

Synthesis of Mononuclear Strontium Complexes with Polyether and β -Diketonato Ligands

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Cite This: *ACS Omega* 2023, 8, 16119–16130

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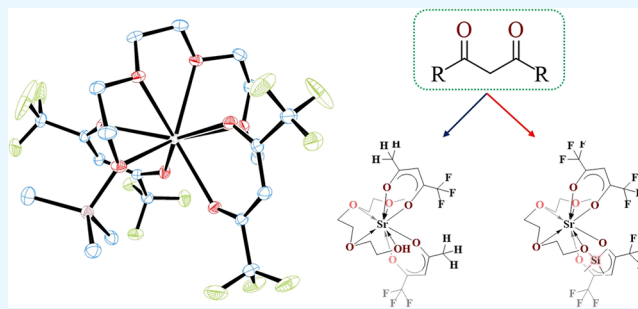
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ABSTRACT: Strontium β -diketonate complexes were synthesized by the substitution reaction of the bis(trimethylsilyl) amide of Sr(btsa)₂·2DME with an ethereal group and β -diketonate ligands. The compounds [Sr(tmge)(btsa)]₂ (1), [Sr(tod)(btsa)]₂ (2), Sr(tmgeH)(tfac)₂ (3), Sr(tmgeH)(acac)₂ (4), Sr(tmgeH)(tmhd)₂ (5), Sr(todH)(tfac)₂ (6), Sr(todH)(acac)₂ (7), Sr(todH)(tmhd)₂ (8), Sr(todH)(hfac)₂ (9), Sr(dmts)(hfac)₂ (10), [Sr(mee)(tmhd)₂]₂ (11), and Sr(dts)(hfac)₂·DME (12) were obtained and analyzed by various techniques, including FT-IR, NMR, TGA (thermogravimetric analyses), and elemental analysis. Complexes 1, 3, 8, 9, 10, 11, and 12 were further structurally confirmed by single-crystal X-ray crystallography, where complexes 1 and 11 showed dimeric structures with μ_2 -O bonds of ethereal groups or tmhd ligands, and complexes 3, 8, 9, 10, and 12 displayed monomeric structures. Interestingly, compounds 10 and 12, which preceded trimethylsilylation of the coordinating ethereal alcohols such as tmhgeH and meeH in the presence of HMDS as by-products due to highly increasing acidity of them, originated from electron-withdrawing two hfac ligands.



INTRODUCTION

Alkaline earth (group 2) metal compounds have numerous uses, including as magnetoresistive materials, ferroelectrics, precursors for thin-film growth, and materials for dynamic random-access memory (DRAM), organic synthesis, and electrically tunable microwave devices.^{1–15} Strontium complexes play a key role in the semiconductor industry because they are used to fabricate thin films containing metal oxides. Among the various ways to fabricate thin films, metal–organic chemical vapor deposition (MOCVD) is particularly attractive for depositing metal-containing materials because it offers the potential for large-area growth.^{16–19} To apply this technique, precursors require various physical properties, such as good volatility and appropriate thermal stability.

However, the development of new Sr complexes is often limited by poor volatility and thermal stability, owing to their high tendency to expand the high-coordination sphere and form oligomeric complexes with low solubility. To overcome these drawbacks, sterically bulky ligands or neutral ligands, such as tetraethylene glycol dimethyl etheral (tetraglyme), tetramethylethylenediamine (TMEDA), β -diketonates, β -diketimines, and cyclopentadienyl groups, have been used to synthesize Sr precursors with a saturated metal center.^{20–25} Among these, β -diketonates such as 2,2,6,6-tetramethylheptane-3,5-dione (tmhd) are used to synthesize Sr β -diketonate complexes because they are promising precursors of Sr-containing thin films.^{26–29} Sr β -diketonate compounds, such as [Sr₃(tmhd)₆(tmhdH)]·C₆H₅Me·C₅H₁₂, [Sr(tmhd)₂(MeOC₂H₄OH)]₂, [Sr(hfa)₂(CH₃O-

(CH₂CH₂O)₄CH₃), [Sr(tmhd)₂(1,10-phenanthroline)], and [Sr(tmhd)₂(triglyme)]³³ (triglyme = Me(OCH₂CH₂)₃OMe) have been reported to be moderately volatile Sr precursors for ALD or MOCVD process.^{30–32} In this study, we extended our previous work on the development of strontium complexes using β -diketonate ligands, such as tfac, acac, tmhd, and hfac, and ethereal groups, such as tmgeH, todH, and meeH ligands.

