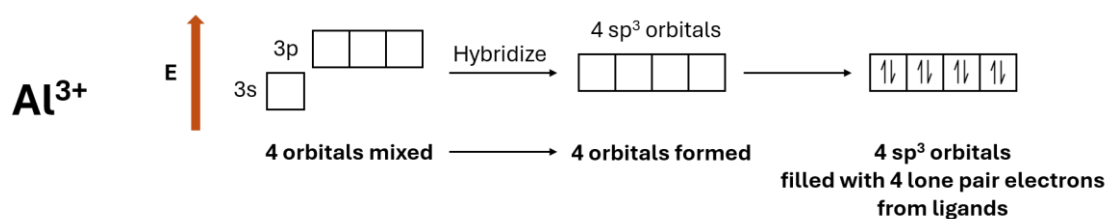


Figure 6.2. Schematic representation of hybridization process of 3s and 3p electron orbitals from Al^{3+} .

While this simple hybridization model provides a useful explanation for the prevalence of tetrahedral geometries in many Group 13 complexes, it does not adequately explain the existence of higher coordination numbers. For example, Al^{3+} can also adopt an octahedral

coordination environment, as observed in tris(acetylacetonato)aluminum(III), $\text{Al}(\text{acac})_3$ (Figure 2.7), where three bidentate acac ligands provide a total of six donor atoms. Such complexes demonstrate that the coordination chemistry of Group 13 metals cannot be fully described by a simple sp^3 hybridization model. Instead, modern descriptions based on molecular orbital theory and the ionic nature of metal–ligand bonding are generally required to account for the ability of Al^{3+} and Ga^{3+} to accommodate coordination numbers greater than four.

In the case of Group 4 transition metals, zirconium and hafnium predominantly exhibit the +4-oxidation state. Numerous studies have shown that Zr^{4+} and Hf^{4+} ions commonly adopt a coordination number of six, resulting in octahedral coordination geometries. For example, Williams *et al.* [122] reported the complexes $[\text{M}(\text{O}^i\text{Bu})_2(\text{mmp})_2]$ ($\text{M} = \text{Zr}, \text{Hf}$; $\text{mmp} = 1$ -methoxy-2-methyl-2-propanolate), in which the metal centers exhibit octahedral coordination (Figure 5.3 in Chapter 5). As discussed previously in Chapter 5, zirconium complexes generally favor six-coordinate geometries. Nevertheless, higher coordination numbers are also accessible due to the relatively large ionic radii of Zr^{4+} and Hf^{4+} . An example is $[\text{Zr}(\text{TFB-TFEA})_4]$, which possesses a coordination number of eight. Similarly, Franceschini *et al.* [100] reported tetrakis(4-iminopent-2-en-2-amido)zirconium, an eight-coordinate complex containing four bidentate β -diketiminato ligands (Figure 6.3).

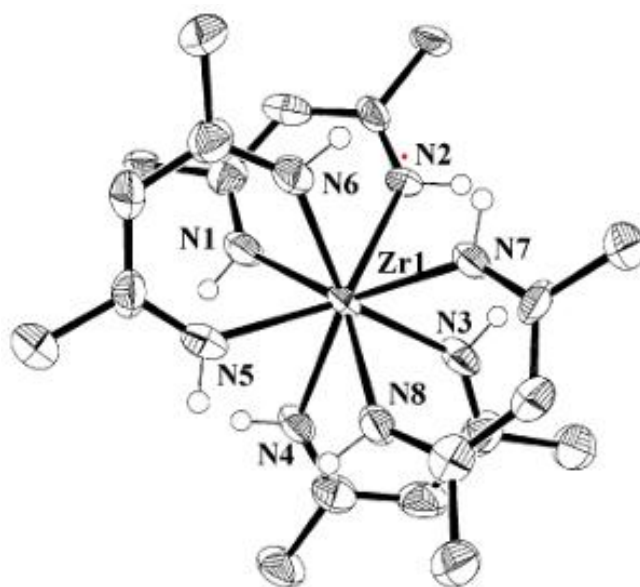


Figure 6.3. Molecular structures of tetrakis(4-iminopent-2-en-2-amido)zirconium. Reproduced from Franceschini *et al.* [100] with permission from American Chemical Society. © American Chemical Society.

The coordination number adopted by a metal ion is strongly influenced by its ionic radius and the steric and geometric constraints imposed by the coordinating ligands. According to

Shannon's effective ionic radii [101], Al^{3+} and Ga^{3+} ions in four-coordinate environments have ionic radii of 0.39 and 0.47 Å, respectively, whereas Zr^{4+} and Hf^{4+} ions in six-coordinate environments possess significantly larger radii of 0.72 and 0.71 Å, respectively. The larger size of Zr^{4+} and Hf^{4+} enables them to accommodate higher coordination numbers when suitable ligands are present. However, the final coordination environment is not governed solely by ionic size but also by the flexibility and donor arrangement of the ligand framework.

This effect is illustrated by the complexes $[\text{M}(\text{mmp})_4]$ ($\text{M} = \text{Zr}, \text{Hf}$) reported by Williams *et al.* [122]. Although each mmp ligand contains both alkoxide and methoxy donor groups and could potentially act as a bidentate ligand, the complexes adopt six-coordinate structures rather than eight-coordinate geometries. In these molecules, only three of the four mmp ligands coordinate in a bidentate fashion, while the methoxy oxygen atoms of the remaining ligands remain uncoordinated (Figure 6.4a and b). This behavior demonstrates that the presence of additional donor atoms does not necessarily result in higher coordination numbers when geometric and steric factors hinder effective chelation. A similar situation is observed for $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$, where the methoxy groups of the TFB-MEA ligands remain non-coordinating despite the ability of the zirconium center to accommodate higher coordination numbers. The inability of the methoxy oxygen atoms to bind to the Zr^{4+} center is therefore attributed to unfavorable geometric constraints within the ligand framework rather than to limitations imposed by the metal ion itself.

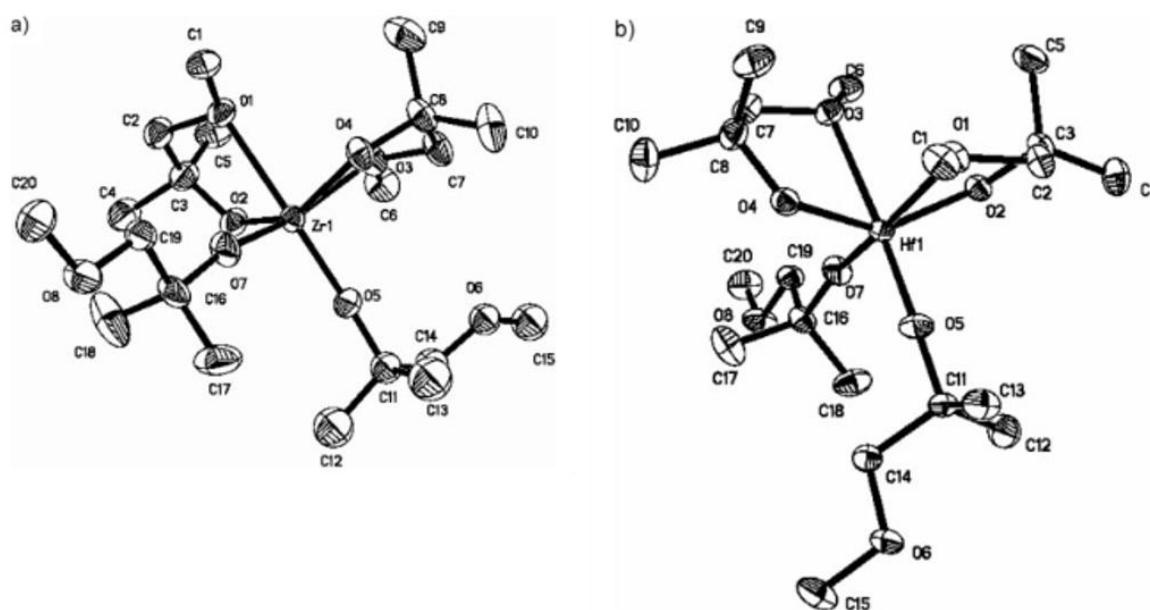


Figure 6.4. Molecular structures of (a) $[\text{Zr}(\text{mmp})_4]$ and (b) $[\text{Hf}(\text{mmp})_4]$. Adapted from Williams *et al.* [122] with permission from Wiley. © Wiley.

Regarding the deposition of $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ thin films using the dual-source precursor system $[\text{Al}(\text{TFB-}i\text{BuA})(\text{O}^i\text{Bu})_2]$ and $[\text{Ga}(\text{TFB-}i\text{BuA})(\text{O}^i\text{Bu})_2]$, the formation of phase-pure $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ is governed primarily by post-deposition crystallization and phase evolution during annealing rather than by the MOCVD process itself. Several studies have reported that alloy formation occurs during high-temperature annealing and that phase separation becomes increasingly likely as the aluminum content increases, particularly for $x_{\text{Al}} > 0.4$ [144]. However, aluminum concentration alone does not determine phase purity. For example, Bhuiyan *et al.* [51] demonstrated the formation of phase-pure β - $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ with an aluminum fraction as high as $x_{\text{Al}} = 0.99$, whereas a γ - $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ phase was observed at $x_{\text{Al}} = 0.29$ [51]. These findings indicate that crystallization kinetics, growth conditions, and thermal treatment can be more influential than composition alone in determining the resulting crystal structure.

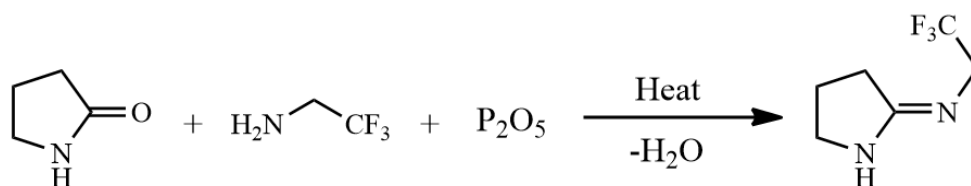
In contrast, the objective of depositing $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ thin films is to stabilize the metastable orthorhombic phase responsible for ferroelectricity. Achieving this phase requires not only careful control of the Hf:Zr ratio but also optimization of the film thickness and post-deposition annealing conditions [145]. Previous studies have shown that the ferroelectric orthorhombic phase is most readily stabilized in ultrathin films, typically with thicknesses below approximately 10 nm, whereas thicker films increasingly favor the thermodynamically stable monoclinic phase [146]. As demonstrated in Chapter 5, co-deposition of the fluorinated β -ketoenamine precursors $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ and $[\text{Hf}(\text{TFB-}i\text{BuA})_2(\text{O}^i\text{Bu})_2]$ produced $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ films with an Hf:Zr ratio of approximately 0.7:0.3, and the films crystallized predominantly in the monoclinic phase. These results indicate that, similar to the $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ system, precursor design alone is insufficient to control the final crystalline phase. Instead, successful preparation of functional mixed-metal oxide thin films requires simultaneous optimization of precursor transport, film composition, thickness, and post-deposition thermal treatment.

6.2. Outlook

In the design of zirconium complexes as SSPs for ZrON thin-film deposition by MOCVD, fluorinated iminopyrrolidine ligands are proposed as a promising ligand platform. Although these ligands coordinate through Zr–N bonds, they function as bidentate N[^]N chelating ligands, which are expected to strengthen the metal–ligand interaction through the chelate effect and thereby improve the thermal stability of the resulting complexes. In addition, the incorporation

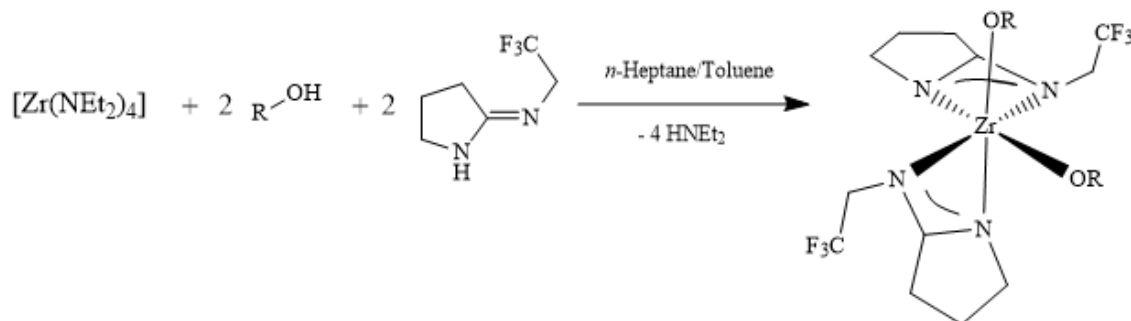
of $-\text{CF}_3$ substituents is anticipated to enhance volatility by reducing intermolecular attractive forces and promoting more favorable sublimation behavior.

The design of this ligand system is inspired by the work of Wasslen *et al.* [147], who reported the synthesis of iminopyrrolidine ligands through the reaction of one equivalent of 2-pyrrolidone with one equivalent of NH_2R ($\text{R} = \text{alkyl}$) in the presence of one equivalent of P_2O_5 under heating conditions, yielding the corresponding iminopyrrolidine ligand (Scheme 5.1). This synthetic approach provides a versatile route for introducing fluorinated substituents while maintaining a rigid N^N-chelating framework suitable for coordination to zirconium.



Scheme 5.1. Reaction scheme for the synthesis of a fluorinated iminopyrrolidine ligand based on Wasslen *et al.* [147].

Furthermore, the incorporation of alkoxo ligands, $-\text{OR}$ ($\text{R} = \text{alkyl}$), is expected to provide additional benefits. The stronger $\text{Zr}-\text{O}$ bonds associated with alkoxo ligands can enhance the overall thermal stability of the complex while maintaining adequate volatility for vapor-phase transport. At the same time, these ligands can act as an internal oxygen source during precursor decomposition, facilitating the formation of ZrON thin films during the deposition process. Consequently, the combination of fluorinated iminopyrrolidine and alkoxo ligands represents a rational molecular design strategy for developing zirconium SSPs (Scheme 5.2) that simultaneously satisfy the requirements of thermal stability, volatility, and appropriate elemental composition for ZrON thin-film growth.



Scheme 5.2. Reaction scheme for the synthesis of a zirconium complex synthesized using fluorinated iminopyrrolidine and ROH ($\text{R} = \text{alkyl}$).

In the synthesis of metal complexes for mixed metal oxide thin-film deposition, while the present study employs a dual-source precursor approach, the development of heterobimetallic Zr–Hf and Al–Ga complexes incorporating pre-organized –Zr–(OR)–Hf– and –Al–(OR)–Ga– structural motifs represent a promising yet largely unexplored strategy for achieving atomic-level mixing of both metals. Such a molecular design would allow the integration of two different metal centers within a single precursor, enabling synchronized decomposition and more controlled oxide network formation during deposition.

This approach could significantly improve compositional homogeneity, phase uniformity, and stoichiometric precision in mixed metal oxide thin films. Although reports on Zr–Hf and Al–Ga heterobimetallic precursors for these systems are currently lacking, related heterobimetallic complexes containing fluorinated ligands have been successfully utilized in the synthesis of other mixed metal oxides [148, 149]. These findings support the feasibility of extending this strategy to Zr–Hf and Al–Ga systems for advanced thin film deposition applications.

For HZO thin-film deposition using the dual-source precursor system $[M(\text{TFB-}t\text{BuA})_2(\text{O}^i\text{Bu})_2]$ ($M = \text{Zr, Hf}$), achieving a stoichiometric 1:1 Zr:Hf ratio requires precise control of precursor delivery to balance the vapor-phase concentrations of the zirconium and hafnium species. Vapor pressure measurements, together with analysis based on the Clausius-Clapeyron equation, provide a means to determine the temperature conditions necessary to generate comparable vapor pressures from both precursors. Because the relative sublimation rates are highly sensitive to temperature and pressure, even small deviations can result in preferential evaporation of one precursor, leading to compositional inhomogeneity in the deposited film. Therefore, careful regulation of both precursor temperatures and reactor pressure is essential for obtaining the desired $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ composition.

In practice, this can be accomplished by placing each precursor in a separated reservoir and controlling their temperatures independently (Figure 6.5). By adjusting the temperature of each reservoir until similar vapor pressures are achieved, comparable amounts of zirconium- and hafnium-containing species can be transported into the deposition zone. Such an approach enables more balanced precursor fluxes and increases the likelihood of obtaining HZO films with compositions close to the targeted 1:1 Zr:Hf ratio.

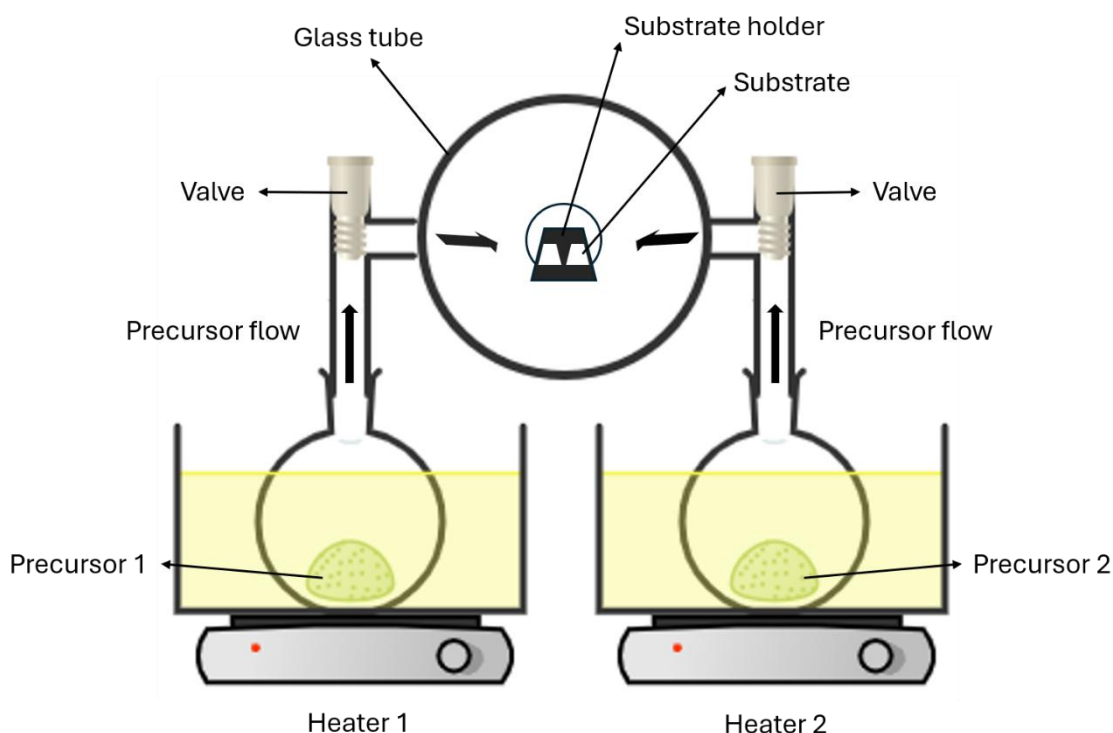


Figure 6.5. Schematic representation of front-view MOCVD with separated reservoirs.

If deviations from the target composition occur, the resulting films are expected to be slightly zirconium-rich. Such a compositional shift may be advantageous because stabilization of the ferroelectric orthorhombic phase generally requires a zirconium content that is equal to or slightly higher than the hafnium content. In contrast, hafnium-rich films tend to favor formation of the thermodynamically stable monoclinic phase, which possesses a centrosymmetric crystal structure and therefore lacks ferroelectric properties [150, 151]. Film thickness is another critical parameter. Previous studies have shown that the orthorhombic phase is preferentially stabilized in ultrathin HZO films, typically below 10 nm, or in a range between 10 and 20 nm [151-155]. Consequently, deposition should be performed for relatively short durations to limit film growth and maintain thicknesses within the range favorable for ferroelectric phase formation.

The deposition of $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ thin films using the dual-source precursor system $[\text{M}(\text{TFB}-t\text{BuA})_2(\text{O}^t\text{Bu})_2]$ ($\text{M} = \text{Zr}, \text{Hf}$) via MOCVD with relatively short deposition times is expected to provide a viable route toward obtaining films suitable for orthorhombic phase formation. To evaluate this possibility, deposition was carried out at 600 °C with precursor reservoir temperatures of 125 °C under reduced pressure ($p \approx 1 \times 10^{-2}$ mbar) for 10 minutes. XRF measurements confirmed the presence of both hafnium and zirconium within the deposited films (Figure 6.6b), indicating successful co-deposition of the two metal species.

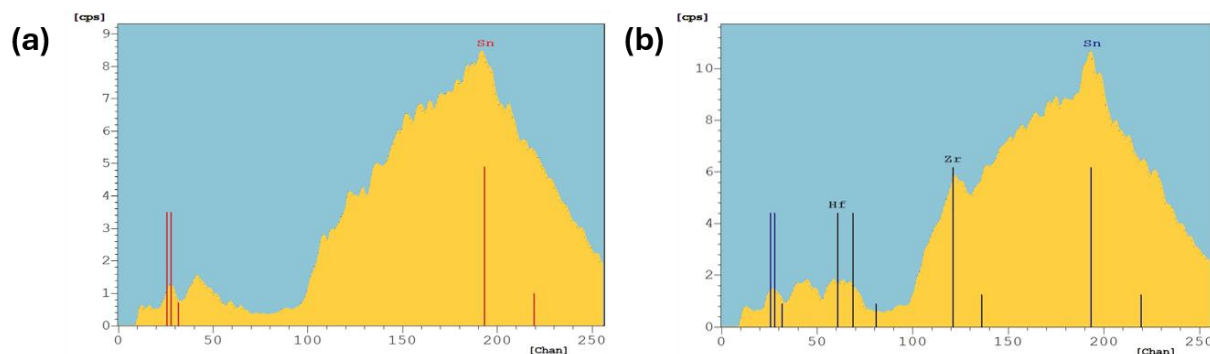


Figure 6.6. XRF result of (a) only FTO substrate and (b) as-deposited $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ thin films ($T_{\text{deposition}} = 600\text{ }^\circ\text{C}$; $T_{\text{sublimation}} = 125\text{ }^\circ\text{C}$; $p \approx 1 \times 10^{-2}\text{ mbar}$; $t_{\text{deposition}} = 10\text{ minutes}$).

Cross-sectional SEM analysis further revealed a film thickness of approximately 300 nm (Figure 6.7a and b).

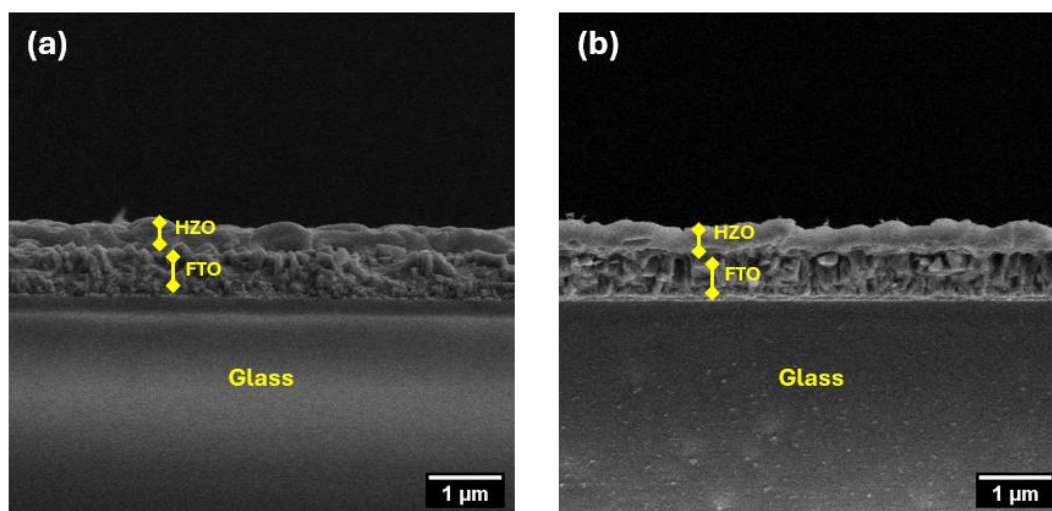


Figure 6.7. Cross-sectional SEM image of (a) as-deposited $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ thin films and (b) calcined $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ thin films ($T_{\text{calcination}} = 350\text{ }^\circ\text{C}$)

Interestingly, after calcination in air at $350\text{ }^\circ\text{C}$ for 3 h, performed to remove residual impurities such as carbon and fluorine and to improve film crystallinity, GIXRD measurements collected at incident angles of $\omega = 0.5^\circ$, 0.75° , and 1° revealed diffraction peaks attributable to orthorhombic HfO_2 , specifically the (102) and (121) reflections (JCPDS no. 21-0904) (Figure 6.8a-c). The observation of an orthorhombic phase is particularly noteworthy because this phase is typically stabilized in ultrathin $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ films, whereas the films obtained in this study are substantially thicker than those commonly reported in the literature.

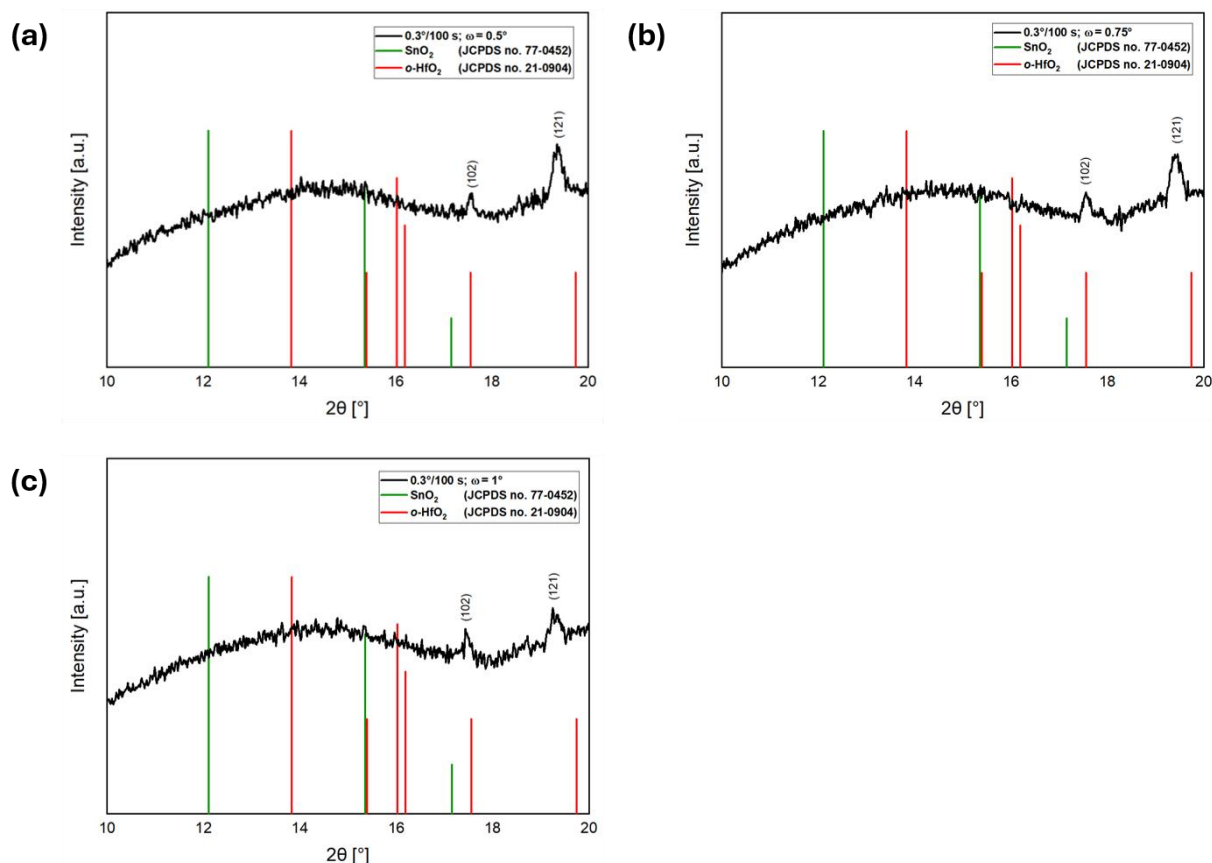


Figure 6.8. Observed GIXRD pattern of calcined $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ thin films with (a) $\omega = 0.5^\circ$, (b) $\omega = 0.75^\circ$, and (c) $\omega = 1^\circ$.

These preliminary results suggest that the combination of MOCVD deposition using $[\text{M}(\text{TFB}-t\text{BuA})_2(\text{O}^i\text{Bu})_2]$ ($\text{M} = \text{Zr}, \text{Hf}$) precursors and calcination at moderate temperatures may provide an alternative pathway for stabilizing orthorhombic $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$, even in comparatively thick films. However, additional studies involving detailed phase analysis, compositional characterization, and ferroelectric measurements are required to confirm the nature of the orthorhombic phase and to elucidate the mechanisms responsible for its stabilization under these conditions.

A similar approach should be adopted for the deposition of $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ using the dual-source precursor system $[\text{M}(\text{TFB}-t\text{BuA})(\text{O}^i\text{Bu})_2]$ ($\text{M} = \text{Al}, \text{Ga}$). Vapor pressure measurements and Clausius-Clapeyron analysis reveal substantial differences in both the enthalpies of sublimation and the vapor pressures of the aluminum and gallium precursors, despite their closely related molecular structures. As a consequence, operating both precursors at the same sublimation temperature would generate markedly different precursor fluxes, leading to poor control over the Al:Ga ratio in the deposited films. To overcome this limitation, each precursor should be placed in a separate reservoir and heated independently until comparable vapor pressures are achieved. Such a strategy is expected to provide improved control over film

composition and enhance compositional homogeneity throughout the deposited layer, analogous to the approach proposed for $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ deposition.

In addition to precise precursor delivery, post-deposition processing is likely to play a critical role in determining the phase evolution of the resulting films. The results obtained in this study suggest that the deposited aluminum gallium oxide layers consist of a mixture of amorphous Al_2O_3 and crystalline $\beta\text{-Ga}_2\text{O}_3$ rather than a single-phase $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ material. Therefore, future investigations should focus on optimizing post-deposition treatments, particularly calcination temperature, atmosphere, and duration, to promote interdiffusion of aluminum and gallium within the oxide network and facilitate the formation of phase-pure $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ thin films. Such studies may provide valuable insights into the conditions required for stabilizing homogeneous aluminum gallium oxide phases and improving the structural and functional properties of these thin films.

7. Experimental Section

7.1. Chemicals and Methods

All chemicals were purchased from commercial suppliers, including Sigma-Aldrich, Thermo Fisher Scientific (USA), Tokyo Chemical Industry (Japan), Deutero GmbH (Germany), Fisher Scientific GmbH (Germany), and Honeywell Riedel-de Haën GmbH (Germany), and were used as received unless otherwise stated.

Solvents were purified prior to use by distillation over sodium. Toluene and tetrahydrofuran (THF) were subsequently stored over sodium wire under a nitrogen atmosphere, whereas *n*-pentane and *n*-heptane were stored over activated 4 Å molecular sieves under nitrogen. All manipulations involving air- and moisture-sensitive compounds were carried out under an inert atmosphere.

For nuclear magnetic resonance (NMR) measurements of the synthesized fluorinated β -ketoenamine ligands, chloroform-*d* (CDCl₃, 99.8% D) was used as received and was not additionally dried over potassium or molecular sieves. In contrast, the deuterated solvents used for NMR characterization of the synthesized metal complexes, namely benzene-*d*₆ (99.0% D) and toluene-*d*₈ (99.0% D), were dried and stored over potassium and activated 4 Å molecular sieves prior to use to minimize moisture contamination.

7.2. Characterization Techniques

Molecular characterization of the synthesized compounds was performed using NMR spectroscopy, elemental analysis (EA), thermal analysis, vapor pressure measurements, and single-crystal X-ray diffraction (SC-XRD). NMR spectra were recorded at room temperature on Bruker Avance NEO 400 and Bruker Avance 300 spectrometers. Measurements on the Bruker Avance NEO 400 were carried out at frequencies of 400 MHz for ¹H NMR, 101 MHz for ¹³C{¹H, ¹⁹F} NMR, and 376 MHz for ¹⁹F NMR. Additional spectra were recorded on a Bruker Avance 300 spectrometer at 300 MHz for ¹H NMR and 282 MHz for ¹⁹F NMR. All spectra were processed and analyzed using MestReNova 15.0.1 software.

Elemental analyses were performed using a HEKAtech CHNS Euro EA 3000 analyzer. Samples were prepared and handled under an argon atmosphere in a glovebox with H₂O and O₂ concentrations maintained below 0.1 ppm to prevent degradation of air- and moisture-sensitive compounds.

The thermal properties of the synthesized complexes were investigated by thermogravimetric and calorimetric techniques. Thermogravimetric-Differential Thermal Analysis (TG-DTA) measurements were conducted using a Seiko TGA/DTA 6300S11 instrument. Approximately 10 mg of sample was placed in aluminum crucibles sealed with vented lids (1.5 mm² opening) and heated at a rate of 5 °C min⁻¹ under a flow of high-purity nitrogen (300 mL min⁻¹). Thermogravimetric-Differential Scanning Calorimetry (TG-DSC) measurements were carried out on a METTLER TOLEDO TGA/DSC 3+ thermal analysis system. Approximately 5 mg of sample was loaded into aluminum crucibles equipped with vented lids (1.5 mm² opening) and heated at 10 °C min⁻¹ under a high-purity nitrogen atmosphere.

Vapor pressure measurements were performed using a Vapor Pressure Analyzer equipped with a Knudsen cell. Measurements were conducted under vacuum conditions (7×10^{-4} Torr), with each temperature step maintained for 180 min to ensure reliable determination of the evaporation behavior and vapor pressure of the compounds.

Single-crystal X-ray diffraction (SC-XRD) data were collected using a Bruker D8 Venture diffractometer and processed with the APEX2 software package. Structure solution and refinement were carried out using ShelXT and ShelXL [156]. Crystallographic Information File (CIF) editing, structural visualization, and crystallographic analyses were performed using PLATON, Olex2 [157], and VESTA [158].

The composition, structure, morphology, and chemical properties of the deposited thin films were investigated using a range of complementary characterization techniques. Qualitative analysis of the metal constituents in thin films obtained from the decomposition of individual metal precursors was carried out by X-ray fluorescence (XRF) spectroscopy using a Fischerscope X-ray XDL 240 instrument. The resulting spectra were evaluated using WinFTM EDXRF software.

The phase composition and crystallinity of the deposited films were examined by X-ray diffraction (XRD). Measurements were performed on a STOE STADI MP vertical diffractometer operated in reflection mode using Bragg-Brentano geometry and molybdenum (Mo) K α radiation ($\lambda = 0.70930$ Å). For Al₂O₃, Ga₂O₃, and (Al_xGa_{1-x})₂O₃ thin films, grazing-incidence X-ray diffraction (GIXRD) measurements were additionally conducted using a Panalytical X'Pert Pro diffractometer equipped with Cu K α radiation ($\lambda = 1.5406$ Å) at a grazing angle of $\omega = 0.5^\circ$. Powder X-ray diffraction (PXRD) analyses were performed using capillary measurements in Debye-Scherrer geometry on a STOE STADI P diffractometer equipped with a Dectris Mythen 1 detector and Mo K α radiation ($\lambda = 0.7107$ Å).

The chemical bonding and vibrational properties of the thin films were investigated by Fourier-transform infrared (FTIR) spectroscopy using a PerkinElmer Spectrum 400 spectrometer. Surface morphology, film thickness, and elemental distribution were analyzed by field-emission scanning electron microscopy (FESEM) using a Zeiss Sigma 300 VP RISE microscope coupled with an energy-dispersive X-ray spectroscopy (EDX) detector (Oxford Instruments Xplore 30).

Further microstructural characterization was carried out by transmission electron microscopy (TEM) using a FEG-type JEOL JEM2200FS microscope equipped with an ultra-high-resolution (UHR) pole piece and operated at an accelerating voltage of 200 kV. TEM images were processed and analyzed using Fiji (ImageJ) software [159], while selected-area electron diffraction (SAED) patterns were evaluated using CrysTBox software [160].

The chemical states and surface compositions of the deposited films were investigated by X-ray photoelectron spectroscopy (XPS). For Al_2O_3 , Ga_2O_3 , and $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ thin films, XPS measurements were carried out using a custom-built instrument equipped with an Al $K\alpha$ X-ray source ($h\nu = 1486.6$ eV). Spectra were collected using a pass energy of 20 eV and subsequently analyzed using CasaXPS software. For $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ thin films, XPS measurements were performed using a PHI 5600 spectrometer equipped with a monochromatic Al $K\alpha$ source (200 W). Survey and high-resolution spectra were acquired at a pass energy of 29.35 eV using a 7 mm X-ray beam (aperture 4, spot size 0.8 mm) and an emission angle of 45° . Charge neutralization (settings 18/5) was applied during acquisition, and all spectra were charge-corrected by referencing the C 1s peak to 284.8 eV.

7.3. Syntheses of the Fluorinated β -Ketoenamine Ligands

Chemicals for the fluorinated β -ketoenamine ligands synthesis were obtained from commercial suppliers and were used without further purification unless stated otherwise. The syntheses of the fluorinated β -ketoenamine ligands were performed under standard ambient laboratory conditions, without the need for specialized atmospheres or controlled environments. Following their preparation, the ligands underwent purification tailored to their physical state: those in liquid form were purified by distillation, while solid ligands were subjected to sublimation. Both purification methods were carried out under reduced pressure ($p \approx 1$ mbar) to ensure the removal of impurities and to achieve high-purity products suitable for subsequent experimental use. The fluorinated β -ketoenamine ligands (*Z*)-1,1,1-trifluoro-4-((2-methoxyethyl)amino)but-3-en-2-one (*H*-TFB-MEA) [38], (*Z*)-4-(*tert*-butylamino)-1,1,1-

trifluorobut-3-en-2-one (*H*-TFB-*t*BuA) [161], and (*Z*)-1,1,1-trifluoro-4-((2,2,2-trifluoroethyl)amino)but-3-en-2-one (*H*-TFB-TFEA) [36] were synthesized following reported procedures.

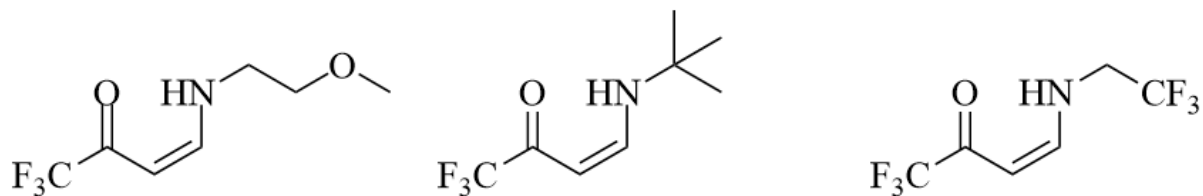
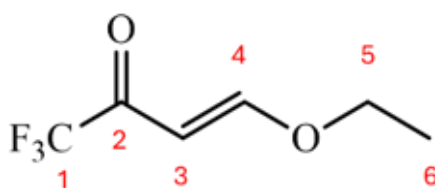


Figure 6.1. Some fluorinated β -ketoenamine ligands used in this study, *H*-TFB-MEA (left), *H*-TFB-*t*BuA (middle), and *H*-TFB-TFEA (right).

Synthesis of (*E*)-4-ethoxy-1,1,1-trifluorobut-3-en-2-one (ETFB)

Ethyl vinyl ether (18 g, 0.25 mol) was introduced into a 250 mL three-neck round-bottom flask, followed by the addition of dichloromethane (50 mL) and pyridine (33 mL). The reaction mixture was cooled to 0 °C and stirred continuously. Trifluoroacetic anhydride (66.5 g, 0.32 mol) was then added dropwise under stirring overnight. Upon complete addition, a dark brown solution was formed. Deionized water (50 mL) was added, resulting in phase separation. The organic layer was collected, and the aqueous phase was extracted with dichloromethane (20 mL $\times$ 3). The combined organic extracts were dried over anhydrous MgSO_4 , filtered, and the solvent was removed under reduced pressure ($p \approx 1$ mbar) to yield a viscous brown residue. The crude product was purified by vacuum distillation at 40 °C ($p \approx 1$ mbar). The colorless liquid product was collected in a 100 mL round-bottom flask cooled to 0 °C, affording 21.734 g (52.98% yield).



^1H NMR (300 MHz, CDCl_3) δ 7.86 (H4, d, 1H), 5.82 (H3, dt, 1H), 4.07 (H5, q, 2H), 1.36 (H6, td, 3H).

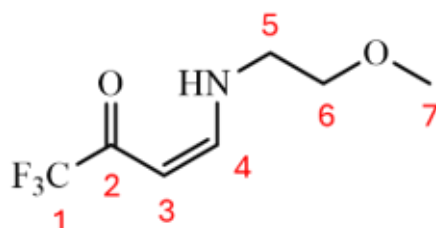
^{19}F NMR (282 MHz, CDCl_3) δ -78.30 (CF_3 of C1).

Anal. Calcd for $\text{C}_6\text{H}_7\text{F}_3\text{O}_2$: C, 49.23; H, 4.20. Found: C, 42.47; H, 3.90 [161].

Synthesis of (*Z*)-1,1,1-trifluoro-4-((2-methoxyethyl)amino)but-3-en-2-one (*H*-TFB-MEA)

ETFB (12.77 g, 0.076 mol) was placed in a 250 mL three-neck round-bottom flask and dissolved in dichloromethane (20 mL). 2-Methoxyethylamine (5.70 g, 0.076 mol) was added

dropwise to the stirred solution from 0 °C to room temperature. The reaction mixture was stirred overnight, during which a dark orange solution formed. After completion of the reaction, the solvent was removed under reduced pressure ($p \approx 1$ mbar), yielding a viscous orange residue. The crude product was purified by vacuum distillation at 95 °C ($p \approx 1$ mbar). The orange liquid product was collected in a 100 mL round-bottom flask, affording 12.37 g (82.62% yield).



