

# Hafnium complexes with versatile $\beta$ -diketiminate ligands: Synthesis, spectroscopic investigation and volatility study



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## ABSTRACT

Synthesis and spectral investigation of four novel  $\beta$ -diketiminate hafnium(IV) chloride complexes cis-dichloro-bis(2,4-bis(phenylimino)pent-3-ene)-hafnium (**4a**), cis-dichloro-bis(2,4-bis(4-methylphenylimino)pent-3-ene)-hafnium (**4b**), cis-dichloro-bis(2,4-bis(4-methoxyphenylimino)pent-3-ene)-hafnium (**4c**) and cis-dichloro-bis(2,4-bis(4-chlorophenylimino)pent-3-ene)-hafnium (**4d**) are reported. All complexes (**4a–d**) were characterized by spectroscopic methods (<sup>1</sup>H NMR, <sup>13</sup>C NMR and mass) and elemental analysis. The solid-state structure of compound **4a** was further examined by single crystal X-ray diffraction. The X-ray structure of **4a** reveals that the complex is monomeric with the hafnium center in a distorted octahedral geometry, and the chloride ligands are in a *cis* arrangement. The thermal stability and volatility of the compounds were probed by TGA/DSC tests demonstrating the potential utility of compounds (**4a–d**) as precursors for CVD/ALD thin film growth below 200 °C.

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## 1. Introduction

The interest in the chemistry of  $\beta$ -diketimines started to grow since the late nineties. The first example for the synthesis of  $\beta$ -diketiminate ligands dates back to 1968, when McGeachin prepared several alkyl-substituted  $\beta$ -diketimines derived from acetylacetone, and some nickel and cobalt complexes [1]. From the end of the nineties, the number of papers appearing in the literature using  $\beta$ -diketiminate ligands has grown extremely fast, and involves a large portion of the main group, transition metal and lanthanide elements. These ligands have several attractive features; for example, their steric and electronic properties can be easily tuned [2], and they can coordinate to the metal center in different bonding models ranging from purely  $\sigma$  and  $\pi$ , to a combination of  $\sigma$  and  $\pi$  donation (Scheme 1A–C) [3]. In particular, some of these  $\beta$ -diketiminate complexes are active for olefin polymerization [3–7], and lactide “living” polymerization [8–11]. However, the utilization of  $\beta$ -diketiminate as ancillary ligands in the synthesis of hafnium complexes still remains relatively poorly explored.

Hafnium dioxide (HfO<sub>2</sub>) thin films have found important technological applications in various fields, from microelectronic and optoelectronic devices to corrosion protection layers [12–15]. Such a broad utilization is the result of its specific properties, including high refractive index, chemical and thermal stability, high density and high dielectric constant [12–15]. Among the methods adopted to date for HfO<sub>2</sub> thin film fabrication (such as sputtering, pulsed laser deposition, sol–gel processing) [16–18], MOCVD is one of the most promising methods due to the possibility of obtaining a good conformal coverage and large area growth under tailored conditions. One of the primary requirements for a successful MOCVD process is the availability of appropriate precursors with adequate volatility and stability [19]. In fact, several existing precursors, including hafnium halides, alkoxides, and amides have certain drawbacks in terms of low volatility, high reactivity towards air and moisture and halogen incorporation into the films [20–22]. A simultaneous solution to these problems is still an open challenge in the field.

Herein, we demonstrate a synthetic pathway for  $\beta$ -diketiminate ligands and their corresponding hafnium(IV) chloride complexes and provide detailed characterization by spectroscopic (<sup>1</sup>H NMR, <sup>13</sup>C NMR and MS) methods, X-ray diffraction, and elemental analysis. Volatility of all four hafnium complexes **4a–d** were assessed by calculating the enthalpy of sublimation from the mass loss rates

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at thermogravimetric isotherms with the purpose of assessing their suitability as precursors to hafnium dioxide (HfO<sub>2</sub>) thin films.

