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Synthesis and characterization of new unsymmetrical β-diketiminate tris(dimethylamido)hafnium(IV) complexes as potential precursors for the MOCVD of HfO_2

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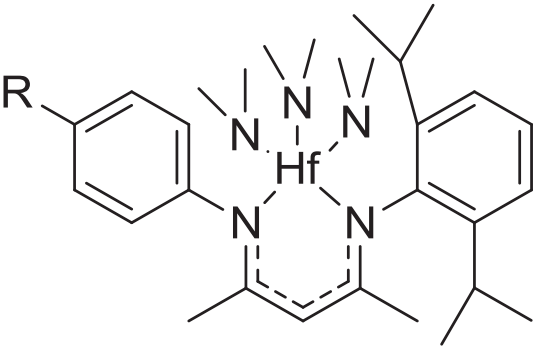

The synthesis and characterization of four new unsymmetrical β-diketiminate tris(dimethylamido) hafnium(IV) complexes, [2-(2,6-diisopropylphenyl)amino-4-(phenyl)imino-2-pentene]tris(dimethylamido)hafnium(IV) (**5a**), [2-(2,6-diisopropylphenyl)amino-4-(4-methylphenyl)imino-2-pentene]tris (dimethylamido)hafnium(IV) (**5b**), [2-(2,6-diisopropyl-phenyl)amino-4-(4-methoxyphenyl)imino-2-pentene]tris(dimethylamido)hafnium(IV) (**5c**), and [2-(2,6-diisopropylphenyl)amino-4-(4-chlorophenyl)imino-2-pentene]tris(dimethylamido)hafnium(IV) (**5d**), are described. Amine elimination reactions work well for introducing unsymmetrical β-diketiminates2-(2,6-diisopropylphenyl)amino-4-(phenyl)imino-2-pentene (**4a**), 2-(2,6-diisopropylphenyl)amino-4-(4-methylphenyl)imino-2-pentene (**4b**), 2-(2,6-diisopropylphenyl)amino-4-(4-methoxyphenyl)imino-2-pentene (**4c**), and 2-(2,6-diisopropylphenyl)amino-4-(4-chlorophenyl)imino-2-pentene (**4d**) to the tetrakis(dimethylamino)hafnium centre. We discuss the synthetic procedures and characterization using ^{1}H NMR, ^{13}C NMR, IR, mass spectroscopy, and elemental analysis. According to the IR and NMR spectra, unsymmetrical β-diketiminate ligands are bidentate, coordinating through two nitrogens to hafnium.

Keywords: Unsymmetrical β-diketiminates; Hafnium compounds; Synthesis; Spectroscopic characterization

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1. Introduction

The metal-organic precursor chemistry of metal oxide materials has developed into a vast field of intense and continuing activity, covering much of materials research due to the diversity of interesting physical and chemical properties of many binary and multi-component metal oxides [1–3]. Hafnium dioxide is one of the promising candidates to replace SiO_2 as the gate oxide material in the submicron generation of complementary metal oxide semiconductor devices because of its relatively high dielectric constant and stability [4]. There are several reports where thin films of HfO_2 have been produced by laser ablation, sputtering, sol–gel, ALD and CVD processes [5, 6]. MOCVD is one of the appealing techniques for deposition of thin films of various materials as it possesses some inherent advantages. The metal-organic compounds used as precursors for this process play a pivotal role in the resulting properties of the films obtained.

The precursor of choice for the deposition of HfO_2 is most often tetrakis(dimethylamido)-hafnium(IV); however, its high reactivity and premature decomposition issues have led to interest in the development of new precursors with the potential of fine tuning their volatility. In this regard, β-ketiminate ligands have shown improved volatility properties in a variety of main group [7–14] and transition metal [15–19] precursors, with the possibility of tuning the volatility properties by changing the ligand structure [20]. It has also been reported that various zirconium β-ketiminates feature high volatility and interesting properties for MOCVD applications [21].

There has been a revival of interest in bidentate β-diketiminate ligands [22] which may be illustrated by the formula $[\{RNC(R^I)\}_2CH]^-$ (figure 1). A major portion of work has focused on more crowded ligands that involve bulky substituents at the nitrogens [23–29]. These have been used to synthesize a variety of transition metal, main group, and lanthanide complexes, a significant number of which have been shown to be effective as either olefin polymerization catalysts or structural models for the metal site metalloproteins [23–29].

However, there are no reports of hafnium-based β-diketiminates for thin film deposition applications. Herein, we report the synthesis and characterization of new unsymmetrical β-diketiminate tris(dimethylamido)hafnium(IV) complexes, [2-(2,6-diisopropylphenyl) amino-4-(phenyl)imino-2-pentene]tris(dimethylamido)hafnium(IV) (**5a**), [2-(2,6-diisopropylphenyl)amino-4-(4-methylphenyl)imino-2-pentene]tris(dimethylamido)hafnium(IV) (**5b**), [2-(2,6-diisopropyl-phenyl)amino-4-(4-methoxyphenyl)imino-2-pentene]tris(dimethylamido) hafnium(IV) (**5c**) and [2-(2,6-diisopropylphenyl)amino-4-(4-chlorophenyl)imino-2-pentene] tris(dimethylamido)hafnium(IV) (**5d**), as potential precursors for the MOCVD of HfO_2.

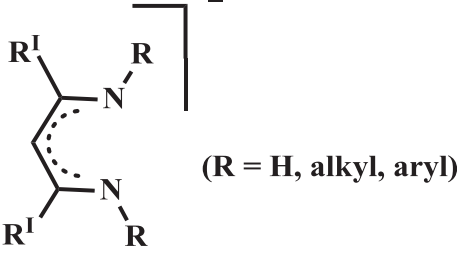


Figure 1. Bidentate, β-diketiminate ligands.