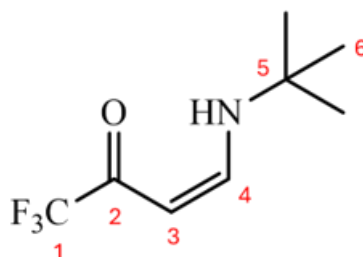
^1H NMR (300 MHz, CDCl_3) δ 10.28 (NH, s, 1H), 7.13 (H4, dd, 1H), 5.31 (H3, dt, 1H), 3.46 (H5, H6, s, 4H), 3.32 (H7, s, 3H).

^{19}F NMR (282 MHz, CDCl_3) δ -76.95 (CF_3 of C1).

Anal. Calcd for $\text{C}_7\text{H}_{10}\text{F}_3\text{NO}_2$: C, 42.64; H, 5.11; N, 7.10. Found: C, 43.77; H, 5.05; N, 7.18.

Synthesis of (Z)-4-(tert-butylamino)-1,1,1-trifluorobut-3-en-2-one (*H*-TFB-*t*BuA)

The synthesis of *H*-TFB-*t*BuA was carried out following the same procedure used for *H*-TFB-MEA. In this case, *tert*-butylamine (8.05 g, 0.11 mol) was used in place of 2-methoxyethylamine, and the ETFB (18.06 g, 0.11 mol) was employed accordingly. The reaction afforded an orange solid. The crude product was purified by sublimation at 45 °C ($p \approx 1$ mbar). The colorless crystal product was collected from a cold finger, affording 16.40 g (76.35% yield).



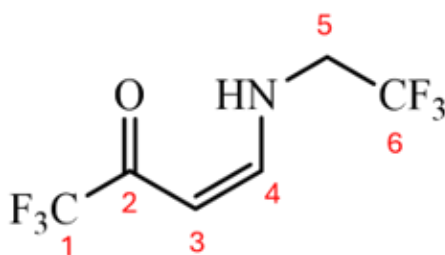
^1H NMR (300 MHz, CDCl_3) δ 10.64 (NH, s, 1H), 7.26 (H4, dd, 1H), 5.36 (H3, dd, 1H), 1.36 (H6, s, 9H).

^{19}F NMR (282 MHz, CDCl_3) δ -76.94 (CF_3 of C1).

Anal. Calcd for $\text{C}_8\text{H}_{12}\text{F}_3\text{NO}$: C, 49.23; H, 6.20; N, 7.18. Found: C, 49.54; H, 6.44; N, 7.02 [161].

Synthesis of (Z)-1,1,1-trifluoro-4-((2,2,2-trifluoroethyl)amino)but-3-en-2-one (H-TFB-TFEA)

The synthesis of **H-TFB-TFEA** was carried out following the same procedure used for **H-TFB-MEA**. In this case, 2,2,2-trifluoroethylamine (8.50 g, 0.108 mol) was used in place of 2-methoxyethylamine, and the ETFB (17.74 g, 0.108 mol) was employed accordingly. The reaction afforded an orange solid. The crude product was purified by sublimation at 30 °C ($p \approx 1$ mbar). The colorless crystal product was collected from a cold finger, affording 20.21 g (84.64% yield).



^1H NMR (300 MHz, CDCl_3) δ 10.64 (NH, s, 1H), 7.26 (H4, dd, 1H), 5.36 (H3, dd, 1H), 1.36 (H6, s, 9H).

^{19}F NMR (282 MHz, CDCl_3) δ -73.33 (CF_3 of C6), -77.38 (CF_3 of C1).

Anal. Calcd for $\text{C}_6\text{H}_5\text{F}_6\text{NO}$: C, 32.59; H, 2.28; N, 6.33. Found: C, 33.02; H, 2.53; N, 6.23 [36].

7.4. Syntheses of Metal Complexes

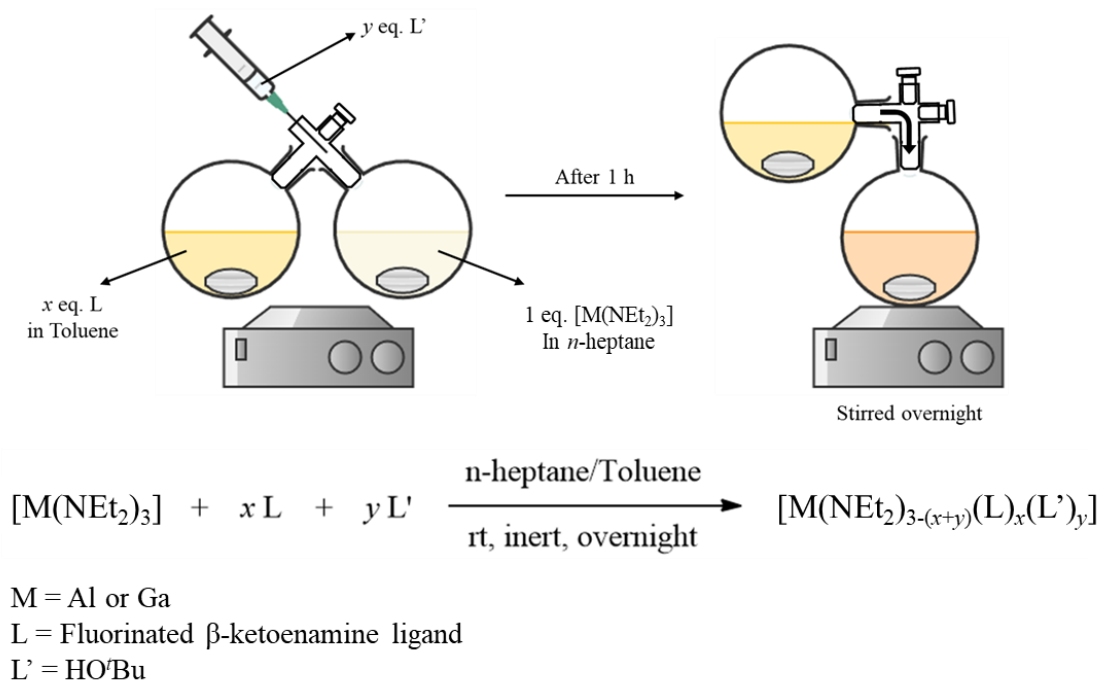
The metal organic complexes described in this work were synthesized under carefully maintained inert conditions to avoid contact with atmospheric moisture and oxygen, both of which are known to compromise the reactivity or purity of sensitive compounds. Throughout the procedures, modified Schlenk line (Stock line) techniques were used (Figure 7.1). All experimental steps, including reagent transfers, reaction setups, and product isolations, were carried out under a continuous flow of dry nitrogen. In this way, an oxygen and moisture-free environment was consistently ensured, which was essential for the stability of the intermediate and final products.



Figure 7.1. Stock line setup for inert condition reaction.

7.4.1. Syntheses of Fluorinated β -Ketoenamine-based Aluminum and Gallium Complexes

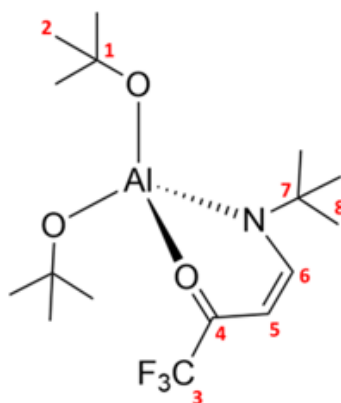
The starting materials, $[\text{Al}(\text{NEt}_2)_3]$ and $[\text{Ga}(\text{NEt}_2)_3]$, were obtained using modified literature methods [162] and purified by vacuum distillation ($p \approx 1$ mbar). The fluorinated β -ketoenamine-based aluminum and gallium complexes were then synthesized according to the general reaction scheme illustrated below.



Scheme 7.1. General reaction scheme for the syntheses of $[\text{M}(\text{NEt}_2)_{3-(x+y)}(\text{L})_x(\text{L}')_y]$ ($\text{M} = \text{Al, Ga}$) complexes.

Synthesis of $[Al(TFB-tBuA)(O^tBu)_2]$

$[Al(NEt_2)_3]$ (1.30 g, 5.34 mmol) was dissolved in *n*-heptane (25 mL) and stirred at room temperature. *tert*-Butyl alcohol (0.79 g, 10.68 mmol) was then added dropwise to the $[Al(NEt_2)_3]$ solution, when an exothermic reaction occurred. The resulting reaction mixture was stirred for 1 hour. Following this, a solution of *H*-TFB-*t*BuA ligand (1.04 g, 5.34 mmol) in toluene (25 mL) was prepared and added slowly to the reaction mixture. The solution turned yellowish, indicating complex formation, and was stirred overnight at room temperature. Afterward, the solvent was removed under reduced pressure ($p \approx 1$ mbar). The reaction afforded the yellow powder. The yellow powder was then purified by sublimation at 86-95 °C, yielding a needle-like colorless crystalline sublimate with a mass of 1.10 g (56.07 % yield). To facilitate crystallization, a mixture of toluene and *n*-heptane was added dropwise to the sublimate, and the resulting solution was stored at -20 °C for several days. Needle-like colorless crystals gradually formed within the yellowish solution, indicating successful crystallization of the target complex.



^1H NMR (400 MHz, C_6D_6) δ 6.91 (H6, d, 1H), 5.17 (H5, dd, 1H), 1.41 (H2, s, 18H), 1.14 (H8, s, 9H).

^{13}C $\{^1H, ^{19}F\}$ NMR (101 MHz, C_6D_6) δ 164.46 (C6), 161.44 (C4), 119.60 (C3), 94.37 (C5), 68.98 (C1), 60.07 (C7), 33.81 (C2), 30.02 (C8).

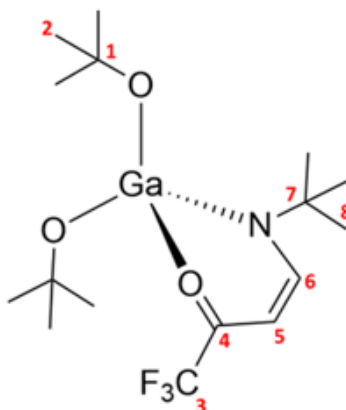
^{19}F NMR (376 MHz, C_6D_6) δ -75.12 (CF_3 of C3).

Anal. Calcd for $AlC_{16}H_{29}O_3NF_3$: C, 52.31; H, 7.97; N, 3.81. Found: C, 51.58; H, 8.78; N, 3.80.

Synthesis of $[Ga(TFB-tBuA)(O^tBu)_2]$

The synthesis of $[Ga(TFB-tBuA)(O^tBu)_2]$ was carried out following the same procedure used for $[Al(TFB-tBuA)(O^tBu)_2]$. In this case, the gallium precursor $[Ga(NEt_2)_3]$ (1.30 g, 4.54 mmol) was used in place of $[Al(NEt_2)_3]$, the *tert*-butyl alcohol (0.67 g, 9.09 mmol) was used, and the fluorinated β -ketoenamine ligand *H*-TFB-*t*BuA (0.89 g, 4.54 mmol) was employed

accordingly. The reaction afforded the yellow powder. The yellow powder was then purified by sublimation at 92-103 °C, yielding a needle-like colorless crystalline sublimate with a mass of 0.90 g (48.30 % yield). To facilitate crystallization, a mixture of toluene and *n*-heptane was added dropwise to the sublimate, and the resulting solution was stored at -20 °C for several days. Needle-like colorless crystals gradually formed within the yellowish solution, indicating successful crystallization of the target complex.



^1H NMR (400 MHz, C_6D_6) δ 6.82 (H6, dd, 1H), 5.07 (H5, dd, 1H), 1.46 (H2, s, 18H), 1.10 (H8, s, 9H).

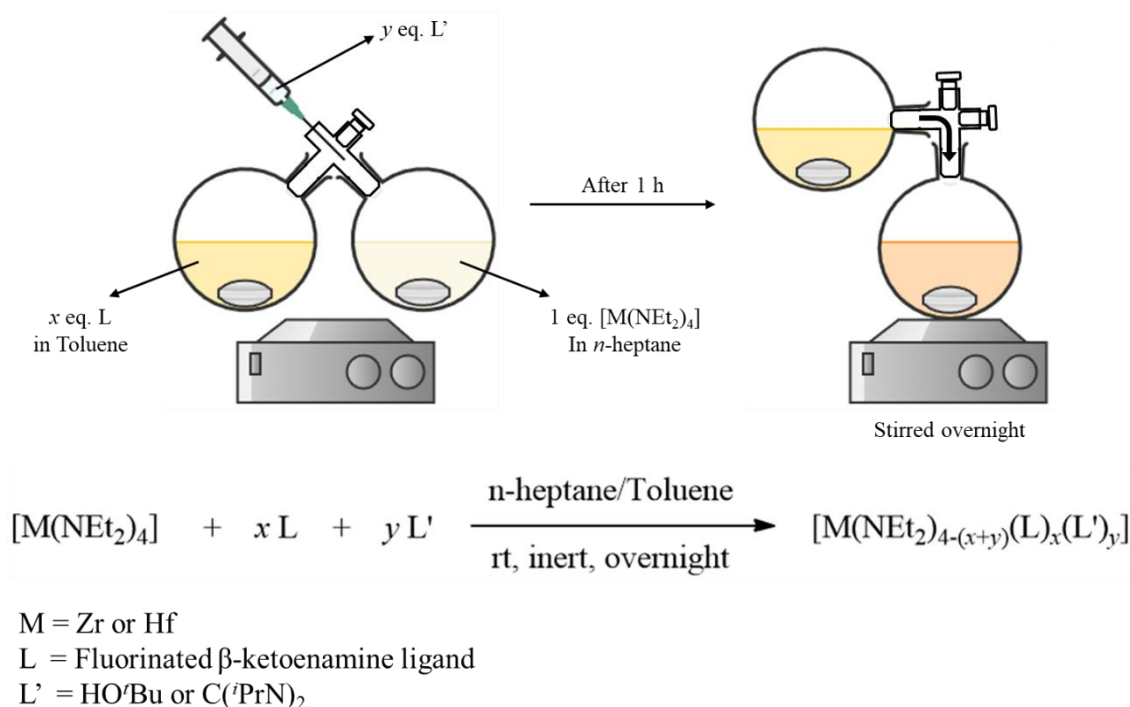
^{13}C $\{^1\text{H}, ^{19}\text{F}\}$ NMR (101 MHz, C_6D_6) δ 163.84 (C6), 163.51 (C4), 119.48 (C3), 92.52 (C5), 71.27 (C1), 60.65 (C7), 33.84 (C2), 30.22 (C8).

^{19}F NMR (376 MHz, C_6D_6) δ -75.11 (CF_3 of C3).

Anal. Calcd for $\text{GaC}_{16}\text{H}_{29}\text{O}_3\text{NF}_3$: C, 46.86; H, 7.14; N, 3.42. Found: C, 44.14; H, 7.28; N, 3.85.

7.4.2. Syntheses of Fluorinated β -Ketoenamine-based Zirconium and Hafnium complexes

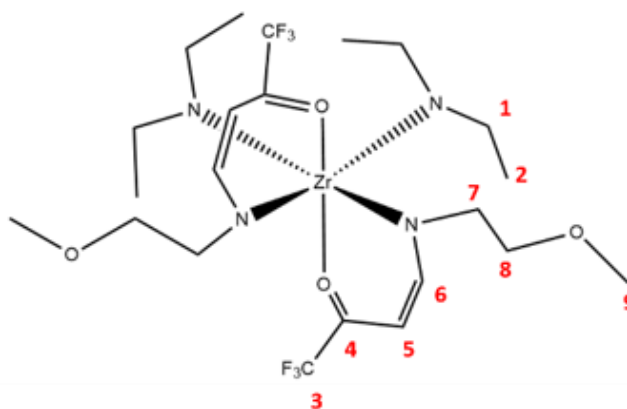
The starting materials, $[\text{Zr}(\text{NEt}_2)_4]$ and $[\text{Hf}(\text{NEt}_2)_4]$, were obtained using modified literature methods [163] and purified by vacuum distillation ($p \approx 1$ mbar). The fluorinated β -ketoenamine-based zirconium and hafnium complexes were then synthesized according to the general reaction scheme illustrated below.



Scheme 6.1. General reaction scheme for the syntheses of $[M(NEt_2)_{4-(x+y)}(L)_x(L')_y]$ (M = Zr, Hf) complexes.

Synthesis of $[Zr(TFB-MEA)_2(NEt_2)_2]$

$[Zr(NEt_2)_4]$ (2.64 g, 6.95 mmol) was dissolved in *n*-heptane (25 mL) and stirred at room temperature. Separately, a solution of the ligand *H*-TFB-MEA (2.54 g, 13.90 mmol) in toluene (25 mL) was prepared and then added slowly to the zirconium solution. Upon addition, the reaction mixture gradually turned orange, indicating the formation of the desired complex. The mixture was allowed to stir overnight at room temperature to ensure complete reaction. Afterward, the solvent was removed under reduced pressure ($p \approx 1$ mbar), yielding an orange powder with a mass of 2.03 g (46.52% yield). To promote crystallization, a mixture of toluene and *n*-heptane was added dropwise to the powder, and the resulting solution was stored at -20 °C for several days. Over time, yellowish crystals were formed in the orange solution, indicating successful crystallization of the product.

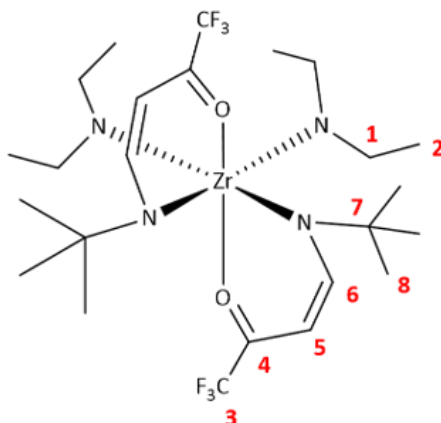


^1H NMR is unable to be assigned.

Anal. Calcd. for $\text{ZrC}_{22}\text{H}_{38}\text{F}_6\text{N}_4\text{O}_4$: C, 42.09; H, 6.10; N, 8.92. Found: C, 45.67; H, 6.39; N, 9.77.

Synthesis of $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)_2]$

The synthesis of $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)_2]$ was carried out following the same procedure used for $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$. In this case, the fluorinated β -ketoenamine ligand *H*-TFB-*t*BuA (1.70 g, 8.70 mmol) was used in place of *H*-TFB-MEA, and the zirconium precursor $[\text{Zr}(\text{NEt}_2)_4]$ (1.65 g, 4.35 mmol) was employed accordingly. The reaction afforded an orange powder with a mass of 1.40 g (51.62 % yield). To facilitate crystallization, a mixture of toluene and *n*-heptane was added dropwise to the residue, and the resulting solution was stored at -20 °C for several days. Yellowish crystals gradually formed within the orange solution, indicating successful crystallization of the target complex.



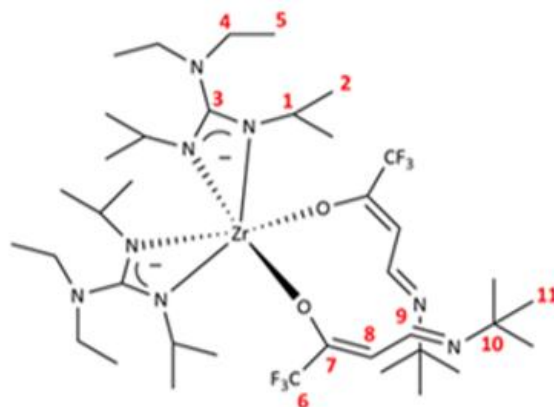
^1H NMR (300 MHz, C_6D_6) δ 7.27 (H6, d, 2H), 5.62 (H5, d, 2H), 3.55 (H1, s, 4H), 3.14 (H1', s, 4H), 1.17 (H2, td, 12H), 0.93 (H8, s, 18H).

^{19}F NMR (282 MHz, C_6D_6) δ -73.58 (CF_3 of C3).

Anal. Calcd. for $\text{ZrC}_{24}\text{H}_{42}\text{F}_6\text{N}_4\text{O}_2$: C, 46.21; H, 6.79; N, 8.98. Found: C, 40.56; H, 5.79; N, 7.29.

Synthesis of $[\text{Zr}(\text{TFB-}t\text{BuA})_2\{\eta^2\text{-(}^i\text{PrN)}_2\text{CNEt}_2\}_2]$

$[\text{Zr}(\text{NEt}_2)_4]$ (0.79 g, 2.07 mmol) was dissolved in *n*-heptane (25 mL) and stirred at room temperature. *N,N'*-Diisopropylcarbodiimide (0.522 g, 4.14 mmol) was then added dropwise to the $[\text{Zr}(\text{NEt}_2)_4]$ solution, when an exothermic reaction occurred. The resulting reaction mixture was stirred for 1 hour. Following this, a solution of *H*-TFB-*t*BuA ligand (0.81 g, 4.14 mmol) in toluene (25 mL) was prepared and added slowly to the reaction mixture. The solution turned yellowish, indicating complex formation, and was stirred overnight at room temperature. Afterward, the solvent was removed under reduced pressure ($p \approx 1$ mbar), yielding a yellowish powder with a mass of 1.30 g (71.70 % yield). To promote crystallization, a mixture of toluene and *n*-heptane was added dropwise to the powder, and the resulting solution was stored at -20 °C for several days. Over time, yellowish crystals were formed in the yellow solution, indicating successful crystallization of the product.



^1H NMR (300 MHz, C_6D_6) δ 8.65 (H9, d, 2H), 6.38 (H8, d, 2H), 3.47 (H1, hept, 4H), 2.83 (H4, q, 8H), 1.36 (H11, s, 18H), 1.27 (H2, d, 24H), 0.81 (H5, t, 12H).

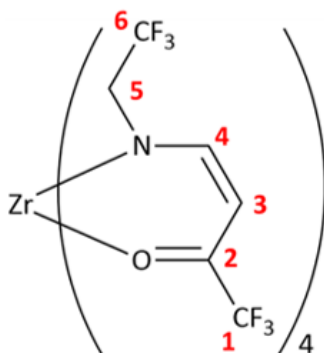
^{19}F NMR (282 MHz, C_6D_6) δ -70.81 (CF_3 of C6).

Anal. Calcd. for $\text{ZrC}_{38}\text{H}_{70}\text{F}_6\text{N}_8\text{O}_2$: C, 52.09; H, 8.05; N, 12.79. Found: C, 41.51; H, 5.82; N, 4.45.

Synthesis of $[\text{Zr}(\text{TFB-TFEA})_4]$

$[\text{Zr}(\text{NEt}_2)_4]$ (1.52 g, 4.01 mmol) was dissolved in *n*-heptane (25 mL) and stirred at room temperature. Separately, a solution of the ligand *H*-TFB-TFEA (3.55 g, 16.06 mmol) in warm *n*-heptane (25 mL) was prepared and then added slowly to the zirconium solution. Upon addition, the reaction mixture gradually turned orange, and an orange precipitate was formed eventually, indicating the formation of the desired complex. The mixture was allowed to stir overnight at room temperature to ensure complete reaction. The solvent was removed under reduced pressure ($p \approx 1$ mbar) to obtain an orange powder that was purified by sublimation at

115-120 °C, yielding a colorless crystalline sublimate with a mass of 2.97 g (76.20 % yield). To promote crystallization, a mixture of toluene and *n*-heptane was added dropwise to the sublimate, and the resulting solution was stored at -20 °C for several days. Over time, colorless crystals were formed in the yellowish solution, indicating successful crystallization of the product.



^1H NMR (400 MHz, C_6D_6) δ 6.87 (H4, d, 4H), 5.24 (H3, dd, 4H), 4.03 (H5, q, 8H).

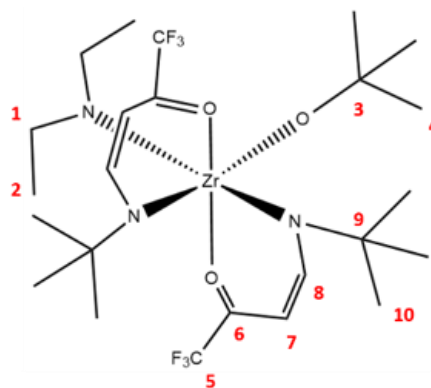
^{13}C $\{^1\text{H}, ^{19}\text{F}\}$ NMR (101 MHz, C_6D_6) δ 168.59 (C2), 159.00 (C3), 124.48 (C4), 119.87 (C1), 98.30 (C6), 58.95 (C5).

^{19}F NMR (376 MHz, C_6D_6) δ -70.61 (CF_3 of C1), -73.19 (CF_3 of C6).

Anal. Calcd. for $\text{ZrC}_{24}\text{H}_{16}\text{F}_{24}\text{N}_4\text{O}_4$: C, 29.67; H, 1.66; N, 5.77. Found: C, 30.23; H, 1.85; N, 5.59.

Synthesis of $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)(\text{O}^i\text{Bu})]$

The synthesis of $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)(\text{O}^i\text{Bu})]$ was carried out following the same procedure used for $[\text{Zr}(\text{TFB-}t\text{BuA})_2\{\eta^2\text{-(}^i\text{PrN)}_2\text{CNEt}_2\}_2]$. In this case, *tert*-butyl alcohol (0.43 g, 5.79 mmol) was used in place of *N, N'*-diisopropylcarbodiimide, the fluorinated β -ketoenamine ligand *H*-TFB-*t*BuA (2.26 g, 11.59 mmol) was used, and the zirconium precursor $[\text{Zr}(\text{NEt}_2)_4]$ (2.20 g, 5.79 mmol) was employed accordingly. The reaction afforded the yellow powder. The yellow powder was then purified by sublimation at 105-110 °C, yielding yellow powder sublimate with a mass of 0.41 g (11.37 % yield). To facilitate crystallization, a mixture of toluene and *n*-heptane was added dropwise to the sublimate, and the resulting solution was stored at -20 °C for several days. Yellow crystals gradually formed within the yellow solution, indicating successful crystallization of the target complex.

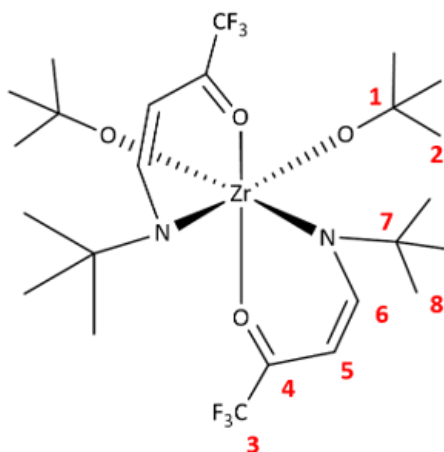


^1H NMR is unable to be assigned.

Anal. Calcd. for $\text{ZrC}_{24}\text{H}_{41}\text{F}_6\text{N}_3\text{O}_3$: C, 46.13; H, 6.61; N, 6.73. Found: C, 47.13; H, 7.82; N, 6.38.

Synthesis of $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{O}^t\text{Bu})_2]$

The synthesis of $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{O}^t\text{Bu})_2]$ was carried out following the same procedure used for $[\text{Zr}(\text{TFB-}t\text{BuA})_2\{\eta^2\text{-(}i\text{PrN)}_2\text{CNEt}_2\}_2]$. In this case, *tert*-butyl alcohol (0.78 g, 10.53 mmol) was used in place of *N, N'*-diisopropylcarbodiimide, the fluorinated β -ketoenamine ligand *H*-TFB-*t*BuA (2.06 g, 10.53 mmol) was used, and the zirconium precursor $[\text{Zr}(\text{NEt}_2)_4]$ (2.00 g, 5.27 mmol) was employed accordingly. The reaction afforded the yellow powder. The yellow powder was then purified by sublimation at 130-135 °C, yielding a colorless crystalline sublimate with a mass of 2.97 g (90.06% yield). To facilitate crystallization, a mixture of toluene and *n*-heptane was added dropwise to the sublimate, and the resulting solution was stored at -20 °C for several days. Colorless crystals gradually formed within the yellowish solution, indicating successful crystallization of the target complex.



^1H NMR (400 MHz, C_6D_6) δ 7.23 (H6, d, 2H), 5.45 (H5, d, 2H), 1.31 (H2, s, 18H), 1.08 (H8, s, 18H).

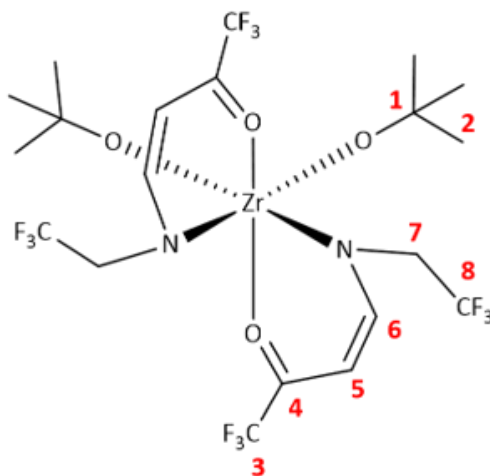
^{13}C $\{^1\text{H}, ^{19}\text{F}\}$ NMR (101 MHz, C_6D_6) δ 158.48 (C6), 156.47 (C4), 120.66 (C3), 97.28 (C5), 78.11 (C1), 62.41 (C7), 32.11 (C2), 30.53 (C8).

^{19}F NMR (376 MHz, C_6D_6) δ -74.48 (CF_3 of C3).

Anal. Calcd. for $\text{ZrC}_{24}\text{H}_{40}\text{O}_4\text{N}_2\text{F}_6$: C, 46.06; H, 6.46; N, 4.48. Found: C, 45.98; H, 6.67; N, 4.51.

Synthesis of $[\text{Zr}(\text{TFB-TFEA})_2(\text{O}^t\text{Bu})_2]$

The synthesis of $[\text{Zr}(\text{TFB-TFEA})_2(\text{O}^t\text{Bu})_2]$ was carried out following the same procedure used for $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{O}^t\text{Bu})_2]$. In this case, the fluorinated β -ketoenamine ligand *H*-TFB-TFEA (3.80 g, 17.20 mmol) was used in place of *H*-TFB-*t*BuA, the *tert*-butyl alcohol (1.27 g, 17.20 mmol) was used, and the zirconium precursor $[\text{Zr}(\text{NEt}_2)_4]$ (3.26 g, 8.59 mmol) was employed accordingly. The reaction afforded the yellow powder. The yellow powder was then purified by sublimation at 93-102 $^\circ\text{C}$, yielding a colorless crystalline sublimate with a mass of 4.35 g (74.78 % yield). To facilitate crystallization, a mixture of toluene and *n*-heptane was added dropwise to the sublimate, and the resulting solution was stored at -20 $^\circ\text{C}$ for several days. Colorless crystals gradually formed within the yellowish solution, indicating successful crystallization of the target complex.



^1H NMR (400 MHz, C_6D_6) δ 6.74 (H6, d, 2H), 5.33 (H5, d, 2H), 4.19 (H7, s, 2H), 3.01 (H7', s, 2H), 1.18 (H2, s, 18H).

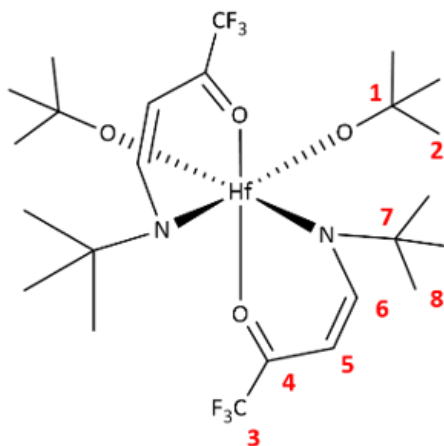
^{13}C NMR (101 MHz, C_6D_6) δ 170.84 (C6), 160.12 (C4), 124.17 (C8), 119.95 (C3), 96.84 (C5), 77.85 (C1), 58.08 (C7), 31.87 (C2).

^{19}F NMR (376 MHz, C_6D_6) δ -70.83 (CF_3 of C8), -75.13 (CF_3 of C3).

Anal. Calcd for $\text{ZrC}_{20}\text{H}_{26}\text{O}_4\text{N}_2\text{F}_{12}$: C, 35.46; H, 3.88; N, 4.14. Found: C, 36.38; H, 3.91; N, 4.22.

Synthesis of $[\text{Hf}(\text{TFB-}t\text{BuA})_2(\text{O}^t\text{Bu})_2]$

The synthesis of $[\text{Hf}(\text{TFB-}t\text{BuA})_2(\text{O}^t\text{Bu})_2]$ was carried out following the same procedure used for $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{O}^t\text{Bu})_2]$. In this case, the hafnium precursor $[\text{Hf}(\text{NEt}_2)_4]$ (3.00 g, 6.42 mmol) was used in place of $[\text{Zr}(\text{NEt}_2)_4]$, the *tert*-butyl alcohol (0.95 g, 12.85 mmol) was used, and the fluorinated β -ketoenamine ligand *H*-TFB-*t*BuA (2.50 g, 12.85 mmol) was employed accordingly. The reaction afforded the yellow powder. The yellow powder was then purified by sublimation at 135-139 °C, yielding a colorless crystalline sublimate with a mass of 3.80 g (82.96% yield). To facilitate crystallization, a mixture of toluene and *n*-heptane was added dropwise to the sublimate, and the resulting solution was stored at -20 °C for several days. Colorless crystals gradually formed within the yellowish solution, indicating successful crystallization of the target complex.



^1H NMR (400 MHz, C_6D_6) δ 7.22 (H6, d, 2H), 5.43 (H5, d, 2H), 1.33 (H2, s, 18H), 1.07 (H8, s, 18H).

^{13}C $\{^1\text{H}, ^{19}\text{F}\}$ NMR (101 MHz, C_6D_6) δ 159.23 (C6), 156.70 (C4), 120.75 (C3), 97.99 (C5), 77.11 (C1), 62.69 (C7), 32.36 (C2), 30.61 (C8).

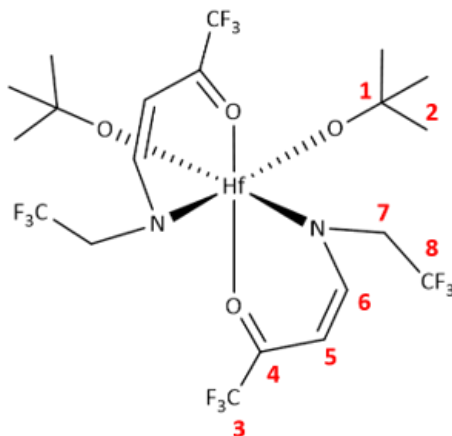
^{19}F NMR (376 MHz, C_6D_6) δ -74.58 (CF_3 of C3).

Anal. Calcd for $\text{HfC}_{24}\text{H}_{40}\text{O}_4\text{N}_2\text{F}_6$: C, 40.40; H, 5.67; N, 3.93. Found: C, 40.74; H, 5.79; N, 4.02.

Synthesis of $[\text{Hf}(\text{TFB-TFEA})_2(\text{O}^t\text{Bu})_2]$

The synthesis of $[\text{Hf}(\text{TFB-TFEA})_2(\text{O}^t\text{Bu})_2]$ was carried out following the same procedure used for $[\text{Zr}(\text{TFB-TFEA})_2(\text{O}^t\text{Bu})_2]$. In this case, the hafnium precursor $[\text{Hf}(\text{NEt}_2)_4]$ (2.85 g, 6.11 mmol) was used in place of $[\text{Zr}(\text{NEt}_2)_4]$, the *tert*-butyl alcohol (0.91 g, 12.21 mmol) was used, and the fluorinated β -ketoenamine ligand *H*-TFB-TFEA (2.70 g, 12.21 mmol) was employed accordingly. The reaction afforded the yellow powder. The yellow powder was then purified by sublimation at 87-95 °C, yielding a colorless crystalline sublimate with a mass

of 2.08 g (44.44% yield). To facilitate crystallization, a mixture of toluene and *n*-heptane was added dropwise to the residue, and the resulting solution was stored at -20°C for several days. Colorless crystals gradually formed within the yellowish solution, indicating successful crystallization of the target complex.



^1H NMR (400 MHz, C_6D_6) δ 6.71 (H6, d, 2H), 5.30 (H5, d, 2H), 4.27 (H7, s, 2H), 2.97 (H7', s, 2H), 1.20 (H2, s, 18H).

^{13}C NMR (101 MHz, C_6D_6) δ 171.18 (C6), 160.16 (C4), 124.19 (C8), 120.05 (C3), 97.48 (C5), 76.91 (C1), 58.08 (C7), 32.14 (C2).

^{19}F NMR (376 MHz, C_6D_6) δ -70.89 (CF_3 of C8), -75.26 (CF_3 of C3).

Anal. Calcd for $\text{HfC}_{20}\text{H}_{26}\text{O}_4\text{N}_2\text{F}_{12}$: C, 31.40; H, 3.43; N, 3.66. Found: C, 32.16; H, 3.42; N, 3.88

7.5. Syntheses of Metal Oxide Thin Films through MOCVD

The thin-film depositions were carried out using a horizontally configured cold-wall MOCVD reactor equipped with a cylindrical glass reaction tube, as illustrated in Figure 7.2 and described in detail in our previous publications [31, 32, 34, 36, 38, 164-168]. In this reactor configuration, the substrate was selectively heated while the reactor walls remained relatively cool, thereby minimizing parasitic gas-phase reactions and unwanted precursor decomposition.

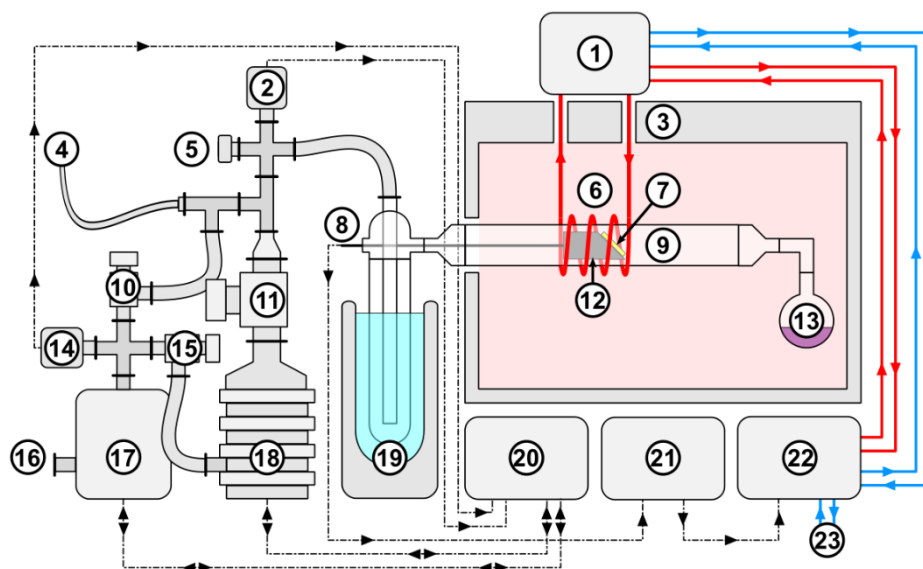


Figure 7.2. Cold-wall MOCVD reactor consisting of (1) water-cooled RF-amplifier, (2) pressure sensor, (3) oven, (4) inert gas supply, (5) overpressure valve, (6) induction coil, (7) substrate, (8) thermocouple, (9) quartz glass reactor tube, (10) bypass valve, (11) main vacuum valve, (12) graphite susceptor, (13) precursor, (14) pressure sensor, (15) exhaust valve, (16) gas exhaust, (17) pre-vacuum pump, (18) high-vacuum pump, (19) liquid nitrogen cooled trap, (20) vacuum controller, (21) temperature controller, (22) RF-generator, (23) cooling water supply. This figure was produced by Dr. Thomas Fischer of the University of Cologne. Reproduced from B. O. A. Fauzi, A. Lichtenberg, C. Hegemann, T. Fischer, M. Schmickler, H. Parala, A. Devi and S. Mathur, *RSC Applied Interfaces*, 2026, 3, 706–720. Licensed under the Creative Commons Attribution 3.0 Unported Licence (CC BY 3.0).

7.5.1. Syntheses of Al_2O_3 , Ga_2O_3 , and $(Al_xGa_{1-x})_2O_3$ Thin Films through MOCVD

Thin film deposition was performed on various substrates, including Si(111), Ti, and fluorine-doped tin oxide (FTO), to assess the adaptability of the process to different surface characteristics and thermal tolerances. All depositions were carried out at a substrate temperature of 600 °C. The growth process proceeded for approximately 2 h under reduced pressure ($p \approx 10^{-2}$ mbar). Throughout the deposition, the precursors were maintained at their respective sublimation temperatures to provide a steady and consistent vapor flux into the reaction chamber. These conditions ensured stable deposition behavior and enabled a systematic evaluation of the precursor performance in CVD-based oxide thin film synthesis.

7.5.2. Syntheses of ZrO_2 , HfO_2 , and $Hf_xZr_{1-x}O_2$ Thin Films through MOCVD

Thin films were deposited on a wide range of substrates, including Si(111), Si(100), Ti, stainless steel, glass, quartz, and fluorine-doped tin oxide (FTO), in order to evaluate the

versatility of the deposition process across different surface chemistries and thermal properties. The deposition temperature was systematically varied between 400 and 600 °C to investigate its influence on film growth and quality. The deposition process was conducted for approximately 2 h under reduced-pressure conditions ($p \approx 10^{-2}$ mbar). During this period, the precursors were maintained at their respective sublimation temperatures to ensure a stable and continuous vapor supply to the reaction zone. These controlled conditions enabled reproducible film growth and allowed assessment of the suitability of the developed precursors for CVD-based oxide thin-film deposition.