## 2. Experimental

### 2.1. General considerations

Unless otherwise noted, all reactions and manipulations were performed under nitrogen in an MBraun Unilab 1200/780 glove box or using conventional Schlenk techniques. All solvents were sparged with nitrogen for 25 min and dried using an MBraun Solvent Purification System (SPS). C<sub>6</sub>D<sub>6</sub> was dried over activated 4 Å molecular sieves. Acetylacetone, aniline, 4-methylaniline, 4-methoxyaniline, 4-chloroaniline, *p*-toluenesulfonic acid, formic acid, magnesium sulfate, 1.6 M *n*-butyllithium hexane solution and hafnium(IV) chloride were procured commercially from Sigma–Aldrich, and were used without further purification. Nuclear magnetic resonance (NMR) spectra were obtained using a 1.0–2.5% solution in deuterated benzene (C<sub>6</sub>D<sub>6</sub>). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Mercury 500 MHz spectrometer. Proton and carbon chemical shifts are reported in parts-per-million ( $\delta$ ) with respect to tetramethylsilane (TMS) as internal reference ( $\delta = 0.0$  ppm). Mass spectra were obtained on a GC–MS instrument operating in TOF–MI<sup>+</sup> mode. CHN analysis was done by Atlantic Microlab using a CE-1108 Elemental Analyzer, and values were within  $\pm 0.4\%$  of the theoretical values. Single crystals suitable for X-ray diffraction study were obtained from methanol and dry dichloromethane by slow evaporation at room temperature.

### 2.2. Synthesis of 2-((phenyl)amino)-4-((phenyl)imino)-2-pentene (3a)

A mixture of aniline (22.78 mL, 0.25 mol), 2,4-pentanedione (12.7 mL, 0.12 mol), and *p*-toluenesulfonic acid (21.3 g, 0.12 mol) in toluene (350 mL) was heated at reflux for 24 h in a Dean–Stark apparatus. The toluene was then decanted off, and the solid residue was treated with diethyl ether (250 mL), water (200 mL), and Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O (53 g, 0.13 mol). After stirring for 25 min, the ether layer was separated and dried with MgSO<sub>4</sub>, and the solvent was removed *in vacuo*. The residue was dried *in vacuo* (10<sup>−2</sup> bar) at 100 °C for 6 h to remove any remaining free aniline, and the residue was crystallized from hexane to give yellow crystals (27 g, 70%) of **3a**. <sup>1</sup>H NMR ( $\delta$  ppm C<sub>6</sub>D<sub>6</sub>, 500 MHz): 13.12 (s, 1H, NH), 7.10–7.07 (m, 4H, Ph), 6.90–6.86 (m, 6H, Ph), 4.76 (s, 1H, CH), 1.79 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR ( $\delta$  ppm C<sub>6</sub>D<sub>6</sub>, 125 MHz, proton decoupled): 159.3 (C=N), 146.2, 129.1, 123.3, 122.7 (Ph), 98.1 (CH), 20.7 (CH<sub>3</sub>). Mass data (TOF MS EI<sup>+</sup>):  $m/z = 250.12$  [M]<sup>+</sup>. Micro Anal. Calc. for C<sub>17</sub>H<sub>18</sub>N<sub>2</sub> (250.34): C, 81.56; H, 7.25; N, 11.19. Found: C, 81.48; H, 7.27; N, 11.21%.

### 2.3. Synthesis of 2-((4-methylphenyl)amino)-4-((4-methylphenyl)imino)-2-pentene (3b)

A mixture of 4-methylaniline (26.8 g, 0.25 mol), 2,4-pentanedione (12.7 mL, 0.12 mol), and *p*-toluenesulfonic acid monohydrate (21.3 g) in toluene (350 mL) was heated at reflux for 24 h in a Dean–Stark apparatus. The toluene was then decanted off, and the solid residue was treated with diethyl ether (250 mL), water

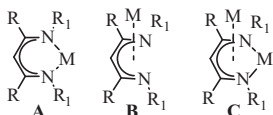
(200 mL), and Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O (53 g). After stirring for 25 min, the ether layer was separated and dried with MgSO<sub>4</sub>, and the solvent was removed *in vacuo*. The residue was dried *in vacuo* (10<sup>−2</sup> bar) at 100 °C for 6 h to remove any remaining free 4-methylaniline, and the residue was crystallized from hexane to give light yellow crystals (27.8 g, 80%) of **3b**. <sup>1</sup>H NMR ( $\delta$  ppm C<sub>6</sub>D<sub>6</sub>, 500 MHz): 13.15 (s, 1H, NH), 6.91 (d,  $J = 8.0$  Hz, 4H, Ph), 6.82 (d,  $J = 8.0$  Hz, 4H, Ph), 4.80 (s, 1H, CH), 2.10 (s, 6H, CH<sub>3</sub>), 1.80 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR ( $\delta$  ppm C<sub>6</sub>D<sub>6</sub>, 125 MHz, proton decoupled): 159.4 (C=N), 143.8, 132.5, 129.6, 122.8 (Ph), 97.6 (CH), 20.7 (CH<sub>3</sub>), 20.7 (CH<sub>3</sub>). Mass data (TOF MS EI<sup>+</sup>):  $m/z = 278.25$  [M]<sup>+</sup>. Micro Anal. Calc. for C<sub>19</sub>H<sub>22</sub>N<sub>2</sub> (278.39): C, 81.97; H, 7.97; N, 10.06. Found: C, 81.87; H, 7.93; N, 10.01%.