The precursors exhibit a high degree of solubility in common organic solvents and could possess promising thermal properties for CVD applications.

2. Experimental

2.1. *General considerations*

Unless otherwise noted, all reactions and manipulations were performed under nitrogen in a MBraunUnilab 1200/780 glovebox or using conventional Schlenk techniques. All solvents were sparged with nitrogen for 25 min and dried using a MBraun Solvent Purification System. C_6D_6 was dried over activated 4 Å molecular sieves. Acetylacetone, aniline, 4-methylaniline, 4-methoxyaniline, 4-chloroaniline, 2,6-diisopropylaniline, *p*-toluenesulfonic acid, formic acid, magnesium sulfate, sodium carbonate, and tetrakis(dimethylamino)hafnium were procured commercially from Sigma–Aldrich chemical company and used without purification. Nuclear magnetic resonance (NMR) spectra were obtained using a 1.0–2.5% solution in deuterated benzene (C_6D_6). ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 500 MHz spectrometer. Proton and carbon chemical shifts are reported in parts-per-million (δ) with respect to tetramethylsilane (TMS) as internal reference ($\delta = 0.0$ ppm). IR spectra were recorded on a Perkin Elmer Paragon 1000 FT-IR spectrometer employing a KBr disk. Mass spectra were obtained on a GC-MS instrument operating in TOF-MI$^+$ mode. CHN analysis was done by Atlantic Microlab using a CE-1108 Elemental Analyzer, and values were within ±0.4% of the theoretical values.

2.2. *Synthesis*

2.2.1. 4-(2,6-Diisopropylphenyl)amino-3-penten-2-one (3). 2,6-Diisopropylaniline (1.77 g, 10.0 mM) was mixed with acetylacetone (1.0 g, 10.0 mM) in 40 mL of methanol containing a catalytic amount (two drops) of formic acid. The solution was heated at 85 °C for 6–8 h. Removal of volatiles afforded pale brown oil. This was then stirred with 20 mL of petroleum ether at −30 °C to precipitate a white solid which was filtered off, washed with 2 × 10 mL cold hexane (−78 °C) and dried *in vacuo*. Yield: 2.30 g (89%). ^{1}H NMR (500 MHz, C_6D_6) δ (ppm): 12.66 (1H, s, NH), 7.11–7.06 (m, 1H, ArH), 6.97–6.94 (m, 2H, ArH), 5.08 (s, 1H, CH=C(CH_3)N), 3.04 (sept, $J = 6.8$ Hz, 2H, CH(CH_3)$_2$), 2.01 (s, 3H, CH_3COC), 1.34 (s, 3H, CH_3CNHAr), 1.02 (d, $J = 6.9$ Hz, 6H, CH(CH_3)$_2$), 0.96 (d, $J = 6.9$ Hz, 6H, CH(CH_3)$_2$). ^{13}C NMR (100 MHz, C_6D_6) δ (ppm): 195.69 (C=O), 162.40 (HC(CNHAr), 146.60 (Ar–C), 134.23 (Ar–C), 128.50 (Ar–C), 123.78 (Ar–C), 95.93 (CH), 29.04 (CH_3C=O), 28.80 (CH(CH_3)$_2$), 24.53 (CH(CH_3)$_2$, 22.61 (CH(CH_3)$_2$), 18.85 (CH_3CNHAr). Mass data (TOF MS EI$^+$): Calcd for $C_{17}H_{25}NO$ [M$^+$] 259.39, found: 259.21. Anal. Calcd for $C_{17}H_{25}NO$: C, 78.72; H, 9.71; N, 5.40. Found: C, 78.61; H, 9.59; N, 5.36. IR (KBr, cm^{-1}) ν: 3418 (m), 2972 (w), 16,015 (s), 1573 (m), 1515 (m), 1467 (w), 1411 (m), 1397 (m), 1344 (m), 1299 (w), 1203 (w), 1137 (m), 1076 (w), 983 (m), 842 (w), 722 (w), 601 (m), 513 (m), 484 (w).

2.2.2. 2-(2,6-Diisopropylphenyl)amino-4-(phenyl)imino-2-pentene (4a). Aniline (4.55 g, 50.00 mM) and *para*-toluenesulfonic acid monohydrate (9.510 g, 50.00 mM) in 100 mL of toluene were stirred for approximately 3 h at room temperature. To the obtained yellow