By combining these three ethereal ligands with different coordination numbers and various β -diketonate ligands with different substituents, we observed the tendency of the molecular structures to be affected by steric hindrance and reactivity of the ligand containing the trifluoromethyl group. The alkoxide ligands of the intermediates [Sr(tmge)(btsa)]₂ (1) and [Sr(tod)(btsa)]₂ (2) take up an acidic proton from the methylene of β -diketonate to afford new complexes 3–9 (Sr(β -diketonate)₂(ROH), ROH = tmgeH or todH). However, when hfacH was used as the β -diketonate, the hydroxyl hydrogen atom of ROH in complexes 1 and 2 was substituted by trimethylsilyl from HMDS, which was produced by the reaction of 1 or 2 with hfacH and existed as a by-product in solution. This resulted in the formation of new complexes 10 and 12, where

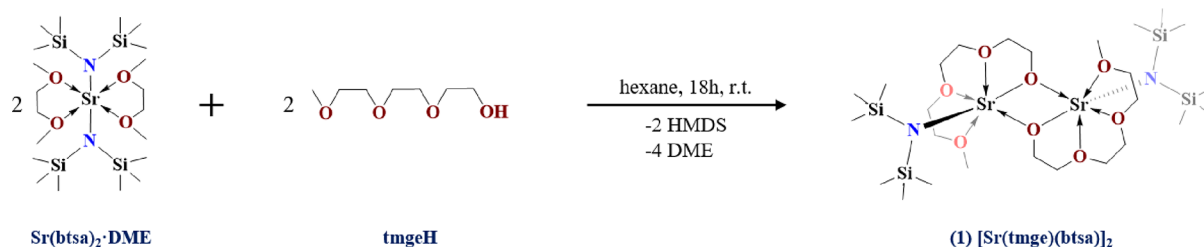