References

1. S. Kumar and D. K. Aswal, in *Recent Advances in Thin Films*, Springer, Singapore, 2020, pp. 1-12.
2. A. Goswami, *Thin Film Fundamentals*, New Age International, New Delhi, 1996, p. 2.
3. G. L. Doll, B. A. Mensah, H. Mohseni and T. W. Scharf, *J. Therm. Spray Technol.*, 2010, **19**, 510-516.
4. A. R. Choi, D. H. Lim, S. Y. Shin, H. J. Kang, D. Kim, J. Y. Kim, Y. Ahn, S. W. Ryu and I. K. Oh, *Chem. Mater.*, 2024, **36**, 2194-2219.
5. A. C. Jones and M. L. Hitchman, in *Chemical Vapour Deposition: Precursors, Processes and Applications*, ed. A. C. Jones and M. L. Hitchman, Royal Society of Chemistry, Cambridge, 2009, ch. 1, pp. 1-36.
6. S. M. George, *Chem. Rev.*, 2010, **110**, 111-131.
7. G. B. Stringfellow, *Organometallic Vapor-Phase Epitaxy: Theory and Practice*, Elsevier, Amsterdam, 1999.
8. H. O. Pierson, *Handbook of Chemical Vapor Deposition: Principles, Technology and Applications*, 2nd edn, William Andrew, Norwich, NY, 1999.
9. K. L. Choy, *Prog. Mater. Sci.*, 2003, **48**, 57-170.
10. S. Ruppi, *Int. J. Refract. Met. Hard Mater.*, 2005, **23**, 306-316.
11. R. Binions, C. J. Carmalt, I. P. Parkin, K. F. Pratt and G. A. Shaw, *Chem. Mater.*, 2004, **16**, 2489-2493.
12. J. H. Choi, H. G. Kim and S. G. Yoon, *J. Mater. Sci.: Mater. Electron.*, 1992, **3**, 87-92.
13. M. Bi, J. Zhu, Y. Luo, H. Cai, X. Li, X. Wang, Y. Wei, X. Wang, C. Hu, J. Hu and G. Zhang, *Coatings*, 2022, **12**, 1731.
14. Z. Akdeniz, M. Caliskan, Z. Cicek and M. P. Tosi, *Z. Naturforsch., A: Phys. Sci.*, 2000, **55**, 575-580.
15. R. Borjas Nevarez, S. M. Balasekaran, E. Kim, P. Weck and F. Poineau, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2018, **74**, 307-311.
16. S. Mathur, H. Shen, R. Rapalaviciute, A. Kareiva and N. Donia, *J. Mater. Chem.*, 2004, **14**, 3259-3265.
17. S. Mathur, M. Veith, R. Rapalaviciute, H. Shen, G. F. Goya, W. L. Martins Filho and T. S. Berquo, *Chem. Mater.*, 2004, **16**, 1906-1913.
18. V. Bhatt and S. Ram, *Chem. Sci. Rev. Lett.*, 2015, **4**, 414-428.
19. D. C. Bradley, *Chem. Rev.*, 1989, **89**, 1317-1322.

20. R. C. Mehrotra and A. Mehrotra, *Inorg. Chim. Acta Rev.*, 1971, **5**, 127-136.
21. D. C. Bradley, R. C. Mehrotra, I. P. Rothwell and A. Singh, *Alkoxo and Aryloxo Derivatives of Metals*, Elsevier, San Diego, 2001, pp. 3-181.
22. P. K. Hon and C. E. Pfluger, *J. Coord. Chem.*, 1973, **3**, 67-76.
23. M. Ohring, *Materials Science of Thin Films: Deposition and Structure*, 2nd edn, Academic Press, San Diego, 2002.
24. K. F. Jensen, in *Proc. 9th Int. Conf. on Chemical Vapor Deposition*, 1984, pp. 3-20.
25. M. E. Coltrin, R. J. Kee and G. H. Evans, *J. Electrochem. Soc.*, 1989, **136**, 819-829.
26. M. Veith, *Mater. Sci. Forum*, 2000, **343**, 531-538.
27. S. Mathur, M. Veith, T. Rügamer, E. Hemmer and H. Shen, *Chem. Mater.*, 2004, **16**, 1304-1312.
28. A. C. Jones, *J. Mater. Chem.*, 2002, **12**, 2576-2590.
29. S. Mishra and S. Daniele, *Chem. Rev.*, 2015, **115**, 8379-8448.
30. U. Atamtürk, E. Jung, T. Fischer and S. Mathur, *Chem. Mater.*, 2022, **34**, 7344-7356.
31. D. Graf, M. Frank, O. Ojelere, I. Gessner, L. Jürgensen, M. Grosch and S. Mathur, *Mater. Today Proc.*, 2020, **33**, 2445-2450.
32. L. Jürgensen, M. Frank, M. Pyeon, L. Czympiel and S. Mathur, *Organometallics*, 2017, **36**, 2331-2337.
33. L. Brückmann, W. Tyrra, S. Stucky and S. Mathur, *Inorg. Chem.*, 2012, **51**, 536-542.
34. U. Atamtürk, V. Brune, S. Mishra and S. Mathur, *Molecules*, 2021, **26**, 5367.
35. M. Frank, L. Jürgensen, J. Leduc, D. Stadler, D. Graf, I. Gessner, F. Zajusch, T. Fischer, M. A. Rose, D. N. Mueller and S. Mathur, *Inorg. Chem.*, 2019, **58**, 10408-10416.
36. L. Jürgensen, D. Höll, M. Frank, T. Ludwig, D. Graf, A. K. Schmidt-Verma and S. Mathur, *Dalton Trans.*, 2020, **49**, 13317-13325.
37. L. Jürgensen, M. Frank, D. Graf, I. Gessner, T. Fischer, K. Welter and S. Mathur, *Z. Phys. Chem.*, 2020, **234**, 911-924.
38. A. Lichtenberg, K. Altuntas, T. Fischer, T. Karimpour, S. Diel, Z. Aytuna and S. Mathur, *Z. Anorg. Allg. Chem.*, 2024, **650**, e202400126.
39. B. O. A. Fauzi, A. Lichtenberg, C. Hegemann, T. Fischer, M. Schmickler, H. Parala, A. Devi and S. Mathur, *RSC Appl. Interfaces*, 2026, **3**, 706-720.
40. D. Grödler, P. Kaden, J. M. Sperling, B. M. Rotermund, B. Scheibe, N. B. Beck, A. Lichtenberg, T. E. Albrecht, S. Mathur and R. Gericke, *Inorg. Chem.*, 2025, **64**, 2321-2328.

41. M. Higashiwaki, K. Sasaki, A. Kuramata, T. Masui and S. Yamakoshi, *Appl. Phys. Lett.*, 2012, **100**, 013504.
42. S. J. Pearton, J. Yang, P. H. Cary, F. Ren, J. Kim, M. J. Tadjer and M. A. Mastro, *Appl. Phys. Rev.*, 2018, **5**, 011301.
43. H. Li, Z. Wu, S. Wu, P. Tian and Z. Fang, *J. Alloys Compd.*, 2023, **960**, 170671.
44. F. Liu, Y. Li, H. Cheng, C. Jin and C. Liu, *Adv. Opt. Mater.*, 2024, **12**, 2400724.
45. B. W. Krueger, C. S. Dandeneau, E. M. Nelson, S. T. Dunham, F. S. Ohuchi and M. A. Olmstead, *J. Am. Ceram. Soc.*, 2016, **99**, 2467-2473.
46. R. Wakabayashi, M. Hattori, K. Yoshimatsu, K. Horiba, H. Kumigashira and A. Ohtomo, *Appl. Phys. Lett.*, 2018, **112**, 232103.
47. C. Z. Zhao and K. Y. Zheng, *J. Phys. Chem. Solids*, 2024, **184**, 111694.
48. W. Hu, S. Li, Y. Hu, L. Wan, S. Jiao, W. Hu, D. N. Talwar, Z. C. Feng, T. Li, J. Xu and L. Wei, *J. Alloys Compd.*, 2021, **864**, 158765.
49. B. J. Baliga, *IEEE Electron Device Lett.*, 2002, **10**, 455-457.
50. A. F. M. Bhuiyan, Z. Feng, J. M. Johnson, H. L. Huang, J. Sarker, M. Zhu, M. R. Karim, B. Mazumder, J. Hwang and H. Zhao, *APL Mater.*, 2020, **8**, 031104.
51. A. A. U. Bhuiyan, L. Meng, H. L. Huang, C. Chae, J. Hwang and H. Zhao, *Phys. Status Solidi RRL*, 2023, **17**, 2300224.
52. M. Veith, O. C. Aktaş, W. Metzger, D. Sossong, H. Ullah Wazir, I. Grobelsek, N. Pütz, G. Wennemuth, T. Pohlemann and M. Oberringer, *Biofabrication*, 2010, **2**, 035001.
53. B. D. Fahlman and A. R. Barron, *Adv. Funct. Mater.*, 2000, **10**, 135-144.
54. M. Valet and D. M. Hoffman, *Chem. Mater.*, 2001, **13**, 2135-2143.
55. C. H. Lin, B. T. Ko, F. C. Wang, C. C. Lin and C. Y. Kuo, *J. Organomet. Chem.*, 1999, **575**, 67-75.
56. B. Prashanth and S. Singh, *Dalton Trans.*, 2014, **43**, 16880-16888.
57. X. Liu, S. H. Chan, F. Wu, Y. Li, S. Keller, J. S. Speck and U. K. Mishra, *J. Cryst. Growth*, 2014, **408**, 78-84.
58. A. Ito, R. Tu and T. Goto, *Surf. Coat. Technol.*, 2010, **204**, 2170-2174.
59. A. Rajib, M. K. Enamul, S. Kurosu, T. Ukai, M. Tokuda, Y. Fujii, T. Hanajiri, R. Ishikawa, K. Ueno and H. Shirai, *J. Vac. Sci. Technol., A*, 2020, **38**, 033413.
60. K. T. Oh, H. Y. Kim, D. H. Kim, J. H. Han, J. Park and J. S. Park, *Ceram. Int.*, 2017, **43**, 8932-8937.
61. Y. Chen, J. Liu, X. Wang, W. Wang, Z. Zeng and Z. Hu, *Catal. Lett.*, 2014, **144**, 1696-1703.

62. R. Kúdela, J. Šoltýs, M. Kučera, R. Stoklas, F. Guemann, M. Blaho, M. Mičušík, O. Pohorelec, M. Gregor, I. Brytavskyi and E. Dobročka, *Appl. Surf. Sci.*, 2018, **461**, 33-38.
63. K. Kim, N. Borojevic, S. Winderbaum, S. Duttagupta, X. Zhang, J. Park and Z. Hameiri, *Sol. Energy*, 2019, **186**, 94-105.
64. K. Djebaili, Z. Mekhalif, A. Boumaza and A. X. P. Djelloul, *J. Spectrosc.*, 2015, **2015**, 868109.
65. T. Tuguhro, N. Kataoka, H. Tanaka, K. Kinoshita and S. Kishida, *Procedia Eng.*, 2017, **216**, 175-181.
66. J. Van den Brand, W. G. Sloof, H. Terryn and J. H. W. De Wit, *Surf. Interface Anal.*, 2004, **36**, 81-88.
67. G. A. Battiston, R. Gerbasi, M. Porchia, R. Bertoncello and F. Caccavale, *Thin Solid Films*, 1996, **279**, 115-118.
68. L. Miinea, S. Suh, S. G. Bott, J.-R. Liu, W.-K. Chu and D. M. Hoffman, *J. Mater. Chem.*, 1999, **9**, 929-935.
69. A. J. Green, J. Speck, G. Xing, P. Moens, F. Allerstam, K. Gumaelius, T. Neyer, A. Arias-Purdue, V. Mehrotra, A. Kuramata and K. Sasaki, *APL Mater.*, 2022, **10**, 029201.
70. S. K. Lee, S. B. Lee, S. Y. Park, Y. S. Yi and C. W. Ahn, *Phys. Rev. Lett.*, 2009, **103**, 095501.
71. H. Qin, P. Sutter and G. Zhou, *J. Am. Ceram. Soc.*, 2014, **97**, 2762-2769.
72. S. H. Park, H. S. Lee, H. S. Ahn and M. Yang, *J. Korean Phys. Soc.*, 2019, **74**, 502-507.
73. C. Zhang, S. Qi, J. Xue, J. Cao, Z. Xie, Y. Liao, Y. Wang, H. Song, A. Qu, G. Hu and Z. Mei, *Adv. Mater. Technol.*, 2025, **10**, 2401215.
74. Y. Liu, Q. Zuo, J. Sun, J. Dai, C. Cheng and H. Huang, *J. Appl. Phys.*, 2024, **135**, 184502.
75. N. Makeswaran, A. K. Battu, R. Swadipta, F. S. Manciu and C. V. Ramana, *ECS J. Solid State Sci. Technol.*, 2019, **8**, Q3249-Q3253.
76. C. H. Tien, B. W. Hsiao, C. M. Chen, M. I. Chen, J. L. Chiang and D. S. Wu, *Ceram. Int.*, 2020, **46**, 24147-24154.
77. S. H. Yuan, S. L. Ou, C. M. Chen, S. Y. Huang, B. W. Hsiao and D. S. Wu, *Ceram. Int.*, 2019, **45**, 702-707.
78. Y. Wang, L. Wang, Y. Dong, Y. Liu, Q. Feng, Y. Zhang, J. Zhang and Y. Hao, *J. Alloys Compd.*, 2025, **1031**, 181060.
79. C. H. Liao, J. Y. Huang, C. S. Huang, C. C. Yang, J. E. Kuo, W. Water, W. S. Tsai, P. A. Miranda Cortez, X. Tang and S. H. Lin, *Processes*, 2024, **13**, 68.

80. P. W. Chen, S. Y. Huang, C. C. Wang, S. H. Yuan and D. S. Wu, *J. Alloys Compd.*, 2019, **791**, 1213-1219.
81. W. Liu, X. Zhu, Y. Ding, H. Tang, P. Xu, T. Huang, Y. Zheng, X. Chen and R. Zhang, *Ceram. Int.*, 2024, **50**, 19856-19863.
82. Z. Akkuly, A. P. Patel, K. K. Subedi, D. Pokhrel, E. Bastola, A. B. Phillips, M. J. Heben and R. Ellingson, in *Proc. 48th IEEE Photovoltaic Specialists Conf. (PVSC)*, IEEE, 2021, pp. 2132-2135.
83. F. Ishikawa and N. Yamamoto, in *Novel Compound Semiconductor Nanowires: Materials, Devices, and Applications*, ed. F. Ishikawa and I. Buyanova, Pan Stanford Publishing, 2018, ch. 8.
84. H. I. Chen, K. C. Chuang, C. H. Chang, W. C. Chen, I. P. Liu and W. C. Liu, *Sens. Actuators, B*, 2017, **246**, 408-414.
85. H. Iwata, H. Ishii, D. Kato, S. Kawashima, K. Kodama, M. Furusawa, M. Tanaka and T. Sekiya, *J. Vac. Sci. Technol., A*, 2018, **36**, 061509.
86. A. S. Kuprin, A. Gilewicz, T. A. Kuznetsova, V. A. Lapitskaya, G. N. Tolmachova, B. Warcholinski, S. M. Aizikovich and E. V. Sadyrin, *Materials*, 2021, **14**, 1483.
87. M. J. Pinzón, J. E. Alfonso, J. J. Olaya, G. I. Cubillos and E. Romero, *Thin Solid Films*, 2014, **572**, 184-188.
88. M. Ahmed and G. Xinxin, *Inorg. Chem. Front.*, 2016, **3**, 578-590.
89. A. Rizzo, M. A. Signore, L. Mirengi and T. Di Luccio, *Thin Solid Films*, 2009, **517**, 5956-5964.
90. V. Streibel, J. L. Schönecker, L. I. Wagner, E. Sirotti, F. Munnik, M. Kuhl, C. M. Jiang, J. Eichhorn, S. Santra and I. D. Sharp, *ACS Appl. Energy Mater.*, 2024, **7**, 4004-4015.
91. Y. H. Wong, V. V. Atuchin, V. N. Kruchinin and K. Y. Cheong, *Appl. Phys. A*, 2014, **115**, 1069-1072.
92. V. V. Atuchin, V. N. Kruchinin, Y. H. Wong and K. Y. Cheong, *Mater. Lett.*, 2013, **105**, 72-75.
93. Q. Guo, T. Wang, Y. Ren, Y. Ran, C. Gao, H. Lu, Z. Jiang and Z. Wang, *Phys. Rev. Mater.*, 2021, **5**, 065201.
94. J. H. Song, J. W. Jeon, Y. H. Kim, J. H. Oh and T. Y. Seong, *Superlattices Microstruct.*, 2013, **62**, 119-127.
95. S. Sinha, T. Vegge and H. A. Hansen, *ChemCatChem*, 2023, **15**, e202300349.
96. A. Banerjee, B. M. Ceballos, C. Kreller, R. Mukundan and G. Pilania, *J. Mater. Sci.*, 2022, **57**, 10213-10224.

97. M. Banerjee, N. B. Srinivasan, H. Zhu, S. J. Kim, K. Xu, M. Winter, H.-W. Becker, D. Rogalla, T. de los Arcos, D. Bekermann, D. Barreca, R. A. Fischer and A. Devi, *Cryst. Growth Des.*, 2012, **12**, 5079-5089.
98. P. L. Franceschini, M. Morstein, H. Berke and H. W. Schmalle, *Inorg. Chem.*, 2003, **42**, 7273-7282.
99. M. Banerjee, R. W. Seidel, M. Winter, H. W. Becker, D. Rogalla and A. Devi, *Dalton Trans.*, 2014, **43**, 2384-2396.
100. M. Al Hareri and D. J. Emslie, *Eur. J. Inorg. Chem.*, 2023, **2023**, e202200594.
101. R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751-767.
102. R. J. Baker, P. E. Colavita, D. M. Murphy, J. A. Platts and J. D. Wallis, *J. Phys. Chem. A*, 2012, **116**, 1435-1444.
103. G. V. Janjić, S. T. Jelić, N. P. Trišović, D. M. Popović, I. S. Đorđević and M. K. Milčić, *Cryst. Growth Des.*, 2020, **20**, 2943-2951.
104. J. Liu, J. P. Glauber, J. Lorenz, D. Rogalla, C. Harms, A. Devi and M. Nolan, *J. Phys. Chem. C*, 2025, **129**, 11173-11182.
105. A. Kashir and H. Hwang, *Phys. Status Solidi A*, 2021, **218**, 2000819.
106. D. Lehninger, A. Prabhu, A. Sünbül, T. Ali, F. Schöne, T. Kämpfe, K. Biedermann, L. Roy, K. Seidel, M. Lederer and L. M. Eng, *Adv. Phys. Res.*, 2023, **2**, 2200108.
107. Q. Luo, Y. Cheng, J. Yang, R. Cao, H. Ma, Y. Yang, R. Huang, W. Wei, Y. Zheng, T. Gong and J. Yu, *Nat. Commun.*, 2020, **11**, 1391.
108. Q. Li, S. Wang, Z. Li, X. Hu, Y. Liu, J. Yu, Y. Yang, T. Wang, J. Meng, Q. Sun and D. W. Zhang, *Nat. Commun.*, 2024, **15**, 2686.
109. X. Yu, N. Zhong, Y. Cheng, T. Xin, Q. Luo, T. Gong, J. Chen, J. Wu, R. Cheng, Z. Fu and K. Tang, *Sci. China Inf. Sci.*, 2025, **68**, 160401.
110. J. Liu, J. Li, J. Wu and J. Sun, *Nanoscale Res. Lett.*, 2019, **14**, 154.
111. M. Jang, J. Jeon, W. C. Lim, K. H. Chae, S. H. Baek and S. K. Kim, *Ceram. Int.*, 2024, **50**, 47910-47915.
112. B. Lee, K. J. Choi, A. Hande, M. J. Kim, R. M. Wallace, J. Kim, Y. Senzaki, D. Shenai, H. Li, M. Rousseau and J. Suydam, *Microelectron. Eng.*, 2009, **86**, 272-276.
113. I. Kärkkänen, A. Shkabko, M. Heikkilä, J. Niinistö, M. Ritala, M. Leskelä, S. Hoffmann-Eifert and R. Waser, *Phys. Status Solidi A*, 2014, **211**, 301-309.
114. A. R. Choi, S. Seo, S. Kim, D. Kim, S. W. Ryu, W. J. Lee and I. K. Oh, *Appl. Surf. Sci.*, 2023, **624**, 157104.

115. L. Aarik, H. Alles, A. Aidla, T. Kahro, K. Kukli, J. Niinistö, H. Mändar, A. Tamm, R. Rammula, V. Sammelselg and J. Aarik, *Thin Solid Films*, 2014, **565**, 37-44.
116. G. D'Acunto, R. Tsyshkevsky, P. Shayesteh, J. J. Gallet, F. Bournel, F. Rochet, I. Pinsard, R. Timm, A. R. Head, M. Kuklja and J. Schnadt, *Chem. Mater.*, 2023, **35**, 529-538.
117. K. Karavaev, K. Kolanek, M. Tallarida, D. Schmeißer and E. Zschech, *Adv. Eng. Mater.*, 2009, **11**, 265-268.
118. J. Niinistö, M. Mäntymäki, K. Kukli, L. Costelle, E. Puukilainen, M. Ritala and M. Leskelä, *J. Cryst. Growth*, 2010, **312**, 245-249.
119. A. Nishida, T. Katayama, T. Endo and Y. Matsuo, *ACS Appl. Mater. Interfaces*, 2025, **17**, 11036-11044.
120. M. Knez, K. Nielsch and L. Niinistö, *Adv. Mater.*, 2007, **19**, 3425-3438.
121. M. Leskelä and M. Ritala, *Angew. Chem. Int. Ed.*, 2003, **42**, 5548-5554.
122. P. A. Williams, J. L. Roberts, A. C. Jones, P. R. Chalker, N. L. Tobin, J. F. Bickley, H. O. Davies, L. M. Smith and T. J. Leedham, *Chem. Vap. Deposition*, 2002, **8**, 163-170.
123. R. Garvie, R. Hannink and R. Pascoe, *Nature*, 1975, **258**, 703-704.
124. R. C. Garvie, R. H. Hannink and R. T. Pascoe, in *Sintering Key Papers*, Springer Netherlands, Dordrecht, 1990, pp. 253-257.
125. R. C. Garvie, *J. Phys. Chem.*, 1965, **69**, 1238-1243.
126. X. Wu, D. Landheer, M. J. Graham, H. W. Chen, T. Y. Huang and T. S. Chao, *J. Cryst. Growth*, 2003, **250**, 479-485.
127. Z. Chen, B. Wang, N. Prud'homme, S. L. Ma, V. Ji and P. Ribot, *Mater. Sci. Forum*, 2011, **675**, 1201-1204.
128. Z. Chen, N. Prud'homme, B. Wang, P. Ribot and V. Ji, *Surf. Coat. Technol.*, 2013, **218**, 7-16.
129. E. M. Huseynov, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, 2023, **286**, 122032.
130. M. M. López Guerrero, A. García de Torres, E. Vereda Alonso, M. T. Siles Cordero and J. M. Cano Pavón, *Ceram. Int.*, 2011, **37**, 607-613.
131. B. Aguirre, R. S. Vemuri, D. Zubia, M. H. Engelhard, V. Shutthanandan, K. K. Bharathi and C. V. Ramana, *Appl. Surf. Sci.*, 2011, **257**, 2197-2202.
132. C. V. Ramana, K. K. Bharathi, A. Garcia and A. L. Campbell, *J. Phys. Chem. C*, 2012, **116**, 9955-9960.
133. J. H. Park, J. Kim, H. Oh, Y. Park and W. Jeon, *Mater. Lett.*, 2025, 139581.
134. W. Zheng, K. H. Bowen, J. Li, I. Dabkowska and M. Gutowski, *J. Phys. Chem. A*, 2005, **109**, 11521-11525.

135. K. T. Jacob, S. Raj and L. Rannesh, *Int. J. Mater. Res.*, 2007, **98**, 776-779.
136. W. Zhang, L. Huang, A. Li and D. Wu, *J. Cryst. Growth*, 2012, **346**, 12-16.
137. M. S. Song, K. Park, K. Lee, J. W. Cho, T. Y. Lee, J. Park and S. C. Chae, *ACS Appl. Electron. Mater.*, 2023, **5**, 117-122.
138. T. Zhang, Y. Fan, Z. Xue, M. Si, Z. Wang, X. Li and Y. Cao, *Mater. Today Electron.*, 2024, **10**, 100124.
139. K. Cao, Q. Zhao, J. Liao, F. Yan, K. Bao, S. Jia, J. Zhang, J. Luo, M. Liao and Y. Zhou, *Microstructures*, 2025, **5**, 2025025.
140. P. Xu, S. Yan, Y. Zhu, J. Zang, P. Luo, G. Li, Q. Yang, Z. Chen, W. Zhang, X. Zheng and M. Tang, *J. Mater. Sci.: Mater. Electron.*, 2023, **34**, 1915.
141. M. A. Jenkins, K. E. Holden, S. W. Smith, M. T. Brumbach, M. D. Henry, C. Weiland, J. C. Woicik, S. T. Jaszewski, J. F. Ihlefeld and J. F. Conley Jr., *ACS Appl. Mater. Interfaces*, 2021, **13**, 14634-14643.
142. M. B. Hachemi, B. Salem, V. Consonni, H. Roussel, A. Garraud, G. Lefevre, S. Labau, S. Basrour and A. Bsiesy, *AIP Adv.*, 2021, **11**, 085004.
143. D. Barreca, A. Milanov, R. A. Fischer, A. Devi and E. Tondello, *Surf. Sci. Spectra*, 2007, **14**, 34-40.
144. Z. Galazka, *IEEE Trans. Semicond. Manuf.*, 2025, **38**, 796-802.
145. F. Wunderwald, B. Xu, A. Kersch, K. M. Holsgrove, Y. C. Kao, C. Richter, S. Enghardt, T. Mikolajick and U. Schroeder, *Small*, 2025, **21**, 2408133.
146. M. H. Park, H. J. Kim, Y. J. Kim, W. Lee, T. Moon and C. S. Hwang, *Appl. Phys. Lett.*, 2013, **102**, 242905.
147. Y. A. Wasslen, A. Kurek, P. A. Johnson, T. C. Pigeon, W. H. Monillas, G. P. Yap and S. T. Barry, *Dalton Trans.*, 2010, **39**, 9046-9054.
148. V. Nahrstedt, D. Stadler, T. Fischer, T. Duchon, D. N. Mueller, C. M. Schneider and S. Mathur, *Inorg. Chem.*, 2021, **60**, 3719-3728.
149. A. Raauf, J. Schlaefer, I. Gessner, A. Lichtenberg, M. Zegke, T. Fischer and S. Mathur, *J. Indian Chem. Soc.*, 2022, **99**, 100347.
150. H. A. Hsain, Y. Lee, G. Parsons and J. L. Jones, *Appl. Phys. Lett.*, 2020, **116**, 192901.
151. S. S. Fields, T. Cai, S. T. Jaszewski, A. Salanova, T. Mimura, H. H. Heinrich, M. D. Henry, K. P. Kelley, B. W. Sheldon and J. F. Ihlefeld, *Adv. Electron. Mater.*, 2022, **8**, 2200601.
152. H. W. Cho, P. Pujar, M. Choi, S. Kang, S. Hong, J. Park, S. Baek, Y. Kim, J. Lee and S. Kim, *npj 2D Mater. Appl.*, 2021, **5**, 46.

153. H. Cho, P. Pujar, M. Choi, M. Naqi, Y. Cho, H. Y. Rho, J. Lee and S. Kim, *ACS Appl. Mater. Interfaces*, 2021, **13**, 60250-60260.
154. S. Shi, H. Xi, T. Cao, W. Lin, Z. Liu, J. Niu, D. Lan, C. Zhou, J. Cao, H. Su and T. Zhao, *Nat. Commun.*, 2023, **14**, 1780.
155. T. Onaya, T. Nabatame, Y. C. Jung, H. Hernandez-Arriaga, J. Mohan, H. S. Kim, N. Sawamoto, C. Y. Nam, E. H. Tsai, T. Nagata and J. Kim, *APL Mater.*, 2021, **9**, 031111.
156. G. M. Sheldrick, *Acta Crystallogr. C*, 2015, **71**, 3-8.
157. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.
158. K. Momma and F. Izumi, *J. Appl. Crystallogr.*, 2011, **44**, 1272-1276.
159. J. Schindelin, I. Arganda-Carreras, E. Frise, V. Kaynig, M. Longair, T. Pietzsch, S. Preibisch, M. Rueden, C. Saalfeld, B. Schmid, J.-Y. Tinevez, D. J. White, V. Hartenstein, K. Eliceiri, P. Tomancak and A. Cardona, *Nat. Methods*, 2012, **9**, 676-682.
160. M. Klinger and A. Jäger, *J. Appl. Crystallogr.*, 2015, **48**, 2012-2018.
161. C. K. Amadi, U. Atamtürk, A. Lichtenberg, A. Raauf and S. Mathur, *Molecules*, 2023, **28**, 2137.
162. C. R. Wade, C. Silvernail, C. Banerjee, A. Soulet, J. McAndrew and J. A. Belot, *Mater. Lett.*, 2007, **61**, 5079-5082.
163. E. Dhaene, C. Seno and J. De Roo, *Dalton Trans.*, 2024, **53**, 11769-11777.
164. R. Fiz, L. Appel, A. Gutiérrez-Pardo, J. Ramírez-Rico and S. Mathur, *ACS Appl. Mater. Interfaces*, 2016, **8**, 21423-21430.
165. D. Graf, J. Schläfer, S. Garbe, A. Klein and S. Mathur, *Chem. Mater.*, 2017, **29**, 5877-5885.
166. J. Altmayer, S. Barth and S. Mathur, *RSC Adv.*, 2013, **3**, 11234-11239.
167. S. Mathur, T. Ruegamer and I. Grobelsek, *Chem. Vap. Deposition*, 2007, **13**, 42-47.
168. R. Müller, F. Hernandez-Ramirez, H. Shen, H. Du, W. Mader and S. Mathur, *Chem. Mater.*, 2012, **24**, 4028-4035.

Abbreviation

ALD	: Atomic Layer Deposition
CMOS	: Complementary Metal-Oxide-Semiconductor
CVD	: Chemical Vapor Deposition
DSC	: Differential Scanning Calorimetry
DTA	: Differential Thermal Analysis
EDX	: Energy-Dispersive X-ray
FeFET	: Ferroelectric Field-Effect Transistor
FTIR	: Fourier Transform Infrared
FTO	: Fluorine-Doped Tin Oxide
GIXRD	: Grazing-Incidence X-ray Diffraction
HEMT	: High-Electron-Mobility Transistor
HS	: Hirshfeld Surface
HZO	: Hafnium Zirconium Oxide
MBE	: Molecular-Beam Epitaxy
MOCVD	: Metal-Organic Chemical Vapor Deposition
MODFET	: Modulation-Doped Field-Effect Transistor
MOSFET	: Metal Oxide Semiconductor Field-Effect Transistor
NMR	: Nuclear Magnetic Resonance
PLD	: Pulsed Laser Deposition
PVD	: Physical Vapor Deposition
SAED	: Selected Area Electron Diffraction
SC-XRD	: Single-Crystal X-ray Diffraction
SEM	: Scanning Electron Microscope
SSP	: Single-Source Precursor
TDMAHf	: Tetrakis(dimethylamido)hafnium
TDMAZr	: Tetrakis(dimethylamido)zirconium
TEM	: Transmission Electron Microscope
TEMAZr	: Tetrakis(ethylmethyldamido)hafnium
TEMAZr	: Tetrakis(ethylmethyldamido)zirconium
TG	: Thermogravimetric
TMAI	: Trimethylaluminum
TMGa	: Trimethylgallium

XPS	: X-ray Photoelectron Spectroscopy
XRD	: X-ray Diffraction
XRF	: X-ray Fluorescence

Appendix

Table of Crystal Details

Table 1. Crystal data and structure refinement for [Al(TFB-*t*BuA)(O^tBu)₂].

Identification code	[Al(TFB- <i>t</i> BuA)(O ^t Bu) ₂]
Empirical formula	C ₁₆ H ₂₉ AlF ₃ NO ₃
Formula weight	367.38
Temperature/K	100.00
Crystal system	triclinic
Space group	P-1
a/Å	6.7295(17)
b/Å	17.215(4)
c/Å	17.528(4)
α/°	92.705(9)
β/°	91.604(9)
γ/°	92.245(8)
Volume/Å ³	2025.9(9)
Z	4
ρ _{calc} /cm ³	1.204
μ/mm ⁻¹	0.139
F(000)	784.0
Crystal size/mm ³	0.11 × 0.03 × 0.02
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.654 to 56.994
Index ranges	-8 ≤ h ≤ 8, -23 ≤ k ≤ 23, 0 ≤ l ≤ 23
Reflections collected	9821
Independent reflections	9821 [R _{int} = ?, R _{sigma} = 0.1149]
Data/restraints/parameters	9821/0/451
Goodness-of-fit on F ²	1.065
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.1857, wR ₂ = 0.4658
Final R indexes [all data]	R ₁ = 0.2380, wR ₂ = 0.4929
Largest diff. peak/hole / e Å ⁻³	1.07/-1.75

Table 2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Al}(\text{TFB}-t\text{BuA})(\text{O}^t\text{Bu})_2]$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	$U(\text{eq})$
Al1	635(4)	2340.6(16)	3648.1(16)	19.5(6)
O2'	2085(10)	2866(4)	4311(4)	23.6(14)
O1	-384(9)	2957(4)	2959(4)	26.7(15)
O2	1964(9)	1622(4)	3229(4)	22.2(13)
N1	-1860(11)	1963(5)	4052(5)	21.1(16)
F3	-4567(10)	3640(5)	1995(5)	58(2)
C2	-2276(14)	3045(6)	2823(5)	22.8(19)
F2	-1698(11)	3411(6)	1559(4)	58(2)
C3	-3806(13)	2715(6)	3183(7)	30(2)
C4	-3538(14)	2202(6)	3780(6)	28(2)
C9	1724(16)	1107(6)	2570(6)	28(2)
C6	113(16)	1132(6)	4851(6)	31(2)
C1	-2652(15)	3610(7)	2195(7)	32(2)
F1	-2077(14)	4336(5)	2439(6)	64(2)
C5	-1951(14)	1425(6)	4717(6)	28(2)
C9'	2112(17)	3626(6)	4655(6)	31(2)
C7	-3362(17)	724(8)	4518(9)	55(4)
C8	-2650(20)	1883(8)	5419(8)	49(3)
C11	2350(20)	1569(10)	1858(7)	57(4)
C12	-439(18)	841(8)	2424(8)	46(3)
C11'	2940(20)	4203(8)	4106(9)	57(4)
C10	3030(30)	417(9)	2694(10)	74(6)
C12'	-20(30)	3852(10)	4776(14)	86(7)
C10'	3240(40)	3623(11)	5391(11)	117(11)

Table 3. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Al}(\text{TFB}-t\text{BuA})(\text{O}^i\text{Bu})_2]$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[\text{h}^2\text{a}^{*2}\text{U}_{11}+2\text{hka}^*\text{b}^*\text{U}_{12}+\dots]$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Al1	10.7(11)	29.5(14)	18.4(13)	0.8(11)	1.7(10)	1.6(10)
O2'	19(3)	27(3)	24(3)	-3(3)	-1(3)	-3(3)
O1	11(3)	35(4)	34(4)	7(3)	-4(3)	1(3)
O2	17(3)	27(3)	22(3)	-8(3)	-1(2)	0(2)
N1	11(3)	30(4)	22(4)	0(3)	-2(3)	1(3)
F3	25(3)	97(6)	55(5)	40(5)	0(3)	19(4)
C2	19(4)	33(5)	17(4)	1(4)	2(3)	10(4)
F2	39(4)	102(7)	39(4)	33(4)	12(3)	24(4)
C3	6(4)	40(6)	43(6)	8(5)	-6(4)	1(4)
C4	15(4)	37(5)	33(5)	7(4)	-2(4)	1(4)
C9	29(5)	33(5)	23(5)	-7(4)	1(4)	8(4)
C6	30(5)	35(5)	27(5)	8(4)	-2(4)	-1(4)
C1	19(5)	41(6)	39(6)	15(5)	-2(4)	4(4)
F1	72(6)	43(4)	80(6)	23(4)	-1(5)	7(4)
C5	19(4)	38(5)	29(5)	6(4)	5(4)	0(4)
C9'	36(6)	26(5)	30(5)	-10(4)	-1(4)	0(4)
C7	24(5)	57(8)	85(11)	42(8)	-16(6)	-14(5)
C8	50(8)	60(8)	41(7)	9(6)	24(6)	22(6)
C11	56(8)	88(11)	26(6)	0(7)	13(6)	-29(8)
C12	31(6)	59(8)	45(7)	-13(6)	-10(5)	-9(5)
C11'	73(10)	38(7)	60(9)	5(6)	26(8)	-9(6)
C10	93(13)	59(9)	67(10)	-38(8)	-37(9)	55(9)
C12'	56(10)	57(9)	141(19)	-46(11)	43(11)	-3(7)
C10'	210(30)	55(10)	76(13)	-8(9)	-99(17)	18(13)

Table 4. Bond Lengths for [Al(TFB-*t*BuA)(O'*i*Bu)₂].

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Al1	O2'	1.699(7)	C3	C4	1.415(14)
Al1	O1	1.786(7)	C9	C11	1.569(16)
Al1	O2	1.706(7)	C9	C12	1.520(15)
Al1	N1	1.941(8)	C9	C10	1.526(15)
O2'	C9'	1.415(12)	C6	C5	1.512(14)
O1	C2	1.305(11)	C1	F1	1.340(14)
O2	C9	1.424(12)	C5	C7	1.528(16)
N1	C4	1.302(11)	C5	C8	1.524(17)
N1	C5	1.524(13)	C9'	C11'	1.516(17)
F3	C1	1.330(12)	C9'	C12'	1.520(19)
C2	C3	1.343(14)	C9'	C10'	1.479(18)
C2	C1	1.525(13)	F2	C1	1.340(14)

Table 5. Bond Angles for [Al(TFB-*t*BuA)(O'*i*Bu)₂].

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2'	Al1	O1	110.8(4)	O2	C9	C10	107.6(9)
O2'	Al1	O2	110.1(3)	C12	C9	C11	106.3(10)
O2'	Al1	N1	112.8(4)	C12	C9	C10	111.2(11)
O1	Al1	N1	97.6(3)	C10	C9	C11	112.2(13)
O2	Al1	O1	111.7(4)	F3	C1	C2	112.9(9)
O2	Al1	N1	113.3(4)	F3	C1	F2	106.6(9)
C9'	O2'	Al1	136.3(7)	F3	C1	F1	105.7(10)
C2	O1	Al1	125.4(6)	F2	C1	C2	111.5(9)
C9	O2	Al1	136.2(6)	F2	C1	F1	109.7(9)
C4	N1	Al1	120.0(7)	F1	C1	C2	110.2(9)
C4	N1	C5	117.4(8)	N1	C5	C7	110.5(9)
C5	N1	Al1	122.5(6)	N1	C5	C8	108.8(9)
O1	C2	C3	127.1(9)	C6	C5	N1	107.6(8)
O1	C2	C1	112.4(8)	C6	C5	C7	108.1(9)
C3	C2	C1	120.4(8)	C6	C5	C8	111.3(10)
C2	C3	C4	122.7(8)	C8	C5	C7	110.5(11)
N1	C4	C3	127.2(9)	O2'	C9'	C10'	108.2(11)
O2	C9	C11	107.9(9)	C11'	C9'	C12'	105.2(13)
O2	C9	C12	111.7(9)	C10'	C9'	C11'	114.0(14)
O2'	C9'	C11'	109.6(10)	C10'	C9'	C12'	111.2(17)
O2'	C9'	C12'	108.5(10)				

Table 6. Torsion Angles for [Al(TFB-*t*BuA)(O^tBu)₂].