suspension, 4-(2,6-diisopropylphenyl)amino-3-penten-2-one (**3**) (12.97 g, 50.00 mM) was added. A Dean–Stark apparatus was attached, and the mixture was heated at reflux for 24 h to remove the water. The reaction mixture was cooled to room temperature, and all the volatiles were removed under reduced pressure to give a yellow solid. The solid was treated with diethyl ether (100 mL), water (100 mL), and sodium carbonate (10.60 g, 100 mM), and the obtained mixture was kept stirring. After complete dissolution, the aqueous phase was separated and extracted with diethyl ether. The combined organic phase was dried over $MgSO_4$ and rotary evaporated to dryness under reduced pressure to afford a brownish yellow solid. Yellow crystals (12.95 g, 77%) were obtained after recrystallization from methanol. ^{1}H NMR (500 MHz, C_6D_6) δ (ppm): 13.14 (s, 1H, NH), 7.16–7.14 (m, 2H, ArH), 7.10–7.09 (m, 2H, ArH), 6.97–6.94 (m, 2H, ArH), 6.88–6.85 (m, 2H, ArH), 4.84 (s, 1H, CH=C(CH_3)N), 3.18 (sept, J = 6.8 Hz, 2H, CH(CH_3)$_2$), 1.82 (s, 3H, CH_3CNHAr), 1.63 (s, 3H, CH_3C=NAr), 1.19 (d, J = 7.0 Hz, 6H, CH(CH_3)$_2$), 1.14 (d, J = 7.0 Hz, 6H, CH(CH_3)$_2$). ^{13}C NMR (100 MHz, C_6D_6) δ (ppm): 163.1 (NCCH_3), 157.3 (NCCH_3), 144.9 (Ar–C), 142.8 (Ar–C), 141.1 (Ar–C), 129.2 (Ar–C), 125.2 (Ar–C), 123.4 (Ar–C), 123.3 (Ar–C), 122.7 (Ar–C), 96.6 (CH), 28.7 (CH(CH_3)$_2$), 24.3 (CH(CH_3)$_2$), 22.7 (CH(CH_3)$_2$), 21.0 (CH_3CNHAr), 20.6 (CH_3C=NAr). M.p.: 93.0 °C. Mass data (TOF MS EI$^+$): Calcd for $C_{23}H_{30}N_2$ [M^+] 334.50, found: 334.49. Anal. Calcd for $C_{23}H_{30}N_2$: C, 82.59; H, 9.04; N, 8.37. Found: C, 82.55; H, 9.01; N, 8.41. IR (KBr, cm^{-1}) ν: 3357 (m), 3055 (w), 2960 (w), 2920 (w), 2875 (w), 1925 (w), 1873 (w), 1800 (w),1740 (w), 1630 (s), 1547 (s), 1489 (w), 1360 (m), 1275 (m), 1260 (m), 1155 (s), 1100 (w), 1030 (w), 800 (s), 798 (s), 750 (s), 699 (m), 595 (w), 501 (w), 425(m).

2.2.3. 2-(2,6-Diisopropylphenyl)amino-4-(4-methylphenyl)imino-2-pentene (4b). 4-Methylaniline (5.35 g, 50.00 mM) and *para*-toluenesulfonic acid monohydrate (9.510 g, 50.00 mM) in 100 mL of toluene were stirred for approximately 3 h at room temperature. To the obtained yellow suspension, 4-(2,6-diisopropylphenyl)amino-3-penten-2-one (**3**) (12.97 g, 50.00 mM) was added and allowed to reflux for 24 h under azeotropic removal of water in a Dean–Stark apparatus. The reaction mixture was cooled to room temperature, and all the volatiles were removed under reduced pressure to give a yellow solid. The solid was treated with diethyl ether (100 mL), water (100 mL), and sodium carbonate (10.60 g, 100 mM), and the obtained mixture was kept stirring. After complete dissolution, the aqueous phase was separated and extracted with diethyl ether. The combined organic phase was dried over $MgSO_4$ and rotary evaporated to dryness under reduced pressure to afford a dark yellow solid. Yellow crystals (14.02 g, 80%) were obtained after recrystallization from methanol. ^{1}H NMR (500 MHz, C_6D_6) δ (ppm): 13.11 (s, 1H, NH), 7.13–7.11 (m, 3H, ArH), 6.89–6.85 (m, 4H, ArH), 4.83 (s, 1H, CH=C(CH_3)N), 3.16 (sept, J = 6.8 Hz, 2H, CH(CH_3)$_2$), 2.05 (s, 3H, CH_3), 1.83 (s, 3H, CH_3CNHAr), 1.63 (s, 3H, CH_3C=NAr), 1.17 (d, 6H, J = 7.0 Hz, CH(CH_3)$_2$), 1.13 (d, J = 7.0 Hz, 6H, CH(CH_3)$_2$). ^{13}C NMR (100 MHz, C_6D_6) δ (ppm): 163.8 (NCCH_3), 156.6 (NCCH_3), 143.7 (Ar–C), 141.6 (Ar–C), 140.5 (Ar–C), 132.8 (Ar–C), 129.8 (Ar–C), 124.8 (Ar–C), 123.4 (Ar–C), 123.1 (Ar–C), 96.4 (CH), 28.7 (CH(CH_3)$_2$), 24.3 (CH(CH_3)$_2$), 22.7 (CH(CH_3)$_2$), 21.1 (CH_3Ar), 20.7 (CH_3CNHAr), 20.5 (CH_3C=NAr). M.p.: 94.0 °C. Mass data (TOF MS EI$^+$): Calcd for $C_{24}H_{32}N_2$ [M^+] 348.52, found: 348.47. Anal. Calcd for $C_{24}H_{32}N_2$: C, 82.71; H, 9.25; N, 8.04. Found: C, 82.69; H, 9.17; N, 8.03. IR (KBr, cm^{-1}) ν: 3357 (m), 3049 (w), 3072 (w), 3015 (w), 2960 (m), 1635 (w), 1598 (s), 1542 (m), 1468 (m), 1439 (m), 1388 (w), 1255 (m), 1236 (s), 1180 (w), 1120 (m), 1105 (m), 1037 (m), 760 (m), 741(m), 664 (w), 615 (w), 602 (w), 557 (w).