Received: January 12, 2023

Accepted: April 11, 2023

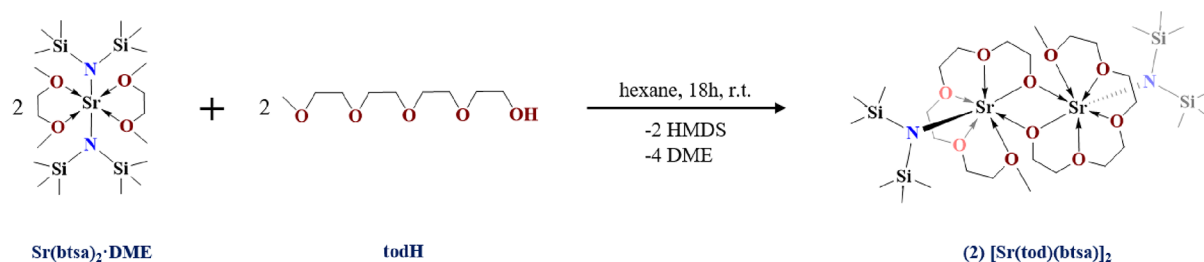
Published: April 28, 2023



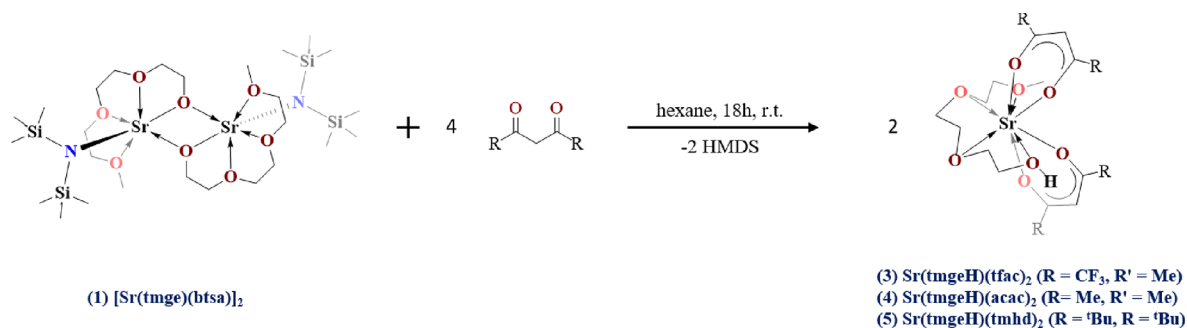
Scheme 1. Synthesis of Complex 1



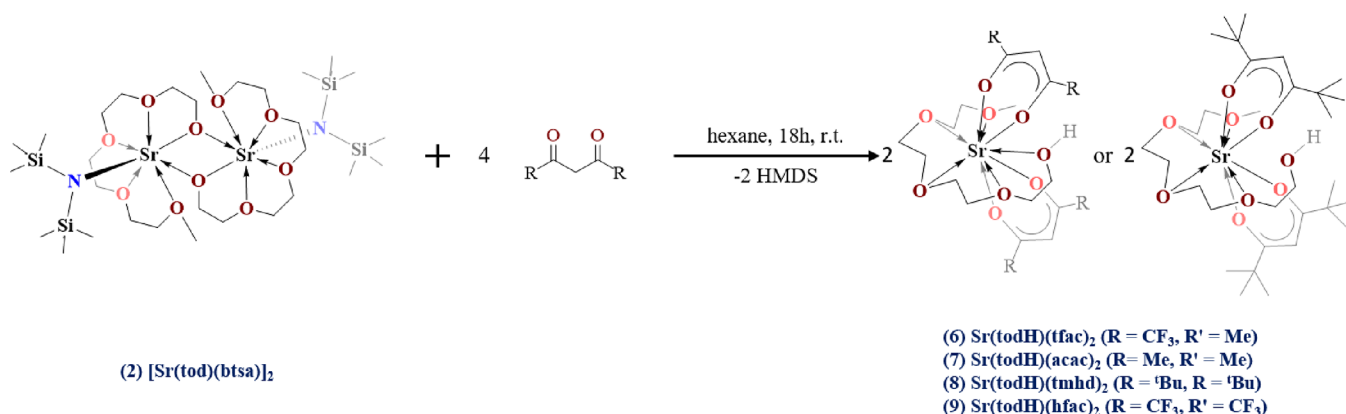
Scheme 2. Synthesis of Complex 2



Scheme 3. Synthesis of Complexes 3–5



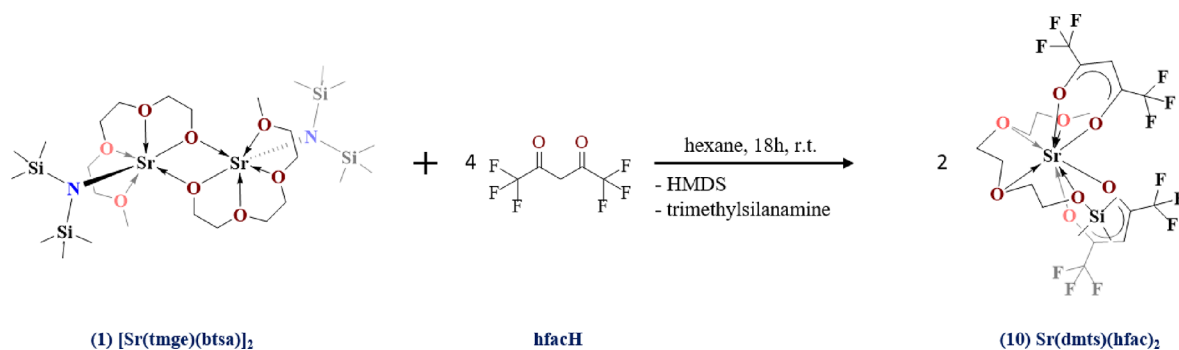
Scheme 4. Synthesis of Complexes 6–9



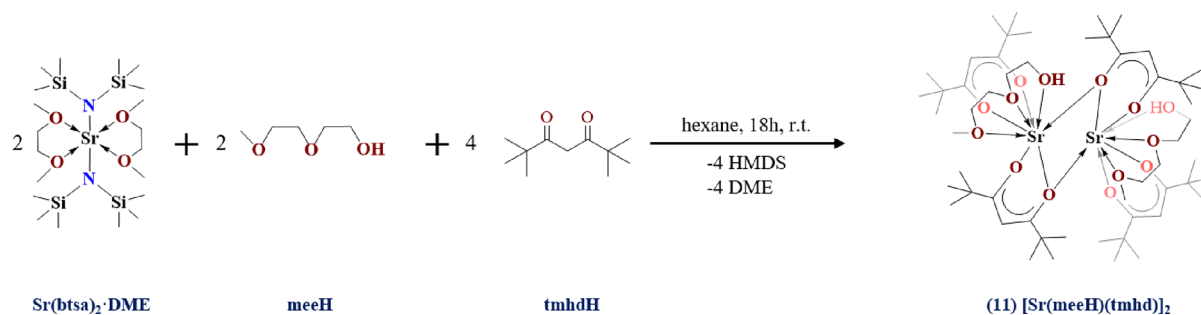
RO-TMS acts as a neutral ligand to coordinate with the Sr metal center ((Sr(hfac)₂(RO-TMS), RO-TMS = 2,2-dimethyl-3,6,9,12-tetraoxa-2-silatrtridecane in **10** or 2,2-dimethyl-3,6,9,12,15-pentaoxa-2-silahexadecane in **12**). The complexes [Sr(tmge)(btsa)]₂ (**1**), [Sr(tod)(btsa)]₂ (**2**), Sr(tmgeH)(tfac)₂ (**3**), Sr(tmgeH)(acac)₂ (**4**), Sr(tmgeH)(tmhd)₂ (**5**), Sr(todH)(tfac)₂ (**6**), Sr(todH)(acac)₂ (**7**), Sr(todH)(tmhd)₂ (**8**), Sr(todH)(hfac)₂ (**9**), Sr(dmts)(hfac)₂ (**10**), [Sr(mee)(tmhd)₂]₂ (**11**), and Sr(dts)(hfac)₂·DME (**12**) were synthesized via controlled substitution reactions using strontium(II)

bis(bis(trimethylsilyl amide)-2DME). In compound **3–9**, tmge and tod ligands were reduced to tmgeH or todH, respectively, by receiving a methine proton from the β-diketone. All complexes were characterized by Fourier transform infrared spectroscopy (FT-IR), elemental analysis (EA), thermogravimetric analysis (TGA), and nuclear magnetic resonance (NMR) spectroscopy. Complexes **1**, **3**, **7**, **9**, **10**, **11**, and **12** were also characterized by X-ray crystallography, where compounds **1** and **11** displayed dimeric structures and compounds **3**, **7**, **9**, **10**, and **12** showed monomeric structures.

