



Syntheses and structures of novel hafnium chloroamido mono-amidinate and mono-guanidinate as precursors for HfO₂ thin film

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ABSTRACT

The reactions between HfCl₂[N(SiMe₃)₂]₂ and one or two equivalents of [ⁱPrNC(Me)NⁱPr]Li and ⁱPr–N=C=N–ⁱPr, at room temperature in toluene, gave the novel chloroamido-amidinato-hafnium HfCl[N(SiMe₃)₂]₂[ⁱPrNC(Me)NⁱPr] (**1**) and chloroamido-guanidinato-hafnium HfCl₂[N(SiMe₃)₂][ⁱPrNC(N(SiMe₃)₂)NⁱPr] (**2**) compounds, respectively. Compounds **1** and **2** were characterized by NMR and X-ray single crystal diffraction analysis. Their reaction towards alcohol was studied in order to check the dependency between molecular structure and HfO₂ Atomic Layer Deposition (ALD) specifications.

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1. Introduction

Amidines and guanidines are popular ligands due to their ease of synthesis and modification, as well as their robust nature [1,2]. The possibility of modulating the steric and electronic characteristics of these ligands can explain their use in coordination chemistry related to homogeneous catalysis, e.g. in Ring Opening Metathesis reactions [3–9] and very recently to materials sciences [10–22].

For applications in nanoscale electronic, the design of hafnium precursors based on amidinate and guanidinate ligands has been the focus of current scientific research in order to elaborate conformational tri-dimensional HfO₂ thin film by conventional or Direct Injection Atomic Layer Deposition (ALD) experiments [10,20–23]. The first step of such process involves the coverage of the substrate by a ligand substitution reaction between the surface species (mainly –OH) and a molecular precursor. This latter has to possess a monomeric structure and a well tailor-made coordination sphere in order to lead to selective heterogeneous surface reaction and to achieve a mono-atomic layer deposition (avoiding particles formation due to further reactions).

While various hafnium derivatives (halides, alkoxides, β-diketonates, alkylamides...) have been considered as precursors to enable such deposition, guanidines and amidines ligands became interesting alternatives to fulfill all the requirements in terms of

by-products, thermal stability and self-limited ALD temperature window, for instance. However, bis-guanidines alkylamide hafnium complexes are generally solids with limited volatility, [20–22] suggesting risk of thermal decomposition in vapor phase and subsequent particle generation. Mono-guanidinate and mono-amidinate alkylamide hafnium complexes have only been claimed in Ref. [23]. Tada et al. disclosed mono-amidinate alkylamide compounds of formula (R₁NC(R₂)NR₃M(NR₄R₅)_n), each R_i being an alkyl group, such as Hf[ⁱPrN(Me)NⁱPr](NMe₂)₃. Mono-amidinate complexes exhibited low volatility for industrial production purpose, and the mono-guanidines disclosed herein present significant advantage over mono-amidinate described by Tada et al. as for instance increased volatility. However, it appears that the mono-amidinate and mono-guanidinate families are claimed either without any precise description [23]. We recently demonstrated that the use of mixed ligand precursor involving monoanionic amidinate or guanidinate ligand appeared to be very promising in terms of tuning the physico-chemical properties of precursors [24]. We then report herein, for the first time, the full characterizations of novel mono-amidinate and mono-guanidinate hafnium-based precursors, and the effects of the coordination sphere nature on volatility and on their reactivities towards –OH species.

2. Experimental

2.1. Materials and apparatus

All reactions and manipulations of air and moisture-sensitive compounds were performed via a dual manifold vacuum/argon

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line using standard Schlenk techniques. Samples preparations were carried in nitrogen filled glove box. All solvents were dried by an MBraun solvent purification system. Deuterated NMR solvents were degassed and dried over activated molecular sieves. ^1H NMR spectra were registered on a Bruker AC-250 spectrometer. Analytical data were obtained from the Service Central d'Analyses du CNRS (Vernaison, France). $^i\text{Pr-N=C=N-}^i\text{Pr}$ was purchased from Sigma–Aldrich and was used as received, $\text{HfCl}_2[\text{N}(\text{SiMe}_3)_2]_2$ was prepared according to the literature [25].

