Synthesis of Heteroleptic Strontium Complexes Containing Substituted Cyclopentadienyl and β-Diketonate Ligands

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The interest in the chemistry and development of strontium precursors for atomic layer deposition (ALD) or chemical vapor deposition (CVD) were driven by several applications such as, $SrTiO_3$ for dynamic random access memories (DRAM),[1] ferroelectrics such as $Ba_xSr_{1-x}TiO_3$ (BSTO),[2] $SrBi_2Ta_2O_9$, and $SrBi_2Nb_2O_9$ for memory devices,[3] high-Tc superconductors such as $Bi_2Sr_2CaCu_2O_{8+\delta}$,[4] electroluminescent films such as SrS:Ce,[5] and mixed-electronic ionic conductors such as $(La_xSr_{1-x})MnO_3$, $(La_xSr_{1-x})CoO_3$ for fuel cell cathodes.[6]

In the synthesis and application of ALD precursor, it is important that the compound should have a good volatile character, stability, and chemical reactivity to allow formation of the target films. In common, the requirements for precursor were achieved by introducing functionalities to the ligands of the homoleptic compounds. But due to the uniformity of the ligands, it is difficult for homoleptic metal precursor to adopt a selective dissociation of one of the ligands. In heteroleptic metal precursors, the difference in reactivity of the ligands leads to a selective dissociation of one of the ligands over the other. On a substrate surface this ability of heteroleptic metal precursors may give more precise self-limiting character which results in formation of high quality films.

The most common volatile precursors of strontium were synthesized using β-diketonates like 2,2,6,6-tetramethyl-3,5-heptanedione[7,8] and highly substituted cyclopentadienes.[9] The studies[10] show that the significant carbon contamination exists on the films in ALD process using strontium β-diketonate complexes, due to the stronger metal-ligand bond and weaker bonds within the ligands, as a result, the ligand bonds breaks before metal-ligand bond. In substituted cyclopentadienyl strontium complexes, the metal-ligand bond dissociation occurs much easier due to the comparatively weaker nature of the bond and stronger intraligand interactions. We expect the combination of β-diketonate ligands with substituted cyclopentadienyl ligands can bring stability, and significantly lower the ligand dissociation energy and the carbon contamination. We selected the substituted cyclopentadiene and 2,2,6,6-tetramethyl-3,5-heptanedione (tmhdH) as ligands for synthesizing heteroleptic strontium precursors. Herein, we report synthesis of strontium complexes containing tri-isopropylcyclopentadienyl and 2,2,6,6-tetramethyl-3,5-heptanedionate as well as 1,3-di-*t*-butylcyclopentadienyl and 2,2,6,6-tetramethyl-3,5-heptanedionate.