2.2.4. 2-(2,6-Diisopropylphenyl)amino-4-(4-methoxyphenyl)imino-2-pentene (4c). To a stirred solution of 4-methoxyaniline (6.150 g, 50.00 mM) in 100 mL of toluene was added *para*-toluenesulfonic acid monohydrate (9.510 g, 50.00 mM), and the mixture was stirred for 3 h at room temperature, then 4-(2,6-diisopropylphenyl)amino-3-penten-2-one (**3**) (12.97 g, 50.00 mM) was added. 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 mM) and kept stirring. After complete dissolution, the aqueous phase was separated and extracted with diethyl ether. The combined organic phases were dried over $MgSO_4$ and rotary evaporated to dryness under reduced pressure to afford a yellow solid. Yellow crystals of **4c** (15.25 g, 84%) were obtained after recrystallization from methanol. ^{1}H NMR (500 MHz, C_6D_6) δ (ppm): 13.04 (s, 1H, NH), 7.14–7.11 (m, 3H, ArH), 6.87–6.84 (m, 2H, ArH), 6.65–6.63 (m, 2H, ArH), 4.84 (s, 1H, CH=C(CH_3)N), 3.26 (s, 3H, OCH_3), 3.17 (sept, J = 6.8 Hz, 2H, CH(CH_3)$_2$), 1.81 (s, 3H, CH_3CNHAr), 1.65 (s, 3H, CH_3C=NAr), 1.19 (d, J = 7.0 Hz, 6H, CH(CH_3)$_2$), 1.14 (d, J = 7.0 Hz, 6H, CH(CH_3)$_2$). ^{13}C NMR (100 MHz, C_6D_6) δ (ppm): 164.1 (NCCH_3), 156.8 (NCCH_3), 156.6 (Ar–C), 144.2 (Ar–C), 140.2 (Ar–C), 136.6 (Ar–C), 125.0 (Ar–C), 124.6 (Ar–C), 123.4 (Ar–C), 114.5 (Ar–C), 95.9 (CH), 54.9 (OCH_3Ar), 28.7 (CH(CH_3)$_2$), 24.2 (CH(CH_3)$_2$), 22.8 (CH(CH_3)$_2$), 21.2 (CH_3CNHAr), 20.3 (CH_3C=NAr). M.p.: 110.0 °C. Mass data (TOF MS EI$^+$): Calcd for $C_{24}H_{32}N_2O$ [M^+] 364.52, found: 364.36. Anal. Calcd for $C_{24}H_{32}N_2O$: C, 79.08; H, 8.85; N, 7.68. Found: C, 79.10; H, 8.72; N, 7.57. IR (KBr, cm^{-1}) ν: 3337 (m), 3054 (m), 2971 (m), 2925 (w), 2878 (m), 2832 (w), 1631 (m), 1548 (m), 1520 (s), 1472 (s), 1400 (s), 1320 (m), 1289 (m), 1260 (w), 1251 (m), 1233 (w), 1169 (m), 1115 (m), 930 (w), 795 (m), 759 (m), 753 (w), 740 (m), 679 (w), 641 (w), 597 (m), 578 (w), 415 (m).

2.2.5. 2-(2,6-Diisopropylphenyl)amino-4-(4-chlorophenyl)imino-2-pentene (4d). To a stirred solution of 4-chloroaniline (6.380 g, 50.00 mM) in 100 mL of toluene was added *para*-toluenesulfonic acid monohydrate (9.510 g, 50.00 mM), and the mixture was stirred for 3 h at room temperature, and then 4-(2,6-diisopropylphenyl)amino-3-penten-2-one (**3**) (12.97 g, 50.00 mM) was added. 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 mM) and kept stirring. After complete dissolution, the aqueous phase was separated and extracted with diethyl ether. The combined organic phases were dried over $MgSO_4$ and rotary evaporated to dryness under reduced pressure to afford a dark yellow solid. Yellow crystals of **4d** (15.10 g, 82%) were obtained after recrystallization from methanol. ^{1}H NMR (500 MHz, C_6D_6) δ (ppm): 12.87 (s, 1H, NH), 7.14–7.08 (m, 3H, ArH), 7.00–6.98 (m, 2H, ArH), 6.63–6.60 (m, 2H, ArH), 4.79 (s, 1H, CH=C(CH_3)N), 3.12 (sept, J = 6.8 Hz, 2H, CH(CH_3)$_2$), 1.69 (s, 3H, CH_3CNHAr), 1.56 (s, 3H, CH_3C=NAr), 1.15 (d, J = 7.0 Hz, 6H, CH(CH_3)$_2$), 1.09 (d, J = 7.0 Hz, 6H, CH(CH_3)$_2$). ^{13}C NMR (100 MHz, C_6D_6) δ (ppm): 161.8 (NCCH_3), 159.2 (NCCH_3), 144.9 (Ar–C), 142.2 (Ar–C), 141.0 (Ar–C), 129.2 (Ar–C), 128.3 (Ar–C), 125.9 (Ar–C), 123.6 (Ar–C), 123.5 (Ar–C), 96.6 (CH), 28.7 (CH(CH_3)$_2$), 24.4 (CH(CH_3)$_2$), 22.7 (CH(CH_3)$_2$), 20.7 (CH_3CNHAr), 20.6 (CH_3C=NAr). M.p.: 116.0 °C. Mass data (TOF MS EI$^+$): Calcd for $C_{23}H_{29}ClN_2$ [M^+] 368.94, found: 368.92. Anal. Calcd for $C_{23}H_{29}ClN_2$: C, 74.88; H,

7.92; Cl, 9.61; N, 7.59. Found: C, 74.89; H, 7.90; Cl, 9.58; N, 7.55. IR (KBr, cm^{-1}) ν: 3351 (m), 3062 (s), 2960 (m), 1670 (s), 1558 (m), 1530 (w), 1495 (m), 1450 (m), 1417 (s), 1325 (m), 1271 (w), 1239 (m), 1215 (w), 1182 (m), 1120 (m), 1051 (m), 1030 (m), 930 (w), 864 (m), 837 (w), 800 (w), 745 (m), 677 (w), 635 (w).