A	B	C	D	Angle/°
Al1	O2'	C9'	C11'	-77.5(13)
Al1	O2'	C9'	C12'	37.0(17)
Al1	O2'	C9'	C10'	157.7(14)
Al1	O1	C2	C3	2.1(16)
Al1	O1	C2	C1	-179.6(7)
Al1	O2	C9	C11	80.2(12)
Al1	O2	C9	C12	-36.2(14)
Al1	O2	C9	C10	-158.5(11)
Al1	N1	C4	C3	1.8(15)
Al1	N1	C5	C6	-12.1(11)
Al1	N1	C5	C7	-129.9(9)
Al1	N1	C5	C8	108.6(9)
O2'	Al1	O1	C2	-119.6(8)
O2'	Al1	O2	C9	-166.1(9)
O1	Al1	O2'	C9'	31.7(11)
O1	Al1	O2	C9	-42.5(10)
O1	C2	C3	C4	-0.4(18)

A	B	C	D	Angle/°
O2	Al1	O2'	C9'	155.8(9)
O2	Al1	O1	C2	117.2(8)
N1	Al1	O2'	C9'	-76.5(10)
N1	Al1	O1	C2	-1.6(9)
N1	Al1	O2	C9	66.5(10)
C2	C3	C4	N1	-1.8(19)
C3	C2	C1	F3	-8.5(16)
C3	C2	C1	F2	-128.4(11)
C3	C2	C1	F1	109.5(12)
C4	N1	C5	C6	171.6(9)
C4	N1	C5	C7	53.7(13)
C4	N1	C5	C8	-67.8(12)
C1	C2	C3	C4	-178.5(10)
C5	N1	C4	C3	178.2(10)
O1	C2	C1	F3	173.1(10)
O1	C2	C1	F2	53.2(12)
O1	C2	C1	F1	-68.9(12)

Table 7. Hydrogen Atom Coordinates ($\text{\AA}\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2\times 10^3$) for $[\text{Al}(\text{TFB-}i\text{BuA})(\text{O}^i\text{Bu})_2]$.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H3	-5122.65	2831.36	3029.32	35
H4	-4710.59	2010.02	4009.13	34
H6A	480.74	808.33	4406.41	46
H6B	128.65	822.69	5306.05	46
H6C	1066.39	1576.02	4927.43	46
H7A	-4737.45	890.97	4505.29	82
H7B	-3210.27	336.09	4905.69	82
H7C	-3043.92	493.4	4016.73	82
H8A	-1549.64	2222.47	5634.36	74
H8B	-3081.36	1520.61	5801.56	74
H8C	-3761.47	2200.18	5271.81	74
H11A	1594.36	2044.31	1840.13	86
H11B	2061.49	1244.51	1390.52	86
H11C	3773.6	1707.62	1899.04	86
H12A	-881.73	523.58	2841.47	69
H12B	-568.84	530.4	1940.07	69
H12C	-1261.83	1296.23	2394.93	69
H11D	4145.72	4002.33	3881.61	85
H11E	3262.82	4702.05	4382.76	85
H11F	1945.17	4277.21	3699.87	85
H10A	4434.94	589.65	2686.28	110
H10B	2748.44	15.36	2285.42	110
H10C	2749.43	201.27	3188.66	110
H12D	-644.75	3967.21	4284	128
H12E	-31.38	4313.02	5124.88	128
H12F	-765.89	3419.87	4995.65	128
H10D	2971.76	3128.92	5630.83	176
H10E	2835.95	4054.07	5729.38	176
H10F	4668.75	3684.83	5299.59	176

Table 8. Crystal data and structure refinement for [Ga(TFB-*t*BuA)(O^{*i*}Bu)₂].

Identification code	[Ga(TFB- <i>t</i> BuA)(O ^{<i>i</i>} Bu) ₂]
Empirical formula	C ₁₆ H ₂₉ F ₃ GaNO ₃
Formula weight	410.132
Temperature/K	100.0
Crystal system	monoclinic
Space group	P2 ₁ /n
<i>a</i> /Å	6.7262(5)
<i>b</i> /Å	17.3261(13)
<i>c</i> /Å	17.4520(11)
α /°	90
β /°	91.707(3)
γ /°	90
Volume/Å ³	2032.9(3)
<i>Z</i>	4
ρ_{calc} /cm ³	1.340
μ /mm ⁻¹	1.392
<i>F</i> (000)	857.8
Crystal size/mm ³	0.11 × 0.08 × 0.03
Radiation	Mo K α (λ = 0.71073)
2 Θ range for data collection/°	4.68 to 56.68
Index ranges	-8 ≤ <i>h</i> ≤ 8, -23 ≤ <i>k</i> ≤ 23, -22 ≤ <i>l</i> ≤ 23
Reflections collected	46556
Independent reflections	5047 [<i>R</i> _{int} = 0.0660, <i>R</i> _{sigma} = 0.0341]
Data/restraints/parameters	5047/0/226
Goodness-of-fit on <i>F</i> ²	1.025
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0454, <i>wR</i> ₂ = 0.1057
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0559, <i>wR</i> ₂ = 0.1142
Largest diff. peak/hole / e Å ⁻³	0.96/-0.77

Table 9. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ga}(\text{TfB}-t\text{BuA})(\text{O}^t\text{Bu})_2]$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Ga1	5721.7(4)	7303.37(16)	3878.00(15)	12.72(9)
F3	505(3)	8726.0(12)	2153.3(11)	37.9(5)
O2'	7248(3)	6541.3(11)	3520.2(10)	18.3(4)
O2	7285(3)	7829.4(11)	4549.5(11)	19.7(4)
O1	4726(3)	7937.0(12)	3077.3(11)	20.4(4)
N1	3160(3)	6971.1(13)	4285.8(12)	15.0(4)
F1	3291(4)	9250.4(17)	2389(2)	91.6(13)
F2	3097(4)	8274(2)	1642.1(14)	89.7(13)
C2	2825(4)	8047.1(16)	2957.9(15)	18.9(5)
C4	1508(4)	7230.4(16)	3985.0(16)	20.9(5)
C3	1296(4)	7747.6(16)	3343.2(17)	21.4(5)
C5	3031(4)	6430.9(16)	4959.9(15)	18.6(5)
C9	7039(4)	8614.2(17)	4789.3(18)	25.2(6)
C9'	6896(4)	6100.7(17)	2836.0(15)	21.1(5)
C8	5121(4)	6134.6(17)	5154.8(16)	21.5(5)
C6	2233(5)	6875(2)	5639.4(17)	32.9(7)
C7	1669(5)	5753.7(19)	4750(2)	31.8(7)
C1	2419(5)	8577(2)	2283(2)	35.4(8)
C10'	4697(5)	5917(2)	2710.2(18)	32.0(7)
C11'	7617(6)	6561(2)	2155.2(18)	39.7(8)
C10	4864(5)	8800(2)	4910(2)	41.1(9)
C12'	8076(6)	5361(2)	2944(2)	45.6(10)
C11	7843(6)	9157(2)	4180(3)	47.0(10)
C12	8230(9)	8694(3)	5536(3)	74.0(17)

Table 10. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for [Ga(TFB-*t*BuA)(O^tBu)₂].**The Anisotropic displacement factor exponent takes the form:**

$$-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots].$$

Atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ga1	7.81(14)	15.21(15)	15.27(15)	0.43(10)	2.41(9)	0.21(10)
F3	23.9(9)	52.1(13)	37.5(11)	10.1(8)	-1.8(8)	22.0(9)
O2'	13.4(8)	24.5(10)	16.9(9)	2.9(7)	1.1(7)	-4.1(7)
O2	16.3(9)	15.0(9)	27.4(10)	0.4(7)	-2.2(7)	-4.8(7)
O1	11.1(8)	26.4(10)	23.8(10)	1.0(7)	3.7(7)	8.7(8)
N1	10.7(9)	16.2(10)	18.2(10)	-1.6(8)	3.8(8)	2.3(8)
F1	59.1(17)	61.5(17)	151(3)	-29.3(14)	-43.5(18)	80(2)
F2	78.4(19)	161(3)	31.5(12)	76(2)	27.5(12)	45.4(16)
C2	18.9(12)	18.0(13)	19.9(12)	3.4(10)	0.8(10)	2.8(10)
C4	11.4(11)	24.5(14)	27.0(14)	-1.9(10)	5.7(10)	4.1(11)
C3	11.9(11)	24.3(14)	27.8(14)	3.7(10)	-0.6(10)	6.3(11)
C5	18.4(12)	19.5(13)	17.9(12)	-0.1(10)	4.4(10)	5.3(10)
C9	25.4(14)	18.0(14)	32.3(15)	0.1(11)	-0.1(12)	-9.2(11)
C9'	24.5(14)	24.0(14)	15.0(12)	3.4(11)	1.8(10)	-4.4(10)
C8	19.7(13)	25.1(14)	19.5(13)	0.9(11)	-1.0(10)	6.0(11)
C6	41.3(18)	34.8(18)	23.5(15)	10.9(14)	17.8(13)	9.1(13)
C7	26.1(15)	28.1(16)	40.5(18)	-9.1(13)	-7.0(13)	13.7(13)
C1	21.5(15)	47(2)	38.4(18)	6.1(14)	3.9(13)	22.0(15)
C10'	30.6(16)	37.6(18)	27.6(16)	-7.9(14)	-0.3(12)	-11.2(13)
C11'	45(2)	54(2)	20.6(15)	-9.6(17)	11.4(14)	-3.6(15)
C10	36.4(18)	23.1(16)	65(2)	-1.7(14)	23.0(17)	-9.9(16)
C12'	60(2)	39(2)	37.1(19)	27.1(18)	-10.5(17)	-19.6(16)
C11	51(2)	21.7(16)	70(3)	-6.6(15)	30(2)	-1.8(17)
C12	109(4)	42(2)	68(3)	16(3)	-46(3)	-32(2)

Table 11. Bond Lengths for [Ga(TFB-*t*BuA)(O^tBu)₂].

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ga1	O2'	1.7959(18)	C2	C3	1.349(4)
Ga1	O2	1.7989(19)	C2	C1	1.512(4)
Ga1	O1	1.8843(19)	C4	C3	1.438(4)
Ga1	N1	1.970(2)	C5	C8	1.526(4)
F3	C1	1.326(4)	C5	C6	1.524(4)
O2'	C9'	1.431(3)	C5	C7	1.527(4)
O2	C9	1.434(3)	C9	C10	1.519(4)
O1	C2	1.303(3)	C9	C11	1.530(5)
N1	C4	1.295(3)	C9	C12	1.516(5)
N1	C5	1.508(3)	C9'	C10'	1.522(4)
F1	C1	1.317(5)	C9'	C11'	1.522(4)
F2	C1	1.328(4)	C9'	C12'	1.517(4)

Table 12. Bond Angles for [Ga(TFB-*t*BuA)(O^tBu)₂].

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	Ga1	O2'	105.66(8)	C7	C5	C8	109.7(2)
O1	Ga1	O2'	111.39(8)	C7	C5	C6	110.6(3)
O1	Ga1	O2	112.08(9)	C10	C9	O2	111.2(2)
N1	Ga1	O2'	115.21(9)	C11	C9	O2	109.5(2)
N1	Ga1	O2	114.41(9)	C11	C9	C10	109.2(3)
N1	Ga1	O1	98.21(8)	C12	C9	O2	106.0(3)
C9'	O2'	Ga1	126.89(16)	C12	C9	C10	110.3(3)
C9	O2	Ga1	126.90(17)	C12	C9	C11	110.7(4)
C2	O1	Ga1	121.96(17)	C10'	C9'	O2'	111.6(2)
C4	N1	Ga1	120.08(18)	C11'	C9'	O2'	108.8(2)
C5	N1	Ga1	122.31(16)	C11'	C9'	C10'	109.1(3)
C5	N1	C4	117.6(2)	C12'	C9'	O2'	105.9(2)
C3	C2	O1	128.5(2)	C12'	C9'	C10'	110.1(3)
C1	C2	O1	111.6(2)	C12'	C9'	C11'	111.3(3)
C1	C2	C3	119.9(2)	F1	C1	F3	106.1(3)
C3	C4	N1	126.6(2)	F2	C1	F3	106.8(3)
C4	C3	C2	124.7(2)	F2	C1	F1	107.8(3)
C8	C5	N1	108.0(2)	C2	C1	F3	113.8(3)
C6	C5	N1	108.9(2)	C2	C1	F1	111.1(3)
C6	C5	C8	109.9(2)	C2	C1	F2	111.0(3)
C7	C5	N1	109.7(2)				

Table 13. Torsion Angles for [Ga(TFB-*t*BuA)(O^tBu)₂].

A	B	C	D	Angle/°
Ga1	O2'	C9'	C10'	-38.8(2)
Ga1	O2'	C9'	C11'	81.7(2)
Ga1	O2'	C9'	C12'	-158.6(3)
Ga1	O2	C9	C10	40.6(2)
Ga1	O2	C9	C11	-80.1(3)
Ga1	O2	C9	C12	160.6(3)
Ga1	O1	C2	C3	-0.9(3)
Ga1	O1	C2	C1	-180.0(2)
Ga1	N1	C4	C3	1.5(3)
Ga1	N1	C5	C8	-7.77(19)
Ga1	N1	C5	C6	111.5(2)
Ga1	N1	C5	C7	-127.3(2)
F3	C1	C2	O1	-178.0(3)
F3	C1	C2	C3	2.9(4)
O2'	Ga1	O2	C9	156.99(18)
O2'	Ga1	O1	C2	122.72(18)
O2	Ga1	O2'	C9'	-161.62(17)

A	B	C	D	Angle/°
O2	Ga1	O1	C2	-119.12(18)
O1	Ga1	O2'	C9'	-39.67(16)
O1	Ga1	O2	C9	35.49(17)
O1	C2	C3	C4	0.1(4)
O1	C2	C1	F1	-58.3(3)
O1	C2	C1	F2	61.5(3)
N1	Ga1	O2'	C9'	71.05(17)
N1	Ga1	O2	C9	-75.19(18)
N1	Ga1	O1	C2	1.48(17)
N1	C4	C3	C2	-0.5(4)
F1	C1	C2	C3	122.5(3)
F2	C1	C2	C3	-117.6(3)
C4	N1	C5	C8	173.7(3)
C4	N1	C5	C6	-67.0(3)
C4	N1	C5	C7	54.2(3)
C4	C3	C2	C1	179.1(3)
C3	C4	N1	C5	-180.0(3)

Table 14. Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ga}(\text{TFB-}i\text{BuA})(\text{O}^i\text{Bu})_2]$.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H4	316(4)	7062.0(16)	4211.0(16)	25.0(7)
H3	-13(4)	7888.4(16)	3178.9(17)	25.6(7)
H8a	5632(13)	5855(11)	4714(5)	32.2(8)
H8b	5997(8)	6571.7(19)	5280(12)	32.2(8)
H8c	5077(6)	5786(10)	5596(8)	32.2(8)
H6a	3120(20)	7308(9)	5764(9)	49.3(11)
H6b	899(16)	7071(12)	5508(5)	49.3(11)
H6c	2170(40)	6530(4)	6083(4)	49.3(11)
H7a	322(9)	5945(2)	4635(14)	47.6(11)
H7b	2170(20)	5490(9)	4298(9)	47.6(11)
H7c	1640(30)	5392(7)	5180(6)	47.6(11)
H10a	4210(10)	5641(13)	3158(6)	47.9(11)
H10b	3948(7)	6398(2)	2639(14)	47.9(11)
H10c	4517(6)	5592(12)	2253(8)	47.9(11)
H11a	6880(30)	7049(8)	2118(10)	59.6(13)
H11b	9041(10)	6668(14)	2226(8)	59.6(13)
H11c	7390(40)	6263(7)	1684(3)	59.6(13)
H10d	4126(10)	8774(16)	4418(3)	61.6(13)
H10e	4311(12)	8425(10)	5267(13)	61.6(13)
H10f	4752(6)	9321(7)	5124(15)	61.6(13)
H12a	9479(9)	5486(2)	3048(17)	68.4(15)
H12b	7560(30)	5071(8)	3377(11)	68.4(15)
H12c	7950(40)	5047(8)	2478(7)	68.4(15)
H11d	9238(14)	9031(12)	4092(13)	70.6(15)
H11e	7060(30)	9094(13)	3701(6)	70.6(15)
H11f	7740(40)	9692(2)	4357(8)	70.6(15)
H12d	7730(40)	8325(17)	5911(8)	111(3)
H12e	9635(12)	8590(20)	5447(5)	111(3)
H12f	8090(50)	9220(8)	5734(13)	111(3)

Table 15. Crystal data and structure refinement for [Zr(TFB-MEA)₂(NEt₂)₂].

Identification code	[Zr(TFB-MEA) ₂ (NEt ₂) ₂]
Empirical formula	C ₂₂ H ₃₈ F ₆ N ₄ O ₄ Zr
Formula weight	627.78
Temperature/K	100.00
Crystal system	triclinic
Space group	P-1
a/Å	9.4389(6)
b/Å	9.4441(5)
c/Å	16.1309(10)
α /°	92.836(2)
β /°	92.847(3)
γ /°	90.381(2)
Volume/Å ³	1434.35(15)
Z	2
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.454
μ/mm^{-1}	0.455
F(000)	648.0
Crystal size/mm ³	0.18 × 0.15 × 0.13
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	4.318 to 77.316
Index ranges	-16 ≤ h ≤ 16, -16 ≤ k ≤ 16, -28 ≤ l ≤ 28
Reflections collected	204458
Independent reflections	16292 [R _{int} = 0.0652, R _{sigma} = 0.0302]
Data/restraints/parameters	16292/0/340
Goodness-of-fit on F ²	1.122
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0293, wR ₂ = 0.0645
Final R indexes [all data]	R ₁ = 0.0358, wR ₂ = 0.0691
Largest diff. peak/hole / e Å ⁻³	0.70/-0.71

Table 16. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Zr1	7709.8(2)	2290.0(2)	2500.1(2)	10.33(2)
F1'	4148.0(8)	-171.0(8)	3863.6(4)	30.51(14)
F1	10170.0(8)	5850.8(8)	1136.1(4)	30.58(15)
F2	11632.7(7)	5149.6(8)	2091.4(5)	32.84(16)
O1	8962.7(7)	3972.5(7)	2169.5(4)	16.03(11)
O1'	6028.0(7)	1036.7(7)	2830.9(4)	16.03(11)
F2'	4850.1(9)	-1632.1(7)	2908.8(5)	32.71(16)
F3'	2758.3(8)	-749.1(9)	2805.0(5)	36.38(17)
F3	10748.6(9)	7241.5(8)	2195.2(5)	36.31(17)
O2	6984.9(9)	4160.5(8)	5114.2(5)	22.68(13)
O2'	5838.9(8)	3014.8(9)	-114.4(5)	22.86(13)
N2	8299.1(8)	927.8(8)	1549.3(5)	15.00(12)
N2'	9072.0(8)	1701.6(8)	3450.5(5)	14.97(12)
N1	6845.7(8)	4273.1(8)	3334.3(5)	15.69(12)
N1'	5725.4(8)	3153.6(8)	1666.4(5)	15.68(12)
C2'	4716.2(9)	771.7(10)	2596.1(6)	17.02(14)
C3'	3921.3(10)	1471.7(12)	2030.7(6)	21.76(17)
C10'	9919.2(10)	2628.7(10)	4038.0(6)	17.72(14)
C10	7370.8(10)	82.3(10)	961.9(6)	17.87(14)
C4'	4445.5(10)	2656.5(11)	1604.5(6)	19.87(16)
C9'	9226.0(11)	186.7(10)	3594.0(6)	19.49(15)
C3	8526.9(12)	6077.1(10)	2969.4(6)	21.75(17)
C9	9812.5(10)	775.3(11)	1407.1(6)	19.40(15)
C6	6078.6(11)	3235.6(11)	4609.2(6)	21.56(17)
C4	7340.7(11)	5553.0(10)	3395.5(6)	20.04(16)
C5	5627.4(10)	4001.6(11)	3841.2(6)	20.69(16)
C8	10323.6(11)	1665.9(12)	712.4(7)	23.85(18)
C2	9228.1(10)	5283.7(9)	2404.3(6)	17.21(14)
C1'	4102.0(11)	-449.4(11)	3041.4(7)	22.63(17)
C11	7344.6(12)	-1490.8(11)	1134.1(7)	25.18(19)
C11'	11491.1(11)	2655.3(12)	3865.8(7)	25.13(19)
C8'	8334.5(12)	-324.1(11)	4288.2(7)	23.74(18)
C1	10447.5(11)	5897.1(11)	1959.2(7)	22.40(17)
C5'	5996.3(11)	4371.8(10)	1159.6(6)	20.75(16)
C7	7540.4(14)	3510.4(13)	5832.8(7)	29.0(2)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
C6'	6764.8(11)	3921.2(11)	392.1(6)	21.71(17)
C7'	6489.5(13)	2460.9(14)	-832.6(7)	29.2(2)

Table 17. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$.

The Anisotropic displacement factor exponent takes the form:

$$-2\pi^2[\text{h}^2\text{a}^{*2}\text{U}_{11}+2\text{hka}^*\text{b}^*\text{U}_{12}+\dots].$$

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Zr1	10.56(3)	10.61(3)	9.71(3)	0.07(2)	-0.08(2)	0.58(2)
F1'	34.6(4)	35.9(4)	21.9(3)	3.7(3)	8.7(3)	-7.9(3)
F1	35.4(4)	35.3(4)	21.9(3)	8.8(3)	4.1(3)	-7.7(3)
F2	19.8(3)	36.6(4)	43.3(4)	13.4(3)	2.9(3)	-3.0(3)
O1	17.3(3)	12.9(2)	17.9(3)	0.5(2)	2.1(2)	-1.4(2)
O1'	12.7(2)	17.7(3)	17.8(3)	2.2(2)	0.3(2)	-1.5(2)
F2'	36.3(4)	20.3(3)	42.8(4)	2.7(3)	13.5(3)	-2.9(3)
F3'	21.8(3)	44.2(4)	43.3(4)	7.9(3)	-0.3(3)	-17.5(3)
F3	43.8(4)	21.9(3)	43.4(4)	-0.2(3)	8.3(3)	-17.4(3)
O2	30.7(4)	21.3(3)	16.0(3)	0.2(2)	2.0(3)	-3.2(3)
O2'	21.0(3)	31.6(4)	15.9(3)	2.2(3)	0.3(2)	-3.3(3)
N2	14.1(3)	17.0(3)	13.6(3)	-3.0(2)	0.8(2)	1.5(2)
N2'	16.2(3)	14.7(3)	13.7(3)	0.7(2)	-2.7(2)	1.5(2)
N1	16.8(3)	16.3(3)	13.8(3)	-0.9(2)	1.0(2)	2.7(2)
N1'	16.2(3)	16.7(3)	14.1(3)	1.4(2)	-1.1(2)	3.0(2)
C2'	13.4(3)	20.2(4)	17.3(3)	-0.7(3)	2.2(3)	-3.0(3)
C3'	13.1(3)	29.6(5)	22.5(4)	2.3(3)	-1.2(3)	-2.2(3)
C10'	17.8(3)	17.9(3)	16.8(3)	-1.1(3)	-4.2(3)	1.0(3)
C10	17.5(3)	18.3(3)	17.0(3)	-4.4(3)	-1.4(3)	1.2(3)
C4'	15.1(3)	25.4(4)	18.8(4)	1.6(3)	-3.3(3)	3.0(3)
C9'	25.4(4)	15.0(3)	17.8(4)	1.8(3)	-3.1(3)	2.6(3)
C3	29.5(5)	13.1(3)	22.4(4)	-1.3(3)	2.2(3)	-2.4(3)
C9	15.0(3)	25.5(4)	17.3(4)	-3.8(3)	1.4(3)	2.5(3)
C6	25.6(4)	20.4(4)	18.9(4)	-3.2(3)	8.1(3)	-4.0(3)
C4	25.4(4)	15.6(3)	18.9(4)	-3.2(3)	1.8(3)	3.1(3)
C5	17.2(4)	25.1(4)	19.5(4)	-6.0(3)	4.8(3)	1.9(3)
C8	20.4(4)	29.4(5)	21.9(4)	-3.3(4)	8.0(3)	-0.7(3)
C2	19.9(4)	14.2(3)	17.5(3)	2.6(3)	-0.9(3)	-3.3(3)
C1'	18.9(4)	25.3(4)	23.8(4)	0.0(3)	4.6(3)	-6.4(3)
C11	26.7(5)	18.7(4)	29.7(5)	-2.9(3)	1.5(4)	-1.9(3)

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C11'	18.2(4)	27.6(5)	29.2(5)	1.3(4)	-2.5(3)	-2.0(3)
C8'	29.2(5)	20.4(4)	21.9(4)	7.0(3)	-2.8(3)	-0.8(3)
C1	25.1(4)	18.6(4)	23.6(4)	3.8(3)	0.2(3)	-6.2(3)
C5'	24.4(4)	18.3(4)	19.2(4)	4.6(3)	-5.8(3)	2.0(3)
C7	37.7(6)	29.8(5)	19.9(4)	4.5(4)	2.9(4)	2.6(4)
C6'	20.2(4)	25.9(4)	19.1(4)	8.2(3)	-3.4(3)	-4.1(3)
C7'	30.3(5)	37.7(6)	20.0(4)	3.4(4)	4.4(4)	2.5(4)

Table 18. Bond Lengths for [Zr(TFB-MEA)₂(NEt₂)₂].

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zr1	O1	2.0807(6)	N2	C9	1.4650(12)
Zr1	O1'	2.0802(6)	N2'	C10'	1.4620(12)
Zr1	N2	2.0533(7)	N2'	C9'	1.4676(12)
Zr1	N2'	2.0519(7)	N1	C4	1.2905(12)
Zr1	N1	2.4214(7)	N1	C5	1.4720(12)
Zr1	N1'	2.4209(7)	N1'	C4'	1.2907(12)
F1'	C1'	1.3377(13)	N1'	C5'	1.4722(12)
F1	C1	1.3391(13)	C2'	C3'	1.3528(14)
F2	C1	1.3405(13)	C2'	C1'	1.5154(14)
O1	C2	1.2960(11)	C3'	C4'	1.4394(15)
O1'	C2'	1.2958(11)	C10'	C11'	1.5233(14)
F2'	C1'	1.3393(13)	C10	C11	1.5251(14)
F3'	C1'	1.3306(12)	C9'	C8'	1.5285(15)
F3	C1	1.3320(12)	C3	C4	1.4400(15)
O2	C6	1.4173(13)	C3	C2	1.3525(14)
O2	C7	1.4177(14)	C9	C8	1.5289(15)
O2'	C6'	1.4192(13)	C6	C5	1.5100(15)
O2'	C7'	1.4170(14)	C2	C1	1.5134(14)
N2	C10	1.4617(12)	C5'	C6'	1.5103(15)

Table 19. Bond Angles for [Zr(TFB-MEA)₂(NEt₂)₂].

Atom	Atom	Atom	Angle/°
O1	Zr1	N1	77.03(3)
O1	Zr1	N1'	90.36(3)
O1'	Zr1	O1	164.12(3)
O1'	Zr1	N1	90.38(3)
O1'	Zr1	N1'	77.06(3)
N2	Zr1	O1	95.01(3)
N2	Zr1	O1'	95.10(3)
N2	Zr1	N1	165.45(3)
N2	Zr1	N1'	92.04(3)
N2'	Zr1	O1	95.11(3)
N2'	Zr1	O1'	94.97(3)
N2'	Zr1	N2	100.90(3)
N2'	Zr1	N1	92.01(3)
N2'	Zr1	N1'	165.43(3)
N1'	Zr1	N1	76.04(3)
C2	O1	Zr1	139.05(6)
C2'	O1'	Zr1	139.01(6)
C6	O2	C7	112.26(8)
C7'	O2'	C6'	112.29(9)
C10	N2	Zr1	127.50(6)
C10	N2	C9	114.01(7)
C9	N2	Zr1	118.48(6)
C10'	N2'	Zr1	127.55(6)
C10'	N2'	C9'	113.90(7)
C9'	N2'	Zr1	118.54(6)
C4	N1	Zr1	127.43(6)
C4	N1	C5	115.49(8)
C5	N1	Zr1	117.07(6)
C4'	N1'	Zr1	127.40(6)
C4'	N1'	C5'	115.52(8)
C5'	N1'	Zr1	117.08(6)

Atom	Atom	Atom	Angle/°
O1'	C2'	C3'	126.55(9)
O1'	C2'	C1'	112.28(8)
C3'	C2'	C1'	121.16(8)
C2'	C3'	C4'	123.28(9)
N2'	C10'	C11'	113.51(8)
N2	C10	C11	113.48(8)
N1'	C4'	C3'	126.05(8)
N2'	C9'	C8'	113.82(8)
C2	C3	C4	123.33(9)
N2	C9	C8	113.81(8)
O2	C6	C5	107.65(8)
N1	C4	C3	126.00(9)
N1	C5	C6	111.16(8)
O1	C2	C3	126.50(9)
O1	C2	C1	112.29(8)
C3	C2	C1	121.21(8)
F1'	C1'	F2'	106.79(9)
F1'	C1'	C2'	111.06(8)
F2'	C1'	C2'	110.85(8)
F3'	C1'	F1'	107.16(8)
F3'	C1'	F2'	107.31(9)
F3'	C1'	C2'	113.36(9)
F1	C1	F2	106.69(9)
F1	C1	C2	111.14(8)
F2	C1	C2	110.89(8)
F3	C1	F1	107.12(8)
F3	C1	F2	107.26(9)
F3	C1	C2	113.42(9)
N1'	C5'	C6'	111.13(8)
O2'	C6'	C5'	107.64(8)

Table 20. Torsion Angles for [Zr(TFB-MEA)₂(NEt₂)₂].

A	B	C	D	Angle/°
Zr1	O1	C2	C3	-8.92(16)
Zr1	O1	C2	C1	171.89(7)
Zr1	O1'	C2'	C3'	-8.86(16)
Zr1	O1'	C2'	C1'	171.89(7)
Zr1	N2	C10	C11	-105.60(9)
Zr1	N2	C9	C8	-98.24(8)
Zr1	N2'	C10'	C11'	-105.54(9)
Zr1	N2'	C9'	C8'	-98.18(8)
Zr1	N1	C4	C3	0.31(15)
Zr1	N1	C5	C6	76.87(8)
Zr1	N1'	C4'	C3'	0.50(15)
Zr1	N1'	C5'	C6'	76.77(8)
O1	C2	C1	F1	59.77(11)
O1	C2	C1	F2	-58.72(11)
O1	C2	C1	F3	-179.47(9)
O1'	C2'	C3'	C4'	-0.57(17)
O1'	C2'	C1'	F1'	59.83(11)
O1'	C2'	C1'	F2'	-58.72(11)
O1'	C2'	C1'	F3'	-179.46(9)
O2	C6	C5	N1	65.28(10)
N1'	C5'	C6'	O2'	65.38(10)

A	B	C	D	Angle/°
C2'	C3'	C4'	N1'	3.82(17)
C3'	C2'	C1'	F1'	-119.46(11)
C3'	C2'	C1'	F2'	121.99(11)
C3'	C2'	C1'	F3'	1.25(14)
C10'	N2'	C9'	C8'	80.50(10)
C10	N2	C9	C8	80.41(10)
C4'	N1'	C5'	C6'	-102.43(10)
C9'	N2'	C10'	C11'	75.92(10)
C3	C2	C1	F1	-119.47(11)
C3	C2	C1	F2	122.03(11)
C3	C2	C1	F3	1.29(14)
C9	N2	C10	C11	75.89(10)
C4	N1	C5	C6	-102.43(10)
C4	C3	C2	O1	-0.57(17)
C4	C3	C2	C1	178.56(9)
C5	N1	C4	C3	179.52(9)
C2	C3	C4	N1	3.95(17)
C1'	C2'	C3'	C4'	178.62(9)
C5'	N1'	C4'	C3'	179.60(9)
C7	O2	C6	C5	-176.47(8)
C7'	O2'	C6'	C5'	-176.52(8)

Table 21. Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H3'	2969.44	1166.07	1908.8	26
H10A	9809.31	2309.65	4606.91	21
H10B	9547.02	3604.63	4017.55	21
H10C	7689.28	192.72	392.88	21
H10D	6394.38	454.3	982.78	21
H4'	3788.35	3115.16	1244.38	24
H9'A	10236.87	-7.44	3734.02	23
H9'B	8951.45	-366.03	3072.62	23
H3	8832.53	7028.34	3091.44	26
H9A	10007.99	-235.01	1267.85	23
H9B	10364.76	1051.01	1928.58	23
H6A	5237.51	2978.77	4914.74	26
H6B	6585.79	2355.43	4453.1	26
H4	6880.25	6209.99	3754.63	24
H5A	4909.6	3422.01	3506.15	25
H5B	5185.66	4913.41	4007.15	25
H8A	9780.66	1403.86	193.22	36
H8B	11333.32	1491.58	639.73	36
H8C	10184.49	2673.08	858.91	36
H11A	6699.85	-1995.15	723.7	38
H11B	7015.27	-1611.86	1693.06	38
H11C	8301.96	-1876.13	1096.08	38
H11D	11612.8	2997.85	3309.92	38
H11E	11873.79	1696.02	3895.72	38
H11F	11998.08	3288.95	4281.01	38
H8'A	7326.76	-187.28	4140.64	36
H8'B	8594.63	220.05	4807.1	36
H8'C	8510.71	-1332.7	4361.89	36
H5'A	6574.81	5089.92	1494.89	25
H5'B	5083.64	4812.03	992.87	25
H7A	7992.45	2615.49	5668.65	43
H7B	6769.19	3322.63	6198.36	43
H7C	8243.56	4143.87	6128.12	43
H6'A	7022.83	4762.06	87.06	26
H6'B	7644.94	3413.94	549.02	26
H7'A	6687.66	3233.79	-1194.82	44

Atom	x	y	z	U(eq)
H7'B	5851.41	1766.46	-1131.81	44
H7'C	7379.5	1999.37	-667.87	44

Table 22. Crystal data and structure refinement for [Zr(TFB-*t*BuA)₂(NEt₂)₂].

Identification code	[Zr(TFB- <i>t</i> BuA) ₂ (NEt ₂) ₂]
Empirical formula	C ₂₄ H ₄₂ F ₆ N ₄ O ₂ Zr
Formula weight	623.83
Temperature/K	100.00
Crystal system	monoclinic
Space group	P2 ₁ /c
<i>a</i> /Å	11.1842(5)
<i>b</i> /Å	15.6050(7)
<i>c</i> /Å	17.5821(9)
α /°	90
β /°	104.990(2)
γ /°	90
Volume/Å ³	2964.2(2)
<i>Z</i>	4
ρ_{calc} /cm ³	1.398
μ /mm ⁻¹	0.435
<i>F</i> (000)	1296.0
Crystal size/mm ³	0.08 × 0.06 × 0.05
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	3.77 to 56.63
Index ranges	-14 ≤ <i>h</i> ≤ 14, -20 ≤ <i>k</i> ≤ 20, -23 ≤ <i>l</i> ≤ 23
Reflections collected	79081
Independent reflections	7376 [<i>R</i> _{int} = 0.0968, <i>R</i> _{sigma} = 0.0452]
Data/restraints/parameters	7376/0/348
Goodness-of-fit on <i>F</i> ²	1.049
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0383, <i>wR</i> ₂ = 0.0802
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0651, <i>wR</i> ₂ = 0.0966
Largest diff. peak/hole / e Å ⁻³	0.70/-0.51

Table 23. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Zr}(\text{TfB-}i\text{BuA})_2(\text{NEt}_2)_2]$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Zr1	7477.9(2)	4237.5(2)	2490.9(2)	14.32(7)
O1	5571.3(15)	4051.6(11)	2135.9(10)	18.1(4)
O1'	9289.4(16)	4669.7(11)	2847.3(11)	19.8(4)
N2'	7769(2)	3273.5(13)	3312.6(13)	18.8(4)
N2	7789.0(19)	3500.9(13)	1594.4(12)	17.5(4)
N1	6720.4(19)	5439.9(13)	1500.5(13)	17.7(4)
N1'	7445(2)	5277.8(14)	3608.8(13)	20.0(4)
C3	4557(2)	4960.8(17)	1100.6(16)	19.3(5)
C4	5602(2)	5487.5(16)	1061.0(16)	19.7(5)
C6'	5383(3)	5896.6(18)	3118.4(16)	25.6(6)
C3'	9685(3)	5550.3(17)	3975.7(16)	24.3(6)
C2	4595(2)	4317.7(16)	1615.7(15)	19.0(5)
C2'	10025(2)	5104.1(17)	3406.2(16)	22.1(5)
C11	6966(2)	3408.8(17)	803.8(15)	20.9(5)
C10'	8543(2)	3307.8(17)	4120.8(16)	21.9(5)
C5'	6252(3)	5459.7(17)	3832.4(16)	22.8(6)
C7'	5719(3)	4597.0(18)	4002.8(17)	27.7(6)
C10	8872(2)	2933.3(17)	1725.9(17)	23.1(6)
C7	8628(3)	5589.0(18)	1080.2(18)	27.0(6)
C1'	11357(2)	5083.2(19)	3360.3(17)	26.6(6)
C4'	8439(3)	5614.0(17)	4054.2(16)	24.2(6)
C1	3426(2)	3839.3(18)	1642.5(17)	23.6(6)
C8	8145(3)	6585.1(17)	2098.6(17)	25.1(6)
C5	7623(2)	6095.1(17)	1335.6(16)	21.4(5)
C6	7061(3)	6748.7(18)	697.7(17)	27.7(6)
C12	6168(3)	2607.0(18)	706.6(17)	25.6(6)
C11'	7181(3)	2430.8(17)	3111.7(17)	26.6(6)
F1	2418.2(14)	4147.7(12)	1141.9(12)	39.1(5)
F1'	11473.6(16)	5401.7(14)	2679.8(11)	42.7(5)
F3	3239.1(16)	3862.7(13)	2358.8(11)	39.3(5)
C8'	6378(3)	6039.5(19)	4548.3(17)	30.8(7)
F3'	12120.7(15)	5532.9(12)	3938.1(11)	38.4(4)
F2'	11793.8(15)	4279.6(11)	3417.2(11)	34.5(4)
F2	3499.3(15)	3008.5(11)	1464.5(11)	34.8(4)
C12'	6082(3)	2287(2)	3452.4(19)	37.3(8)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
C9'	9775(3)	2843(2)	4233.1(19)	34.5(7)
C9	9893(3)	3257(2)	1375(2)	37.0(7)

Table 24. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Zr}(\text{TFB-}i\text{BuA})_2(\text{NEt}_2)_2]$.

The Anisotropic displacement factor exponent takes the form:

$$-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots].$$

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Zr1	15.46(11)	12.95(11)	14.30(11)	-0.1(1)	3.40(8)	-0.28(9)
O1	17.7(8)	17.4(9)	19.4(9)	1.5(7)	4.9(7)	0.7(7)
O1'	19.7(9)	18.7(9)	20.0(10)	-1.1(7)	3.2(7)	-1.7(7)
N2'	24.8(11)	14.8(10)	16.5(11)	1.1(8)	4.6(9)	-0.3(8)
N2	17.1(10)	17.5(10)	17.8(11)	-2.2(8)	4.5(8)	0.1(8)
N1	18.6(10)	15.1(10)	18.8(11)	0.3(8)	3.8(8)	-0.9(8)
N1'	25.3(11)	17.0(10)	17.7(11)	0.5(8)	5.5(9)	2.7(9)
C3	15.6(12)	20.7(13)	20.0(13)	-0.8(10)	1.5(10)	1.1(10)
C4	25.7(13)	14.8(11)	18.4(13)	0.3(10)	5.4(10)	0.3(10)
C6'	29.7(14)	26.8(14)	20.9(14)	-1.8(11)	7.5(11)	6.4(11)
C3'	27.1(14)	20.9(13)	19.8(14)	-3.0(11)	-3.3(11)	-4.9(11)
C2	18.1(12)	19.6(12)	20.2(13)	-5.2(10)	6.6(10)	-0.5(10)
C2'	21.4(12)	20.6(13)	21.1(14)	4.1(11)	-0.1(10)	-3.0(10)
C11	22.2(12)	22.1(13)	18.3(13)	-0.8(10)	5.2(10)	-0.1(10)
C10'	28.0(13)	17.1(12)	19.0(13)	0.2(10)	3.2(11)	-0.3(10)
C5'	29.8(14)	20.7(13)	19.3(14)	1.4(11)	9.3(11)	5.6(11)
C7'	34.5(15)	28.0(14)	25.7(15)	2.0(12)	17.1(12)	3.5(12)
C10	22.1(13)	23.8(13)	23.8(14)	-4.7(11)	6.8(11)	2.0(11)
C7	25.7(14)	26.0(15)	31.0(16)	4.8(12)	10.5(12)	-4.1(11)
C1'	21.0(13)	32.1(15)	24.0(15)	0.5(12)	0.5(11)	-4.5(11)
C4'	33.0(14)	20.4(13)	17.4(13)	-3.8(10)	3.0(11)	-0.3(11)
C1	20.3(12)	24.6(14)	27.1(15)	-2.7(11)	8.4(11)	-2.9(11)
C8	27.4(14)	18.5(13)	27.0(15)	2.3(11)	2.9(11)	-4.6(11)
C5	23.3(13)	18.5(12)	21.4(14)	3.9(10)	4.0(10)	-4.3(10)
C6	27.5(14)	23.0(14)	29.7(16)	8.4(12)	1.8(12)	-7.2(11)
C12	25.2(13)	27.8(14)	22.7(14)	-2.3(11)	4.2(11)	-3.8(11)
C11'	36.6(15)	18.1(13)	23.5(15)	0.1(11)	5.2(12)	-4.8(11)
F1	15.2(8)	45.4(11)	52.6(12)	12.8(9)	1.5(8)	-3.5(7)
F1'	28.1(9)	64.6(13)	35.8(11)	16.2(10)	8.9(8)	-9.5(9)
F3	31.5(9)	59.7(12)	32.7(10)	-6.2(9)	19.0(8)	-11.9(9)

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C8'	42.1(17)	29.5(15)	21.2(15)	1.5(12)	8.7(13)	11.3(13)
F3'	24.1(8)	40.2(10)	43.1(11)	-6.7(8)	-5.4(8)	-8.8(8)
F2'	25.0(8)	34.6(10)	42.5(11)	-2.9(8)	6.3(8)	5.3(7)
F2	29.8(9)	23.8(9)	53.3(12)	-4.0(8)	15.1(8)	-8.9(7)
C12'	49.0(19)	33.2(17)	30.0(17)	-4.4(14)	10.6(15)	-20.2(15)
C9'	31.3(16)	37.8(17)	30.7(17)	-1.2(14)	1.2(13)	10.9(13)
C9	27.9(15)	41.6(18)	47(2)	2.3(15)	19.3(14)	5.4(13)

Table 25. Bond Lengths for [Zr(TFB-*t*BuA)₂(NEt₂)₂].