It has been well known that the stability of strontium complexes depends on the steric effects of the ligands and its ability to shield the central metal atom as well as metal-ligand bond strength. Among them, the ligand's steric factor is very important in precursor chemistry to prevent the complexes from forming the oligomers that ultimately lead to low volatility. So the use of substituted cyclopentadienyl ligands with sterically bulky 2,2,6,6-tetramethyl-3,5-heptanedionate (tmhd) should provide the much needed "encapsulation" to larger alkaline earth metal. To get the desired products the reactions were carried out by substitution of iodide ions from strontium iodide (SrI_2) one by one, first with substituted cyclopentadienyl potassium salt and then with sodium salt of 2,2,6,6-tetramethyl-3,5-heptanedione (Scheme 1). In the first step a THF solution of strontium iodide was treated with an equimolar solution of the respective cyclopentadienyl potassium salt in THF. This part of the reaction, to get mono cyclopentadienyl strontium complexes were studied in detail by several groups.[11-13] The resulted products are mono cyclopentadienyl strontium iodide, which exists as a dimer with coordination of a THF molecule on each strontium atom. In the second step the mono cyclopentadienyl strontium iodide was treated with sodium salt of 2,2,6,6-tetramethyl-3,5-heptanedione in THF. The product was extracted to toluene and dried from the solvents to get the pure products as Sr($^iPr_3$Cp)(tmhd) (**1**) and Sr($^tBu_2$Cp)(tmhd) (**2**). Both the compounds were characterized by NMR, IR spectroscopy, and elemental analysis as well as thermogravimetric analysis to study the decomposition character. ^1H NMR spectra of the complex **1** in C_6D_6 show [$^iPr_3$Cp]-ring hydrogen resonance peak at δ 6.20 which is shifted down field compared to the [Sr($^iPr_3$Cp)$_2$][14] (δ 5.70). The β-C*H* proton from the tmhd ligand appears at δ 5.90 which again shifts slightly down field compared to the [Sr(tmhd)$_2$THF$_4$][15] where the β-C*H* proton was at δ 5.88. The -C(C*H$_3$*)$_3$ protons also show a down field shift (δ 1.24) from the analogous peaks of [Sr(tmhd)$_2$THF$_4$] (δ 1.22). In the case of the complex **2** the proton NMR spectra show the [$^tBu_2$Cp] ring appears at δ 6.07, 6.32 and 6.35 undergoing a down field shift with respect to the [Sr($^tBu_3$Cp)$_2$][9] (δ 5.96), while the tmhd protons of **2** are resonating at δ 6.01 (β-C*H*)
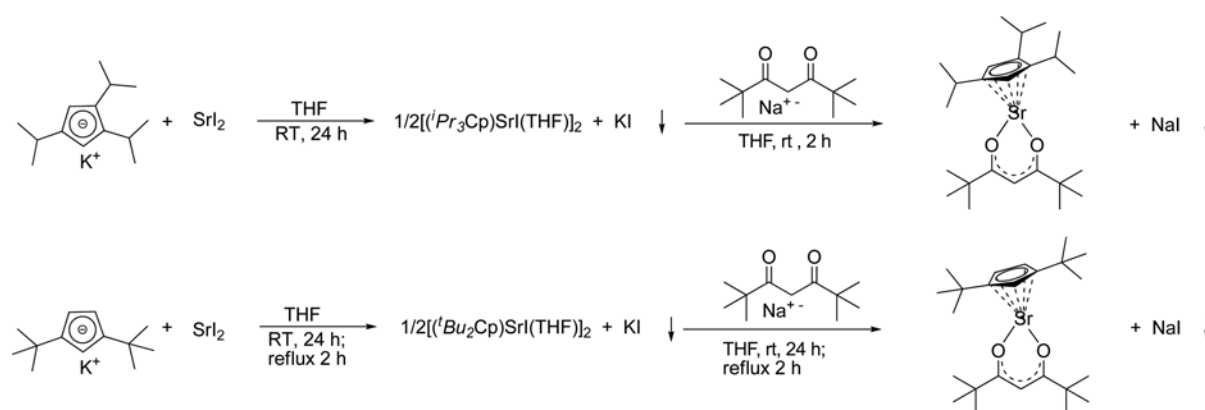
Scheme 1. Preparation of compound **1** and **2**.

and δ 1.25 (-C(CH_3)$_3$) with both exhibiting down field shift corresponding to the respective protons from the [Sr(tmhd)$_2$ (THF)$_4$] complex. The absence of any THF in the final products shows that the highly substituted cyclopentadienyl and tetramethylheptanedionate can stabilize the central strontium ion without additional coordination of solvent molecules.

FT-IR spectra of the complexes exhibit peaks at 473 cm^{-1} (**1**) and 475 cm^{-1} (**2**) which was assigned as Sr–O bond stretching vibrations[16] and confirmed the presence of tmhd in the compound. The strong peaks at 1589 cm^{-1} (**1**) and 1600 cm^{-1} (**2**) were C–C partial double bond as well as from the C–O partial double bond of tmhd ligand of the complexes. On comparison with the sodium salt of tmhd ligand, the C–C, C–O partial double peaks undergo a red shift indicating the strong bonding with the strontium metal. The medium intensity peaks at 1452 cm^{-1} (**1**) and 1454 cm^{-1} (**2**) were originated from the aromatic C–C double bonds of the cyclopentadienyl ligands, shifts to lower wave number corresponding to the peaks in K(^{i}Pr$_3$Cp) and K(^{t}Bu$_2$Cp) (1457 cm^{-1} and 1461 cm^{-1} respectively). The aromatic CH stretching vibrations of the cyclopentadienyl ligands in the complexes were noted as very weak peaks at 3060 cm^{-1} (**1**) and 3064 cm^{-1} (**2**) respectively. The FT-IR and NMR spectroscopic analyses support a strong bonding of the strontium ion with both the anionic ligands. Elemental analysis of the compounds **1** and **2** are carried out with extreme care and minimum exposure to air. Even with our best efforts, results show a low value for carbon, which reflects the high air-sensitivity of the compound, which is not uncommon in strontium complexes.[17]