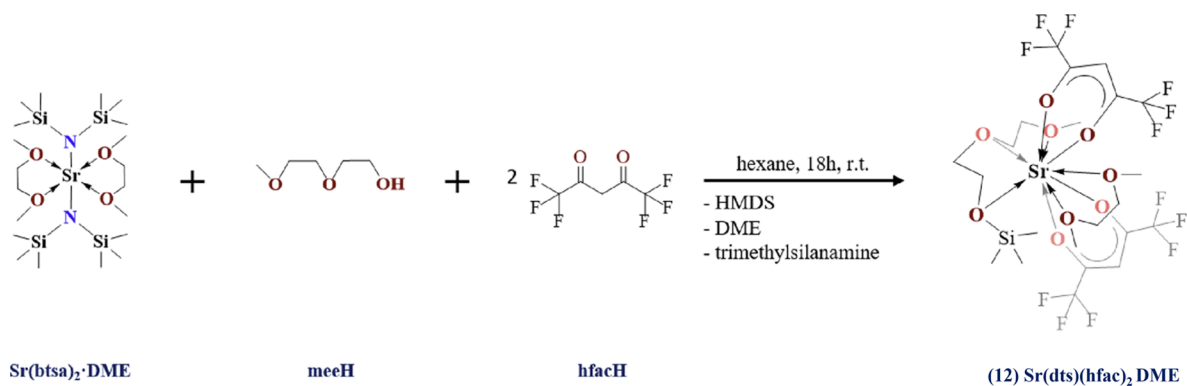
Scheme 5. Synthesis of Complex 10



Scheme 6. Synthesis of Complex 11



Scheme 7. Synthesis of Complex 12



RESULTS AND DISCUSSION

Various strontium complexes have been synthesized using three etheral ligands to investigate the properties of the strontium complexes according to the number of coordinating oxygen atoms on their properties. Interestingly, we observed various Sr compound tendencies that were affected by steric hindrance, electron density, and the coordination number of the central metal. In this study, new strontium complexes were synthesized by substitution reactions. (Schemes 1 and 2). In the first step, $\text{Sr}(\text{btsa})_2 \cdot 2\text{DME}$ was allowed to react in a hexane solution with an equivalent amount of tmgeH or todH at room temperature to obtain $[\text{Sr}(\text{tmge})(\text{btsa})]_2$ (1) and $[\text{Sr}(\text{tod})(\text{btsa})]_2$ (2), respectively. Two complexes were purified by recrystallization from saturated toluene solution at -30°C as white solids in moderate yields of 80–85%. In the case of the mee ligand with a relatively low number of coordinating oxygen atoms, the desired intermediate was not synthesized; therefore, compounds 11 and 12 were synthesized through an *in situ* reaction. In the second step, complexes 1 and 2 were reacted in hexane with various β -diketones, such as tfacH ,

acacH , tmhdH , and hfacH , at room temperature. The products $\text{Sr}(\text{tmgeH})(\text{tfac})_2$ (3), $\text{Sr}(\text{tmgeH})(\text{acac})_2$ (4), $\text{Sr}(\text{tmgeH})(\text{tmhd})_2$ (5), $\text{Sr}(\text{todH})(\text{tfac})_2$ (6), $\text{Sr}(\text{todH})(\text{acac})_2$ (7), $\text{Sr}(\text{todH})(\text{tmhd})_2$ (8), $\text{Sr}(\text{todH})(\text{hfac})_2$ (9), and $\text{Sr}(\text{dmts})(\text{hfac})_2$ (10) were obtained in a moderate yield of 80–90% as white powders (Schemes 3–5). Complexes $[\text{Sr}(\text{meeH})(\text{tmhd})_2]_2$ (11) and $\text{Sr}(\text{dts})(\text{hfac})_2 \cdot \text{DME}$ (12) were prepared using a procedure similar to a previously reported one.³³ The $\text{Sr}(\text{btsa})_2 \cdot 2\text{DME}$ solution in hexane was first treated with an equivalent ratio of meeH , followed by the addition of tmhdH or hfacH (as shown in Schemes 6 and 7), and the reaction mixture was stirred overnight at room temperature. X-Ray-quality crystals of the complexes were obtained from saturated toluene solutions of 1 and hexane solutions of 3, 8, 9, 10, 11, and 12 at -30°C . In single X-ray crystallography, complexes 1 and 11 showed dimeric structures, whereas complexes 3, 8, 9, 10, and 12 displayed monomeric structures, which will be discussed in detail later. Surprisingly, the hydroxyl hydrogen of tmgeH in complex 1 was substituted with a trimethylsilyl group to afford $\text{Sr}(\text{dmts})(\text{hfac})_2$ (10). In addition, $\text{Sr}(\text{dts})$ -

(hfac)₂ (**12**) was considered to be prepared by the same mechanism as **10**, although intermediate like (**1**) was not synthesized. The electron density of the strontium atom is changed by the highly electronegative fluorine atoms contained in hfac, which affects the acidity of H in tmgeH and meeH with three or four oxygen atoms, and silylation of alcohol from HMDS existing as a reaction by-product proceeded. However, when using a todH ligand with five oxygen atoms, silylation of alcohol was not observed, which could be attributed to the high steric hindrance and more abundant electron density than tmgeH and meeH. In addition, different trends were observed according to the number of fluorine atoms in β -diketone. Unlike when hfac with six fluorine atoms was used, silylation did not occur in the case of tfac with three fluorine atoms. To the best of our knowledge, this is the first example showing that the hydrogen atom of an alcohol is substituted with TMS according to the electron density of the central metal, which depends on the coordination number of the ligand and the number of fluorine atoms.