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zr1	O1	2.0814(17)	C3'	C2'	1.352(4)
Zr1	O1'	2.0725(17)	C3'	C4'	1.439(4)
Zr1	N2'	2.053(2)	C2	C1	1.517(3)
Zr1	N2	2.052(2)	C2'	C1'	1.514(4)
Zr1	N1	2.551(2)	C11	C12	1.520(4)
Zr1	N1'	2.557(2)	C10'	C9'	1.523(4)
O1	C2	1.298(3)	C5'	C7'	1.533(4)
O1'	C2'	1.297(3)	C5'	C8'	1.527(4)
N2'	C10'	1.462(3)	C10	C9	1.517(4)
N2'	C11'	1.472(3)	C7	C5	1.533(4)
N2	C11	1.462(3)	C1'	F1'	1.333(3)
N2	C10	1.470(3)	C1'	F3'	1.343(3)
N1	C4	1.291(3)	C1'	F2'	1.340(3)
N1	C5	1.516(3)	C1	F1	1.328(3)
N1'	C5'	1.512(3)	C1	F3	1.329(3)
N1'	C4'	1.294(3)	C1	F2	1.341(3)
C3	C4	1.446(4)	C8	C5	1.523(4)
C3	C2	1.345(4)	C5	C6	1.526(4)
C6'	C5'	1.534(4)	C11'	C12'	1.516(4)

Table 26. Bond Angles for [Zr(TFB-*t*BuA)₂(NEt₂)₂].

Atom	Atom	Atom	Angle/°
O1	Zr1	N1	76.36(7)
O1	Zr1	N1'	95.82(7)
O1'	Zr1	O1	168.98(7)
O1'	Zr1	N1	95.35(7)
O1'	Zr1	N1'	76.61(7)
N2'	Zr1	O1	94.15(8)
N2'	Zr1	O1'	93.50(8)
N2'	Zr1	N1	169.65(8)
N2'	Zr1	N1'	87.45(8)
N2	Zr1	O1	93.19(7)
N2	Zr1	O1'	93.89(8)
N2	Zr1	N2'	95.89(9)
N2	Zr1	N1	88.86(8)
N2	Zr1	N1'	170.14(8)
N1	Zr1	N1'	89.40(7)
C2	O1	Zr1	140.94(16)
C2'	O1'	Zr1	141.04(17)
C10'	N2'	Zr1	127.13(16)
C10'	N2'	C11'	112.4(2)
C11'	N2'	Zr1	120.42(17)
C11	N2	Zr1	126.52(16)
C11	N2	C10	112.4(2)
C10	N2	Zr1	120.89(17)
C4	N1	Zr1	123.38(17)
C4	N1	C5	115.9(2)
C5	N1	Zr1	120.43(15)
C5'	N1'	Zr1	120.55(16)
C4'	N1'	Zr1	122.78(18)
C4'	N1'	C5'	116.4(2)
C2	C3	C4	124.8(2)
N1	C4	C3	127.5(2)
C2'	C3'	C4'	124.8(2)
O1	C2	C3	126.0(2)
O1	C2	C1	113.3(2)

Atom	Atom	Atom	Angle/°
C3	C2	C1	120.7(2)
O1'	C2'	C3'	125.9(2)
O1'	C2'	C1'	112.9(2)
C3'	C2'	C1'	121.3(2)
N2	C11	C12	113.2(2)
N2'	C10'	C9'	113.4(2)
N1'	C5'	C6'	106.6(2)
N1'	C5'	C7'	107.4(2)
N1'	C5'	C8'	115.2(2)
C7'	C5'	C6'	110.7(2)
C8'	C5'	C6'	108.4(2)
C8'	C5'	C7'	108.5(2)
N2	C10	C9	114.3(2)
F1'	C1'	C2'	111.5(2)
F1'	C1'	F3'	107.1(2)
F1'	C1'	F2'	107.3(2)
F3'	C1'	C2'	113.0(2)
F2'	C1'	C2'	111.2(2)
F2'	C1'	F3'	106.5(2)
N1'	C4'	C3'	128.0(3)
F1	C1	C2	113.1(2)
F1	C1	F3	107.7(2)
F1	C1	F2	106.8(2)
F3	C1	C2	111.3(2)
F3	C1	F2	106.4(2)
F2	C1	C2	111.3(2)
N1	C5	C7	106.5(2)
N1	C5	C8	107.0(2)
N1	C5	C6	115.0(2)
C8	C5	C7	111.9(2)
C8	C5	C6	107.6(2)
C6	C5	C7	108.8(2)
N2'	C11'	C12'	113.3(2)

Table 27. Torsion Angles for [Zr(TFB-*t*BuA)₂(NEt₂)₂].

A	B	C	D	Angle/°
Zr1	O1	C2	C3	-6.2(4)
Zr1	O1	C2	C1	175.22(18)
Zr1	O1'	C2'	C3'	-8.9(5)
Zr1	O1'	C2'	C1'	172.08(19)
Zr1	N2'	C10'	C9'	-103.7(3)
Zr1	N2'	C11'	C12'	-103.8(2)
Zr1	N2	C11	C12	-97.9(2)
Zr1	N2	C10	C9	-105.5(2)
Zr1	N1	C4	C3	8.0(4)
Zr1	N1	C5	C7	56.1(2)
Zr1	N1	C5	C8	-63.8(2)
Zr1	N1	C5	C6	176.70(18)
Zr1	N1'	C5'	C6'	-64.2(2)
Zr1	N1'	C5'	C7'	54.6(2)
Zr1	N1'	C5'	C8'	175.61(17)
Zr1	N1'	C4'	C3'	6.4(4)
O1	C2	C1	F1	176.2(2)
O1	C2	C1	F3	54.8(3)
O1	C2	C1	F2	-63.7(3)
O1'	C2'	C1'	F1'	59.4(3)
O1'	C2'	C1'	F3'	180.0(2)
O1'	C2'	C1'	F2'	-60.3(3)
C3	C2	C1	F1	-2.5(4)

A	B	C	D	Angle/°
C3	C2	C1	F3	-123.8(3)
C3	C2	C1	F2	117.7(3)
C4	N1	C5	C7	-117.7(3)
C4	N1	C5	C8	122.5(2)
C4	N1	C5	C6	3.0(3)
C4	C3	C2	O1	-2.3(4)
C4	C3	C2	C1	176.1(2)
C3'	C2'	C1'	F1'	-119.7(3)
C3'	C2'	C1'	F3'	0.9(4)
C3'	C2'	C1'	F2'	120.6(3)
C2	C3	C4	N1	-0.4(4)
C2'	C3'	C4'	N1'	-0.7(5)
C11	N2	C10	C9	79.4(3)
C10'	N2'	C11'	C12'	76.9(3)
C5'	N1'	C4'	C3'	-179.6(3)
C10	N2	C11	C12	76.9(3)
C4'	N1'	C5'	C6'	121.7(3)
C4'	N1'	C5'	C7'	-119.5(3)
C4'	N1'	C5'	C8'	1.5(3)
C4'	C3'	C2'	O1'	0.1(5)
C4'	C3'	C2'	C1'	179.0(3)
C5	N1	C4	C3	-178.5(2)
C11'	N2'	C10'	C9'	75.4(3)

Table 28. Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)_2]$.

Atom	x	y	z	U(eq)
H4	5449.01	5918.3	665.79	24
H6'A	5736.59	6447.91	3021.65	38
H6'B	4574.14	5991.82	3223.34	38
H6'C	5282.6	5529.21	2654.06	38
H3'	10316.18	5843.37	4351.66	29
H11A	7470.97	3392.81	417.3	25
H11B	6420.32	3917.4	684.67	25
H10A	8084.19	3049.99	4475.42	26
H10B	8707.01	3915.06	4275.95	26
H7'A	5607.36	4223.56	3541.58	42
H7'B	4917.89	4690.06	4119.19	42
H7'C	6290.76	4325.94	4456.44	42
H10C	8597.65	2364.45	1497.13	28
H10D	9215.2	2855.96	2299.93	28
H7A	9001.82	5171.93	1489.33	40
H7B	9266.01	5984.16	1001.34	40
H7C	8257.61	5287.24	586.57	40
H4'	8333.23	5943.65	4486.42	29
H8A	7475.68	6895.58	2244.21	38
H8B	8770.76	6993.66	2024.13	38
H8C	8525.55	6181.21	2518.39	38
H6A	6702.38	6450.1	200.65	42
H6B	7707.24	7142.83	629.05	42
H6C	6412.43	7072.96	853.75	42
H12A	5616.5	2591.91	173.61	38
H12B	5673.63	2613.58	1092.34	38
H12C	6700.84	2098.55	791.1	38
H11C	7803.25	1977.54	3308.69	32
H11D	6903.21	2377.15	2531.57	32
H8'A	6930.37	5769.75	5010.73	46
H8'B	5561.33	6127.5	4644.12	46
H8'C	6722.18	6593.44	4449.56	46
H12D	5414.01	2681.72	3203.88	56
H12E	6331.34	2391.07	4021.3	56
H12F	5791.96	1694.9	3352.17	56
H9'A	10257.75	3116.34	3908	52

Atom	x	y	z	U(eq)
H9'B	9621.96	2242.2	4075.28	52
H9'C	10236.29	2871.19	4788.19	52
H9A	9557.92	3353.36	809.41	55
H9B	10557.62	2831.14	1460	55
H9C	10221.8	3796.98	1630.71	55
H3	3810(30)	5080(19)	757(18)	27(8)

Table 29. Crystal data and structure refinement for [Zr(TFB-*t*BuA)₂{ η^2 -(*i*PrN)₂CNEt₂}₂].

Identification code	[Zr(TFB- <i>t</i> BuA) ₂ { η^2 -(<i>i</i> PrN) ₂ CNEt ₂ } ₂]
Empirical formula	C ₃₈ H ₇₀ F ₆ N ₈ O ₂ Zr
Formula weight	876.24
Temperature/K	100(2)
Crystal system	monoclinic
Space group	P2 ₁ /c
<i>a</i> /Å	11.1783(4)
<i>b</i> /Å	16.6168(5)
<i>c</i> /Å	27.9964(11)
α /°	90
β /°	92.335(2)
γ /°	90
Volume/Å ³	5195.9(3)
<i>Z</i>	4
ρ_{calc} /cm ³	1.120
μ /mm ⁻¹	0.268
<i>F</i> (000)	1856.0
Crystal size/mm ³	0.170 × 0.160 × 0.080
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	3.646 to 56.628
Index ranges	-14 ≤ <i>h</i> ≤ 14, -22 ≤ <i>k</i> ≤ 22, -36 ≤ <i>l</i> ≤ 37
Reflections collected	99843
Independent reflections	12911 [<i>R</i> _{int} = 0.1110, <i>R</i> _{sigma} = 0.0657]
Data/restraints/parameters	12911/0/514
Goodness-of-fit on <i>F</i> ²	1.050
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0988, <i>wR</i> ₂ = 0.2904
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1312, <i>wR</i> ₂ = 0.3240
Largest diff. peak/hole / e Å ⁻³	5.03/-0.60

Table 30. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Zr}(\text{TFB}-t\text{BuA})_2\{\eta^2-(i\text{PrN})_2\text{CNEt}_2\}_2]$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Zr1	7455.5(4)	2900.0(3)	2079.0(2)	17.20(17)
O1'	8602(3)	2480(2)	2600.0(14)	25.0(8)
F2	3981(3)	3813(3)	2435.0(15)	43.6(10)
O1	6372(3)	3285(2)	2590.8(13)	23.4(8)
F1'	10800(4)	3201(2)	2614.2(17)	46.1(10)
F3'	11007(4)	1936(3)	2519.8(17)	48.0(10)
F1	3596(3)	3446(3)	3135.0(14)	50.6(12)
F2'	11433(4)	2463(3)	3201.7(17)	56.2(13)
N2'	8017(4)	4107(3)	1855.4(15)	19.2(8)
F3	4152(4)	2578(3)	2628.8(19)	51.7(12)
N3	6883(4)	1712(3)	1812.1(16)	21.2(9)
N3'	8892(4)	3024(3)	1552.5(16)	20.8(9)
N2	6005(4)	2807(3)	1501.2(16)	21.3(9)
N1	7268(5)	4190(3)	3989.6(17)	29.7(10)
N4	5294(4)	1532(3)	1208.1(17)	26.1(10)
N4'	9677(4)	4313(3)	1345.0(17)	26.8(10)
N1'	7869(5)	1700(3)	4003.8(18)	35.7(12)
C12'	8885(5)	3824(3)	1577.7(17)	20.2(10)
C2	5636(5)	3460(3)	2935.2(18)	20.9(10)
C3	5926(5)	3726(3)	3379.6(19)	23.6(10)
C3'	9146(6)	2129(3)	3409(2)	28.2(12)
C12	6033(5)	2006(3)	1499.0(18)	20.7(10)
C4'	7966(6)	1960(3)	3580(2)	30.0(12)
C14	6440(6)	934(3)	2526(2)	29.0(12)
C13'	8080(5)	4914(3)	2069.5(18)	21.8(10)
C4	7127(5)	3887(3)	3575.1(19)	23.6(10)
C15'	8540(6)	4863(3)	2587.4(19)	28.6(12)
C2'	9369(5)	2358(3)	2963(2)	24.9(11)
C13	6807(5)	894(3)	2010(2)	24.4(11)
C16	3546(6)	1137(4)	1670(2)	34.9(13)
C10	6222(6)	3817(4)	861(2)	30.5(12)
C9'	8631(6)	2101(4)	860(2)	34.2(13)
C17'	9270(7)	5028(4)	1087(2)	36.3(14)
C11	5369(5)	3269(3)	1120.8(19)	25.6(11)
C11'	9518(5)	2589(4)	1180(2)	26.4(11)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
C1	4347(5)	3318(4)	2790(2)	27.0(11)
C9	4367(6)	3767(4)	1330(2)	35.1(14)
C5	8479(6)	4355(4)	4196(2)	32.2(13)
C1'	10651(5)	2490(4)	2829(2)	30.6(12)
C18'	10967(5)	4155(4)	1403(2)	30.5(12)
C15	8009(6)	467(4)	1969(2)	32.8(13)
C14'	6867(7)	5312(4)	2033(3)	41.6(16)
C18	5750(6)	822(4)	966(2)	35.4(14)
C17	3994(5)	1592(4)	1247(2)	33.1(13)
C7	8762(7)	3694(4)	4559(3)	44.0(17)
C6'	5683(7)	1422(5)	3802(3)	48.9(19)
C6	9479(6)	4400(5)	3836(3)	42.6(16)
C10'	10470(6)	2034(4)	1402(3)	37.6(15)
C19'	11591(6)	4766(4)	1721(3)	42.3(16)
C8	8397(8)	5161(4)	4451(3)	47.1(18)
C7'	6360(8)	2171(4)	4545(3)	44.4(17)
C5'	6666(7)	1506(4)	4185(2)	37.3(15)
C8'	6837(9)	707(4)	4447(3)	50(2)
C19	5614(8)	901(6)	429(3)	53(2)
C16'	9549(10)	4952(7)	562(3)	78(3)

Table 31. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Zr}(\text{TFB-}i\text{BuA})_2\{\eta^2\text{-(}i\text{PrN)}_2\text{CNEt}_2\}_2]$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[\text{h}^2\text{a}^{*2}\text{U}_{11}+2\text{hka}^*\text{b}^*\text{U}_{12}+\dots]$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Zr1	17.2(3)	19.2(3)	15.1(3)	-0.67(16)	-0.24(17)	0.07(17)
O1'	26(2)	27(2)	22.0(18)	3.3(15)	-6.0(15)	1.9(15)
F2	30.2(19)	58(3)	42(2)	11.8(19)	-7.7(17)	4.1(18)
O1	23.1(18)	30(2)	17.3(17)	-2.8(14)	4.8(14)	1.2(15)
F1'	37(2)	36(2)	66(3)	10.1(19)	3.2(19)	-6.7(17)
F3'	34(2)	46(2)	65(3)	-10(2)	7(2)	8.1(18)
F1	23.3(18)	97(4)	32(2)	-11(2)	8.7(15)	-12(2)
F2'	29(2)	92(4)	47(2)	10(2)	-16.8(18)	-9(2)
N2'	22(2)	19(2)	17(2)	-2.2(15)	3.8(16)	1.4(16)
F3	35(2)	37(2)	82(3)	-20(2)	-11(2)	-10.3(17)
N3	22(2)	21(2)	21(2)	-0.9(16)	-2.3(17)	-0.2(16)
N3'	21(2)	21(2)	20(2)	-5.8(16)	6.3(17)	0.0(16)

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
N2	23(2)	22(2)	19(2)	0.5(16)	-1.2(17)	2.9(17)
N1	36(3)	34(3)	19(2)	2.4(18)	-1.9(19)	-8(2)
N4	26(2)	29(2)	23(2)	1.1(18)	-3.9(18)	-7.4(19)
N4'	28(2)	27(2)	27(2)	-0.9(18)	8.4(19)	-2.8(19)
N1'	50(3)	33(3)	24(2)	8(2)	-7(2)	-10(2)
C12'	20(2)	26(2)	15(2)	-2.6(18)	-0.9(18)	-1.3(19)
C2	20(2)	23(2)	20(2)	1.0(18)	3.9(19)	-1.3(19)
C3	26(3)	26(3)	19(2)	0.4(19)	2(2)	1(2)
C3'	33(3)	24(3)	26(3)	1(2)	-11(2)	0(2)
C12	20(2)	25(3)	17(2)	-0.8(18)	2.3(18)	-2.0(19)
C4'	43(3)	26(3)	20(3)	0(2)	-6(2)	-6(2)
C14	34(3)	25(3)	27(3)	5(2)	0(2)	1(2)
C13'	29(3)	17(2)	19(2)	0.9(18)	5(2)	0.1(19)
C4	26(3)	26(3)	19(2)	6.2(19)	1(2)	-4(2)
C15'	43(3)	22(3)	21(3)	-3(2)	1(2)	-1(2)
C2'	27(3)	20(2)	27(3)	-1(2)	-8(2)	4(2)
C13	28(3)	20(2)	25(3)	-1.1(19)	-3(2)	-3(2)
C16	34(3)	38(3)	33(3)	3(3)	3(3)	0(3)
C10	39(3)	29(3)	23(3)	4(2)	-3(2)	-5(2)
C9'	34(3)	36(3)	33(3)	-15(2)	4(3)	-3(2)
C17'	50(4)	36(3)	24(3)	11(2)	10(3)	-1(3)
C11	27(3)	31(3)	18(2)	5(2)	-5(2)	0(2)
C11'	25(3)	33(3)	22(3)	-10(2)	6(2)	-1(2)
C1	25(3)	33(3)	24(3)	-3(2)	2(2)	-1(2)
C9	34(3)	40(3)	30(3)	5(3)	-2(2)	17(3)
C5	36(3)	37(3)	23(3)	7(2)	-8(2)	-10(3)
C1'	27(3)	33(3)	31(3)	2(2)	-9(2)	0(2)
C18'	21(3)	39(3)	33(3)	-10(2)	10(2)	-5(2)
C15	34(3)	26(3)	38(3)	1(2)	-1(3)	6(2)
C14'	43(4)	36(3)	45(4)	-14(3)	-9(3)	16(3)
C18	39(3)	35(3)	32(3)	-10(2)	4(3)	-12(3)
C17	22(3)	43(3)	34(3)	7(3)	-5(2)	-9(2)
C7	52(4)	43(4)	36(3)	13(3)	-19(3)	-17(3)
C6'	52(4)	63(5)	32(3)	5(3)	1(3)	-29(4)
C6	30(3)	59(4)	38(4)	6(3)	-6(3)	-11(3)
C10'	29(3)	39(3)	44(4)	-15(3)	4(3)	10(3)
C19'	37(4)	44(4)	46(4)	-18(3)	-1(3)	-1(3)
C8	60(5)	39(4)	41(4)	-2(3)	-14(3)	-10(3)

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C7'	62(5)	36(3)	36(4)	-3(3)	6(3)	-12(3)
C5'	59(4)	31(3)	21(3)	2(2)	1(3)	-14(3)
C8'	85(6)	32(3)	34(4)	9(3)	10(4)	-10(4)
C19	57(5)	69(5)	33(4)	-15(4)	-1(3)	-12(4)
C16'	101(8)	106(8)	28(4)	24(5)	26(5)	37(7)

Table 32. Bond Lengths for [Zr(TFB-*t*BuA)₂{ η^2 -(*i*PrN)₂CNEt₂}₂].

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zr1	O1	2.018(4)	N4'	C17'	1.454(8)
Zr1	O1'	2.026(4)	N4'	C18'	1.468(7)
Zr1	N3	2.197(4)	N1'	C4'	1.271(8)
Zr1	N2'	2.200(4)	N1'	C5'	1.491(9)
Zr1	N3'	2.233(4)	C2	C3	1.347(7)
Zr1	N2	2.248(4)	C2	C1	1.500(8)
O1'	C2'	1.319(6)	C3	C4	1.454(8)
F2	C1	1.341(7)	C3'	C2'	1.338(8)
O1	C2	1.325(6)	C3'	C4'	1.449(9)
F1'	C1'	1.339(7)	C14	C13	1.520(8)
F3'	C1'	1.335(8)	C13'	C14'	1.509(8)
F1	C1	1.322(7)	C13'	C15'	1.521(8)
F2'	C1'	1.334(7)	C2'	C1'	1.513(8)
N2'	C12'	1.352(6)	C13	C15	1.528(8)
N2'	C13'	1.469(6)	C16	C17	1.507(8)
F3	C1	1.324(7)	C10	C11	1.523(8)
N3	C12	1.357(7)	C9'	C11'	1.539(8)
N3	C13	1.470(7)	C17'	C16'	1.518(9)
N3'	C12'	1.331(7)	C11	C9	1.528(8)
N3'	C11'	1.470(6)	C11'	C10'	1.523(9)
N2	C12	1.332(7)	C5	C7	1.522(8)
N2	C11	1.473(7)	C5	C8	1.522(10)
N1	C4	1.269(7)	C5	C6	1.536(9)
N1	C5	1.476(8)	C18'	C19'	1.503(8)
N4	C12	1.382(7)	C18	C19	1.513(10)
N4	C18	1.460(8)	C6'	C5'	1.510(10)
N4	C17	1.466(8)	C7'	C5'	1.543(9)
N4'	C12'	1.384(7)	C5'	C8'	1.524(9)

Table 33. Bond Angles for [Zr(TFB-*t*BuA)₂{ η^2 -(*i*PrN)₂CNEt₂}₂].

Atom	Atom	Atom	Angle/°
O1	Zr1	O1'	88.75(16)
O1	Zr1	N3	110.56(16)
O1'	Zr1	N3	95.87(16)
O1	Zr1	N2'	95.73(16)
O1'	Zr1	N2'	109.83(16)
N3	Zr1	N2'	143.62(16)
O1	Zr1	N3'	155.26(16)
O1'	Zr1	N3'	93.23(17)
N3	Zr1	N3'	93.78(16)
N2'	Zr1	N3'	60.45(15)
O1	Zr1	N2	95.53(16)
O1'	Zr1	N2	155.61(16)
N3	Zr1	N2	60.15(16)
N2'	Zr1	N2	93.65(16)
N3'	Zr1	N2	92.77(17)
C2'	O1'	Zr1	168.7(4)
C2	O1	Zr1	174.2(4)
C12'	N2'	C13'	121.9(4)
C12'	N2'	Zr1	93.8(3)
C13'	N2'	Zr1	136.5(3)
C12	N3	C13	121.8(4)
C12	N3	Zr1	94.7(3)
C13	N3	Zr1	136.2(3)
C12'	N3'	C11'	122.2(5)
C12'	N3'	Zr1	92.9(3)
C11'	N3'	Zr1	143.0(4)
C12	N2	C11	121.9(5)
C12	N2	Zr1	93.2(3)
C11	N2	Zr1	142.9(4)
C4	N1	C5	120.6(5)
C12	N4	C18	121.4(5)
C12	N4	C17	119.2(5)
C18	N4	C17	117.1(5)
C12'	N4'	C17'	121.4(5)
C12'	N4'	C18'	119.2(5)
C17'	N4'	C18'	119.1(5)
C4'	N1'	C5'	120.2(6)

Atom	Atom	Atom	Angle/°
N3	C12	N4	124.1(5)
N1'	C4'	C3'	119.2(6)
N2'	C13'	C14'	110.1(5)
N2'	C13'	C15'	110.4(4)
C14'	C13'	C15'	110.9(5)
N1	C4	C3	119.7(5)
O1'	C2'	C3'	128.6(6)
O1'	C2'	C1'	112.2(5)
C3'	C2'	C1'	119.2(5)
N3	C13	C14	109.9(4)
N3	C13	C15	109.7(5)
C14	C13	C15	111.3(5)
N4'	C17'	C16'	109.9(6)
N2	C11	C10	111.3(5)
N2	C11	C9	110.1(4)
C10	C11	C9	110.0(5)
N3'	C11'	C10'	110.7(5)
N3'	C11'	C9'	111.0(5)
C10'	C11'	C9'	110.0(5)
F1	C1	F3	107.3(5)
F1	C1	F2	105.0(5)
F3	C1	F2	106.0(5)
F1	C1	C2	114.0(5)
F3	C1	C2	112.5(5)
F2	C1	C2	111.4(5)
N1	C5	C7	106.8(5)
N1	C5	C8	105.9(6)
C7	C5	C8	109.7(5)
N1	C5	C6	115.7(5)
C7	C5	C6	109.7(6)
C8	C5	C6	108.9(6)
F2'	C1'	F3'	106.3(5)
F2'	C1'	F1'	106.9(5)
F3'	C1'	F1'	105.7(5)
F2'	C1'	C2'	113.4(5)
F3'	C1'	C2'	111.8(5)
F1'	C1'	C2'	112.2(5)

Atom	Atom	Atom	Angle/°
N3'	C12'	N2'	112.6(5)
N3'	C12'	N4'	123.8(5)
N2'	C12'	N4'	123.6(5)
O1	C2	C3	127.7(5)
O1	C2	C1	112.7(4)
C3	C2	C1	119.6(5)
C2	C3	C4	126.2(5)
C2'	C3'	C4'	124.7(5)
N2	C12	N3	111.9(5)
N2	C12	N4	124.0(5)

Atom	Atom	Atom	Angle/°
N4'	C18'	C19'	112.0(5)
N4	C18	C19	111.7(6)
N4	C17	C16	112.8(5)
N1'	C5'	C6'	114.8(5)
N1'	C5'	C8'	104.7(6)
C6'	C5'	C8'	109.5(6)
N1'	C5'	C7'	107.1(5)
C6'	C5'	C7'	110.8(7)
C8'	C5'	C7'	109.7(5)

Table 34. Torsion Angles for [Zr(TFB-*t*BuA)₂{ η^2 -(*i*PrN)₂CNEt₂}₂].

A	B	C	D	Angle/°
C11'	N3'	C12'	N2'	163.2(5)
Zr1	N3'	C12'	N2'	-4.7(4)
C11'	N3'	C12'	N4'	-16.7(8)
Zr1	N3'	C12'	N4'	175.4(5)
C13'	N2'	C12'	N3'	158.6(5)
Zr1	N2'	C12'	N3'	4.7(5)
C13'	N2'	C12'	N4'	-21.5(8)
Zr1	N2'	C12'	N4'	-175.3(4)
C17'	N4'	C12'	N3'	135.0(6)
C18'	N4'	C12'	N3'	-51.5(7)
C17'	N4'	C12'	N2'	-44.9(8)
C18'	N4'	C12'	N2'	128.6(5)
O1	C2	C3	C4	0.7(9)
C1	C2	C3	C4	179.5(5)
C11	N2	C12	N3	165.5(5)
Zr1	N2	C12	N3	-1.8(4)
C11	N2	C12	N4	-13.8(8)
Zr1	N2	C12	N4	178.9(5)
C13	N3	C12	N2	156.5(5)
Zr1	N3	C12	N2	1.8(5)
C13	N3	C12	N4	-24.2(8)
Zr1	N3	C12	N4	-178.9(5)
C18	N4	C12	N2	138.0(6)
C17	N4	C12	N2	-59.8(7)

A	B	C	D	Angle/°
C12	N3	C13	C14	-105.3(6)
Zr1	N3	C13	C14	36.6(7)
C12	N3	C13	C15	132.0(5)
Zr1	N3	C13	C15	-86.1(6)
C12'	N4'	C17'	C16'	-119.0(7)
C18'	N4'	C17'	C16'	67.5(8)
C12	N2	C11	C10	-119.3(6)
Zr1	N2	C11	C10	39.4(8)
C12	N2	C11	C9	118.3(6)
Zr1	N2	C11	C9	-83.0(7)
C12'	N3'	C11'	C10'	120.5(6)
Zr1	N3'	C11'	C10'	-79.9(7)
C12'	N3'	C11'	C9'	-117.2(6)
Zr1	N3'	C11'	C9'	42.4(8)
O1	C2	C1	F1	176.5(5)
C3	C2	C1	F1	-2.5(8)
O1	C2	C1	F3	54.0(7)
C3	C2	C1	F3	-124.9(6)
O1	C2	C1	F2	-64.9(6)
C3	C2	C1	F2	116.2(6)
C4	N1	C5	C7	-103.5(7)
C4	N1	C5	C8	139.7(6)
C4	N1	C5	C6	18.9(8)
O1'	C2'	C1'	F2'	172.6(5)

A	B	C	D	Angle/°
C18	N4	C12	N3	-41.2(8)
C17	N4	C12	N3	121.0(6)
C5'	N1'	C4'	C3'	-178.7(5)
C2'	C3'	C4'	N1'	175.8(6)
C12'	N2'	C13'	C14'	138.3(5)
Zr1	N2'	C13'	C14'	-81.4(6)
C12'	N2'	C13'	C15'	-98.9(6)
Zr1	N2'	C13'	C15'	41.4(7)
C5	N1	C4	C3	179.8(5)
C2	C3	C4	N1	175.0(6)
Zr1	O1'	C2'	C3'	98(2)
Zr1	O1'	C2'	C1'	-83(2)
C4'	C3'	C2'	O1'	0.5(10)
C4'	C3'	C2'	C1'	-178.2(5)

A	B	C	D	Angle/°
C3'	C2'	C1'	F2'	-8.5(8)
O1'	C2'	C1'	F3'	-67.2(6)
C3'	C2'	C1'	F3'	111.7(6)
O1'	C2'	C1'	F1'	51.3(7)
C3'	C2'	C1'	F1'	-129.8(6)
C12'	N4'	C18'	C19'	-106.2(6)
C17'	N4'	C18'	C19'	67.5(7)
C12	N4	C18	C19	-118.5(6)
C17	N4	C18	C19	79.0(7)
C12	N4	C17	C16	-78.8(7)
C18	N4	C17	C16	84.2(7)
C4'	N1'	C5'	C6'	16.0(9)
C4'	N1'	C5'	C8'	136.1(6)
C4'	N1'	C5'	C7'	-107.4(7)

Table 35. Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Zr}(\text{TFB-}t\text{BuA})_2\{\eta^2\text{-(}^i\text{PrN)}_2\text{CNEt}_2\}_2]$.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H3	5283.25	3817.52	3584.92	28
H3'	9810.01	2072.01	3629.45	34
H4'	7273.48	2043.68	3378.27	36
H14A	7079.12	1189.15	2722.74	44
H14B	6302.36	387.47	2644.44	44
H14C	5703.11	1249.12	2544.99	44
H13'	8653.17	5245.26	1887.71	26
H4	7802.9	3765.04	3393.44	28
H15A	7952.83	4580.88	2776.58	43
H15B	8663.91	5407.78	2714.7	43
H15C	9300.63	4569.21	2604.65	43
H13	6183.1	587.73	1819.75	29
H16A	3703.56	561.32	1630.55	52
H16B	2682.71	1224.34	1691.58	52
H16C	3960.31	1330.14	1963.41	52
H10A	6546.12	4225.43	1083.44	46
H10B	5788.26	4081.69	593.55	46
H10C	6879.52	3496.37	739.85	46
H9'A	8268.35	1677.53	1050.02	51

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H9'B	9056.86	1856.43	597.53	51
H9'C	8002.47	2458.77	728.7	51
H17A	9674.25	5509.16	1224.89	44
H17B	8396.35	5093.97	1117.66	44
H11	5002.92	2881.79	884	31
H11'	9921.31	2992.29	975.49	32
H9A	3860.12	3415.9	1517.67	53
H9B	3883.3	4014.46	1070.33	53
H9C	4716.32	4188.06	1537.42	53
H18A	11323.83	4163.34	1084.87	37
H18B	11092.21	3611.86	1540.77	37
H15D	8180.9	399.27	1631.31	49
H15E	7973.29	-62.34	2122.73	49
H15F	8642.32	789.26	2127.99	49
H14D	6589.03	5337.46	1696.34	62
H14E	6925.91	5857.72	2163.7	62
H14F	6296.5	4998.52	2213.75	62
H18C	5309.18	340.33	1070.06	43
H18D	6606.21	747.65	1059.99	43
H17C	3595.74	1378.5	951.27	40
H17D	3769.99	2165.5	1275.89	40
H7A	8188.78	3717.98	4814.23	66
H7B	9575.35	3768.98	4695.91	66
H7C	8704.61	3168.17	4400.82	66
H6'A	5547.38	1942.51	3644.03	73
H6'B	4943.94	1246.74	3947.68	73
H6'C	5918.27	1023.1	3565.99	73
H6A	9546.39	3880.84	3673.62	64
H6B	10239.61	4527.44	4005.81	64
H6C	9288.23	4820.91	3600	64
H10D	11055.82	2352.3	1590.79	56
H10E	10876.16	1748.8	1148.2	56
H10F	10091.9	1642.11	1609.63	56
H19A	11506.27	5300.98	1576.49	64
H19B	12442.08	4628.55	1759.29	64
H19C	11231.49	4765.61	2034.36	64
H8A	8236.06	5587.23	4215.13	71
H8B	9154.65	5271.52	4626.74	71

Atom	x	y	z	U(eq)
H8C	7746.03	5142.03	4674.82	71
H7'A	7027.16	2235.86	4779.54	67
H7'B	5635.68	2020.59	4709.33	67
H7'C	6221.83	2679.69	4373.84	67
H8'A	7110.98	298.84	4223.41	76
H8'B	6074.24	537.28	4574.86	76
H8'C	7434.91	772.2	4709.42	76
H19D	5889.64	404.75	278.82	80
H19E	6095.32	1355.39	322.85	80
H19F	4770.73	992.83	335.89	80
H16D	9383.18	5464.48	400.11	117
H16E	9049.35	4528.47	414.04	117
H16F	10395.71	4812.8	534.78	117

Table 36. Crystal data and structure refinement for [Zr(TFB-TFEA)₄].

Identification code	[Zr(TFB-TFEA) ₄]
Empirical formula	C ₂₄ H ₁₆ F ₂₄ N ₄ O ₄ Zr
Formula weight	971.63
Temperature/K	100.00
Crystal system	triclinic
Space group	P-1
a/Å	10.2516(5)
b/Å	18.0006(9)
c/Å	19.1006(9)
α/°	108.641(2)
β/°	90.000(2)
γ/°	90.000(2)
Volume/Å ³	3339.8(3)
Z	4
ρ _{calc} /g/cm ³	1.932
μ/mm ⁻¹	0.503
F(000)	1904.0
Crystal size/mm ³	0.13 × 0.13 × 0.11
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.768 to 56.726
Index ranges	-13 ≤ h ≤ 13, -24 ≤ k ≤ 24, -25 ≤ l ≤ 25
Reflections collected	216707
Independent reflections	16655 [R _{int} = 0.0593, R _{sigma} = 0.0253]
Data/restraints/parameters	16655/0/1080
Goodness-of-fit on F ²	1.116
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0506, wR ₂ = 0.1225
Final R indexes [all data]	R ₁ = 0.0597, wR ₂ = 0.1275
Largest diff. peak/hole / e Å ⁻³	1.18/-0.79

Table 37. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Zr}(\text{TFB-TFEA})_4]$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Zr1	4011.0(3)	2501.1(2)	7498.6(2)	16.60(7)
F17	2191(2)	327.4(11)	6673.8(12)	36.1(5)
F12	2198(2)	4674.6(11)	8326.3(12)	36.0(5)
F22	5886(2)	4539.5(12)	6416.4(13)	40.3(5)
O4	2405(2)	3099.4(12)	7224.7(11)	21.0(4)
F5	5899(2)	471.0(12)	7462.4(13)	42.0(5)
O1	2406(2)	1904.1(12)	7774.8(11)	21.0(4)
F4	5892(2)	461.7(12)	8577.1(13)	40.6(5)
F24	5899(2)	4531.3(12)	7531.9(13)	41.8(5)
O3	5613(2)	1793.1(12)	6992.2(12)	22.2(4)
O2	5618(2)	3208.4(12)	8002.4(12)	22.1(4)
F18	394(2)	392.2(13)	6115.6(14)	42.8(5)
F10	2193(3)	4933.6(13)	9498.5(13)	48.1(6)
F8	8098(2)	3638.0(14)	9273.3(13)	42.6(5)
F14	7615(2)	485.3(13)	6212.8(16)	48.9(6)
F16	2181(3)	67.3(13)	5502.1(13)	48.4(6)
F13	8090(2)	1368.4(14)	5721.8(13)	43.3(5)
F11	401(2)	4609.0(13)	8885.9(14)	42.5(5)
F15	8137(2)	1643.5(15)	6899.0(13)	46.7(6)
F7	8140(2)	3357.7(15)	8096.4(13)	45.8(6)
F9	7623(2)	4516.5(13)	8779.9(16)	49.0(6)
F19	278(2)	4050.0(16)	7251.7(15)	55.3(7)
F3	278(2)	952.9(16)	7747.4(15)	55.3(7)
F1	-172(2)	2138.7(15)	8310(2)	60.2(8)
F6	7688(2)	666.3(14)	8084.8(18)	55.4(7)
F23	7685(2)	4334.6(14)	6907.5(18)	55.4(7)
F20	-177(2)	2863.2(15)	6694(2)	60.5(8)
F21	173(2)	3639.9(19)	6081.3(14)	56.7(7)
F2	181(2)	1358.1(19)	8916.1(14)	56.9(7)
N3	3269(3)	1614.5(14)	6332.9(14)	21.7(5)
N2	3276(2)	3388.6(14)	8664.1(14)	21.5(5)
N1	4807(2)	1889.7(14)	8377.1(14)	21.5(5)
N4	4804(2)	3111.7(15)	6618.4(14)	21.9(5)
C4	4133(3)	1761.7(18)	8905.1(17)	25.4(6)
C22	4125(3)	3243.6(18)	6094.4(17)	25.4(6)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
C3	2756(3)	1736.9(18)	8940.0(17)	25.8(6)
C10	3976(3)	3659.1(18)	9263.0(17)	27.2(6)
C16	3968(3)	1345.5(18)	5735.9(18)	28.0(7)
C21	2749(3)	3263.3(18)	6058.4(17)	26.1(6)
C15	5356(3)	1316.2(19)	5704.5(18)	29.7(7)
C2	2013(3)	1752.6(17)	8355.8(17)	22.1(6)
C17	1882(3)	1405.5(18)	6221.8(17)	24.5(6)
C9	5362(3)	3687.6(19)	9292.7(18)	28.7(7)
C20	2007(3)	3252.5(17)	6640.4(17)	22.4(6)
C5	6206(3)	1701.1(18)	8404.2(19)	26.4(6)
C18	1663(4)	547(2)	6129.4(19)	31.5(7)
C11	1888(3)	3598.2(18)	8776.1(17)	24.2(6)
C8	6062(3)	3523.5(17)	8661.5(18)	24.6(6)
C6	6410(3)	824(2)	8128(2)	31.2(7)
C19	555(3)	3451.9(18)	6662.4(18)	26.9(6)
C7	7499(3)	3754(2)	8699(2)	30.7(7)
C13	7490(3)	1246(2)	6293(2)	31.5(7)
C23	6201(3)	3302.0(18)	6589.8(19)	26.2(6)
C14	6053(3)	1480.6(18)	6334.5(18)	25.6(6)
C24	6409(3)	4178(2)	6865(2)	32.3(7)
C1	558(3)	1550.3(19)	8337.5(18)	27.1(6)
C12	1671(4)	4456(2)	8872.2(19)	31.6(7)

Table 38. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Zr}(\text{TFB-TFEA})_4]$. The Anisotropic displacement factor exponent takes the form:

$$-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots].$$

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Zr1	20.13(13)	13.78(12)	15.82(13)	4.61(9)	0.08(9)	0.00(9)
F17	44.2(12)	22.8(9)	44.5(12)	15.5(9)	0.3(9)	1.1(8)
F12	43.5(12)	22.8(9)	44.7(12)	14.9(9)	0.9(9)	-1.7(8)
F22	47.7(13)	29.2(11)	51.7(14)	23.5(10)	-1.0(10)	-2.9(9)
O4	24.7(10)	18.6(10)	20.3(10)	7.0(8)	-0.8(8)	1.5(8)
F5	60.5(15)	21.5(10)	41.6(12)	6.9(9)	3.0(10)	2.9(9)
O1	24.6(10)	19.6(10)	20.0(10)	7.8(8)	0.6(8)	-2.0(8)
F4	49.1(13)	30.0(11)	50.5(13)	24.0(10)	1.0(10)	2.8(9)
F24	59.5(14)	20.8(10)	42.3(13)	6.2(9)	-3.0(10)	-2.4(9)
O3	24.2(10)	18.2(10)	22.7(10)	4.5(8)	2.4(8)	3.0(8)

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
O2	24.2(10)	17.6(10)	23.6(11)	5.3(8)	-1.8(8)	-2.2(8)
F18	38.5(12)	34.1(11)	53.6(14)	11.2(10)	-7.2(10)	-14.5(9)
F10	67.1(16)	25.4(11)	40.4(13)	-5.6(9)	-11.7(11)	8.7(10)
F8	38.1(12)	48.4(13)	40.6(13)	13.2(10)	-17.1(9)	1.0(10)
F14	38.5(12)	30.6(11)	79.6(18)	20.4(12)	14.0(12)	9.9(9)
F16	68.8(16)	25.2(11)	39.0(13)	-6.8(9)	11.4(11)	-9.0(10)
F13	38.3(12)	47.7(13)	43.6(13)	14.0(11)	17.1(10)	-0.2(10)
F11	39.0(12)	33.4(11)	52.6(14)	10.3(10)	7.0(10)	14.3(9)
F15	28.7(11)	59.7(15)	40.0(13)	-0.5(11)	2.1(9)	4.3(10)
F7	27.4(11)	59.4(15)	40.1(13)	1.1(11)	-0.8(9)	-3.0(10)
F9	36.3(12)	31.0(11)	82.2(19)	21.5(12)	-13.6(12)	-9.7(9)
F19	37.5(13)	54.5(15)	52.0(15)	-13.5(12)	-10.9(11)	19.6(11)
F3	38.9(13)	53.4(15)	51.6(15)	-14.0(12)	11.4(11)	-20.2(11)
F1	26.8(11)	40.2(13)	122(3)	38.0(15)	3.0(13)	2.5(9)
F6	27.6(11)	37.4(13)	108(2)	32.9(14)	5.3(12)	8.8(9)
F23	26.9(11)	37.2(13)	109(2)	32.8(14)	-4.5(12)	-9.0(9)
F20	26.9(11)	40.5(13)	123(3)	39.2(15)	-1.4(13)	-2.1(9)
F21	41.6(13)	94(2)	46.1(14)	38.6(15)	-3.3(11)	21.1(13)
F2	40.9(13)	97(2)	45.6(14)	40.4(15)	3.5(10)	-20.7(13)
N3	28.2(13)	16.7(11)	21.0(12)	7.0(9)	-1.9(9)	-1.4(9)
N2	26.7(13)	17.9(11)	20.7(12)	7.1(9)	1.9(9)	1.1(9)
N1	24.5(13)	16.9(11)	23.3(12)	7.0(10)	-2.0(9)	1.7(9)
N4	25.2(13)	18.1(12)	22.0(12)	5.8(10)	2.1(9)	-1.8(9)
C4	36.7(17)	20.7(14)	20.4(14)	8.7(11)	-3.9(12)	0.9(12)
C22	36.6(17)	19.2(14)	21.8(14)	8.5(11)	3.6(12)	-1.1(12)
C3	33.9(17)	23.7(15)	21.7(15)	9.9(12)	3.9(12)	1.9(12)
C10	40.4(18)	21.9(15)	18.1(14)	4.4(11)	2.4(12)	1.2(12)
C16	41.7(19)	20.3(14)	20.1(15)	3.8(12)	-2.3(12)	-1.2(12)
C21	34.4(17)	23.3(15)	21.9(15)	9.2(12)	-4.5(12)	-1.0(12)
C15	39.7(18)	25.3(16)	22.4(15)	5.4(12)	6.9(13)	3.3(13)
C2	26.1(15)	15.8(13)	23.5(14)	4.9(11)	3.5(11)	0.6(10)
C17	30.7(16)	20.9(14)	21.5(14)	6.1(11)	-4.7(11)	-1.7(11)
C9	38.3(18)	25.5(15)	21.2(15)	5.8(12)	-7.1(12)	-2.5(13)
C20	27.6(15)	15.1(13)	24.3(15)	6.1(11)	-3.3(11)	-0.6(10)
C5	23.4(15)	23.6(15)	34.3(17)	12.1(13)	-5.0(12)	-0.4(11)
C18	39.9(19)	22.5(15)	29.3(17)	4.3(13)	-2.1(14)	-4.3(13)
C11	30.7(16)	20.7(14)	21.1(14)	6.5(11)	3.3(11)	3.2(11)
C8	30.0(16)	16.7(13)	25.4(15)	4.6(11)	-5.9(12)	1.1(11)

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C6	27.1(16)	24.8(16)	45(2)	15.6(14)	-0.3(14)	3.5(12)
C19	31.1(16)	21.3(14)	28.2(16)	7.8(12)	-3.0(12)	2.6(12)
C7	30.0(17)	26.8(16)	33.1(18)	6.5(13)	-8.1(13)	-1.6(12)
C13	33.2(18)	25.0(16)	33.4(18)	5.2(13)	10.2(14)	1.2(13)
C23	24.9(15)	23.3(15)	33.1(17)	12.6(13)	4.5(12)	0.6(11)
C14	28.4(16)	17.9(14)	29.4(16)	6.0(12)	6.3(12)	-1.1(11)
C24	28.5(17)	24.6(16)	47(2)	15.2(15)	1.3(14)	-4.3(12)
C1	30.1(16)	23.2(15)	27.7(16)	7.6(12)	3.5(12)	-2.8(12)
C12	38.7(19)	23.8(16)	28.3(17)	2.7(13)	1.7(13)	5.1(13)

Table 39. Bond Lengths for [Zr(TFB-TFEA)₄].