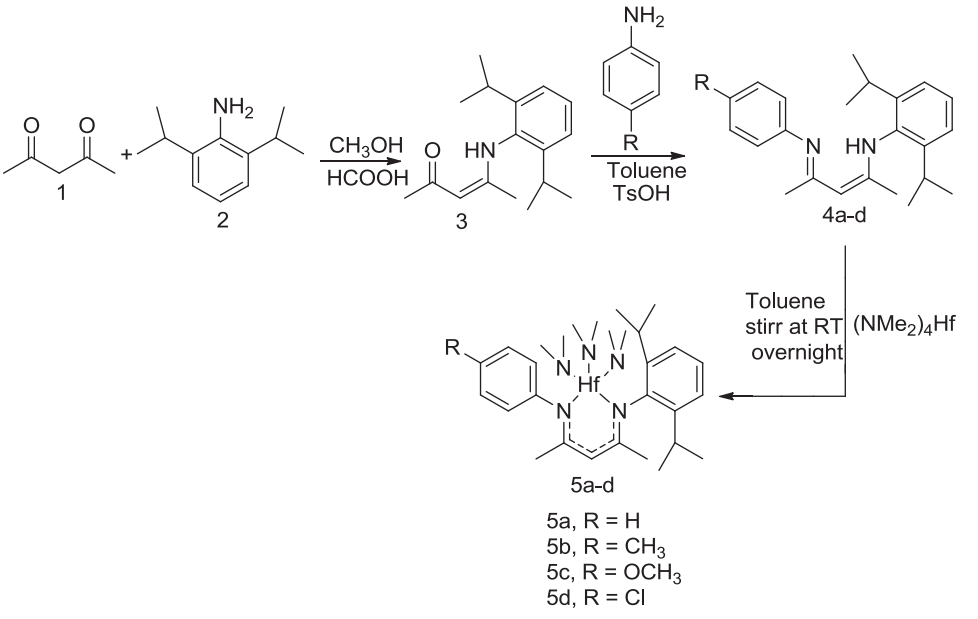
2.2.6. [2-(2,6-Diisopropylphenyl)amino-4-(phenyl)imino-2-pentene]tris(dimethyl-amino)-hafnium(IV) (5a). 2-(2,6-Diisopropylphenyl)amino-4-(phenyl)imino-2-pentene (**4a**) (3.30 g, 10.0 mM) in 40 mL of dry toluene was added via cannula to 40 mL of dry toluene solution of $Hf[N(CH_3)_2]_4$ (3.54 g, 10.0 mM) under a nitrogen atmosphere at room temperature. The reaction mixture turned bright red immediately. The reaction mixture was then heated to reflux overnight. The brownish yellow solution was filtered, and the filtrate was concentrated in vacuum and layered with dried *n*-hexane to give **5a** as a brown-yellow solid (3.0 g, 47%). ^{1}H NMR (500 MHz, C_6D_6) δ (ppm): 7.19–7.14 (m, 4H, ArH), 7.07–7.04 (m, 1H, ArH), 6.95–6.92 (m, 1H, ArH), 6.84–6.82 (m, 2H, ArH), 5.11 (s, 1H, CH=C(CH_3)N), 3.13 (sept, J = 6.8 Hz, 2H, CH(CH_3)$_2$), 2.81 (s, 18H, N(CH_3)$_2$), 1.73 (s, 3H, CH_3CNHAr), 1.60 (s, 3H, CH_3C=NAr), 1.38 (d, J = 7.0 Hz, 6H, CH(CH_3)$_2$), 1.16 (d, J = 7.0 Hz, 6H, CH(CH_3)$_2$). ^{13}C NMR (100 MHz, C_6D_6) δ (ppm): 166.48(NCCH_3), 165.93 (NCCH_3), 150.88 (Ar–C), 147.02 (Ar–C), 141.78 (Ar–C), 129.52 (Ar–C), 125.56 (Ar–C), 125.24 (Ar–C), 124.04 (Ar–C), 124.00 (Ar–C), 101.43 (CH), 43.37 (N(CH_3)$_2$), 29.05 (CH(CH_3)$_2$), 25.81 (CH(CH_3)$_2$), 24.93 (CH(CH_3)$_2$), 24.62 (CH_3CNHAr), 24.39 (CH_3C=NAr). Mass data (TOF MS EI$^+$): m/z = 629.15 [M^+–CH_3]. Micro analysis calculated for $C_{29}H_{47}N_5Hf$ (644.20): Calcd: C, 54.07%; H, 7.35%; N, 10.87%; Hf, 27.71%. Found: C, 54.01%; H, 7.39%; N, 10.85%; Hf, 27.69%. IR (KBr, cm^{-1}) ν: 2963 (w), 2917 (w), 2901(w), 2869 (w), 1919 (w), 1871 (w), 1801 (w), 1745 (w), 1487 (w), 1359 (m), 1263 (m), 1257 (m), 1153 (s), 1103 (w), 1031 (w), 807 (s), 795 (s), 755 (s), 700 (m), 596 (w), 500 (w), 421(m).