2.2. Synthesis

2.2.1. $\text{HfCl}[\text{N}(\text{SiMe}_3)_2]_2[{}^i\text{PrNC}(\text{Me})\text{N}^i\text{Pr}]$ (**1**)

A solution of MeLi 1.6 M in hexane (6.50 ml, 10.40 mmol) was added dropwise to a stirred solution of ${}^i\text{Pr-N=C=N-}^i\text{Pr}$ (1.31 g, 10.40 mmol) in diethyl ether (25 ml) at -30°C . The mixture was then warmed to room temperature and stirred for 6 h. The above reactant mixture was added to a solution of $\text{HfCl}_2[\text{N}(\text{SiMe}_3)_2]_2$ (6.00 g, 10.51 mmol) in toluene (40 ml) and stirred for 20 h. The resulting white suspension was filtered. The filtrate was concentrated under vacuum and stored at -18°C , yielding colorless crystals of compound **1** (6.20 g, 80%). ^1H NMR (25 $^\circ\text{C}$, CDCl_3): δ_{H} 0.3 [s, $\text{HfCl}[\text{N}(\text{SiMe}_3)_2]_2[{}^i\text{PrNC}(\text{Me})\text{N}^i\text{Pr}]$, 36H], 1.25 [d, $J^3 = 6.4$ Hz, $\text{HfCl}[\text{N}(\text{SiMe}_3)_2]_2[(\text{CH}_3)_2\text{CHNC}(\text{Me})\text{NCH}(\text{CH}_3)_2]$, 12H], 1.96 [s, $\text{HfCl}[\text{N}(\text{SiMe}_3)_2]_2[({}^i\text{PrNC}(\text{Me})\text{N}^i\text{Pr})]$, 3H], 3.87 [sept., $J^3 = 6.4$ Hz, $\text{HfCl}[\text{N}(\text{SiMe}_3)_2]_2[(\text{CH}_3)_2\text{CHNC}(\text{Me})\text{NCH}(\text{CH}_3)_2]$, 2H]. Anal. Calc. for $\text{C}_{20}\text{H}_{54}\text{Cl}_2\text{N}_4\text{Si}_4\text{Hf}$: C, 35.48; H, 8.04; N, 8.28; Hf, 26.37. Found: C, 35.15; H, 8.10; N, 8.39; Hf, 26.27%.

2.2.2. $\text{HfCl}_2[\text{N}(\text{SiMe}_3)_2]_2[{}^i\text{PrNC}(\text{N}(\text{SiMe}_3)_2)\text{N}^i\text{Pr}]$ (**2**)

A solution of ${}^i\text{Pr-N=C=N-}^i\text{Pr}$ (0.25 g, 1.95 mmol) in toluene (2 ml) was added to a solution of $\text{HfCl}_2[\text{N}(\text{SiMe}_3)_2]_2$ (1.11 g, 1.95 mmol) in toluene (20 ml). After stirring for 20 h at room temperature, the solvent was removed under reduced pressure to give a white powder. Crystals of complex **2** were obtained at -18°C in hexane (1.14 g, 82%). ^1H NMR (250 MHz, CDCl_3): δ_{H} 0.29, 0.33 [s [1:2], $\text{HfCl}_2[\text{N}(\text{SiMe}_3)_2]_2[{}^i\text{PrNC}(\text{N}(\text{SiMe}_3)_2)\text{N}^i\text{Pr}]$, 36H], 1.25–1.34 [d, $J^3 = 6.3$ Hz, $\text{HfCl}_2[\text{N}(\text{SiMe}_3)_2]_2[(\text{CH}_3)_2\text{CHNC}(\text{N}(\text{SiMe}_3)_2)\text{NCH}(\text{CH}_3)_2]$, 12H], 3.58, 4.10, 4.23 [sept. [1:1:1], $J^3 = 6.3$ Hz, $\text{HfCl}_2[\text{N}(\text{SiMe}_3)_2]_2[(\text{CH}_3)_2\text{CHNC}(\text{N}(\text{SiMe}_3)_2)\text{NCH}(\text{CH}_3)_2]$, 2H]. Anal. Calc. for $\text{C}_{18}\text{H}_{50}\text{Cl}_2\text{N}_4\text{Si}_4\text{Hf}$: C, 32.77; H, 7.24; N, 8.05; Hf, 25.63. Found: C, 33.2; H, 7.11; N, 7.91; Hf, 25.40%.