NMR. NMR spectra of the respective complexes were recorded using C₆D₆ both as the solvent and standard at room temperature. The –OH peak was absent in the spectra of **1** and **2**, whereas the spectra of **3–9** and **11** showed –OH peaks of tmgeH and todH, indicating that these ligands were reduced to tmgeH and todH by β -diketonate ligands (Figures S2–S12). The spectra of **10** and **12** displayed trimethyl silyl peaks at 0.01 and 0.08 ppm, respectively, as a result of trimethylsilylation of alcohol with HMDS from **1** and **2**. The ¹H NMR spectra of complexes **1** and **2** showed a single peak for the two btsa groups at δ = 0.44 and 0.45 ppm, respectively, which was a downfield shift from the btsa group of Sr(btsa)₂·2DME (0.39 ppm). The CH₃ protons of the tmge for complexes **1–12** appeared at δ_{H} = 3.37, 3.35, 3.19, 3.13, 3.20, 3.19, 3.34, 3.28, 3.18, 3.06, 3.10, and 3.06 ppm, respectively. The β -CH protons of the diketone ligands (tfac, acac, tmhd, and hfac) for compounds **3–12** appeared at δ_{H} = 5.75, 5.34, 5.86, 5.80, 5.36, 5.85, 6.28, 6.33, 5.81, and 6.28 ppm, respectively, as singlets. In the spectra of **3, 4, 5, 6, 7, 8, and 11**, the –CH₃, –2(CH₃), and –2(CH₃)₃ moieties of β -diketonate ligands appeared at δ = 1.86, 2.01, 1.35, 1.87, 2.01, 1.38, and 1.31 ppm. The ¹⁷F NMR signals of –CF₃ and –2(CF₃) at **3, 6, 10, and 12** were observed at –76.85, –76.65, –76.75, and –76.78 ppm, respectively (Figures S26–S30).

FT-IR Spectra. The FT-IR spectra of complexes **1, 2, 10, and 12** showed strong peaks at ν = 2937 cm^{–1} (**1**), 2934 cm^{–1} (**2**), 2943 cm^{–1} (**10**), and 2934 cm^{–1} (**12**) (Si–CH₃ stretching vibration) and middle peak ν = 1243 cm^{–1} (**1**), 1241 cm^{–1} (**2**), 1259 cm^{–1} (**10**), and 1255 cm^{–1} (**12**) (Si–CH₃ rocking vibration), respectively, showing the remaining btsa group in **1** and **2** and trimethylsilylation of alcohol in **10** and **12**.

In complexes **3–9** and **11**, the FT-IR spectra showed the presence of –OH stretching middle peaks at ν = 3272 cm^{–1} (**3**), 3336 cm^{–1} (**4**), 3321 cm^{–1} (**5**), 3280 cm^{–1} (**6**), 3214 cm^{–1} (**7**), 3335 cm^{–1} (**8**), 3509 cm^{–1} (**9**), and 3177 cm^{–1} (**11**), respectively, which means that tmge and tod were reduced to tmgeH and todH, respectively. In complexes **3–12**, the FT-IR spectra showed peaks for C=O stretching in coordinated β -diketonates at 1638 cm^{–1} (**3**), 1652 cm^{–1} (**4**), 1606 cm^{–1} (**5**), 1643 cm^{–1} (**6**), 1613 cm^{–1} (**7**), 1591 cm^{–1} (**8**), 1673 cm^{–1} (**9**), 1670 cm^{–1} (**10**), 1593 cm^{–1} (**11**), and 1673 cm^{–1} (**12**), respectively, indicating that the reaction proceeded successfully.

Crystal Structure. X-Ray-quality crystals of the complexes were obtained from saturated toluene solutions of **1** and saturated solutions of hexane **3, 8, 9, 10, 11, and 12** at –30 °C. Complexes **1, 3, 8, 9, 10, and 11** crystallized in a monoclinic space group, where the etheral group ligands formed a 5-membered ring composed of Sr–O–C–C–O. Complexes **12** crystallized in a triclinic space group (Tables S1 and S2). Complex **1** formed dimers with oxygen atoms of the etheral group, bridging the two metal centers by μ_2 -O bonding, which is similar to the previously reported results (Figure 1).^{9,34–36}