Mass spectra of the complexes **1** and **2** display the dominant peaks at *m/z* 726, 271, 184, and 127 which correspond to Sr$_2$(thd)$_3^+$, Sr(thd)$^+$, (CH$_3$)$_3$CC$_3$H$_2$O$_2$C(CH$_3$)$_3^+$ and C$_3$H$_2$O$_2$C(CH$_3$)$_3^+$, respectively.[18] Complex **1** exhibits the peak at *m/z* 192 which corresponds to ^{i}Pr$_3$Cp$^+$ while complex **2** has a peak at *m/z* 355 which is assigned as (^{t}Bu$_2$Cp)$_2^+$.[19] It is well known that the electron ionization spectra of strontium complexes containing 2,2,6,6-tetra-methyl-3,5-heptanedionate (tmhd) show fragments of the type and M$_2$L$_3^+$, M$_3$L$_5^+$, M$_4$L$_7^+$, which are the results of ion-molecule reactions in the mass spectrometer source.[20,21] The

bond between the strontium and the respective substituted cyclopentadienyl moieties in complex **1** and **2** are weak with respect to the Sr–tmhd bond, which indeed leads to dissociation of cyclopentadienyl part even with little favorable condition and the formation of Sr$_x$(tmhd)$_y$ species. We assume that 1,3-di-*t*-butylcyclopentadienyl species formed during mass analysis might be susceptible for dimerization while tri-isopropylcyclopentadienyl species remained in the monomeric form due to its sterically hindered nature. These results show the presence of both tmhd and substituted cyclopentadienyl part in the complexes and so the formation of desired strontium complexes.

Thermogravimetric analyses of the complexes (Fig. 1) were done at a temperature range of room temperature to 900 °C and a constant flow of nitrogen was maintained during the measurement. Complex **1** shows a step by step loss of mass during the analysis which indicates the compound decomposition with loss of ligands in steps. Considering the very strong bonding character of β-diketones and relatively weaker bonding of cyclopentadienyl ligands with strontium, the first and major step in the graph 124-340 °C where a mass loss of ~31% occurs may come from the loss of tri-isopropyl cyclopentadienyl ligand. A second weight loss of 23% occurs in the range of 340-430 °C. Finally with two more mass losses in the 430-500 °C and 750-800 °C range, 27% of nonvolatile residue remained at the end. The high
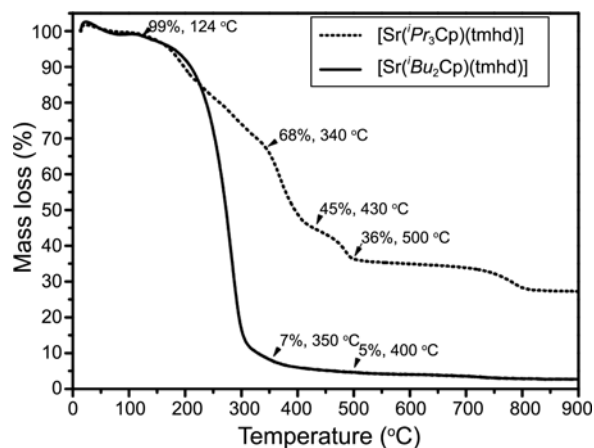

Figure 1. Thermogravimetric plot of complex **1** and **2**.

amount of residues indicates the self decomposition of the complex **1** during the TG analysis, which reflects the temperature instability of the complex. The TG analysis of the complex **2** resulted in single step decomposition with 7% residue at 350 ℃, which is slightly lower compared to the [Sr($^{t}Bu_3$Cp)$_2$][9] (10% residue at ~310 ℃) and [Sr(tmhd)$_2$-(THF)$_4$] (9.5% residue at ~380 ℃). This shows the complex's volatility and stability at these temperatures. Furthermore, the volatility of the complex **1** and **2** were studied under vacuum (0.05 Torr), starting from room temperature in which the complex **1** remains completely nonvolatile up to 180 ℃, on the other hand, the complex **2** exhibited volatility and sublimed at 140 ℃ with a moderate 40% yield without any component separation. This sublimation temperature of the complex **2** is much lower than those of [Sr(tmhd)$_2$] (230 ℃/0.05 Torr) and [Sr($^{t}Bu_3$Cp)$_2$] (120-180 ℃/0.04 Torr).

It has been known that strontium-tmhd bond is much stronger in nature compared to strontium-cyclopentadienyl bonds. In complexes **1** and **2**, the bonding between strontium and cyclopentadienyls might have been further weakened by steric friction between substituents on cyclopentadienyls and *t*-butyl groups on tmhd. We assume that complex **1** with tri-isopropylcyclopentadienyl group might be experiencing more steric friction than that of complex **2** where two *t*-butyl groups were present on cyclopentadienyl which eventually causing the destabilization of complex **1** and decomposition upon heating without sublimation.