2.2.7. [2-(2,6-Diisopropylphenyl)amino-4-(4-methylphenyl)imino-2-pentene]tris (dimethyl-amino)hafnium(IV) (5b). 2-(2,6-Diisopropylphenyl)amino-4-(4-methylphenyl) imino-2-pentene (3.48 g, 10.0 mM) and $Hf[N(CH_3)_2]_4$ (3.54 g, 10.0 mM) were dissolved in dry toluene (80 mL) under a nitrogen atmosphere at room temperature. The reaction mixture turned bright yellow immediately. The reaction mixture was then heated to reflux overnight. The yellow solution was filtered, and the filtrate was concentrated in vacuum and layered with dried *n*-hexane to give **5b** as a light-yellow solid (3.15 g, 49%). ^{1}H NMR (500 MHz, C_6D_6) δ (ppm): 7.16–7.14 (m, 1H, ArH), 7.07–7.04 (m, 1H, ArH), 6.99–6.98 (m, 2H, ArH), 6.89–6.88 (m, 1H, ArH), 6.75–6.74 (m, 2H, ArH), 5.12 (s, 1H, CH=C(CH_3)N), 3.15 (sept, J = 6.8 Hz, 2H, CH(CH_3)$_2$), 2.82 (s, 18H, N(CH_3)$_2$), 2.14 (s, 3H, CH_3), 1.76 (s, 3H, CH_3CNHAr), 1.61 (s, 3H, CH_3C=NAr), 1.39 (d, 6H, J = 7.0 Hz, CH(CH_3)$_2$), 1.17 (d, J = 7.0 Hz, 6H, CH(CH_3)$_2$). ^{13}C NMR (100 MHz, C_6D_6) δ (ppm): 166.25 (NCCH_3), 166.26 (NCCH_3), 148.28 (Ar–C), 147.11 (Ar–C), 141.83 (Ar–C), 132.81 (Ar–C), 129.80 (Ar–C), 125.06 (Ar–C), 124.04 (Ar–C), 123.43 (Ar–C), 101.36 (CH), 43.72 (N(CH_3)$_2$), 29.04 (CH(CH_3)$_2$), 24.96 (CH(CH_3)$_2$), 24.43 (CH(CH_3)$_2$), 21.98 (CH_3Ar), 20.81 (CH_3CNHAr), 20.62 (CH_3C=NAr). Mass data (TOF MS EI$^+$): m/z = 643.21 [M^+–CH_3]. Micro analysis calculated for $C_{30}H_{49}N_5Hf$ (658.23): Calcd: C, 54.74%; H, 7.50%; N, 10.64%; Hf, 27.12%. Found: C, 54.71%; H, 7.48%; N, 10.67%; Hf, 27.10%. IR (KBr, cm^{-1}) ν: 2961 (m), 2815(w), 1630 (w), 1541 (m), 1470 (m), 1440 (m), 1389 (w), 1251 (m),

1235 (s), 1181 (w), 1119 (m), 1100 (m), 1039 (m), 761 (m), 740(m), 667 (w), 610 (w), 601 (w), 555 (w).

2.2.8. [2-(2,6-Diisopropylphenyl)amino-4-(4-methoxyphenyl)imino-2-pentene]tris (dimethyl-amino)hafnium(IV) (5c). 2-(2,6-Diisopropylphenyl)amino-4-(4-methoxyphenyl) imino-2-pentene (3.64 g, 10.0 mM) in 40 mL of toluene was added dropwise to a stirred solution of $Hf[N(CH_3)_2]_4$ (3.54 g, 10.0 mM) in 40 mL of toluene under a nitrogen atmosphere at room temperature. Upon completion of the addition, a yellow solid precipitated. The solid was allowed to settle, and the supernatant was decanted via cannula. The yellow solid was pure as judged by ^{1}H NMR but could be recrystallized from pentane if necessary. The filtrate was reduced in volume and placed in a −80 °C freezer to yield another crop of yellow solid (4.50 g, 67%). ^{1}H NMR (500 MHz, C_6D_6) δ (ppm): 7.16–7.13 (m, 2H, ArH), 7.02–7.04 (m, 1H, ArH), 6.81–6.80 (m, 2H, ArH), 6.77–6.75 (m, 2H, ArH), 5.12 (s, 1H, $CH{=}C(CH_3)N$), 3.32 (s, 3H, OCH_3), 3.15 (sept, J = 6.8 Hz, 2H, $CH(CH_3)_2$), 2.83 (s, 18H, $N(CH_3)_2$), 1.75 (s, 3H, CH_3CNHAr), 1.61 (s, 3H, $CH_3C{=}NAr$), 1.39 (d, J = 7.0 Hz, 6H, $CH(CH_3)_2$), 1.17 (d, J = 7.0 Hz, 6H, $CH(CH_3)_2$). ^{13}C NMR (100 MHz, C_6D_6) δ (ppm): 166.55 ($NCCH_3$), 166.18 ($NCCH_3$), 164.42 (Ar–C), 147.13 (Ar–C), 143.97 (Ar–C), 141.83 (Ar–C), 126.02 (Ar–C), 125.52 (Ar–C), 124.04 (Ar–C), 113.38 (Ar–C), 101.28 (CH), 54.86 (OCH_3Ar), 43.45 ($N(CH_3)_2$), 29.05 ($CH(CH_3)_2$), 25.81 ($CH(CH_3)_2$), 24.93 ($CH(CH_3)_2$), 24.39 (CH_3CNHAr), 22.76 ($CH_3C{=}NAr$). Mass data (TOF MS EI$^+$): m/z = 659.21[M^+–CH_3]. Micro analysis calculated for $C_{30}H_{49}N_5HfO$ (674.23): Calcd: C, 53.44%; H, 7.33%; N, 10.39%; Hf, 26.47%. Found: C, 53.39%; H, 7.19%; N, 10.54%; Hf, 26.41%. IR (KBr, cm^{-1}) ν: 2925 (w), 2830 (w), 1510 (s), 1470 (s), 1401 (s), 1321 (m), 1290 (m), 1261 (w), 1249 (m), 1237 (w), 1173 (m), 1121 (m), 931 (w), 797 (m), 760 (m), 750 (w), 741 (m), 680 (w), 640 (w), 600 (m), 575 (w), 410 (m).