### 2.4. Synthesis of 2-((4-methoxyphenyl)amino)-4-((4-methoxyphenyl)imino)-2-pentene (3c)

To a stirred solution of 4-methoxyaniline (6.150 g, 50.00 mmol) in 80 mL of toluene was added *p*-toluenesulfonic acid monohydrate (9.510 g, 50.00 mmol), and the mixture was stirred for 3 h at room temperature, then 4-(4-methoxyphenyl)amino-3-penten-2-one (**2<sup>1</sup>c**) (10.26 g, 50.00 mmol) was added to it. A Dean–Stark apparatus was attached and the mixture was heated to reflux for 24 h. The reaction mixture was cooled and dried under reduced pressure to give a yellow solid. The obtained solid was treated with diethyl ether (100 mL), water (100 mL) and sodium carbonate (10.60 g, 100.0 mmol), and kept stirring. After complete dissolution, the aqueous phase was separated and extracted with diethyl ether. The combined organic phases were dried over MgSO<sub>4</sub> and rotary evaporated to dryness under reduced pressure to afford a yellow solid. Yellow crystals of **3c** (11.95 g, 77%) were obtained after recrystallization from methanol. <sup>1</sup>H NMR ( $\delta$  ppm C<sub>6</sub>D<sub>6</sub>, 500 MHz): 13.08 (s, 1H, NH), 6.83 (d,  $J = 8.0$  Hz, 4H, Ph), 6.70 (d,  $J = 8.0$  Hz, 4H, Ph), 4.83 (s, 1H, CH), 3.30 (s, 6H, OCH<sub>3</sub>), 1.84 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR ( $\delta$  ppm C<sub>6</sub>D<sub>6</sub>, 125 MHz, proton decoupled): 159.9 (C=N), 156.5, 139.4, 124.4, 114.4 (Ph), 97.0 (CH), 54.9 (OCH<sub>3</sub>), 20.6 (CH<sub>3</sub>). Mass data (TOF MS EI<sup>+</sup>):  $m/z = 310.17$  [M]<sup>+</sup>. Micro Anal. Calc. for C<sub>19</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub> (310.39): C, 73.52; H, 7.14; N, 9.03. Found: C, 73.41; H, 7.15; N, 9.00%.

### 2.5. Synthesis of 2-((4-chlorophenyl)amino)-4-((4-chlorophenyl)imino)-2-pentene (3d)

To a stirred solution of 4-chloroaniline (6.380 g, 50.00 mmol) in 80 mL of toluene was added *p*-toluenesulfonic acid monohydrate (9.510 g, 50.00 mmol), and the mixture was stirred for 3 h at room temperature, then 4-(4-chlorophenyl)amino-3-penten-2-one (**2<sup>1</sup>d**) (10.48 g, 50.00 mmol) was added to it. A Dean–Stark apparatus was attached and the mixture was heated to reflux for 24 h. The reaction mixture was cooled and dried under reduced pressure to give a yellow solid. The obtained solid was treated with diethyl ether (100 mL), water (100 mL) and sodium carbonate (10.60 g, 100.0 mmol), and kept stirring. After complete dissolution, the aqueous phase was separated and extracted with diethyl ether. The combined organic phases were dried over MgSO<sub>4</sub> and rotary evaporated to dryness under reduced pressure to afford a yellow solid. Yellow crystals of **3d** (11.95 g, 77%) were obtained after recrystallization from methanol. <sup>1</sup>H NMR ( $\delta$  ppm C<sub>6</sub>D<sub>6</sub>, 500 MHz): 12.81 (s, 1H, NH), 7.01 (d,  $J = 8.0$  Hz, 4H, Ph), 6.53 (d,  $J = 8.0$  Hz, 4H, Ph), 4.70 (s, 1H, CH), 1.65 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR ( $\delta$  ppm C<sub>6</sub>D<sub>6</sub>, 125 MHz, proton decoupled): 159.5 (C=N), 144.5, 129.1, 128.8, 123.86 (Ph), 98.4 (CH), 20.5 (CH<sub>3</sub>). Mass data (TOF MS EI<sup>+</sup>):  $m/z = 319.11$  [M]<sup>+</sup>. Micro Anal. Calc. for C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>Cl<sub>2</sub> (319.23): C, 63.96; H, 5.05; N, 8.78; Cl, 22.21. Found: C, 63.91; H, 5.15; N, 8.69; Cl, 22.21%.



**Scheme 1.** Coordination modes of  $\beta$ -diketiminato ligands (A–C).

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