A new class of the heteroleptic strontium complexes containing substituted cyclopentadienyl and tetramethyl heptanedionate (tmhd) were synthesized and characterized. The highly substituted ligand mixtures can stabilize the central strontium metal ion and eventually prevent from undergoing oligomerization. The thermogravimetric analyses show the temperature instability for the complex **1** and stepwise decomposition while heating. Complex **2** displays temperature stability and a steady loss of mass in the temperature region of 125-350 ℃ with 7% residue at the end. The cyclopentadineyl part of the complex tend be more reactive than that of tetramethylheptanedionate and we expect this factor can be effectively suitable during the application of these precursors for the selective decomposition for making thin films containing strontium oxide. The studies to explore these compounds as a possible strontium precursor for the growth of thin films of SrTiO$_3$ (STO), and Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ (BSTO) using ALD techniques are in progress.

Experimental

NMR spectra were recorded on Bruker 300 MHz spectrometer with THF-d_8 and C$_6$D$_6$ as solvent and standard. IR spectra were obtained from Nicolet Nexus FT-IR spectrophotometer. Elemental analyses were carried out on Thermo Scientific OEA Flash 2000 Analyzer. Thermogravimetric analyses were carried out on SETARAM 92-18 TG-DTA instrument.

Tri-isopropylcyclopentadiene and its potassium salt was prepared using the literature procedure.[22] The potassium salt

of 1,3-di-*t*-butylcyclopentadiene was prepared in an exactly similar fashion. The sodium salt of the 2,2,6,6-tetramethyl-3,5-heptanedione was prepared by modification of the literature procedure for Na(hfac).[23] All reactions were carried out in inert dry condition using standard Schlenk techniques or in argon filled glove box. Toluene and THF were purified by Innovative Technology PS-MD-4 solvent purification system. All other chemicals were purchased from Aldrich and used as received.

Synthesis of [Sr($^{i}Pr_3$Cp)I(THF)]$_2$. Strontium iodide (0.40 g, 1.20 mmol) was dissolved in 100 mL of THF and slowly added 2,3,5-tri-isopropylcyclopentadiene potassium salt (0.27 g, 1.20 mmol) in 50 mL of THF. The reaction mixture was stirred at room temperature for 24 h. Potassium iodide precipitate formed was filtered out and THF removed to get yellow powder. Yield is 0.34 g (59%). ^{1}H NMR (C$_6$D$_6$) δ 1.32 (d, br, 6H, CH(CH_3)$_2$), 1.34 (d, br, 12H, CH(CH_3)$_2$), 1.34 (m, br, 4H, THF), 2.95 (septet, br, 1H, CH(CH$_3$)$_2$), 3.00 (septet, br, 2H, CH(CH$_3$)$_2$), 3.54 (m, br, 4H, THF), 5.81 (s, 2H, Cp ring CH). FT-IR (KBr, cm^{-1}): 3060 (w), 2958 (vs), 2868 (m), 1463 (m), 1380 (m), 1361 (m), 1031 (m), 783 (m), 680 (w), 519 (w).

Synthesis of [Sr($^{t}Bu_2$Cp)I(THF)]$_2$. Strontium iodide (0.40 g, 1.20 mmol) was dissolved in 100 mL of THF and carefully added 1,3-di-*t*-butylcyclopentadiene potassium salt (0.26 g, 1.20 mmol) in 50 mL of THF. The reaction mixture was stirred at room temperature for 24 h, and then refluxed for 2 h. Potassium iodide precipitate formed was filtered out and the filtrate was dried to get yellow powder. Yield is 0.35 g (61%). ^{1}H NMR (THF-d_8) δ 1.06 (s, br, 18H, C(CH_3)$_3$), 1.68 (s, br, 4H, THF), 3.54 (s, br, 4H, THF), 5.72 (d, $J = 4.14$ Hz, 1H, Cp ring CH), 6.01 (d, $J = 4.68$ Hz, 1H, Cp ring CH), 6.20-6.30 (m, 1H, Cp ring CH). FT-IR (KBr, cm^{-1}): 3063 (w), 3961 (vs), 2901 (m), 2867 (m), 1475 (m), 1460 (m), 1391 (w), 1361 (m), 1257 (m), 1227 (m), 1199 (m), 1031 (m), 873 (m), 806 (w), 633 (w).