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zr1	O4	2.122(2)	N4	C22	1.302(4)
Zr1	O1	2.122(2)	N4	C23	1.478(4)
Zr1	O3	2.114(2)	C4	C3	1.414(5)
Zr1	O2	2.116(2)	C22	C21	1.413(5)
Zr1	N3	2.410(3)	C3	C2	1.359(4)
Zr1	N2	2.409(3)	C10	C9	1.422(5)
Zr1	N1	2.423(2)	C16	C15	1.425(5)
Zr1	N4	2.424(3)	C21	C20	1.352(4)
F17	C18	1.339(4)	C15	C14	1.348(5)
F12	C12	1.340(4)	C2	C1	1.533(4)
F22	C24	1.342(4)	C17	C18	1.515(4)
O4	C20	1.298(4)	C9	C8	1.352(5)
F5	C6	1.333(4)	C20	C19	1.529(4)
O1	C2	1.289(4)	C5	C6	1.510(4)
F4	C6	1.343(4)	C11	C12	1.512(4)
F24	C24	1.335(4)	C8	C7	1.526(5)
O3	C14	1.283(4)	C13	C14	1.528(5)
O2	C8	1.287(4)	C23	C24	1.510(5)
F18	C18	1.329(4)	F15	C13	1.328(4)
F10	C12	1.341(4)	F7	C7	1.319(4)
F8	C7	1.331(4)	F9	C7	1.338(4)
F14	C13	1.335(4)	F19	C19	1.316(4)
F16	C18	1.342(4)	F3	C1	1.317(4)
F13	C13	1.330(4)	F1	C1	1.312(4)
F11	C12	1.329(4)	F6	C6	1.337(4)

Atom	Atom	Length/Å
F23	C24	1.335(4)
F20	C19	1.315(4)
F21	C19	1.319(4)
F2	C1	1.317(4)
N3	C16	1.302(4)

Atom	Atom	Length/Å
N3	C17	1.469(4)
N2	C10	1.306(4)
N2	C11	1.471(4)
N1	C4	1.302(4)
N1	C5	1.479(4)

Table 40. Bond Angles for [Zr(TFB-TFEA)₄].

Atom	Atom	Atom	Angle/°
O4	Zr1	N3	76.46(8)
O4	Zr1	N2	75.31(8)
O4	Zr1	N1	144.13(8)
O4	Zr1	N4	73.20(8)
O1	Zr1	O4	78.28(8)
O1	Zr1	N3	75.33(8)
O1	Zr1	N2	76.51(8)
O1	Zr1	N1	73.19(8)
O1	Zr1	N4	144.12(8)
O3	Zr1	O4	140.27(8)
O3	Zr1	O1	115.91(8)
O3	Zr1	O2	77.91(8)
O3	Zr1	N3	72.43(9)
O3	Zr1	N2	142.24(9)
O3	Zr1	N1	73.41(8)
O3	Zr1	N4	76.28(8)
O2	Zr1	O4	115.91(8)
O2	Zr1	O1	140.31(8)
O2	Zr1	N3	142.20(9)
O2	Zr1	N2	72.43(8)
O2	Zr1	N1	76.31(8)
O2	Zr1	N4	73.39(8)
N3	Zr1	N1	115.64(8)
N3	Zr1	N4	77.19(8)
N2	Zr1	N3	143.40(9)
N2	Zr1	N1	77.24(8)
N2	Zr1	N4	115.60(8)
N1	Zr1	N4	140.74(9)
N2	C11	C12	111.4(3)

Atom	Atom	Atom	Angle/°
O2	C8	C9	126.0(3)
O2	C8	C7	114.5(3)
C9	C8	C7	119.4(3)
F5	C6	F4	105.8(3)
F5	C6	F6	107.4(3)
F5	C6	C5	114.0(3)
F4	C6	C5	112.9(3)
F6	C6	F4	106.8(3)
F6	C6	C5	109.6(3)
F19	C19	F21	107.2(3)
F19	C19	C20	110.7(3)
F20	C19	F19	106.8(3)
F20	C19	F21	107.2(3)
F20	C19	C20	111.8(3)
F21	C19	C20	112.7(3)
F8	C7	F9	106.6(3)
F8	C7	C8	111.9(3)
F7	C7	F8	107.8(3)
F7	C7	F9	107.6(3)
F7	C7	C8	112.2(3)
F9	C7	C8	110.5(3)
N5	C28	C27	126.3(3)
F14	C13	C14	110.8(3)
F13	C13	F14	107.1(3)
F13	C13	C14	111.9(3)
F15	C13	F14	107.4(3)
F15	C13	F13	107.4(3)
F15	C13	C14	111.9(3)
N4	C23	C24	110.7(3)

Atom	Atom	Atom	Angle/°
C20	O4	Zr1	136.0(2)
C2	O1	Zr1	136.0(2)
C14	O3	Zr1	137.1(2)
C8	O2	Zr1	137.1(2)
C16	N3	Zr1	125.9(2)
C16	N3	C17	113.5(3)
C17	N3	Zr1	120.15(19)
C10	N2	Zr1	126.1(2)
C10	N2	C11	113.5(3)
C11	N2	Zr1	120.04(19)
C4	N1	Zr1	126.1(2)
C4	N1	C5	112.9(3)
C5	N1	Zr1	120.72(19)
C22	N4	Zr1	126.0(2)
C22	N4	C23	112.9(3)
C23	N4	Zr1	120.83(19)
N1	C4	C3	125.6(3)
N4	C22	C21	125.8(3)
C2	C3	C4	120.8(3)
C14	C15	C16	119.8(3)
O1	C2	C3	126.7(3)
O1	C2	C1	113.5(3)
C3	C2	C1	119.8(3)
N3	C17	C18	111.4(3)
C8	C9	C10	120.0(3)
O4	C20	C21	126.4(3)
O4	C20	C19	113.3(3)
C21	C20	C19	120.3(3)
N1	C5	C6	110.4(3)
F17	C18	F16	105.5(3)

Atom	Atom	Atom	Angle/°
O3	C14	C15	126.1(3)
O3	C14	C13	114.7(3)
C15	C14	C13	119.1(3)
F22	C24	C23	112.8(3)
F24	C24	F22	105.8(3)
F24	C24	F23	107.4(3)
F24	C24	C23	113.8(3)
F23	C24	F22	107.1(3)
F23	C24	C23	109.6(3)
F3	C1	C2	110.8(3)
F1	C1	F3	106.8(3)
F1	C1	F2	107.4(3)
F1	C1	C2	111.5(3)
F2	C1	F3	107.0(3)
F2	C1	C2	113.0(3)
F12	C12	F10	105.6(3)
F12	C12	C11	112.9(3)
F10	C12	C11	112.9(3)
F11	C12	F12	107.4(3)
F11	C12	F10	107.6(3)
F11	C12	C11	110.1(3)
N2	C10	C9	125.6(3)
N3	C16	C15	125.8(3)
C20	C21	C22	120.9(3)
F17	C18	C17	113.1(3)
F18	C18	F17	107.4(3)
F18	C18	F16	107.4(3)
F18	C18	C17	110.3(3)
F16	C18	C17	112.7(3)

Table 41. Torsion Angles for [Zr(TFB-TFEA)₄].

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Zr1	O4	C20	C21	-21.9(5)	C21	C20	C19	F20	119.5(3)
Zr1	O4	C20	C19	159.5(2)	C21	C20	C19	F21	-1.5(4)
Zr1	O1	C2	C3	-22.2(5)	C17	N3	C16	C15	-166.5(3)
Zr1	O1	C2	C1	159.7(2)	O1	C2	C1	F2	176.8(3)
Zr1	O3	C14	C15	-22.7(5)	O2	C8	C7	F8	-143.5(3)
Zr1	O3	C14	C13	160.6(2)	O2	C8	C7	F7	-22.2(4)
Zr1	O2	C8	C9	-22.3(5)	O2	C8	C7	F9	97.8(3)
Zr1	O2	C8	C7	160.5(2)	F14	C13	C14	O3	97.4(3)
Zr1	N3	C16	C15	20.7(4)	F14	C13	C14	C15	-79.6(4)
Zr1	N3	C17	C18	-113.5(2)	F13	C13	C14	O3	-143.0(3)
Zr1	N2	C10	C9	20.7(4)	F13	C13	C14	C15	39.9(4)
Zr1	N2	C11	C12	-113.8(2)	F15	C13	C14	O3	-22.4(4)
Zr1	N1	C4	C3	19.7(4)	F15	C13	C14	C15	160.6(3)
Zr1	N1	C5	C6	-110.5(3)	N3	C16	C15	C14	9.1(5)
Zr1	N4	C22	C21	18.8(4)	N3	C17	C18	F17	52.5(4)
Zr1	N4	C23	C24	-110.4(3)	N3	C17	C18	F18	172.8(3)
O4	C20	C19	F19	57.1(4)	N3	C17	C18	F16	-67.2(4)
O4	C20	C19	F20	-61.9(4)	N2	C10	C9	C8	9.2(5)
O4	C20	C19	F21	177.2(3)	N2	C11	C12	F12	52.8(4)
O1	C2	C1	F3	56.7(4)	N2	C11	C12	F10	-66.9(4)
O1	C2	C1	F1	-62.1(4)	N2	C11	C12	F11	172.8(3)
C4	N1	C5	C6	75.6(3)	N1	C4	C3	C2	8.3(5)
C4	C3	C2	O1	-10.9(5)	N1	C5	C6	F5	53.4(4)
C4	C3	C2	C1	167.0(3)	N1	C5	C6	F4	-67.3(4)
C22	N4	C23	C24	75.2(3)	N1	C5	C6	F6	173.8(3)
C22	C21	C20	O4	-11.8(5)	N4	C22	C21	C20	9.6(5)
C22	C21	C20	C19	166.6(3)	N4	C23	C24	F22	-67.2(4)
C3	C2	C1	F3	-121.5(3)	N4	C23	C24	F24	53.3(4)
C3	C2	C1	F1	119.7(3)	N4	C23	C24	F23	173.6(3)
C3	C2	C1	F2	-1.4(4)	C9	C8	C7	F8	39.2(4)
C10	N2	C11	C12	72.9(3)	C9	C8	C7	F7	160.5(3)
C10	C9	C8	O2	-12.6(5)	C9	C8	C7	F9	-79.5(4)
C10	C9	C8	C7	164.4(3)	C5	N1	C4	C3	-166.7(3)
C16	N3	C17	C18	73.2(3)	C11	N2	C10	C9	-166.5(3)
C16	C15	C14	O3	-12.4(5)	C23	N4	C22	C21	-167.1(3)
C16	C15	C14	C13	164.3(3)	C21	C20	C19	F19	-121.6(3)

Table 42. Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Zr}(\text{TFB-TFEA})_4]$.

Atom	x	y	z	U(eq)
H4	4606.25	1677.77	9300.65	31
H22	4595.63	3334.72	5701.38	30
H3	2345.81	1709.02	9376.91	31
H10	3520.54	3853.77	9718.25	33
H16	3511.06	1151.43	5280.84	34
H21	2338.95	3284.45	5619.05	31
H15	5789.44	1181.25	5241.11	36
H17A	1562.67	1517.64	5776.78	29
H17B	1375.63	1731.7	6651.54	29
H9	5796.51	3821.95	9755.86	34
H5A	6526.52	1916.44	8918.58	32
H5B	6711.15	1946.83	8094.78	32
H11A	1567.68	3483.7	9219.72	29
H11B	1381.18	3274.21	8345.34	29
H23A	6519.11	3086.16	6074.99	31
H23B	6708.02	3056.4	6898.52	31

Table 43. Crystal data and structure refinement for [Zr(TFB-*t*BuA)₂(NEt₂)(O^{*i*}Bu)].

Identification code	[Zr(TFB- <i>t</i> BuA) ₂ (NEt ₂)(O ^{<i>i</i>} Bu)]
Empirical formula	C ₂₄ H ₄₁ F ₆ N ₃ O ₃ Zr
Formula weight	624.82
Temperature/K	100.0
Crystal system	monoclinic
Space group	P2 ₁ /n
<i>a</i> /Å	9.8561(3)
<i>b</i> /Å	16.9853(6)
<i>c</i> /Å	17.8596(6)
α /°	90
β /°	97.9390(10)
γ /°	90
Volume/Å ³	2961.20(17)
<i>Z</i>	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.402
μ/mm^{-1}	0.437
<i>F</i> (000)	1296.0
Crystal size/mm ³	0.15 × 0.08 × 0.05
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	4.478 to 56.59
Index ranges	-12 ≤ <i>h</i> ≤ 13, -22 ≤ <i>k</i> ≤ 22, -23 ≤ <i>l</i> ≤ 23
Reflections collected	99734
Independent reflections	7334 [<i>R</i> _{int} = 0.0392, <i>R</i> _{sigma} = 0.0163]
Data/restraints/parameters	7334/0/345
Goodness-of-fit on <i>F</i> ²	1.043
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0559, <i>wR</i> ₂ = 0.1454
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0614, <i>wR</i> ₂ = 0.1506
Largest diff. peak/hole / e Å ⁻³	3.13/-1.83

Table 44. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Zr}(\text{TfB}-t\text{BuA})_2(\text{NEt}_2)(\text{O}^i\text{Bu})]$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Zr1	4858.3(3)	6135.6(2)	2552.7(2)	17.53(10)
F3	6707(2)	3935.9(13)	689.4(14)	38.7(5)
F1'	3311(2)	8580.2(14)	4183.8(13)	40.5(5)
O1'	3584(2)	6913.5(13)	3044.7(13)	23.6(4)
O1	5984(2)	5492.5(14)	1858.5(13)	23.8(5)
F2'	1748(2)	7746.2(18)	3783.9(15)	51.7(7)
O2	6454(2)	6388.4(14)	3248.8(13)	27.2(5)
F1	7895(2)	4978.8(17)	961.7(16)	51.4(7)
F2	7573(3)	4166.1(18)	1838.9(15)	55.1(8)
F3'	3524(3)	7375.9(16)	4532.1(13)	51.0(7)
N1	3070(2)	5812.9(15)	1466.8(14)	17.8(5)
N1'	5344(2)	7421.3(15)	1929.3(14)	18.7(5)
N2	4151(3)	5217.1(17)	3063.6(16)	27.9(6)
C5'	6072(3)	7480.6(18)	1238.7(17)	19.5(5)
C4	3237(3)	5256.1(18)	1002.4(17)	21.5(6)
C5	1650(3)	6176.0(19)	1382.1(18)	22.0(6)
C6'	5301(3)	6970.9(19)	615.9(17)	23.6(6)
C7'	7528(3)	7167(2)	1467.3(19)	26.5(6)
C4'	5201(3)	8067.5(19)	2286.7(19)	24.6(6)
C2	5706(3)	4961.4(17)	1345.4(16)	18.4(5)
C2'	3811(3)	7635.0(19)	3265.8(18)	23.6(6)
C3	4477(3)	4816.3(19)	940.5(19)	26.2(6)
C3'	4554(3)	8178(2)	2959(2)	28.9(7)
C1'	3102(4)	7839(2)	3943(2)	31.1(7)
C8'	6162(4)	8319(2)	928(2)	29.5(7)
C13	7615(4)	6390(2)	3808.7(19)	29.3(7)
C7	998(3)	5938(2)	2079.5(19)	29.3(7)
C1	6966(3)	4504(2)	1206(2)	30.8(7)
C6	1813(3)	7067(2)	1347(2)	30.5(7)
C8	694(3)	5916(2)	675(2)	31.5(7)
C15	7138(4)	6625(3)	4549(2)	46.9(11)
C16	8635(5)	6983(3)	3595(3)	52.9(12)
C14	8211(7)	5563(3)	3846(3)	73.6(19)
C11	3748(6)	4387(3)	2818(3)	63.9(14)
C9	2657(12)	5260(4)	4066(3)	119(4)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
C12	4965(7)	3839(4)	3003(5)	88(2)
C10	3902(6)	5098(8)	3804(6)	202(8)

Table 45. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for [Zr(TFB-*t*BuA)₂(NEt₂)(O^{*i*}Bu)]. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Zr1	19.52(15)	17.90(16)	14.72(15)	-2.44(9)	0.76(10)	0.19(10)
F3	33.9(11)	37.5(12)	43.6(13)	-20.8(10)	1.7(9)	12.1(9)
F1'	43.4(13)	39.7(12)	40.6(12)	-22.0(10)	13.8(10)	-0.6(10)
O1'	24.7(11)	23.7(11)	23.9(11)	-7.1(8)	8.3(8)	-3.1(8)
O1	20.1(10)	25.4(11)	24.7(11)	-8.6(9)	-1.4(8)	4.3(8)
F2'	28.0(11)	75.5(19)	56.0(15)	-31.3(14)	21.9(11)	-11.4(11)
O2	29.2(12)	27.2(11)	22.6(11)	-5.5(9)	-5.7(9)	-1.3(9)
F1	25.5(11)	63.6(17)	69.3(17)	-29.0(14)	21.4(11)	-7.2(11)
F2	49.9(15)	67.1(18)	43.5(14)	-11.2(13)	-10.6(11)	39.1(14)
F3'	75.8(19)	52.0(15)	29.6(12)	-3.1(11)	22.9(12)	11.8(13)
N1	14.2(10)	19.9(11)	19.7(11)	1.7(9)	3.3(9)	0.9(9)
N1'	15.8(11)	21.0(12)	19.5(11)	0.2(9)	2.9(9)	-0.3(9)
N2	32.7(14)	24.5(13)	23.4(13)	-2.3(10)	-6.7(11)	2.2(11)
C5'	19.0(13)	20.4(13)	19.5(13)	1.1(10)	4.3(10)	-1.5(10)
C4	18.0(13)	21.1(14)	24.0(14)	-2.6(11)	-1.9(11)	-1.0(11)
C5	15.6(13)	29.3(16)	21.2(14)	-0.9(11)	2.8(11)	3.5(11)
C6'	26.5(15)	25.4(15)	19.6(14)	0.0(11)	5.3(11)	-1.2(12)
C7'	18.2(13)	31.6(16)	30.8(16)	2.1(13)	7.4(12)	0.0(12)
C4'	23.2(14)	20.9(14)	30.5(16)	-4.2(12)	6.4(12)	-5.4(11)
C2	19.7(13)	16.6(12)	19.1(13)	-2.2(10)	3.5(10)	2.4(10)
C2'	19.1(13)	28.0(15)	23.7(14)	-10.1(12)	3.0(11)	-0.1(11)
C3	22.9(14)	22.5(15)	32.2(16)	-10.7(12)	-0.3(12)	3.7(12)
C3'	29.4(16)	25.8(16)	33.3(17)	-13.7(13)	10.5(13)	-5.1(13)
C1'	28.6(16)	36.3(18)	30.4(17)	-12.9(14)	10.8(13)	-3.3(14)
C8'	36.0(18)	23.9(15)	29.4(16)	4.9(13)	7.5(14)	-2.9(13)
C13	27.1(16)	36.1(18)	22.8(15)	-4.1(13)	-3.3(12)	-0.5(13)
C7	16.5(13)	46(2)	25.5(15)	-0.2(14)	5.2(12)	1.4(13)
C1	22.0(15)	37.0(18)	32.3(17)	-11.5(14)	0.1(13)	7.8(13)
C6	23.3(15)	28.8(17)	39.2(19)	2.8(14)	4.0(13)	8.4(13)
C8	19.2(14)	46(2)	27.5(16)	-6.4(15)	-2.3(12)	7.7(14)

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C15	31.3(19)	84(3)	25.0(17)	-11.5(19)	1.7(14)	-11(2)
C16	37(2)	84(4)	37(2)	1(2)	1.5(17)	-22(2)
C14	95(4)	56(3)	60(3)	-6(3)	-26(3)	38(3)
C11	68(3)	60(3)	63(3)	12(3)	5(3)	1(3)
C9	253(12)	72(4)	35(3)	1(3)	32(5)	-58(6)
C12	75(4)	60(4)	131(7)	31(4)	20(4)	8(3)
C10	33(3)	385(18)	190(9)	249(12)	24(4)	21(6)

Table 46. Bond Lengths for [Zr(TFB-*t*BuA)₂(NEt₂)(O^tBu)].

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zr1	O1'	2.098(2)	N2	C11	1.512(7)
Zr1	O1	2.083(2)	N2	C10	1.392(9)
Zr1	O2	1.914(2)	C5'	C6'	1.527(4)
Zr1	N1	2.495(2)	C5'	C7'	1.532(4)
Zr1	N1'	2.527(3)	C5'	C8'	1.535(4)
Zr1	N2	1.982(3)	C4	C3	1.450(4)
F3	C1	1.335(4)	C5	C7	1.533(4)
F1'	C1'	1.337(4)	C5	C6	1.524(5)
O1'	C2'	1.297(4)	C5	C8	1.532(4)
O1	C2	1.288(4)	C4'	C3'	1.447(5)
F2'	C1'	1.335(4)	C2	C3	1.345(4)
O2	C13	1.412(4)	C2	C1	1.515(4)
F1	C1	1.338(5)	C2'	C3'	1.341(5)
F2	C1	1.333(4)	C2'	C1'	1.518(4)
F3'	C1'	1.332(5)	C13	C15	1.517(5)
N1	C4	1.283(4)	C13	C16	1.508(6)
N1	C5	1.518(4)	C13	C14	1.521(6)
N1'	C5'	1.513(4)	C11	C12	1.519(9)
N1'	C4'	1.287(4)	C9	C10	1.400(13)

Table 47. Bond Angles for [Zr(TFB-*t*BuA)₂(NEt₂)(O^{*i*}Bu)].

Atom	Atom	Atom	Angle/°
O1'	Zr1	N1	93.69(8)
O1'	Zr1	N1'	78.52(8)
O1	Zr1	O1'	168.04(9)
O1	Zr1	N1	78.42(8)
O1	Zr1	N1'	92.41(9)
O2	Zr1	O1'	94.15(10)
O2	Zr1	O1	92.69(9)
O2	Zr1	N1	169.47(9)
O2	Zr1	N1'	84.47(9)
O2	Zr1	N2	100.81(11)
N1	Zr1	N1'	90.22(8)
N2	Zr1	O1'	91.94(11)
N2	Zr1	O1	96.40(11)
N2	Zr1	N1	85.94(10)
N2	Zr1	N1'	169.48(10)
C2'	O1'	Zr1	129.4(2)
C2	O1	Zr1	135.4(2)
C13	O2	Zr1	166.8(2)
C4	N1	Zr1	121.63(19)
C4	N1	C5	115.7(2)
C5	N1	Zr1	122.07(18)
C5'	N1'	Zr1	123.82(18)
C4'	N1'	Zr1	118.6(2)
C4'	N1'	C5'	116.4(3)
C11	N2	Zr1	134.0(3)
C10	N2	Zr1	132.1(7)
C10	N2	C11	93.8(7)
N1'	C5'	C6'	108.2(2)
N1'	C5'	C7'	107.0(2)
N1'	C5'	C8'	114.4(3)
C6'	C5'	C7'	110.5(3)
C6'	C5'	C8'	108.1(3)
C7'	C5'	C8'	108.7(3)
N1	C4	C3	127.9(3)
N1	C5	C7	107.2(2)

Atom	Atom	Atom	Angle/°
N1	C5	C6	107.8(2)
N1	C5	C8	114.7(3)
C6	C5	C7	110.8(3)
C6	C5	C8	108.0(3)
C8	C5	C7	108.3(3)
N1'	C4'	C3'	127.8(3)
O1	C2	C3	126.7(3)
O1	C2	C1	112.2(3)
C3	C2	C1	121.0(3)
O1'	C2'	C3'	127.3(3)
O1'	C2'	C1'	112.3(3)
C3'	C2'	C1'	120.4(3)
C2	C3	C4	124.8(3)
C2'	C3'	C4'	125.3(3)
F1'	C1'	C2'	113.8(3)
F2'	C1'	F1'	106.5(3)
F2'	C1'	C2'	111.1(3)
F3'	C1'	F1'	106.6(3)
F3'	C1'	F2'	107.0(3)
F3'	C1'	C2'	111.5(3)
O2	C13	C15	107.4(3)
O2	C13	C16	109.0(3)
O2	C13	C14	107.4(3)
C15	C13	C14	111.6(4)
C16	C13	C15	110.0(3)
C16	C13	C14	111.2(4)
F3	C1	F1	106.5(3)
F3	C1	C2	113.7(3)
F1	C1	C2	111.0(3)
F2	C1	F3	107.2(3)
F2	C1	F1	106.8(3)
F2	C1	C2	111.3(3)
N2	C11	C12	109.9(5)
N2	C10	C9	124.6(5)

Table 48. Torsion Angles for [Zr(TFB-*t*BuA)₂(NEt₂)(O'*i*Bu)].

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Zr1	O1'	C2'	C3'	33.1(5)	O1	C2	C1	F1	-61.5(4)
Zr1	O1'	C2'	C1'	-147.7(2)	O1	C2	C1	F2	57.3(4)
Zr1	O1	C2	C3	21.4(5)	N1	C4	C3	C2	-4.3(6)
Zr1	O1	C2	C1	-160.8(2)	N1'	C4'	C3'	C2'	-10.2(6)
Zr1	O2	C13	C15	-92.1(10)	C5'	N1'	C4'	C3'	-179.9(3)
Zr1	O2	C13	C16	148.7(9)	C4	N1	C5	C7	110.9(3)
Zr1	O2	C13	C14	28.1(12)	C4	N1	C5	C6	-129.7(3)
Zr1	N1	C4	C3	-10.1(5)	C4	N1	C5	C8	-9.4(4)
Zr1	N1	C5	C7	-60.4(3)	C5	N1	C4	C3	178.6(3)
Zr1	N1	C5	C6	59.0(3)	C4'	N1'	C5'	C6'	-137.6(3)
Zr1	N1	C5	C8	179.3(2)	C4'	N1'	C5'	C7'	103.3(3)
Zr1	N1'	C5'	C6'	55.4(3)	C4'	N1'	C5'	C8'	-17.1(4)
Zr1	N1'	C5'	C7'	-63.6(3)	C3	C2	C1	F3	-3.5(5)
Zr1	N1'	C5'	C8'	176.0(2)	C3	C2	C1	F1	116.5(4)
Zr1	N1'	C4'	C3'	-12.2(5)	C3	C2	C1	F2	-124.7(4)
Zr1	N2	C11	C12	92.4(6)	C3'	C2'	C1'	F1'	-0.5(5)
Zr1	N2	C10	C9	90.0(12)	C3'	C2'	C1'	F2'	119.6(4)
O1'	C2'	C3'	C4'	3.2(6)	C3'	C2'	C1'	F3'	-121.1(4)
O1'	C2'	C1'	F1'	-179.7(3)	C1'	C2'	C3'	C4'	-175.9(3)
O1'	C2'	C1'	F2'	-59.6(4)	C1	C2	C3	C4	-176.0(3)
O1'	C2'	C1'	F3'	59.7(4)	C11	N2	C10	C9	-92.4(13)
O1	C2	C3	C4	1.6(6)	C10	N2	C11	C12	-85.1(6)
O1	C2	C1	F3	178.5(3)					

Table 49. Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for [Zr(TFB-*t*BuA)₂(NEt₂)(O'*i*Bu)].

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H4	2452.83	5115.09	657.44	26
H6'A	5256.31	6428.18	797.05	35
H6'B	5780.8	6981.31	170.68	35
H6'C	4369.99	7176.21	480.22	35
H7'A	8008.89	7501.4	1865.63	40
H7'B	8021.23	7172.1	1027.04	40
H7'C	7484.58	6626.83	1655.43	40
H4'	5564.49	8527.05	2085.13	30
H3	4417.74	4394.62	588	31

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H3'	4664.54	8675.65	3202.16	35
H8'A	5246.05	8554.78	849.65	44
H8'B	6530.3	8299.51	446.28	44
H8'C	6766.91	8636.98	1290.87	44
H7A	919.99	5362.82	2097.48	44
H7B	84.23	6173.2	2049.85	44
H7C	1571.8	6124.01	2536.95	44
H6A	2417.7	7247.74	1795.61	46
H6B	914.03	7317.89	1330.26	46
H6C	2211.76	7207.58	891.77	46
H8A	1116.3	6039.44	223.82	47
H8B	-181.75	6193.78	652.15	47
H8C	536.67	5346.92	698.08	47
H15A	6791.85	7166.64	4511.12	70
H15B	7908.55	6591.43	4958.35	70
H15C	6406.46	6269.47	4656.47	70
H16A	8977.96	6809.77	3132.4	79
H16B	9400.8	7026.78	4005.42	79
H16C	8187.61	7496.25	3508.13	79
H14A	7505.55	5185.47	3946.35	110
H14B	8985.72	5535.39	4253.24	110
H14C	8524.94	5434.72	3363.52	110
H11A	3430.97	4377.96	2267.82	77
H11B	2984.28	4207.2	3082.47	77
H9A	2313.96	5773.27	3874.43	179
H9B	2797.47	5268.53	4620.27	179
H9C	1988.6	4850.71	3888.12	179
H12A	5675.45	3979.16	2692.86	132
H12B	4671.77	3294.64	2895.93	132
H12C	5334.02	3889.98	3539.13	132
H10A	4608.31	5404.24	4128.61	242
H10B	4101.56	4536.4	3917.49	242

Table 50. Crystal data and structure refinement for [Zr(TFB-*t*BuA)₂(O^{*i*}Bu)₂].

Identification code	[Zr(TFB- <i>t</i> BuA) ₂ (O ^{<i>i</i>} Bu) ₂]
Empirical formula	C ₂₄ H ₄₀ F ₆ N ₂ O ₄ Zr
Formula weight	625.80
Temperature/K	100.00
Crystal system	monoclinic
Space group	P2 ₁ /n
<i>a</i> /Å	9.8124(5)
<i>b</i> /Å	17.2234(7)
<i>c</i> /Å	17.9667(8)
α /°	90
β /°	97.349(2)
γ /°	90
Volume/Å ³	3011.5(2)
<i>Z</i>	4
ρ_{calc} /cm ³	1.380
μ /mm ⁻¹	0.432
<i>F</i> (000)	1296.0
Crystal size/mm ³	0.05 × 0.04 × 0.02
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	4.506 to 56.608
Index ranges	-13 ≤ <i>h</i> ≤ 13, -22 ≤ <i>k</i> ≤ 22, -23 ≤ <i>l</i> ≤ 23
Reflections collected	83300
Independent reflections	7479 [<i>R</i> _{int} = 0.0902, <i>R</i> _{sigma} = 0.0421]
Data/restraints/parameters	7479/12/346
Goodness-of-fit on <i>F</i> ²	1.053
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0497, <i>wR</i> ₂ = 0.1242
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0767, <i>wR</i> ₂ = 0.1411
Largest diff. peak/hole / e Å ⁻³	1.65/-0.80

Table 51. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Zr}(\text{TFB}-t\text{BuA})_2(\text{O}^t\text{Bu})_2]$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Zr1	5054.1(3)	3857.9(2)	7480.5(2)	17.65(10)
F2	3306(2)	6057.9(13)	9311.1(14)	43.7(6)
O2'	3442(2)	3619.5(14)	6806.1(13)	27.9(5)
O1	3934(2)	4438.9(13)	8224.7(13)	25.2(5)
O1'	6345(2)	3123.4(14)	6955.3(14)	29.7(5)
F3'	6637(3)	1515.1(15)	5783.5(14)	49.6(6)
F1	2092(3)	5031.6(16)	9102.0(18)	58.2(8)
F3	2403(3)	5797.0(17)	8186.0(16)	63.0(9)
O2	5701(3)	4767.9(15)	7025.9(15)	34.3(6)
F1'	6393(3)	2700.4(18)	5456.3(15)	63.3(8)
F2'	8174(3)	2335(2)	6187.0(17)	68.1(9)
N1	6908(3)	4164.7(16)	8526.5(15)	23.0(6)
N1'	4616(3)	2590.0(16)	8070.6(16)	23.3(6)
C5'	3932(3)	2498.9(19)	8772.3(19)	23.4(7)
C5	8320(3)	3807(2)	8601.2(19)	25.9(7)
C4	6763(4)	4744(2)	8962(2)	27.9(7)
C6'	4699(4)	3000(2)	9392.4(19)	28.3(7)
C8'	2449(3)	2785(2)	8588(2)	29.9(8)
C2'	6106(3)	2426(2)	6709(2)	27.5(7)
C2	4258(4)	5012.5(19)	8678(2)	25.9(7)
C4'	4734(3)	1967(2)	7685(2)	27.5(7)
C9'	2304(4)	3554(2)	6246(2)	31.3(8)
C3	5523(4)	5187(2)	9020(2)	31.9(8)
C3'	5357(4)	1881(2)	7002(2)	29.4(7)
C6	8989(4)	4037(2)	7914(2)	33.6(8)
C1	3027(4)	5481(2)	8827(2)	37.8(9)
C1'	6824(4)	2235(2)	6036(2)	36.6(9)
C8	8152(4)	2925(2)	8623(2)	36.1(9)
C7'	3913(4)	1664(2)	9068(2)	38.7(9)
C7	9271(4)	4044(3)	9307(2)	38.6(9)
C12'	1413(5)	2894(3)	6451(3)	45.9(10)
C10'	2871(5)	3375(4)	5511(2)	56.0(13)
C11'	1521(5)	4310(3)	6198(3)	59.9(14)
C11	4904(5)	5719(3)	6114(3)	55.8(13)
C9	6092(6)	5359(4)	6558(3)	76(2)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
C10	7210(7)	5800(4)	6856(4)	92(2)
C12	6899(9)	4834(5)	5930(5)	108(3)

Table 52. Anisotropic Displacement Parameters (Å²×10³) for [Zr(TFB-*t*BuA)₂(O^{*i*}Bu)₂].

The Anisotropic displacement factor exponent takes the form:

$$-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...].$$

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Zr1	17.88(15)	18.64(15)	16.18(15)	-1.38(12)	1.24(10)	-1.57(11)
F2	44.1(13)	36.3(12)	50.5(14)	-18.4(11)	5.1(11)	9.6(10)
O2'	26.7(12)	31.5(12)	23.5(12)	-4.0(10)	-4.1(10)	-1.0(10)
O1	24.8(12)	26.2(11)	24.8(12)	-6.9(9)	3.3(9)	2.4(9)
O1'	27.3(13)	32.5(13)	30.9(13)	-8.3(10)	9.4(10)	-5.1(10)
F3'	53.6(15)	48.7(15)	48.1(15)	-25.1(12)	13.4(12)	2.7(12)
F1	35.1(13)	57.0(16)	87(2)	-29.8(15)	26.5(14)	-6.7(11)
F3	60.1(17)	69.3(18)	52.8(16)	-14.8(14)	-18.9(14)	42.2(15)
O2	38.9(15)	30.9(13)	32.0(14)	7.3(11)	0.2(11)	-10.3(11)
F1'	91(2)	67.4(19)	36.8(15)	1.8(13)	28.1(15)	17.9(16)
F2'	26.7(13)	113(3)	68.1(19)	-43.1(18)	21.9(13)	-10.3(14)
N1	20.0(13)	28.2(14)	20.9(14)	1.1(11)	3.4(11)	-0.3(11)
N1'	17.7(13)	26.6(14)	25.5(14)	1.1(11)	2.7(11)	-1.5(10)
C5'	22.6(16)	25.2(16)	23.6(16)	4.1(13)	6.9(13)	-0.6(12)
C5	21.3(16)	30.3(17)	25.9(17)	-1.9(13)	1.8(13)	-0.8(13)
C4	26.5(17)	27.6(17)	27.9(18)	-3.1(14)	-2.8(14)	-2.6(13)
C6'	30.0(18)	31.9(18)	23.3(17)	4.4(14)	5.3(14)	2.1(14)
C8'	19.6(16)	38.6(19)	32.3(19)	3.4(15)	6.2(14)	-0.1(14)
C2'	21.5(16)	35.0(18)	26.6(18)	-10.5(14)	5.9(13)	2.8(13)
C2	26.9(17)	23.0(16)	27.8(17)	-4.9(13)	3.5(14)	1.6(13)
C4'	24.6(17)	23.7(16)	34.1(19)	-1.4(14)	3.1(14)	-3.9(13)
C9'	23.0(17)	42(2)	27.1(18)	0.2(15)	-4.7(14)	-6.0(15)
C3	31.5(19)	27.0(17)	36(2)	-8.9(15)	-1.7(15)	3.5(14)
C3'	25.3(17)	27.1(17)	36(2)	-6.6(14)	2.7(15)	-0.5(13)
C6	22.7(17)	45(2)	34(2)	-0.2(16)	7.5(15)	-3.9(15)
C1	30.5(19)	38(2)	43(2)	-16.1(18)	0.6(17)	7.6(16)
C1'	32(2)	46(2)	34(2)	-10.2(17)	11.2(16)	1.1(16)
C8	27.4(19)	31.9(19)	49(2)	7.0(17)	6.8(17)	6.6(15)
C7'	45(2)	32.5(19)	40(2)	7.7(17)	9.0(18)	0.7(17)
C7	25.2(18)	53(2)	37(2)	-6.8(18)	-0.3(16)	7.7(16)

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C12'	41(2)	54(3)	41(2)	-2(2)	-0.6(19)	-18(2)
C10'	36(2)	101(4)	30(2)	-6(2)	-1.6(18)	-17(2)
C11'	45(3)	50(3)	80(4)	13(3)	-8(3)	13(2)
C11	46(3)	51(3)	69(3)	31(2)	2(2)	-5(2)
C9	62(3)	86(4)	70(4)	54(3)	-31(3)	-46(3)
C10	88(3)	85(3)	100(3)	11.5(18)	3.3(18)	-8.6(18)
C12	110(3)	111(3)	106(3)	5.4(19)	21.2(19)	2.3(19)

Table 53. Bond Lengths for [Zr(TFB-*t*BuA)₂(O'*Bu*)₂].