2.2.9. [2-(2,6-Diisopropylphenyl)amino-4-(4-chlorophenyl)imino-2-pentene]tris (dimethyl-amino)hafnium(IV) (5d). 2-(2,6-Diisopropylphenyl)amino-4-(4-chlorophenyl) imino-2-pentene (3.68 g, 10 mM) in 40 mL of toluene was added dropwise via cannula to a stirred solution of $Hf[N(CH_3)_2]_4$ (3.54 g, 10.0 mM) in 40 mL of toluene under a nitrogen atmosphere at room temperature. The reaction mixture was then heated to reflux overnight. The orange-yellow solution was filtered, and the filtrate was concentrated in vacuum and layered with dried *n*-hexane to give **5d** as a yellow solid (4.0 g, 59%). ^{1}H NMR (500 MHz, C_6D_6) δ (ppm): 7.19–7.14 (m, 3H, ArH), 7.07–7.04 (m, 1H, ArH), 6.95–6.92 (m, 1H, ArH), 6.84–6.82 (m, 2H, ArH), 5.13 (s, 1H, $CH{=}C(CH_3)N$), 3.13 (sept, J = 6.8 Hz, 2H, $CH(CH_3)_2$), 2.81 (s, 18H, $N(CH_3)_2$), 1.73 (s, 3H, CH_3CNHAr), 1.60 (s, 3H, $CH_3C{=}NAr$), 1.38 (d, J = 7.0 Hz, 6H, $CH(CH_3)_2$), 1.16 (d, J = 7.0 Hz, 6H, $CH(CH_3)_2$). ^{13}C NMR (100 MHz, C_6D_6) δ (ppm): 166.48 ($NCCH_3$), 165.93 ($NCCH_3$), 150.88 (Ar–C), 147.52 (Ar–C), 141.78 (Ar–C), 130.01 (Ar–C), 129.73 (Ar–C), 127.61 (Ar–C), 124.04 (Ar–C), 124.00 (Ar–C), 101.44 (CH), 43.37 ($N(CH_3)_2$), 29.05 ($CH(CH_3)_2$), 25.81 ($CH(CH_3)_2$), 24.93 ($CH(CH_3)_2$), 24.62 (CH_3CNHAr), 24.39 ($CH_3C{=}NAr$). Mass data (TOF MS EI$^+$): m/z = 663.61 [M^+–CH_3]. Micro analysis calculated for $C_{29}H_{46}N_5ClHf$ (678.65): Calcd: C, 51.32%; H, 6.83%; N, 10.32%; Cl, 5.22%; Hf, 26.30%. Found: C, 51.29%; H, 6.81%; N, 10.30%; Cl, 5.17%; Hf, 26.25%. IR (KBr, cm^{-1}) ν: 2901 (m), 2820 (w), 1530 (w), 1491 (m), 1449 (m), 1420 (s), 1315 (m), 1270 (w), 1235 (m), 1223 (w), 1181 (m), 1129 (m), 1057 (m), 1033 (m), 931 (w), 862 (m), 836 (w), 801 (w), 743 (m), 675 (w), 631 (w).



Scheme 1. Synthesis of β-diketiminate tris(dimethylamido)hafnium(IV) complexes.

3. Results and discussion

3.1. *Synthesis*

The synthetic pathway for unsymmetrical β-diketiminates described in this work is outlined in scheme 1. As depicted in scheme 1, the unsymmetrical β-diketimines **4a–d** were synthesized in two steps: (1) condensation of acetylacetone with one equiv. of primary aromatic amine 2,6-diisopropylaniline in methanol, with formic acid as catalyst, afforded the (Z)-4-(2,6-diisopropylphenylamino)pent-3-en-2-one intermediate **3** and (2) another equiv. of the other aromatic amine (aniline, 4-methylaniline, 4-methoxyaniline, and 4-chloroaniline) was pre-treated with para-toluenesulfonic acid in a 1:1 ratio for 3 h to afford para-toluenesulfonate, which was then reacted with the (Z)-4-(2,6-diisopropylphenylamino)pent-3-en-2-one intermediate **3** to give unsymmetrical β-diketimines (**4a–d**) in good yields. The reaction of tetrakis(dimethylamido)hafnium(IV) and β-diketiminates in toluene at 110 °C under a nitrogen atmosphere leads to formation of β-diketiminate tris(dimethylamido)hafnium(IV) complexes (**5a–d**) in moderate yields (scheme 1). The transformation proceeds by evolution of amine by-products as a result of the transamination reaction. Despite the efforts to crystallize β-diketiminate tris(dimethylamido)hafnium(IV) complexes (**5a–d**) using several methods, no suitable single crystals were obtained. All the compounds were fully characterized by ^{1}H, ^{13}C NMR, IR, mass spectroscopy, and elemental analysis. All the unsymmetrical β-diketiminate tris(dimethylamido)hafnium(IV) complexes have high degree of solubility in common organic solvents.