2.2.3. $\text{HfCl}(\text{O}^i\text{Pr})[\text{N}(\text{SiMe}_3)_2]_2[{}^i\text{PrNC}(\text{Me})\text{N}^i\text{Pr}]$ (**3**)

A solution of ${}^i\text{PrOH}$ (0.16 g, 2.80 mmol) in diethylether (4 ml) was added to a solution of $\text{HfCl}[\text{N}(\text{SiMe}_3)_2]_2[{}^i\text{PrNC}(\text{Me})\text{N}^i\text{Pr}]$ (**1**) (0.92 g, 1.36 mmol) in diethylether (15 ml). After stirring for 20 h at room temperature, the solvent was removed under reduced pressure to give a white powder of **3** (0.71 g, 91%). ^1H NMR (250 MHz, CDCl_3): δ_{H} 0.30 [s, $\text{HfCl}(\text{O}^i\text{Pr})[\text{N}(\text{SiMe}_3)_2]_2[{}^i\text{PrNC}(\text{Me})\text{N}^i\text{Pr}]$, 18H], 1.24 [d, $J^3 = 6.5$ Hz, $\text{HfCl}(\text{O}^i\text{Pr})[\text{N}(\text{SiMe}_3)_2]_2[(\text{CH}_3)_2\text{CHNC}(\text{Me})\text{NCH}(\text{CH}_3)_2]$, 12H], 1.28 [d, $J^3 = 6.3$ Hz, $\text{HfCl}(\text{O}^i\text{Pr})[\text{N}(\text{SiMe}_3)_2]_2[({}^i\text{PrNC}(\text{Me})\text{N}^i\text{Pr})]$, 6H], 2.00 [s, $\text{HfCl}(\text{O}^i\text{Pr})[\text{N}(\text{SiMe}_3)_2]_2[({}^i\text{PrNC}(\text{Me})\text{N}^i\text{Pr})]$, 3H], 3.87 [sept., $J^3 = 6.5$ Hz, $\text{HfCl}(\text{O}^i\text{Pr})[\text{N}(\text{SiMe}_3)_2]_2[(\text{CH}_3)_2\text{CHNC}(\text{Me})\text{NCH}(\text{CH}_3)_2]$, 2H], 4.46 [broad peak, $\text{HfCl}(\text{O}^i\text{Pr})[\text{N}(\text{SiMe}_3)_2]_2[({}^i\text{PrNC}(\text{Me})\text{N}^i\text{Pr})]$, 1H]. Anal. Calc. for $\text{C}_{18}\text{H}_{50}\text{Cl}_2\text{N}_4\text{Si}_4\text{Hf}$: C, 35.59; H, 7.20; N, 7.33; Hf, 31.12. Found: C, 35.21; H, 7.13; N, 7.67; Hf, 31.52%.

2.3. X-Ray crystal structure determination for **1–2**

The data were processed using the KAPPA CCD analysis programs [26]. The lattice constants were refined by least-squares refinements. Empirical absorption correction (multi-scan [27]) was applied to the data sets. The data collection has been performed at 293 K. The structure has been solved by direct methods using the

SIR97 program [28] combined with Fourier difference syntheses and refined against F using the CRYSTALS program [29]. Hydrogen atoms have been found either by Fourier difference or located theoretically based on the conformation and environment of the supporting atom and then refined. All the atomic displacement parameters for non-hydrogen atoms have been refined anisotropically.