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zr1	O2'	1.910(2)	N1'	C4'	1.291(4)
Zr1	O1	2.091(2)	C5'	C6'	1.529(5)
Zr1	O1'	2.098(2)	C5'	C8'	1.532(5)
Zr1	O2	1.913(2)	C5'	C7'	1.534(5)
Zr1	N1	2.499(3)	C5	C6	1.523(5)
Zr1	N1'	2.489(3)	C5	C8	1.529(5)
F2	C1	1.326(4)	C5	C7	1.531(5)
O2'	C9'	1.409(4)	C4	C3	1.452(5)
O1	C2	1.293(4)	C2'	C3'	1.341(5)
O1'	C2'	1.292(4)	C2'	C1'	1.511(5)
F3'	C1'	1.325(5)	C2	C3	1.347(5)
F1	C1	1.342(5)	C2	C1	1.505(5)
F3	C1	1.347(5)	C4'	C3'	1.446(5)
O2	C9	1.405(5)	C9'	C12'	1.508(5)
F1'	C1'	1.340(5)	C9'	C10'	1.529(6)
F2'	C1'	1.328(5)	C9'	C11'	1.508(6)
N1	C5	1.506(4)	C11	C9	1.464(7)
N1	C4	1.287(4)	C9	C10	1.385(8)
N1'	C5'	1.510(4)	C9	C12	1.715(10)

Table 54. Bond Angles for [Zr(TFB-*t*BuA)₂(O^{*i*}Bu)₂].

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2'	Zr1	O1	92.77(10)	C8	C5	C7	107.4(3)
O2'	Zr1	O1'	94.79(10)	N1	C4	C3	127.6(3)
O2'	Zr1	O2	101.43(11)	O1'	C2'	C3'	126.9(3)
O2'	Zr1	N1	170.60(10)	O1'	C2'	C1'	113.2(3)
O2'	Zr1	N1'	84.69(10)	C3'	C2'	C1'	119.8(3)
O1	Zr1	O1'	166.68(10)	O1	C2	C3	126.6(3)
O1	Zr1	N1	79.02(9)	O1	C2	C1	112.6(3)
O1	Zr1	N1'	90.80(9)	C3	C2	C1	120.8(3)
O1'	Zr1	N1	92.43(9)	N1'	C4'	C3'	128.1(3)
O1'	Zr1	N1'	79.03(9)	O2'	C9'	C12'	108.5(3)
O2	Zr1	O1	96.37(11)	O2'	C9'	C10'	106.9(3)
O2	Zr1	O1'	92.85(11)	O2'	C9'	C11'	108.9(3)
O2	Zr1	N1	84.18(10)	C12'	C9'	C10'	110.2(4)
O2	Zr1	N1'	170.29(10)	C11'	C9'	C12'	110.9(4)
N1'	Zr1	N1	90.81(9)	C11'	C9'	C10'	111.3(4)
C9'	O2'	Zr1	170.6(2)	C2	C3	C4	125.6(3)
C2	O1	Zr1	131.4(2)	C2'	C3'	C4'	125.0(3)
C2'	O1'	Zr1	128.4(2)	F2	C1	F1	106.5(3)
C9	O2	Zr1	168.6(3)	F2	C1	F3	107.0(3)
C5	N1	Zr1	123.6(2)	F2	C1	C2	114.5(3)
C4	N1	Zr1	119.6(2)	F1	C1	F3	106.9(3)
C4	N1	C5	115.8(3)	F1	C1	C2	111.0(3)
C5'	N1'	Zr1	124.5(2)	F3	C1	C2	110.6(3)
C4'	N1'	Zr1	117.9(2)	F3'	C1'	F1'	106.1(3)
C4'	N1'	C5'	116.2(3)	F3'	C1'	F2'	106.5(3)
N1'	C5'	C6'	108.6(3)	F3'	C1'	C2'	114.8(3)
N1'	C5'	C8'	107.3(3)	F1'	C1'	C2'	111.0(3)
N1'	C5'	C7'	114.4(3)	F2'	C1'	F1'	106.7(4)
C6'	C5'	C8'	110.0(3)	F2'	C1'	C2'	111.3(3)
C6'	C5'	C7'	107.7(3)	O2	C9	C11	111.9(4)
C8'	C5'	C7'	108.8(3)	O2	C9	C12	101.3(5)
N1	C5	C6	108.0(3)	C11	C9	C12	105.5(5)
N1	C5	C8	107.9(3)	C10	C9	O2	115.4(5)
N1	C5	C7	114.9(3)	C10	C9	C11	121.0(5)
C6	C5	C8	109.7(3)	C10	C9	C12	97.7(6)
C6	C5	C7	108.8(3)				

Table 55. Torsion Angles for [Zr(TFB-*t*BuA)₂(O'*i*Bu)₂].

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Zr1	O1	C2	C3	-29.7(5)	O1'	C2'	C1'	F1'	-61.8(4)
Zr1	O1	C2	C1	152.8(3)	O1'	C2'	C1'	F2'	56.9(5)
Zr1	O1'	C2'	C3'	-33.7(5)	N1	C4	C3	C2	7.5(6)
Zr1	O1'	C2'	C1'	148.9(3)	N1'	C4'	C3'	C2'	10.3(6)
Zr1	O2	C9	C11	67(2)	C5'	N1'	C4'	C3'	-179.0(3)
Zr1	O2	C9	C10	-149.0(14)	C5	N1	C4	C3	-178.8(3)
Zr1	O2	C9	C12	-44.7(18)	C4	N1	C5	C6	-107.0(3)
Zr1	N1	C5	C6	61.5(3)	C4	N1	C5	C8	134.5(3)
Zr1	N1	C5	C8	-57.1(3)	C4	N1	C5	C7	14.7(4)
Zr1	N1	C5	C7	-176.8(2)	C4'	N1'	C5'	C6'	139.8(3)
Zr1	N1	C4	C3	12.3(5)	C4'	N1'	C5'	C8'	-101.3(3)
Zr1	N1'	C5'	C6'	-53.8(3)	C4'	N1'	C5'	C7'	19.5(4)
Zr1	N1'	C5'	C8'	65.1(3)	C3	C2	C1	F2	-0.2(6)
Zr1	N1'	C5'	C7'	-174.1(2)	C3	C2	C1	F1	-120.8(4)
Zr1	N1'	C4'	C3'	13.7(5)	C3	C2	C1	F3	120.8(4)
O1	C2	C3	C4	-2.1(6)	C3'	C2'	C1'	F3'	0.3(5)
O1	C2	C1	F2	177.5(3)	C3'	C2'	C1'	F1'	120.6(4)
O1	C2	C1	F1	56.9(4)	C3'	C2'	C1'	F2'	-120.7(4)
O1	C2	C1	F3	-61.5(4)	C1	C2	C3	C4	175.3(4)
O1'	C2'	C3'	C4'	-3.6(6)	C1'	C2'	C3'	C4'	173.6(3)
O1'	C2'	C1'	F3'	177.9(3)					

Table 56. Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for [Zr(TFB-*t*BuA)₂(O'*i*Bu)₂].

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H4	7561.61	4900.54	9282.59	33
H6'A	5643.53	2810.02	9510.96	42
H6'B	4231.72	2971.39	9842.06	42
H6'C	4714.42	3540.07	9221.69	42
H8'A	2450.59	3327.88	8424.81	45
H8'B	1978.31	2743.86	9035.64	45
H8'C	1968.44	2465.97	8185.01	45
H4'	4365.76	1507.08	7872.8	33
H3	5610.56	5639.25	9325.9	38
H3'	5225.54	1401.08	6741.6	35
H6A	8397.15	3876.95	7458.31	50

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H6B	9883.66	3779.82	7931.48	50
H6C	9116.24	4600.98	7908.47	50
H8A	7744.87	2779.16	9073.75	54
H8B	9053.06	2677.3	8634.34	54
H8C	7549.65	2754.11	8176.01	54
H7'A	3297.86	1347.35	8718.19	58
H7'B	3585.47	1663.98	9561.07	58
H7'C	4843.73	1447.67	9114.3	58
H7A	9474.18	4599.82	9286.48	58
H7B	10129.04	3747.52	9335.9	58
H7C	8819.19	3935.07	9752.02	58
H12A	1962.6	2418.57	6518.17	69
H12B	651.36	2817.09	6048.43	69
H12C	1045.59	3018.38	6918.91	69
H10A	3548.02	3770.4	5419.64	84
H10B	2116.92	3376.39	5096.41	84
H10C	3310.09	2863.05	5545.17	84
H11A	1265.8	4440.82	6692.7	90
H11B	687.88	4257.42	5837.17	90
H11C	2099.23	4723.49	6032.48	90
H11D	4408.89	5327.32	5788.32	84
H11E	5216.71	6135.59	5805.26	84
H11F	4290.62	5934.8	6450.99	84
H10D	6941.41	6138.72	7250.88	138
H10E	7526.86	6117.35	6459.67	138
H10F	7954.41	5455.42	7070.15	138
H12D	7538.02	4464.55	6203.07	162
H12E	7407.05	5187.52	5638.91	162
H12F	6211.21	4550.78	5590.71	162

Table 57. Crystal data and structure refinement for [Hf(TFB-*t*BuA)₂(O^{*i*}Bu)₂].

Identification code	[Hf(TFB- <i>t</i> BuA) ₂ (O ^{<i>i</i>} Bu) ₂]
Empirical formula	C ₂₄ H ₄₀ F ₆ HfN ₂ O ₄
Formula weight	713.07
Temperature/K	100.00
Crystal system	monoclinic
Space group	P2 ₁ /n
<i>a</i> /Å	9.8037(6)
<i>b</i> /Å	17.2112(10)
<i>c</i> /Å	17.9261(12)
α /°	90
β /°	97.076(2)
γ /°	90
Volume/Å ³	3001.7(3)
<i>Z</i>	4
ρ_{calc} /cm ³	1.578
μ /mm ⁻¹	3.542
<i>F</i> (000)	1424.0
Crystal size/mm ³	0.13 × 0.1 × 0.07
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	4.518 to 56.598
Index ranges	-13 ≤ <i>h</i> ≤ 12, -22 ≤ <i>k</i> ≤ 22, -23 ≤ <i>l</i> ≤ 23
Reflections collected	69998
Independent reflections	7449 [<i>R</i> _{int} = 0.0479, <i>R</i> _{sigma} = 0.0238]
Data/restraints/parameters	7449/0/346
Goodness-of-fit on <i>F</i> ²	1.086
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0234, <i>wR</i> ₂ = 0.0468
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0275, <i>wR</i> ₂ = 0.0484
Largest diff. peak/hole / e Å ⁻³	1.09/-0.97

Table 58. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Hf}(\text{TFB}-t\text{BuA})_2(\text{O}^t\text{Bu})_2]$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Hf1	4933.0(2)	6171.4(2)	2507.1(2)	14.33(3)
F1	1812.5(19)	7702.1(15)	3793.2(13)	59.9(7)
F2	3568(2)	7321.0(12)	4534.1(11)	53.3(6)
F3	3372.4(19)	8512.5(11)	4207.5(10)	40.0(4)
F1'	7898.9(19)	4986.8(12)	887.3(13)	49.9(5)
F2'	6679.3(18)	3957.7(10)	695.3(10)	35.4(4)
F3'	7603(2)	4235.3(13)	1814.6(12)	54.6(6)
O1	3648.2(17)	6897.4(10)	3034.0(10)	21.7(4)
O1'	6063.8(17)	5591.6(10)	1776.7(10)	19.8(3)
O2	6536.8(18)	6412.6(11)	3176.1(10)	23.2(4)
O2'	4276(2)	5264.9(11)	2959.9(10)	26.8(4)
N1	5378.2(19)	7419.6(12)	1914.0(11)	17.4(4)
N1'	3102(2)	5874.5(12)	1477.0(12)	18.2(4)
C1	3161(3)	7788.0(18)	3953.9(16)	29.8(6)
C2	3897(2)	7597.8(15)	3281.1(15)	21.4(5)
C3	4672(3)	8135.5(15)	2991.2(15)	22.4(5)
C4	5285(2)	8042.5(15)	2305.0(14)	20.7(5)
C5	6069(2)	7507.0(14)	1209.7(14)	19.0(5)
C6	5306(3)	7000.9(15)	594.9(14)	22.5(5)
C7	7552(3)	7228.4(16)	1396.3(15)	24.7(5)
C8	6077(3)	8340.6(16)	906.8(17)	29.8(6)
C1'	6972(3)	4543.5(17)	1175.5(17)	29.2(6)
C2'	5734(3)	5011.0(14)	1325.4(14)	19.5(5)
C3'	4470(3)	4832.9(15)	992.5(15)	23.0(5)
C4'	3240(3)	5284.5(15)	1049.1(15)	21.6(5)
C5'	1686(2)	6244.0(15)	1399.4(14)	20.6(5)
C6'	1864(3)	7122.5(16)	1388.2(18)	29.7(6)
C7'	994(3)	5997.8(17)	2084.3(16)	26.9(6)
C8'	753(3)	6012.8(19)	680.4(16)	32.1(6)
C9	7680(3)	6456.7(17)	3740.8(15)	25.2(5)
C10	8456(3)	5696(2)	3760(2)	50.1(9)
C11	8589(3)	7122(2)	3548.3(18)	38.3(7)
C12	7120(3)	6616(2)	4482.5(17)	44.4(9)
C9'	3842(3)	4726.4(19)	3480.9(19)	40.2(8)
C10'	5084(3)	4294(2)	3850(2)	47.4(9)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
C11'	2774(4)	4216(2)	3105(3)	72.9(15)
C12'	3188(5)	5206(3)	4084(3)	72.6(14)

Table 59. Anisotropic Displacement Parameters (Å²×10³) for [Hf(TFB-*t*BuA)₂(O'*i*Bu)₂].

The Anisotropic displacement factor exponent takes the form:

$$-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...].$$

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Hf1	14.91(5)	15.06(5)	12.91(5)	-1.06(4)	1.24(3)	-1.36(4)
F1	24.5(9)	99.0(18)	59.8(14)	-42.0(13)	20.0(9)	-13.3(10)
F2	84.3(16)	51.6(12)	29.3(10)	1.5(9)	27.9(10)	12.9(11)
F3	45.0(10)	39.8(10)	36.7(10)	-20.5(8)	11.1(8)	3.6(8)
F1'	30.1(9)	46.6(11)	77.3(15)	-25.3(11)	24.3(10)	-6.2(8)
F2'	35.7(9)	27.9(9)	42.3(10)	-15.1(7)	3.8(8)	8.9(7)
F3'	52.8(12)	59.6(13)	45.4(12)	-12.5(10)	-17.4(9)	38.0(11)
O1	20.1(8)	23.2(9)	22.8(9)	-6.2(7)	6.9(7)	-4.2(7)
O1'	18.8(8)	17.9(8)	21.9(9)	-3.8(7)	-0.4(7)	0.9(6)
O2	24.6(9)	24.1(9)	19.2(9)	-3.0(7)	-4.6(7)	-0.5(7)
O2'	34.6(10)	23.6(10)	21.8(10)	4.6(8)	1.8(8)	-8.6(8)
N1	13.7(9)	19.9(10)	18.6(10)	2.0(8)	2.2(7)	-0.5(7)
N1'	16.6(9)	19.6(10)	18.5(10)	1.5(8)	2.9(8)	0.1(8)
C1	25.6(13)	36.8(16)	28.1(15)	-11.7(12)	8.0(11)	-0.6(11)
C2	16.9(11)	23.9(12)	23.0(13)	-8.1(10)	0.6(9)	1.1(9)
C3	22.5(12)	20.6(12)	23.7(13)	-6.6(10)	1.0(10)	-1.1(10)
C4	20.3(11)	17.3(11)	24.0(13)	1.1(10)	1.0(9)	-2.7(9)
C5	18.2(11)	20.7(12)	18.5(12)	3.3(9)	4.6(9)	0.4(9)
C6	23.9(12)	27.5(13)	16.6(12)	2.3(10)	3.8(9)	0.6(10)
C7	18.1(11)	30.6(14)	26.3(14)	3.1(11)	6.0(10)	-0.5(10)
C8	34.0(15)	25.6(14)	30.9(15)	8.2(11)	7.7(12)	-1.7(11)
C1'	24.0(13)	28.4(14)	34.1(16)	-11.0(12)	-0.5(11)	5.0(11)
C2'	22.8(12)	15.4(11)	20.3(12)	-1.2(9)	3.3(9)	3.0(9)
C3'	24.5(12)	19.0(12)	24.5(13)	-7.0(10)	-0.9(10)	2.0(10)
C4'	19.8(11)	19.7(12)	24.1(13)	-1.3(10)	-1.8(10)	-2.1(9)
C5'	16.8(10)	25.0(13)	19.8(12)	0.3(10)	0.8(9)	0.7(9)
C6'	21.9(12)	26.6(14)	40.8(17)	5.8(12)	4.2(11)	7.3(10)
C7'	18.7(12)	32.7(15)	30.3(15)	-0.9(11)	7.5(10)	1.2(10)
C8'	20.2(12)	46.7(18)	27.8(15)	-7.9(13)	-2.8(10)	8.2(12)
C9	21.5(12)	31.2(14)	20.9(13)	0.6(11)	-4.8(10)	-5.8(10)

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C10	33.0(17)	46(2)	69(3)	14.5(18)	-6.3(16)	10.8(15)
C11	35.8(16)	44.5(18)	34.7(17)	-5.1(14)	4.4(13)	-18.0(14)
C12	33.6(16)	78(3)	20.1(15)	-2.3(15)	-1.6(12)	-13.3(16)
C9'	43.4(17)	35.9(17)	38.5(18)	21.0(14)	-6.8(14)	-16.2(14)
C10'	39.9(18)	41.7(19)	59(2)	26.3(17)	-1.6(16)	-3.7(15)
C11'	53(2)	41(2)	115(4)	35(2)	-29(2)	-22.9(18)
C12'	94(4)	73(3)	57(3)	21(2)	38(3)	9(3)

Table 60. Bond Lengths for [Hf(TFB-*t*BuA)₂(O'*i*Bu)₂].

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Hf1	O1	2.0816(17)	N1'	C5'	1.518(3)
Hf1	O1'	2.0728(17)	C1	C2	1.515(4)
Hf1	O2	1.9022(17)	C2	C3	1.342(4)
Hf1	O2'	1.9069(18)	C3	C4	1.443(4)
Hf1	N1	2.460(2)	C5	C6	1.526(4)
Hf1	N1'	2.465(2)	C5	C7	1.528(3)
F1	C1	1.326(3)	C5	C8	1.534(4)
F2	C1	1.336(4)	C1'	C2'	1.508(3)
F3	C1	1.335(3)	C2'	C3'	1.343(4)
F1'	C1'	1.338(4)	C3'	C4'	1.449(3)
F2'	C1'	1.334(3)	C5'	C6'	1.523(4)
F3'	C1'	1.342(4)	C5'	C7'	1.534(4)
O1	C2	1.297(3)	C5'	C8'	1.538(4)
O1'	C2'	1.301(3)	C9	C10	1.513(4)
O2	C9	1.417(3)	C9	C11	1.517(4)
O2'	C9'	1.418(3)	C9	C12	1.525(4)
N1	C4	1.290(3)	C9'	C10'	1.508(5)
N1	C5	1.512(3)	C9'	C11'	1.465(5)
N1'	C4'	1.290(3)	C9'	C12'	1.560(6)

Table 61. Bond Angles for [Hf(TFB-*t*BuA)₂(O^{*i*}Bu)₂].

Atom	Atom	Atom	Angle/°
O1	Hf1	N1	79.71(7)
O1	Hf1	N1'	92.23(7)
O1'	Hf1	O1	167.47(7)
O1'	Hf1	N1	90.59(7)
O1'	Hf1	N1'	79.85(7)
O2	Hf1	O1	94.72(7)
O2	Hf1	O1'	92.20(7)
O2	Hf1	O2'	101.91(8)
O2	Hf1	N1	84.55(7)
O2	Hf1	N1'	170.61(7)
O2'	Hf1	O1	92.47(8)
O2'	Hf1	O1'	96.31(8)
O2'	Hf1	N1	170.32(7)
O2'	Hf1	N1'	84.06(7)
N1	Hf1	N1'	90.51(7)
C2	O1	Hf1	127.89(15)
C2'	O1'	Hf1	130.61(15)
C9	O2	Hf1	169.08(17)
C9'	O2'	Hf1	163.7(2)
C4	N1	Hf1	117.56(16)
C4	N1	C5	116.1(2)
C5	N1	Hf1	124.71(15)
C4'	N1'	Hf1	119.25(16)
C4'	N1'	C5'	115.9(2)
C5'	N1'	Hf1	123.73(15)
F1	C1	F2	107.2(3)
F1	C1	F3	106.7(2)
F1	C1	C2	111.3(2)
F2	C1	C2	111.3(2)
F3	C1	F2	106.1(2)
F3	C1	C2	113.8(2)
O1	C2	C1	112.6(2)
O1	C2	C3	126.9(2)
C3	C2	C1	120.5(2)
C2	C3	C4	124.7(2)
N1	C4	C3	128.3(2)

Atom	Atom	Atom	Angle/°
N1	C5	C6	108.43(19)
N1	C5	C7	107.34(19)
N1	C5	C8	114.3(2)
C6	C5	C7	110.3(2)
C6	C5	C8	107.5(2)
C7	C5	C8	109.0(2)
F1'	C1'	F3'	106.9(2)
F1'	C1'	C2'	111.4(2)
F2'	C1'	F1'	106.5(2)
F2'	C1'	F3'	107.0(2)
F2'	C1'	C2'	113.8(2)
F3'	C1'	C2'	110.8(2)
O1'	C2'	C1'	112.1(2)
O1'	C2'	C3'	126.7(2)
C3'	C2'	C1'	121.2(2)
C2'	C3'	C4'	125.2(2)
N1'	C4'	C3'	127.8(2)
N1'	C5'	C6'	108.2(2)
N1'	C5'	C7'	107.5(2)
N1'	C5'	C8'	114.3(2)
C6'	C5'	C7'	110.3(2)
C6'	C5'	C8'	107.7(2)
C7'	C5'	C8'	108.9(2)
O2	C9	C10	108.7(2)
O2	C9	C11	108.2(2)
O2	C9	C12	107.1(2)
C10	C9	C11	110.6(3)
C10	C9	C12	111.7(3)
C11	C9	C12	110.3(3)
O2'	C9'	C10'	108.7(3)
O2'	C9'	C11'	110.2(3)
O2'	C9'	C12'	107.0(3)
C10'	C9'	C12'	109.6(3)
C11'	C9'	C10'	113.5(3)
C11'	C9'	C12'	107.7(4)

Table 62. Torsion Angles for [Hf(TFB-*t*BuA)₂(O'*i*Bu)₂].

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Hf1	O1	C2	C1	-149.63(18)	F3	C1	C2	O1	-178.4(2)
Hf1	O1	C2	C3	32.3(4)	F3	C1	C2	C3	-0.2(4)
Hf1	O1'	C2'	C1'	-153.50(18)	F1'	C1'	C2'	O1'	-57.5(3)
Hf1	O1'	C2'	C3'	28.8(4)	F1'	C1'	C2'	C3'	120.4(3)
Hf1	O2	C9	C10	49.8(10)	F2'	C1'	C2'	O1'	-177.9(2)
Hf1	O2	C9	C11	169.9(8)	F2'	C1'	C2'	C3'	-0.1(4)
Hf1	O2	C9	C12	-71.1(10)	F3'	C1'	C2'	O1'	61.4(3)
Hf1	O2'	C9'	C10'	-87.2(8)	F3'	C1'	C2'	C3'	-120.7(3)
Hf1	O2'	C9'	C11'	148.0(6)	O1	C2	C3	C4	5.3(4)
Hf1	O2'	C9'	C12'	31.1(8)	O1'	C2'	C3'	C4'	3.2(5)
Hf1	N1	C4	C3	-14.6(3)	C1	C2	C3	C4	-172.7(2)
Hf1	N1	C5	C6	53.5(2)	C2	C3	C4	N1	-10.8(4)
Hf1	N1	C5	C7	-65.6(2)	C4	N1	C5	C6	-141.5(2)
Hf1	N1	C5	C8	173.44(17)	C4	N1	C5	C7	99.4(2)
Hf1	N1'	C4'	C3'	-13.0(4)	C4	N1	C5	C8	-21.5(3)
Hf1	N1'	C5'	C6'	55.9(2)	C5	N1	C4	C3	179.3(2)
Hf1	N1'	C5'	C7'	-63.3(2)	C1'	C2'	C3'	C4'	-174.3(3)
Hf1	N1'	C5'	C8'	175.75(18)	C2'	C3'	C4'	N1'	-7.8(5)
F1	C1	C2	O1	-57.8(3)	C4'	N1'	C5'	C6'	-136.2(2)
F1	C1	C2	C3	120.4(3)	C4'	N1'	C5'	C7'	104.6(3)
F2	C1	C2	O1	61.7(3)	C4'	N1'	C5'	C8'	-16.4(3)
F2	C1	C2	C3	-120.1(3)	C5'	N1'	C4'	C3'	178.6(2)

Table 63. Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for [Hf(TFB-*t*BuA)₂(O'*i*Bu)₂].

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H3	4829.06	8611.13	3256.85	27
H4	5669.78	8498.41	2117	25
H6A	5305.08	6460.6	767.31	34
H6B	5767	7032.48	140.67	34
H6C	4357.3	7184.68	481.9	34
H7A	8028.65	7557.41	1791.86	37
H7B	8021.92	7260.33	945.46	37
H7C	7555.39	6688.89	1571.19	37
H8A	5146.6	8556.89	870.83	45
H8B	6387.52	8337.29	407.67	45

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H8C	6702.12	8659.98	1248.52	45
H3'	4374.93	4374.03	696.05	28
H4'	2438.49	5127	733.05	26
H6'A	2460.95	7286.73	1839.46	45
H6'B	964.23	7373.4	1377.79	45
H6'C	2280.79	7272.99	940.05	45
H7'A	884.1	5431.87	2083.79	40
H7'B	89.76	6245.44	2061.5	40
H7'C	1566.53	6158.82	2545.29	40
H8'A	1223.49	6124.02	240.72	48
H8'B	-104.47	6310.61	646.67	48
H8'C	545.43	5456.46	695.79	48
H10A	7896.4	5283.7	3945.95	75
H10B	9321	5745.34	4094.24	75
H10C	8653.17	5565.47	3251.89	75
H11A	8962.87	7005.44	3078.36	58
H11B	9345.85	7189.91	3954.1	58
H11C	8045.51	7600.86	3488.02	58
H12A	6657.7	7122.23	4456.9	67
H12B	7879.28	6620.05	4892.7	67
H12C	6461.92	6209.13	4574.54	67
H10D	5552.44	4040.09	3463.82	71
H10E	4791.42	3900.87	4192.63	71
H10F	5713.59	4660.47	4133.89	71
H11D	1998.83	4530.36	2878.4	109
H11E	2459.06	3858.64	3473.9	109
H11F	3151.23	3917.22	2712.63	109
H12D	3883.08	5551.78	4346.72	109
H12E	2846.42	4851.85	4446.68	109
H12F	2423.69	5516.81	3837.91	109

Table 64. Crystal data and structure refinement for [Zr(TFB-TFEA)₂(O^tBu)₂].

Identification code	[Zr(TFB-TFEA) ₂ (O ^t Bu) ₂]
Empirical formula	C ₂₀ H ₂₆ F ₁₂ N ₂ O ₄ Zr
Formula weight	677.65
Temperature/K	100.00
Crystal system	triclinic
Space group	P-1
a/Å	9.5522(4)
b/Å	9.9151(4)
c/Å	15.2858(6)
α/°	86.728(2)
β/°	78.184(2)
γ/°	76.128(2)
Volume/Å ³	1375.68(10)
Z	2
ρ _{calc} /g/cm ³	1.636
μ/mm ⁻¹	0.509
F(000)	680.0
Crystal size/mm ³	0.11 × 0.1 × 0.05
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.232 to 56.674
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -20 ≤ l ≤ 20
Reflections collected	95372
Independent reflections	6858 [R _{int} = 0.0417, R _{sigma} = 0.0177]
Data/restraints/parameters	6858/0/358
Goodness-of-fit on F ²	1.072
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0289, wR ₂ = 0.0686
Final R indexes [all data]	R ₁ = 0.0328, wR ₂ = 0.0704
Largest diff. peak/hole / e Å ⁻³	0.54/-0.31

Table 65. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Zr}(\text{TFB-TFEA})_2(\text{O}^t\text{Bu})_2]$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Zr1	2849.3(2)	2364.6(2)	7321.0(2)	13.02(5)
F4'	-16.6(12)	5244.5(11)	8717.1(7)	27.5(2)
F2'	7224.4(12)	3279.0(12)	5647.8(8)	30.2(2)
F3	-836.1(13)	276.4(11)	8697.9(8)	30.8(2)
F4	2765.4(14)	5544.5(12)	9757.7(8)	33.9(3)
F5	3183.9(14)	5841.4(12)	8331.4(8)	33.6(3)
O1'	4620.4(12)	3284.2(12)	6829.1(8)	18.3(2)
F2	-1645.2(13)	1337.0(13)	9956.5(8)	34.4(3)
O2'	4116.4(12)	669.3(11)	7603.6(8)	18.3(2)
F3'	6775.4(14)	5502.7(13)	5715.6(9)	39.3(3)
O1	817.8(12)	2232.1(12)	8102.1(8)	17.9(2)
F6'	-154.4(14)	7139.1(11)	7951.1(8)	34.5(3)
F1	-2127.5(12)	2382.9(12)	8737.7(8)	31.9(3)
F6	4922.6(15)	5704.7(13)	9060.1(8)	38.1(3)
F5'	-1987.6(12)	6156.8(13)	8217.7(8)	37.1(3)
F1'	7071.1(13)	4259.9(15)	6894.9(8)	40.6(3)
O2	2262.8(13)	1880.4(12)	6273.6(8)	19.2(2)
N1	2984.9(15)	3070.3(14)	8786.0(9)	17.1(3)
N1'	1681.1(15)	4720.4(14)	6961.4(9)	16.6(3)
C4	2202.4(19)	2776.1(17)	9533.0(11)	19.6(3)
C3	904(2)	2249.7(17)	9640.5(11)	21.4(3)
C6'	-511.7(19)	5901.6(18)	8014.9(13)	24.4(4)
C4'	2288.1(19)	5624.9(17)	6490.0(11)	21.2(3)
C7'	5266.0(18)	-465.8(17)	7758.5(11)	19.0(3)
C5	4233.8(19)	3636.0(18)	8887.0(12)	21.6(3)
C6	3766(2)	5183.7(19)	9008.9(12)	25.2(4)
C7	1611.6(18)	1194.5(17)	5730.6(11)	19.3(3)
C2	313.9(18)	2037.0(16)	8942.4(11)	17.9(3)
C2'	4854.8(18)	4405.1(17)	6415.3(11)	18.2(3)
C5'	66.9(18)	5086.9(18)	7159.1(12)	20.7(3)
C1	-1082(2)	1507.6(18)	9094.5(12)	23.7(3)
C9'	6723(2)	-96(2)	7356.9(14)	28.5(4)
C3'	3838(2)	5524.0(18)	6223.8(12)	22.4(3)
C1'	6488(2)	4372(2)	6162.9(13)	25.2(4)
C8	2733(2)	-109(2)	5358.9(14)	33.5(4)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
C10'	5110(2)	-1729.5(18)	7300.2(15)	30.6(4)
C9	251(2)	822(2)	6310.8(13)	32.8(4)
C10	1177(2)	2186(2)	4980.9(13)	28.0(4)
C8'	5106(2)	-690(2)	8765.9(13)	34.8(5)

Table 66. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Zr}(\text{TFB-TFEA})_2(\text{O}^t\text{Bu})_2]$.

The Anisotropic displacement factor exponent takes the form:

$$-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...].$$

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Zr1	11.87(7)	12.19(7)	15.88(8)	-1.58(5)	-3.80(5)	-3.28(5)
F4'	27.6(5)	28.5(5)	22.5(5)	-3.2(4)	-7.0(4)	3.4(4)
F2'	20.0(5)	32.8(6)	34.7(6)	-4.3(5)	2.3(4)	-5.5(4)
F3	35.5(6)	25.6(5)	34.6(6)	-4.3(5)	-2.7(5)	-16.1(5)
F4	45.1(7)	24.3(5)	30.9(6)	-10.2(5)	-3.1(5)	-7.0(5)
F5	47.6(7)	28.7(6)	34.2(6)	7.4(5)	-22.6(5)	-17.1(5)
O1'	14.7(5)	19.0(5)	22.7(6)	0.5(4)	-4.7(4)	-6.0(4)
F2	36.3(6)	41.7(7)	26.6(6)	0.0(5)	6.1(5)	-22.4(5)
O2'	16.4(5)	12.8(5)	24.5(6)	0.2(4)	-4.2(5)	-0.6(4)
F3'	33.3(6)	32.4(6)	52.3(8)	2.1(5)	5.9(6)	-20.5(5)
O1	15.3(5)	21.6(6)	17.4(6)	-1.5(4)	-3.1(4)	-5.0(4)
F6'	42.1(7)	18.8(5)	39.6(7)	-6.1(5)	-7.5(5)	-0.2(5)
F1	17.9(5)	35.6(6)	42.7(7)	1.6(5)	-6.2(5)	-7.6(4)
F6	47.2(7)	43.5(7)	39.2(7)	3.4(5)	-20.8(6)	-31.0(6)
F5'	17.5(5)	46.1(7)	39.5(7)	-7.8(5)	-3.3(5)	7.8(5)
F1'	25.7(6)	68.5(9)	36.7(7)	-4.2(6)	-11.4(5)	-23.4(6)
O2	19.1(6)	22.4(6)	18.8(6)	-5.5(4)	-4.8(5)	-8.1(5)
N1	17.0(6)	14.6(6)	20.5(7)	-2.1(5)	-7.1(5)	-2.2(5)
N1'	16.0(6)	17.6(6)	16.5(6)	-2.7(5)	-5.1(5)	-2.0(5)
C4	24.3(8)	17.0(7)	18.4(8)	-2.4(6)	-9.2(6)	-1.4(6)
C3	26.5(9)	20.6(8)	17.6(8)	1.6(6)	-3.2(7)	-7.9(7)
C6'	19.5(8)	22.8(8)	27.4(9)	-1.2(7)	-6.0(7)	2.9(6)
C4'	24.5(8)	17.5(7)	20.5(8)	0.4(6)	-7.1(7)	-1.1(6)
C7'	18.0(8)	16.2(7)	21.8(8)	0.7(6)	-5.5(6)	-0.7(6)
C5	19.0(8)	26.7(8)	21.1(8)	-4.0(6)	-7.3(6)	-5.4(6)
C6	32.5(9)	26.3(9)	23.7(9)	-0.3(7)	-11.7(7)	-14.8(7)
C7	21.6(8)	21.3(8)	18.9(8)	-3.0(6)	-7.9(6)	-8.6(6)
C2	16.4(7)	15.1(7)	20.8(8)	0.0(6)	-0.7(6)	-3.6(6)

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C2'	18.2(7)	20.3(7)	17.9(8)	-2.8(6)	-1.8(6)	-8.9(6)
C5'	16.7(7)	21.2(8)	23.6(8)	-0.5(6)	-8.0(6)	0.1(6)
C1	22.9(8)	24.2(8)	24.6(9)	-1.2(7)	-0.9(7)	-10.0(7)
C9'	17.3(8)	31.4(10)	35.5(10)	-1.4(8)	-5.2(7)	-3.1(7)
C3'	26.0(9)	19.4(8)	21.8(8)	2.2(6)	-2.0(7)	-8.2(7)
C1'	22.4(8)	29.5(9)	25.8(9)	-2.6(7)	-1.4(7)	-12.1(7)
C8	40.3(11)	26.9(9)	34.2(11)	-12.4(8)	-15.3(9)	0.0(8)
C10'	34.9(10)	16.5(8)	42.1(11)	-2.8(7)	-14.7(9)	-2.9(7)
C9	35.8(11)	45.0(12)	27.0(10)	-2.1(8)	-6.5(8)	-27.0(9)
C10	34.9(10)	26.7(9)	26.8(9)	1.8(7)	-13.4(8)	-10.2(8)
C8'	40.2(11)	34.5(10)	22.7(9)	4.8(8)	-5.9(8)	3.2(9)

Table 67. Bond Lengths for [Zr(TFB-TFEA)₂(O^tBu)₂].

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zr1	O1'	2.0974(11)	F1'	C1'	1.336(2)
Zr1	O2'	1.9059(11)	O2	C7	1.4203(18)
Zr1	O1	2.0890(11)	N1	C4	1.290(2)
Zr1	O2	1.9214(11)	N1	C5	1.472(2)
Zr1	N1	2.4211(14)	N1'	C4'	1.290(2)
Zr1	N1'	2.4204(14)	N1'	C5'	1.468(2)
F4'	C6'	1.334(2)	C4	C3	1.433(2)
F2'	C1'	1.339(2)	C3	C2	1.353(2)
F3	C1	1.342(2)	C6'	C5'	1.510(2)
F4	C6	1.337(2)	C4'	C3'	1.433(2)
F5	C6	1.339(2)	C7'	C9'	1.523(2)
O1'	C2'	1.291(2)	C7'	C10'	1.522(2)
F2	C1	1.335(2)	C7'	C8'	1.525(3)
O2'	C7'	1.4185(19)	C5	C6	1.503(3)
F3'	C1'	1.335(2)	C7	C8	1.520(3)
O1	C2	1.297(2)	C7	C9	1.527(3)
F6'	C6'	1.343(2)	C7	C10	1.524(2)
F1	C1	1.342(2)	C2	C1	1.518(2)
F6	C6	1.344(2)	C2'	C3'	1.350(2)
F5'	C6'	1.344(2)	C2'	C1'	1.522(2)

Table 68. Bond Angles for [Zr(TFB-TFEA)₂(OⁱBu)₂].

Atom	Atom	Atom	Angle/°
O1'	Zr1	N1	86.30(5)
O1'	Zr1	N1'	76.20(5)
O2'	Zr1	O1'	92.42(5)
O2'	Zr1	O1	102.50(5)
O2'	Zr1	O2	102.31(5)
O2'	Zr1	N1	84.19(5)
O2'	Zr1	N1'	167.95(5)
O1	Zr1	O1'	155.84(5)
O1	Zr1	N1	76.59(5)
O1	Zr1	N1'	87.06(5)
O2	Zr1	O1'	104.80(5)
O2	Zr1	O1	90.60(5)
O2	Zr1	N1	166.70(5)
O2	Zr1	N1'	84.70(5)
N1'	Zr1	N1	91.03(4)
C2'	O1'	Zr1	138.68(11)
C7'	O2'	Zr1	169.63(11)
C2	O1	Zr1	135.95(10)
C7	O2	Zr1	159.19(11)
C4	N1	Zr1	125.58(11)
C4	N1	C5	114.04(14)
C5	N1	Zr1	119.20(10)
C4'	N1'	Zr1	127.57(11)
C4'	N1'	C5'	115.10(14)
C5'	N1'	Zr1	116.34(10)
N1	C4	C3	126.31(15)
C2	C3	C4	122.75(16)
F4'	C6'	F6'	106.61(15)
F4'	C6'	F5'	107.05(15)
F4'	C6'	C5'	113.41(14)
F6'	C6'	F5'	106.89(14)
F6'	C6'	C5'	112.25(15)
F5'	C6'	C5'	110.26(15)
N1'	C4'	C3'	125.85(15)
O2'	C7'	C9'	107.94(14)
O2'	C7'	C10'	107.64(14)
O2'	C7'	C8'	107.97(14)

Atom	Atom	Atom	Angle/°
C9'	C7'	C8'	110.91(16)
C10'	C7'	C9'	110.74(15)
C10'	C7'	C8'	111.48(16)
N1	C5	C6	110.82(14)
F4	C6	F5	107.01(16)
F4	C6	F6	107.04(14)
F4	C6	C5	112.30(15)
F5	C6	F6	106.99(15)
F5	C6	C5	112.54(14)
F6	C6	C5	110.65(16)
O2	C7	C8	108.24(14)
O2	C7	C9	108.31(14)
O2	C7	C10	108.21(13)
C8	C7	C9	110.65(16)
C8	C7	C10	111.06(16)
C10	C7	C9	110.27(15)
O1	C2	C3	126.96(15)
O1	C2	C1	112.39(14)
C3	C2	C1	120.65(15)
O1'	C2'	C3'	127.25(15)
O1'	C2'	C1'	111.74(15)
C3'	C2'	C1'	121.00(15)
N1'	C5'	C6'	110.83(14)
F3	C1	C2	110.87(14)
F2	C1	F3	107.10(14)
F2	C1	F1	107.50(15)
F2	C1	C2	113.47(15)
F1	C1	F3	106.67(14)
F1	C1	C2	110.90(14)
C2'	C3'	C4'	122.69(16)
F2'	C1'	C2'	111.42(14)
F3'	C1'	F2'	106.80(15)
F3'	C1'	F1'	107.40(15)
F3'	C1'	C2'	113.44(16)
F1'	C1'	F2'	107.09(16)
F1'	C1'	C2'	110.39(15)

Table 69. Torsion Angles for [Zr(TFB-TFEA)₂(O^tBu)₂].