3.2. *^{1}H NMR and ^{13}C NMR spectra*

^{1}H and ^{13}C NMR spectra of the β-diketimines and their corresponding β-diketiminate tris(dimethylamido)hafnium(IV) complexes were recorded in C_6D_6 solution. The ^{1}H NMR spectra of all the unsymmetrical β-diketimines show a characteristic downfield shift in the range δ = 12.87–13.14 ppm for the NH proton and high field shift of δ = 4.79–4.84 ppm for the methyne proton attributable to the formation of unsymmetrical β-diketimines from (Z)-4-(2,6-diisopropylphenylamino)pent-3-en-2-one and amines [30, 31]. Two sharp singlets observed at 1.69–1.83 and 1.56–1.65 ppm are assigned to protons of the two methyl groups (CH_3C=NAr and CH_3CNHAr) of the unsymmetrical β-diketiminates. The resonance due to the four CH_3 protons ($CH(CH_3)_2$) was observed as two doublets at 1.15–1.19 and 1.09–1.14 ppm while that of CH appeared as a septet at 3.12–3.18 ppm. In the ^{1}H NMR spectra of unsymmetrical β-diketiminate tris(dimethylamido)hafnium(IV) complexes (**5a–d**), the chemical shifts around 12.87–13.14 ppm, which correspond to the NH moiety, completely disappear after reaction and the presence of new signals at 2.83–2.81 ppm suggest chelation of the ligand to the hafnium center. The other signals [methyne protons, methyl protons (CH_3C=NAr and CH_3CNHAr), CH_3 protons ($CH(CH_3)_2$), and CH protons] in β-diketiminate tris(dimethylamido)hafnium(IV) complexes (**5a–d**) did not show any significant shift.

The ^{13}C NMR is in good agreement with the proposed unsymmetrical β-diketiminates and their corresponding β-diketiminate tris(dimethylamido)hafnium(IV) complexes as well. The ^{13}C NMR spectra of unsymmetrical β-diketiminates showed peaks at 164.1–161.8 and 159.2–156.6 ppm, which are assigned to carbon of $NCCH_3$. The methyne carbon is at 95.9–96.6 ppm. Four peaks at 24.3–28.7, 20.3–20.6, 21–22.8, and 20.7–21.2 ppm are due to carbons of the six methyl groups (CH_3C=NAr, CH_3CNHAr, and $CH(CH_3)_2$), respectively. In the ^{13}C NMR spectra of unsymmetrical β-diketiminate tris(dimethylamido)hafnium(IV) complexes (**5a–d**), the appearance of peaks at 166.55–166.25 ($NCCH_3$) and 166.26–165.93 ($NCCH_3$) ppm in the downfield region and the presence of new signals in the region 43.72–43.37 ppm ($N(CH_3)_2$) further supports the chelation of the ligand to the hafnium center. However, the methyne carbon and carbons of the six methyl groups (CH_3C=NAr, CH_3CNHAr, and $CH(CH_3)_2$) did not shift.

3.3. *FT-IR spectra*

The FT-IR spectra for **4a–d** and **5a–d** are recorded in the solid state using the KBr disk technique from 400 to 4000 cm^{-1}. Great care was taken to ensure inert transfer between the glove box unit and the FT-IR instrument. In order to ascertain the mode of bonding of unsymmetrical β-diketiminates to the hafnium center, the IR spectra of the free ligands were compared with those of hafnium complexes. In the IR spectra of all the unsymmetrical β-diketimines (**4a–d**), the (C=N) bands are observed at 1645–1557 (ν) cm^{-1}; the position of these bands varies with the molecular structure, though no regularity can be pointed out. The sharp bands at 1400–1500 cm^{-1} are attributed to deformation of –CH_3. The bands at 3055–3072 (ν) cm^{-1} are typical of the NH group. Weak bands at 3000–2900 cm^{-1} arise from C–CH_3 asymmetric stretching vibrations. Weak to medium absorptions from 3100 to 3000 cm^{-1} correspond to the =C–H stretch of aromatic rings. In IR spectra of all the unsymmetrical β-diketiminate tris(dimethylamido)hafnium(IV) complexes (**5a–d**), the bands characteristic of NH and C=N are not observed, suggesting chelation of the ligand to the hafnium center through both nitrogens. Appearance of new bands at 2815–2901 of N–CH_3 further supports formation of the hafnium complexes. The weak bands at 3010–2925 cm^{-1}

arise from C–CH_3 asymmetric stretching vibrations. Weak to medium absorptions from 3108 to 3005 cm^{-1} correspond to =C–H stretch of the aromatic ring.

3.4. *Mass spectral and elemental analysis*

In the present investigation, the TOF MS EI^+ spectra of all the unsymmetrical β-diketiminates (**4a–d**) show the molecular ion peaks at *m/z* $[M^+] = 334.49$, 348.47, 364.36, and 368.92, respectively, supporting the total molecular weight of the β-diketiminates.

The TOF MS EI^+ spectra of the unsymmetrical β-diketiminate tris(dimethyl-amido)hafnium(IV) complexes (**5a–d**) show the molecular ion peaks at *m/z* $[M^+–CH_3] = 629.15$, 643.21, 659.21, and 663.61, respectively, supporting the monomeric nature of the complexes and also their purity.

The elemental analyses show 1 : 1 (metal : ligand) stoichiometry for all the unsymmetrical β-diketiminate tris(dimethylamido)hafnium(IV) complexes (**5a–d**).

4. Summary and conclusions

A series of new β-diketiminate tris(dimethylamido)hafnium(IV) complexes (**5a–d**) were synthesized in high yields and structurally characterized. Amide substitution reactions were shown to be convenient routes for the synthesis of β-diketiminate tris(dimethylamido)hafnium(IV) complexes. According to ^1H, ^{13}C NMR and IR spectral results, the unsymmetrical β-diketimines are bidentate coordinating through nitrogens to hafnium. β-Diketiminate tris (dimethylamido)hafnium(IV) complexes are monomeric. This work represents the first literature report of the synthesis and characterization of β-diketiminate tris(dimethylamido) hafnium(IV) complexes. These compounds are conveniently obtained by a simple and straightforward synthesis route, which is amenable to scale-up applications. Detailed MOCVD studies using these compounds are currently in progress.

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