Synthesis of Sr($^{i}Pr_3$Cp)(tmhd) (1). To a 100 mL of THF solution of [Sr($^{i}Pr_3$Cp)I(THF)]$_2$ (0.34 g, 0.36 mmol), sodium salt of 2,2,6,6-tetramethyl-3,5-heptanedione (0.15 g, 0.72 mmol) in THF (10 mL) was added and stirred at room temperature for 24 h. The resultant was filtered and dried to get yellow solid. It is then re-dissolved in toluene and filtered and the filtrate was dried. Yield is 0.19 g (57%). Anal. Calcd for SrC$_{25}$H$_{42}$O$_2$: C, 64.96; H, 9.16. Found: C, 62.36; H, 9.00. ^{1}H NMR (C$_6$D$_6$) δ 1.06 (d, 6H, $J = 6.87$ Hz, CH(CH_3)$_2$), 1.10 (d, 6H, $J = 6.84$ Hz, CH(CH_3)$_2$), 1.12 (d, 6H, $J = 6.87$ Hz, CH(CH_3)$_2$), 1.24 (s, 18H, C(CH_3)$_3$), 2.57 (septet, $J = 6.84$ Hz, 1H, CH(CH$_3$)$_2$), 2.80 (septet, 2H, $J = 6.89$ Hz, CH(CH$_3$)$_2$), 5.90 (s, 1H, β-CH), 6.20 (s, 2H, Cp ring CH). (^{13}C, C$_6$D$_6$) δ 22.9 (2C, CH(CH$_3$)$_2$), 23.2 (2C, CH(CH$_3$)$_2$), 26.3 (2C, CH(CH$_3$)$_2$), 27.0 (1C, CH(CH$_3$)$_2$), 28.9 (1C, CH(CH$_3$)$_2$), 29.0 (6C, C(CH$_3$)$_3$), 30.2 (1C, CH(CH$_3$)$_2$), 41.6 (2C, C(CH$_3$)$_3$), 91.5 (2C, diketone α-C), 124.0 (2C, Cp ring), 141.6 (1C, Cp ring), 143.9 (1C, Cp ring), 152.3 (1C, Cp ring), 201.6 (1C, β-CH). FT-IR (KBr, cm^{-1}): 3060 (vw), 2958 (s), 2869 (m), 1589 (s), 1576 (s), 1535 (m), 1504 (s), 1452 (m), 1411 (vs), 1389 (s), 1358 (s),

1223 (w), 1184 (w), 1131 (w), 865 (w), 814 (w), 792 (w), 473 (w). EI-MS (*m/z*, relative intensity): 726 (60), 271 (30), 192 (40), 184 (10), 127 (100).

Synthesis of Sr($^{t}Bu_2$Cp)(tmhd) (2). To a 100 mL solution of [Sr($^{t}Bu_2$Cp)I(THF)]$_2$ (0.35 g, 0.37 mmol) in THF, sodium salt of 2,2,6,6-tetramethyl heptanedione (tmhd) (0.15 g, 0.74 mmol) in 10 mL of THF was added and stirred at room temperature for 24 h and then refluxed for 2 h. The resultant was then dried and re-dissolved in toluene and filtered. The filtrate was dried to get brown color solid. Yield is 0.16 g (48%). Anal. Calcd for SrC$_{24}$H$_{40}$O$_2$: C, 64.32; H, 9.00. Found: C, 59.20; H, 8.56. ^{1}H NMR (C$_6$D$_6$) δ 1.15 (s, 18H, Cp, C(CH_3)$_3$), 1.25 (s, 18H, C(CH_3)$_3$), 6.01 (s, 1H, β-CH), 6.07 (s, 1H, Cp ring CH), 6.32 (s, 1H, Cp ring CH), 6.35 (s, 1H, Cp ring CH). (^{13}C, C$_6$D$_6$) δ 29.0 (6C, C(CH$_3$)$_3$), 29.1 (3C, Cp, C(CH$_3$)$_3$), 31.0 (3C, Cp, C(CH$_3$)$_3$), 40.9 (2C, Cp, C(CH$_3$)$_3$), 41.4 (2C, C(CH$_3$)$_3$), 91.5 (2C, diketone α-C), 120.1 (1C, Cp ring), 126.0 (1C, Cp ring), 127.3 (1C, Cp ring), 200.4 (1C, β-CH). FT-IR (KBr, cm^{-1}): 3064 (vw), 2960 (s), 2869 (m), 1600 (s), 1580 (s), 1508 (s), 1454 (m), 1420 (vs), 1389 (s), 1359 (s), 1222 (w), 1130 (w), 866 (w), 793 (w), 475 (w). EI-MS (*m/z*, relative intensity): 726 (100), 355 (100), 271 (70), 184 (5), 127 (55).

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