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Zr1	O1'	C2'	C3'	7.3(3)	O1	C2	C1	F1	-57.06(19)
Zr1	O1'	C2'	C1'	-174.12(12)	F6'	C6'	C5'	N1'	64.73(18)
Zr1	O2'	C7'	C9'	-8.2(7)	F5'	C6'	C5'	N1'	-176.21(14)
Zr1	O2'	C7'	C10'	-127.7(6)	N1	C4	C3	C2	-2.1(3)
Zr1	O2'	C7'	C8'	111.8(6)	N1	C5	C6	F4	63.26(19)
Zr1	O1	C2	C3	21.1(3)	N1	C5	C6	F5	-57.6(2)
Zr1	O1	C2	C1	-158.55(12)	N1	C5	C6	F6	-177.20(14)
Zr1	O2	C7	C8	-88.5(3)	N1'	C4'	C3'	C2'	2.9(3)
Zr1	O2	C7	C9	31.6(4)	C4	N1	C5	C6	-86.53(18)
Zr1	O2	C7	C10	151.1(3)	C4	C3	C2	O1	1.7(3)
Zr1	N1	C4	C3	-14.4(2)	C4	C3	C2	C1	-178.63(15)
Zr1	N1	C5	C6	105.21(14)	C3	C2	C1	F3	-118.45(18)
Zr1	N1'	C4'	C3'	-13.2(2)	C3	C2	C1	F2	2.1(2)
Zr1	N1'	C5'	C6'	101.20(14)	C3	C2	C1	F1	123.24(17)
F4'	C6'	C5'	N1'	-56.2(2)	C4'	N1'	C5'	C6'	-89.32(18)
O1'	C2'	C3'	C4'	1.7(3)	C5	N1	C4	C3	178.17(16)
O1'	C2'	C1'	F2'	58.0(2)	C5'	N1'	C4'	C3'	178.72(16)
O1'	C2'	C1'	F3'	178.59(14)	C3'	C2'	C1'	F2'	-123.30(18)
O1'	C2'	C1'	F1'	-60.82(19)	C3'	C2'	C1'	F3'	-2.7(2)
O1	C2	C1	F3	61.25(19)	C3'	C2'	C1'	F1'	117.84(18)
O1	C2	C1	F2	-178.18(14)	C1'	C2'	C3'	C4'	-176.75(16)

Table 70. Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for [Zr(TFB-TFEA)₂(O^tBu)₂].

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H4	2517.12	2922.69	10063.22	24
H3	438.61	2041.38	10226.48	26
H4'	1650.62	6430.15	6302.6	25
H5A	5025.11	3414.62	8350.04	26
H5B	4629.88	3196.25	9410.99	26
H5'A	-303.73	4228.81	7215.79	25
H5'B	-296.8	5647.95	6659.84	25
H9'A	6782.48	83.67	6714.76	43
H9'B	7536.65	-870.1	7450.3	43
H9'C	6788.39	737.03	7647.07	43
H3'	4162.49	6275.1	5899.3	27

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H8A	3621.78	146.2	5020.61	50
H8B	2316.24	-578.84	4963.66	50
H8C	2983.37	-733.19	5852.84	50
H10A	4140.92	-1915.22	7541.91	46
H10B	5878.31	-2537.59	7407.69	46
H10C	5208.66	-1549.62	6656	46
H9A	543.36	192.32	6793.49	49
H9B	-225.86	364.76	5943.85	49
H9C	-437.68	1670.17	6567.43	49
H10D	501.97	3039.93	5238.13	42
H10E	691.27	1743.77	4611.14	42
H10F	2059.84	2410.82	4611.19	42
H8'A	5198.55	144.49	9041.51	52
H8'B	5878.28	-1484	8889.49	52
H8'C	4139.75	-875.91	9014.15	52

Table 71. Crystal data and structure refinement for [Hf(TFB-TFEA)₂(O^tBu)₂].

Identification code	[Hf(TFB-TFEA) ₂ (O ^t Bu) ₂]
Empirical formula	C ₂₀ H ₂₆ F ₁₂ HfN ₂ O ₄
Formula weight	764.92
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	9.5367(7)
b/Å	9.9051(7)
c/Å	15.2811(12)
α/°	86.736(3)
β/°	78.509(3)
γ/°	76.131(3)
Volume/Å ³	1373.25(18)
Z	2
ρ _{calc} /g/cm ³	1.850
μ/mm ⁻¹	3.908
F(000)	744.0
Crystal size/mm ³	0.06 × 0.05 × 0.02
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.236 to 56.812
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -20 ≤ l ≤ 20
Reflections collected	82302
Independent reflections	6866 [R _{int} = 0.0771, R _{sigma} = 0.0371]
Data/restraints/parameters	6866/0/358
Goodness-of-fit on F ²	1.100
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0320, wR ₂ = 0.0670
Final R indexes [all data]	R ₁ = 0.0400, wR ₂ = 0.0694
Largest diff. peak/hole / e Å ⁻³	1.86/-1.52

Table 72. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Hf}(\text{TFB-TFEA})_2(\text{O}^i\text{Bu})_2]$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Hf1	2822.3(2)	2396.4(2)	7325.7(2)	15.56(5)
F4'	-36(3)	5258(3)	8733.1(16)	30.4(5)
O1'	807(3)	2255(3)	8096.6(17)	18.7(5)
O1	4592(3)	3285(3)	6838.6(17)	19.5(5)
F1'	7187(3)	3271(3)	5651.1(17)	33.5(6)
F1	-829(3)	275(3)	8684.1(17)	33.0(6)
F6'	-2011(3)	6169(3)	8231.1(18)	39.9(7)
F3	-2121(3)	2384(3)	8731.1(17)	34.2(6)
F4	3148(3)	5880(3)	8344.0(17)	36.9(6)
F5'	-176(3)	7149(3)	7967.2(18)	37.6(6)
F5	2760(3)	5545(3)	9764.0(17)	36.2(6)
O2	4075(3)	685(3)	7604.5(18)	21.3(6)
F2	-1629(3)	1333(3)	9941.7(17)	37.5(6)
O2'	2240(3)	1934(3)	6266.7(17)	22.1(6)
F3'	7062(3)	4242(3)	6898.6(18)	44.1(7)
F2'	6750(3)	5499(3)	5720.0(19)	42.1(7)
F6	4900(3)	5737(3)	9065.7(19)	42.4(7)
N1'	1660(3)	4731(3)	6980(2)	18.2(6)
N1	2984(3)	3085(3)	8768(2)	18.3(6)
C2	320(4)	2038(4)	8939(2)	19.0(7)
C3'	3810(5)	5525(4)	6239(3)	25.0(8)
C3	928(4)	2237(4)	9625(3)	24.4(8)
C2'	4834(4)	4409(4)	6425(2)	20.7(8)
C4	2208(4)	2775(4)	9524(3)	23.3(8)
C5'	39(4)	5106(4)	7179(3)	23.5(8)
C1	-1067(4)	1501(4)	9083(3)	25.6(8)
C4'	2265(4)	5641(4)	6510(3)	23.1(8)
C7'	1595(4)	1240(4)	5730(3)	22.4(8)
C1'	6459(5)	4366(5)	6164(3)	29.8(9)
C6	3744(5)	5211(4)	9010(3)	27.2(9)
C6'	-530(4)	5912(4)	8029(3)	27.3(9)
C5	4229(4)	3664(4)	8875(3)	23.0(8)
C10	6681(4)	-48(5)	7354(3)	31.2(10)
C7	5230(4)	-441(4)	7761(3)	22.0(8)
C10'	1152(5)	2212(5)	4974(3)	30.9(9)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
C8'	250(5)	844(5)	6303(3)	36.3(11)
C9'	2739(5)	-66(5)	5362(3)	39.0(11)
C9	5091(5)	-1715(4)	7300(3)	34.0(10)
C8	5086(5)	-672(5)	8759(3)	36.9(11)

Table 73. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Hf}(\text{TFB-TFEA})_2(\text{O}^t\text{Bu})_2]$.

The Anisotropic displacement factor exponent takes the form:

$$-2\pi^2[\text{h}^2\text{a}^2\text{U}_{11}+2\text{hka}^*\text{b}^*\text{U}_{12}+\dots].$$

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Hf1	13.84(7)	14.64(8)	19.03(8)	-3.11(5)	-3.33(5)	-4.08(5)
F4'	28.4(12)	31.4(13)	26.5(12)	-4.4(10)	-7.2(10)	5.3(10)
O1'	14.7(12)	22.8(13)	19.8(13)	-4.6(10)	0.2(10)	-8.7(10)
O1	15.9(12)	20.3(13)	24.4(14)	-1.2(11)	-4.6(10)	-7.5(10)
F1'	23.1(12)	35.6(14)	39.1(14)	-5.2(11)	2.2(10)	-6.8(11)
F1	36.1(14)	29.4(13)	37.4(14)	-5.3(11)	-2.5(11)	-18.1(11)
F6'	20.6(12)	48.7(17)	42.6(16)	-7.5(13)	-4.2(11)	7.1(11)
F3	19.2(11)	40.1(15)	42.8(15)	1.0(12)	-5.6(10)	-6.7(11)
F4	51.2(16)	33.2(14)	36.7(14)	8.7(11)	-23.9(13)	-19.3(12)
F5'	45.2(15)	20.7(12)	44.0(16)	-7.4(11)	-8.0(12)	-0.8(11)
F5	47.3(16)	27.6(13)	33.4(14)	-12.0(11)	-3.5(12)	-8.8(12)
O2	20.0(13)	17.2(13)	26.0(14)	-2.7(11)	-3.8(11)	-2.8(11)
F2	39.5(15)	45.3(16)	29.3(14)	-1.8(12)	6.8(11)	-23.3(13)
O2'	22.2(13)	25.7(14)	20.8(14)	-6.8(11)	-3.0(10)	-9.3(11)
F3'	26.8(13)	76(2)	39.0(15)	-6.1(14)	-10.2(11)	-26.5(14)
F2'	36.6(15)	35.7(15)	54.9(18)	2.5(13)	4.9(13)	-22.5(12)
F6	51.2(17)	47.8(17)	44.9(16)	2.8(13)	-22.8(13)	-33.3(14)
N1'	19.1(15)	18.2(15)	16.5(15)	-5.5(12)	-4.9(12)	-0.5(12)
N1	17.8(15)	16.2(15)	21.8(16)	-4.3(12)	-6.4(12)	-2.4(12)
C2	20.3(17)	14.9(17)	19.7(18)	1.3(14)	0.3(14)	-3.6(14)
C3'	31(2)	19.6(19)	26(2)	2.4(16)	-5.2(16)	-10.4(16)
C3	28(2)	22(2)	24(2)	0.7(16)	-4.4(16)	-6.9(16)
C2'	22.2(18)	24(2)	17.9(18)	-4.0(15)	0.0(14)	-12.2(15)
C4	28(2)	18.9(19)	22.6(19)	-2.0(15)	-9.5(16)	-0.1(16)
C5'	18.1(18)	24(2)	27(2)	0.0(16)	-9.2(15)	0.7(15)
C1	26(2)	24(2)	26(2)	-2.0(16)	1.5(16)	-9.3(16)
C4'	25.7(19)	20.3(19)	23(2)	-0.7(15)	-8.4(15)	-1.3(16)
C7'	26.5(19)	24(2)	20.4(19)	-4.1(15)	-7.0(15)	-9.2(16)

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C1'	26(2)	35(2)	30(2)	-0.9(18)	-2.8(17)	-11.6(18)
C6	35(2)	30(2)	24(2)	-0.6(17)	-9.8(17)	-17.6(18)
C6'	19.2(18)	26(2)	33(2)	-1.7(17)	-5.2(16)	2.3(16)
C5	19.9(18)	29(2)	21.8(19)	-5.7(16)	-8.0(15)	-5.0(16)
C10	20.8(19)	34(2)	35(2)	-3.8(19)	-3.4(17)	0.5(17)
C7	21.7(18)	19.7(19)	22.6(19)	-2.8(15)	-4.0(15)	-0.6(15)
C10'	39(2)	30(2)	31(2)	2.8(18)	-16.6(19)	-13.9(19)
C8'	39(2)	48(3)	31(2)	-6(2)	-7.4(19)	-26(2)
C9'	45(3)	35(3)	37(3)	-16(2)	-17(2)	2(2)
C9	36(2)	21(2)	47(3)	-2.4(19)	-17(2)	-3.7(18)
C8	42(3)	35(3)	27(2)	1.6(19)	-4.8(19)	4(2)

Table 74. Bond Lengths for [Hf(TFB-TFEA)₂(O^tBu)₂].

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Hf1	O1'	2.076(2)	F2'	C1'	1.336(5)
Hf1	O1	2.077(3)	F6	C6	1.346(5)
Hf1	O2	1.906(3)	N1'	C5'	1.473(5)
Hf1	O2'	1.924(3)	N1'	C4'	1.293(5)
Hf1	N1'	2.392(3)	N1	C4	1.306(5)
Hf1	N1	2.389(3)	N1	C5	1.476(5)
F4'	C6'	1.333(5)	C2	C3	1.340(5)
O1'	C2	1.302(4)	C2	C1	1.513(5)
O1	C2'	1.295(5)	C3'	C2'	1.347(6)
F1'	C1'	1.338(5)	C3'	C4'	1.427(6)
F1	C1	1.340(5)	C3	C4	1.423(6)
F6'	C6'	1.348(5)	C2'	C1'	1.513(5)
F3	C1	1.343(5)	C5'	C6'	1.499(6)
F4	C6	1.331(5)	C7'	C10'	1.521(6)
F5'	C6'	1.340(5)	C7'	C8'	1.523(6)
F5	C6	1.334(5)	C7'	C9'	1.530(6)
O2	C7	1.415(4)	C6	C5	1.504(6)
F2	C1	1.333(5)	C10	C7	1.530(6)
O2'	C7'	1.411(4)	C7	C9	1.525(6)
F3'	C1'	1.347(5)	C7	C8	1.512(6)

Table 75. Bond Angles for [Hf(TFB-TFEA)₂(OⁱBu)₂].

Atom	Atom	Atom	Angle/°
O1'	Hf1	O1	156.71(10)
O1'	Hf1	N1'	87.03(10)
O1'	Hf1	N1	77.14(10)
O1	Hf1	N1'	76.96(10)
O1	Hf1	N1	86.19(10)
O2	Hf1	O1'	101.88(11)
O2	Hf1	O1	92.43(11)
O2	Hf1	O2'	102.09(11)
O2	Hf1	N1'	168.69(11)
O2	Hf1	N1	84.45(11)
O2'	Hf1	O1'	91.04(10)
O2'	Hf1	O1	103.94(11)
O2'	Hf1	N1'	84.50(11)
O2'	Hf1	N1	167.53(11)
N1	Hf1	N1'	90.87(10)
C2	O1'	Hf1	135.4(2)
C2'	O1	Hf1	138.4(2)
C7	O2	Hf1	168.5(2)
C7'	O2'	Hf1	158.0(2)
C5'	N1'	Hf1	116.7(2)
C4'	N1'	Hf1	127.4(3)
C4'	N1'	C5'	114.9(3)
C4	N1	Hf1	125.4(3)
C4	N1	C5	113.6(3)
C5	N1	Hf1	119.9(2)
O1'	C2	C3	126.6(4)
O1'	C2	C1	112.0(3)
C3	C2	C1	121.5(3)
C2'	C3'	C4'	123.4(4)
C2	C3	C4	123.4(4)
O1	C2'	C3'	126.5(3)
O1	C2'	C1'	112.1(3)
C3'	C2'	C1'	121.4(4)
N1	C4	C3	125.9(4)
N1'	C5'	C6'	111.1(3)
F1	C1	F3	106.7(3)
F1	C1	C2	111.5(3)

Atom	Atom	Atom	Angle/°
F3	C1	C2	110.8(3)
F2	C1	F1	107.3(3)
F2	C1	F3	106.9(3)
F2	C1	C2	113.2(3)
N1'	C4'	C3'	125.5(4)
O2'	C7'	C10'	108.6(3)
O2'	C7'	C8'	108.9(3)
O2'	C7'	C9'	107.9(3)
C10'	C7'	C8'	110.4(4)
C10'	C7'	C9'	110.7(4)
C8'	C7'	C9'	110.3(4)
F1'	C1'	F3'	106.6(4)
F1'	C1'	C2'	111.8(3)
F3'	C1'	C2'	110.0(3)
F2'	C1'	F1'	107.1(3)
F2'	C1'	F3'	107.3(4)
F2'	C1'	C2'	113.7(4)
F4	C6	F5	107.4(4)
F4	C6	F6	107.0(3)
F4	C6	C5	112.8(3)
F5	C6	F6	106.8(3)
F5	C6	C5	112.2(3)
F6	C6	C5	110.3(4)
F4'	C6'	F6'	106.7(3)
F4'	C6'	F5'	106.5(3)
F4'	C6'	C5'	113.8(3)
F6'	C6'	C5'	110.3(3)
F5'	C6'	F6'	106.7(3)
F5'	C6'	C5'	112.3(4)
N1	C5	C6	110.8(3)
O2	C7	C10	107.4(3)
O2	C7	C9	107.8(3)
O2	C7	C8	108.3(3)
C9	C7	C10	110.5(3)
C8	C7	C10	111.3(4)
C8	C7	C9	111.4(4)

Table 76. Torsion Angles for [Hf(TFB-TFEA)₂(O^tBu)₂].

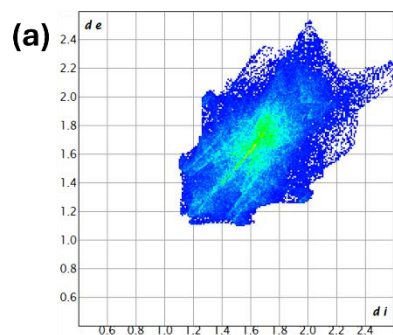
A	B	C	D	Angle/°	A	B	C	D	Angle/°
Hf1	O1'	C2	C3	21.4(6)	F4	C6	C5	N1	-57.6(4)
Hf1	O1'	C2	C1	-158.1(3)	F5	C6	C5	N1	63.8(4)
Hf1	O1	C2'	C3'	7.0(6)	F6	C6	C5	N1	-177.2(3)
Hf1	O1	C2'	C1'	-173.8(3)	N1'	C5'	C6'	F4'	-56.0(5)
Hf1	O2	C7	C10	-11.8(14)	N1'	C5'	C6'	F6'	-176.0(3)
Hf1	O2	C7	C9	-130.9(11)	N1'	C5'	C6'	F5'	65.1(4)
Hf1	O2	C7	C8	108.5(12)	C2	C3	C4	N1	-3.1(6)
Hf1	O2'	C7'	C10'	152.4(5)	C3'	C2'	C1'	F1'	-123.4(4)
Hf1	O2'	C7'	C8'	32.1(8)	C3'	C2'	C1'	F3'	118.4(4)
Hf1	O2'	C7'	C9'	-87.6(7)	C3'	C2'	C1'	F2'	-2.0(6)
Hf1	N1'	C5'	C6'	101.3(3)	C3	C2	C1	F1	-117.7(4)
Hf1	N1'	C4'	C3'	-12.5(6)	C3	C2	C1	F3	123.5(4)
Hf1	N1	C4	C3	-14.1(5)	C3	C2	C1	F2	3.5(5)
Hf1	N1	C5	C6	105.5(3)	C2'	C3'	C4'	N1'	2.0(7)
O1'	C2	C3	C4	2.3(6)	C4	N1	C5	C6	-86.2(4)
O1'	C2	C1	F1	61.8(4)	C5'	N1'	C4'	C3'	179.4(4)
O1'	C2	C1	F3	-56.9(4)	C1	C2	C3	C4	-178.2(4)
O1'	C2	C1	F2	-177.0(3)	C4'	N1'	C5'	C6'	-89.3(4)
O1	C2'	C1'	F1'	57.4(5)	C4'	C3'	C2'	O1	2.4(6)
O1	C2'	C1'	F3'	-60.9(4)	C4'	C3'	C2'	C1'	-176.8(4)
O1	C2'	C1'	F2'	178.8(3)	C5	N1	C4	C3	178.3(4)

Table 77. Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for [Hf(TFB-TFEA)₂(O^tBu)₂].

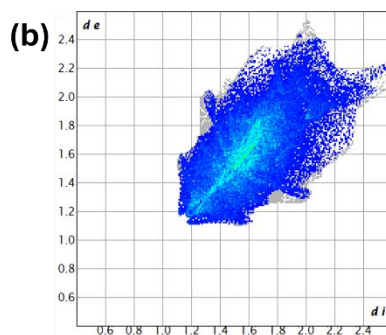
Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H3'	4132.69	6273.77	5909.87	30
H3	482.16	2005.87	10209.13	29
H4	2525.46	2922.81	10054.23	28
H5'A	-336.18	4250.2	7232.94	28
H5'B	-326.62	5672.69	6680.01	28
H4'	1627.37	6455.36	6330.66	28
H5A	5016.12	3459.38	8337.06	28
H5B	4637.07	3215.92	9395.2	28
H10A	6735.25	115.16	6710.58	47
H10B	7507.03	-806.34	7454.71	47
H10C	6730.1	800.41	7635.01	47

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H10D	443.2	3053.69	5223.03	46
H10E	701.55	1743.13	4595.03	46
H10F	2026.03	2466	4615.59	46
H8'A	553.75	213.2	6784.27	54
H8'B	-218.67	379.88	5933	54
H8'C	-449.9	1684.65	6561.32	54
H9'A	3614.07	200.84	5014.82	58
H9'B	2322.95	-557.25	4975.83	58
H9'C	3012.4	-676.34	5857.94	58
H9A	4128.32	-1914.35	7539.48	51
H9B	5870.2	-2516.18	7407.7	51
H9C	5184.36	-1532.85	6656.37	51
H8A	5136.49	175.98	9039.35	55
H8B	5887.66	-1440.63	8880.78	55
H8C	4139.06	-901.53	9003.49	55

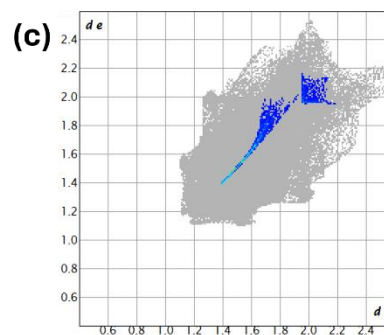
Hirshfeld Surface (HS) Fingerprints



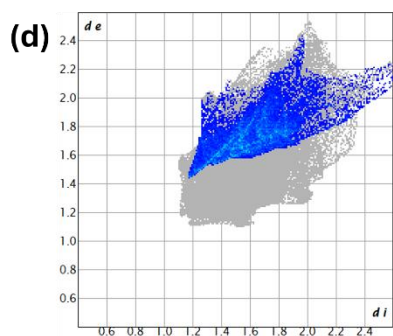
100% HS area for all interactions



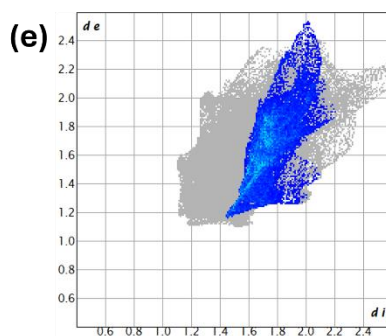
57.2% HS area of H...H



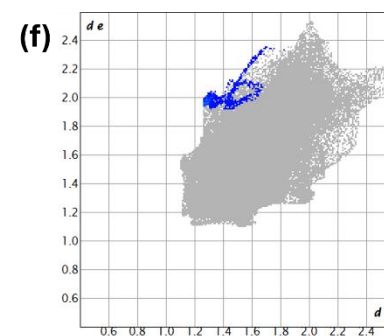
2.5% HS area of F...F



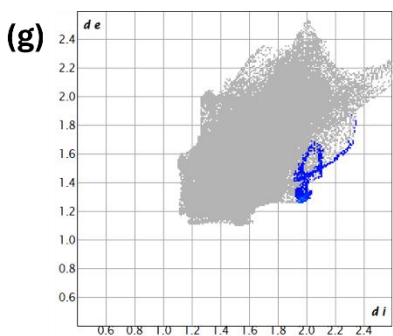
16.9% HS area of H...F



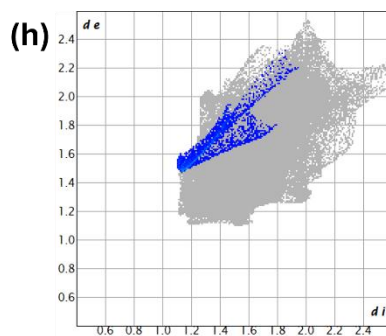
17.4% HS area of F...H



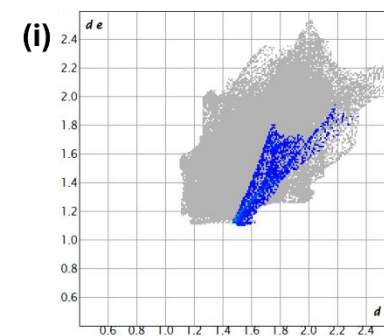
0.7% HS area of H...C



0.7% HS area of C...H

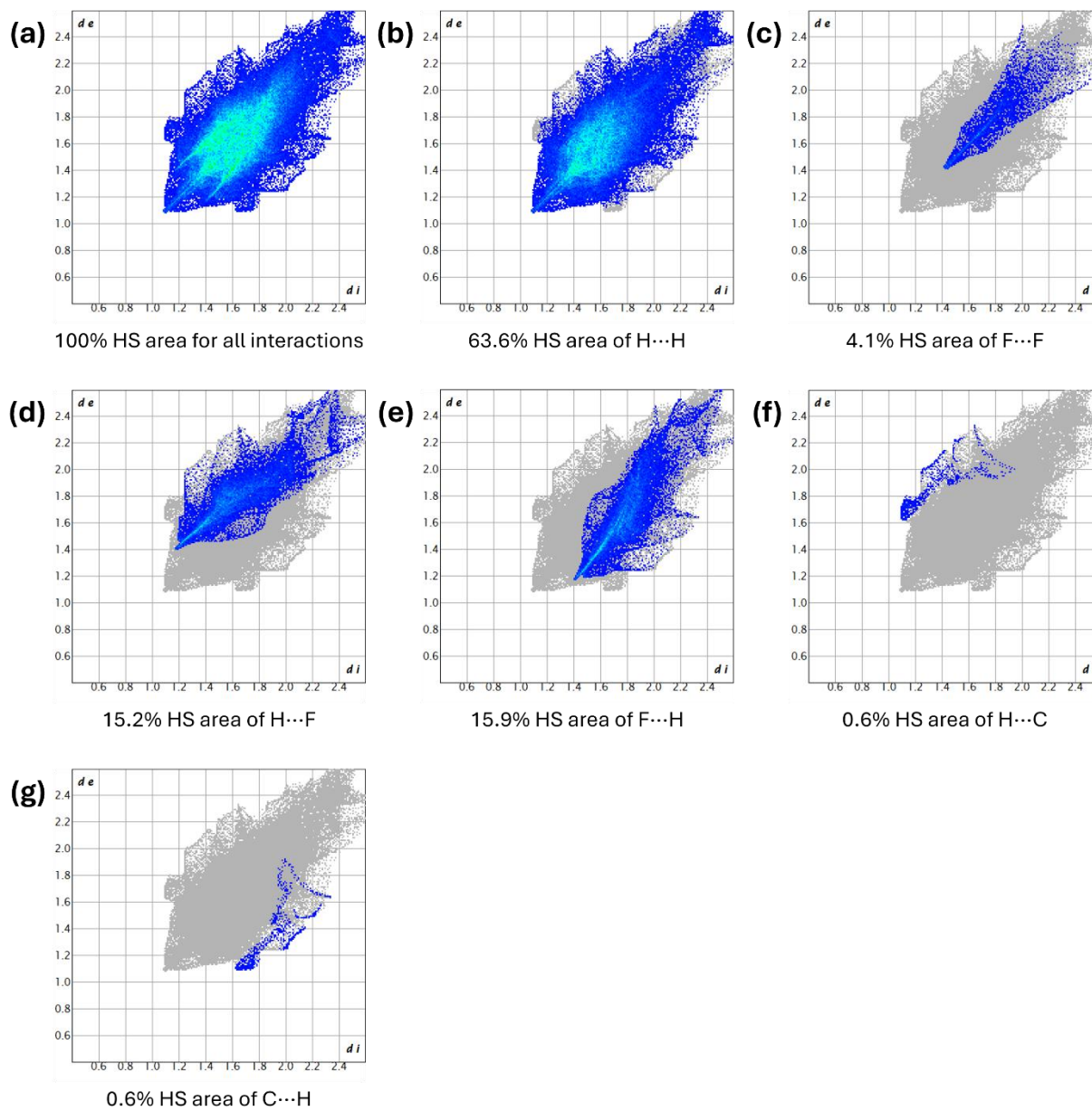


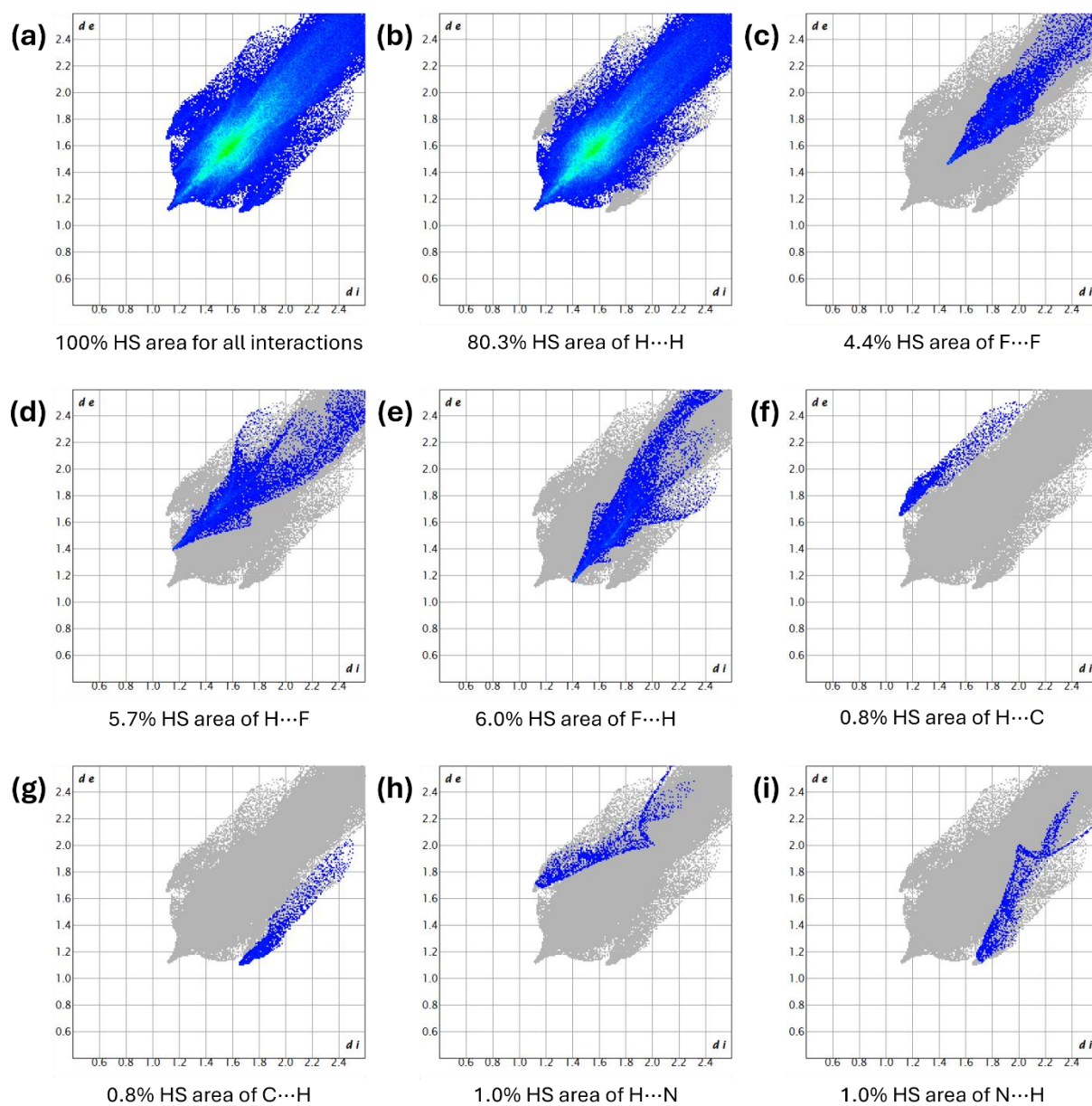
2.2% HS area of H...O



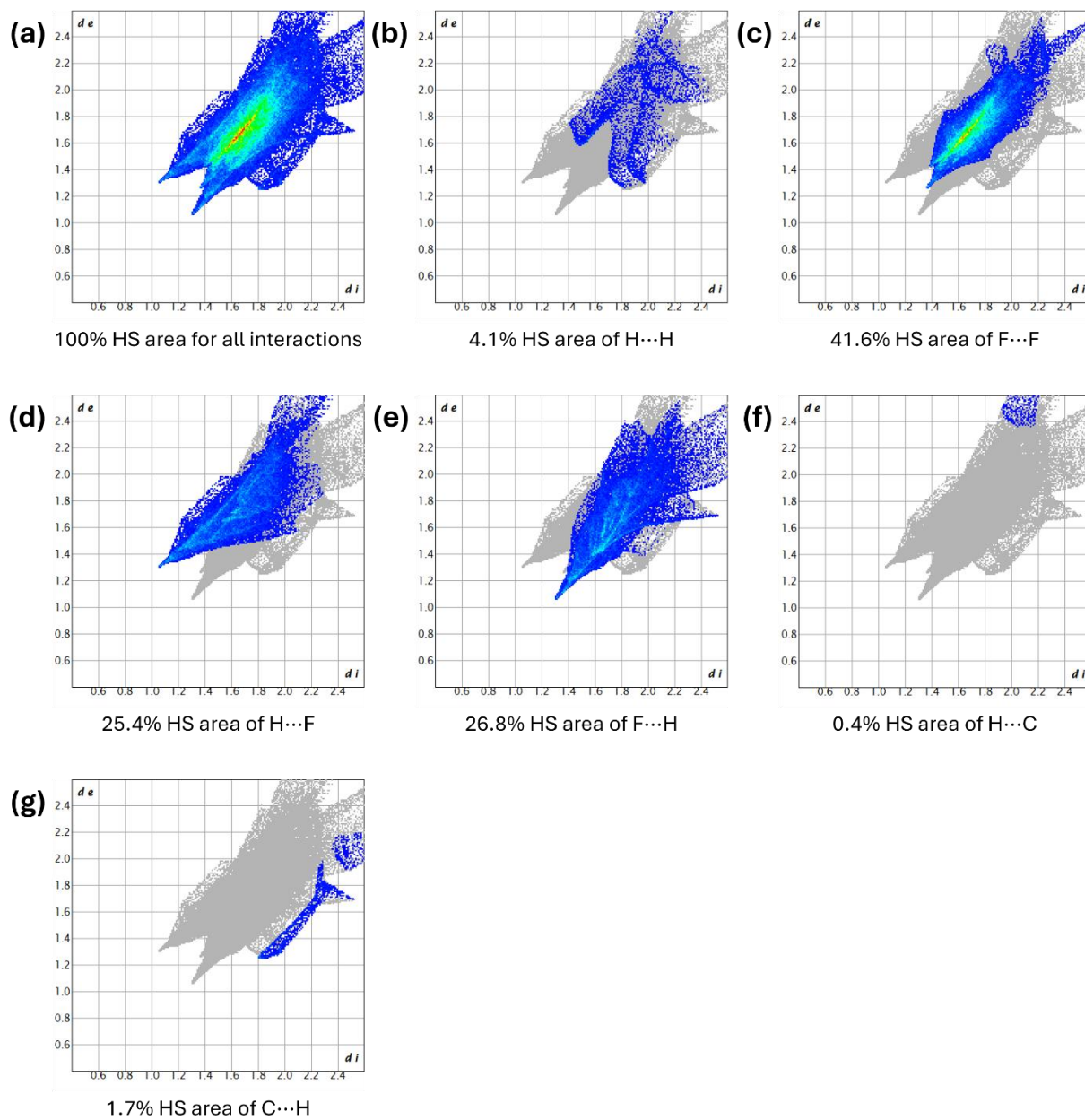
2.4% HS area of O...H

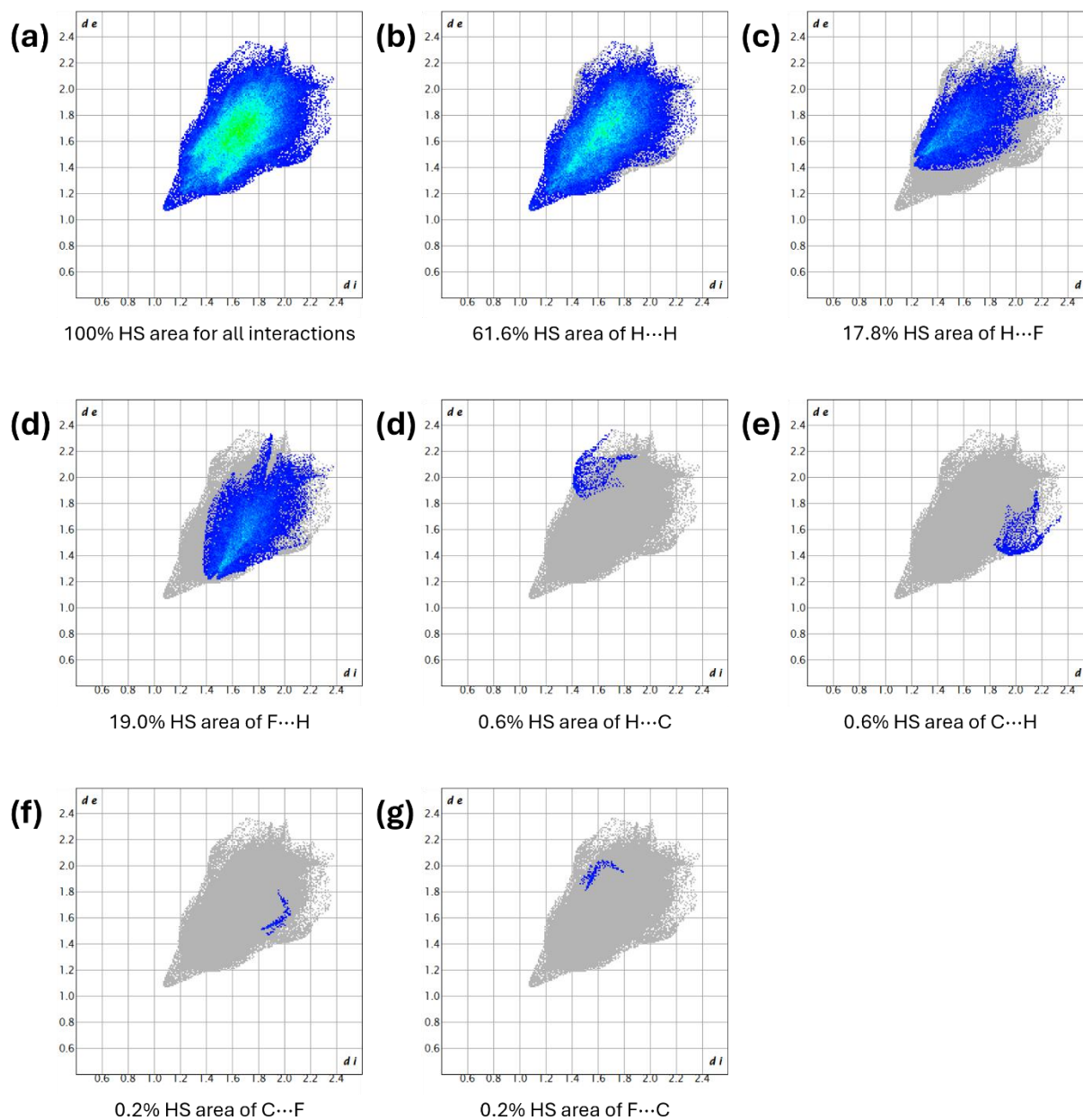
HS fingerprint of $[\text{Zr}(\text{TFB-MEA})_2(\text{NEt}_2)_2]$

HS fingerprint of $[\text{Zr}(\text{TFB-}t\text{BuA})_2(\text{NEt}_2)_2]$



HS fingerprint of $[\text{Zr}(\text{TFB-}t\text{BuA})_2\{\eta^2\text{-(}i\text{PrN)}_2\text{CNEt}_2\}_2]$

HS fingerprint of $[\text{Zr}(\text{TFB-TFEA})_4]$



HS fingerprint of $[\text{Zr}(\text{TFB-tBuA})_2(\text{NEt}_2)(\text{O'Bu})]$

Teilpublikationen:

Billy Oktora Abdilah, Andreas Lichtenberg, Corinna Hegemann, Thomas Fischer, Marcel Schmickler, Harish Parala, Anjana Devi, and Sanjay Mathur. "**Hf_xZr_{1-x}O₂ thin films from chemical vapor deposition of fluorinated β -ketoenamine precursors.**" *RSC Applied Interfaces*, **3**(3), (2026), p706-720.