3. Results and discussion

3.1. Syntheses and characterizations of complexes **1** and **2**

The novel mono-amidinate $\text{HfCl}[\text{N}(\text{SiMe}_3)_2]_2[{}^i\text{PrNC}(\text{Me})\text{N}^i\text{Pr}]$ (**1**) was synthesized by metathesis reaction between $\text{HfCl}_2[\text{N}(\text{SiMe}_3)_2]_2$ and one or two equivalents of $[{}^i\text{PrNC}(\text{Me})\text{N}^i\text{Pr}]\text{Li}$, as shown in Scheme 1. Similarly, the insertion reaction in Hf–N bond between one or two equivalents of ${}^i\text{Pr-N=C=N-}^i\text{Pr}$ and $\text{HfCl}_2[\text{N}(\text{SiMe}_3)_2]_2$ led only to the original mono-guanidinate precursor $\text{HfCl}_2[\text{N}(\text{SiMe}_3)_2]_2[{}^i\text{PrNC}(\text{N}(\text{SiMe}_3)_2)\text{N}^i\text{Pr}]$ (**2**). This is the first examples of mono-substituted amidinato and guanidinato hafnium complexes to be structurally characterized. While hafnium-center is only five-fold coordinated, it can be assumed that the high steric shielding of the hafnium-center cannot be overcome after the first substitution or insertion reactions. Removing the solvent in vacuum yielded **1** and **2** in the form of white powders. Crystalline, colorless samples were obtained by recrystallization from toluene, diethylether or hexane at -18°C . The compounds were highly soluble in most of the organic solvents such as hexane, toluene, diethylether. Elemental analysis and ^1H NMR data revealed that both compounds were chemically pure as prepared.

NMR results at room temperature displayed only one set of signals for derivative **1** while compound **2** exhibited several sets of signals. Both possessed an internal mirror plane along the Hf–chloro–amidinate and Hf–amido–guanidinato plane, for **1** and **2** respectively, and were thus not chiral. These data indicated a higher steric hindrance for compound **2**, suggesting that the rotation barriers of C–N(SiMe_3)₂ and N–CHMe₂ bonds cannot be overcome.

3.2. X-ray structure of **1–2**

Single crystals of **1** and **2** were obtained by recrystallization from solvent at -18°C (Figs. 1 and 2). They were transferred from Schlenk tubes to paratone oil and mounted on a capillary and then on the goniometer. They crystallized in a monoclinic crystal system. Crystallographic data and selected bond lengths and bond angles are summarized in Tables 1 and 2, respectively.

3.2.1. X-ray structure of $\text{HfCl}[\text{N}(\text{SiMe}_3)_2]_2[{}^i\text{PrNC}(\text{Me})\text{N}^i\text{Pr}]$ (**1**)

The Hf atom is surrounded by five atoms forming a distorted base square pyramid. This environment is composed by four nitrogen atoms, two belonging to the two silyl-amido ligands L1 (N1 and N10) and two belonging to the amidinate ligand L2 (N19 and N21), and one chlorine atom. Hf–N and Hf–Cl bond lengths (average: 2.14 Å and 2.42 Å, respectively) are in agreement with those recently reported in the literature [8–10]. It has to be noticed that the Hf–NL1 bond lengths are slightly shorter than the Hf–NL2 ones (average: 2.07 Å versus 2.20 Å, respectively) due to the more basic character of the silyl-amido group. With a dihedral angle of 358.99° and 359.81° around the nitrogen atoms of the silyl-amido groups, it indicated a sp^2 hybridisation of the nitrogen atoms and a strong π -donating effect of these amido groups. The bite angle of the bidentate amidinate ligand (N(19)–Hf–N(21) = 60.09°) is similar to the ones in related complex such as $\text{HfCl}_2[{}^i\text{BuNC}(\text{Me})\text{N}^i\text{Bu}]$ [10]. C–N bond lengths within the amidinate core are similar (1.332 and 1.343 Å) showing no difference in the Hf-to-ligand interaction of the two metallacycle nitrogen groups.

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