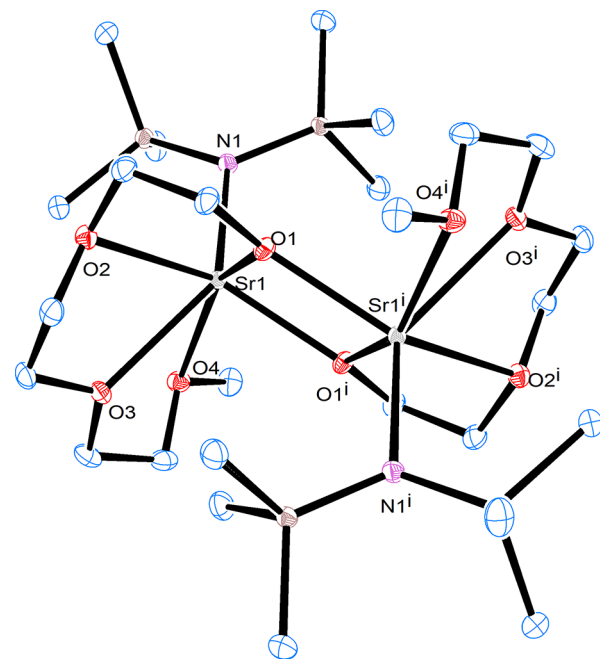


Figure 1. ORTEP drawing of the crystal structure of [Sr(tmge)(btsa)]₂ (**1**). The ellipsoids represent a probability 30%.

In complexes **1**, each of the strontium atoms was bonded to one etheral group ligand and one btsa ligand, where the strontium metal centers showed octahedral geometry in **1**, with the N atom of the btsa group remaining in the equatorial region. The distances between the two metal centers in the dimeric structures of **1** were 3.8054(4), which are comparable to those previously reported for [Sr(btsa)(L¹)₂] (3.8360(4) Å), [Sr(dadamb)(btsa)]₂ (3.8610(4) Å), and [Sr(demamp)(btsa)]₂ (3.8193(3) Å) (Table 1).^{9,34,36} In complexes **1** and **11**, which showed a dimeric structure, molecule barycenter is located on an inversion center. Complex **3** showed a monomeric structure, where the strontium ion bonded two tfac ligands and coordinated to one tmgeH, which obtained a proton from tfacH (Figure 2). In complex **3**, the strontium metal center displayed a distorted square antiprismatic geometry, where the strontium atom was satisfied by eight oxygen atoms from two tfac ligands and one tmgeH ligand.

This coordination is similar to that of Ca(thd)₂(triglyme) and Ba(thd)₂(triglyme) complexes, where the central metal atoms have eight coordination sites.²⁰ In complex **3**, the Sr–O (tfac oxygen) lengths were in the range of 2.477–2.545 Å (average 2.5132 Å), which are comparable to those of [Sr(thd)₂(triethylenetetramine)] (2.513 Å) and slightly shorter than those of [Sr(thd)₂(tetraethylenepentamine)] (2.546 Å) (Table 2). The average O–Sr–O chelate angle between the metal and tmgeH ligand is 62.9°, which is smaller than the N–

Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for 1

bond lengths (Å)	1	bond angles (°)	1
Sr1–O1 ⁱ	2.399(10)	O1 ⁱ –Sr1–O1	76.81(4)
Sr1–O1	2.456(11)	O1 ⁱ –Sr1–N1	115.66(4)
Sr1–N1	2.500(13)	O1–Sr1–N1	115.78(4)
Sr1–O3	2.608(11)	O1 ⁱ –Sr1–O3	101.18(4)
Sr1–O2	2.655(11)	O1–Sr1–O3	99.73(4)
Sr1–O4	2.665(11)	N1–Sr1–O3	132.97(4)
Sr1–O5		O1 ⁱ –Sr1–O2	134.70(4)
Sr...Sr ⁱ	3.805(4)	O1–Sr1–O2	66.73(3)
		N1–Sr1–O2	104.03(4)
		O3–Sr1–O2	61.61(3)
		O1 ⁱ –Sr1–O4	85.82(4)
		O1–Sr1–O4	151.25(3)
		N1–Sr1–O4	92.44(4)
		O3–Sr1–O4	61.08(3)
		O2–Sr1–O4	114.16(3)
		Sr1–O1–Sr1 ⁱ	103.19(4)

Sr–N chelate angles of [Sr(thd)₂(triethylenetetramine)] (63.1(4)–64.6 (3)°) and [Sr(thd)₂(tetraethylenepentamine)] (61.5(4)–64.0 (3)°).³⁷

Complexes **8** and **9** showed a monomeric structure, where strontium ions are bonded to two tmhd or hfac ligands and coordinated to one todH ligand, which was obtained from the proton of the tmhdH or hfacH ligand. The crystal structure of **9** showed a nonacoordinate metal center and tricapped trigonal prismatic geometry, whereas **8** showed a bicapped trigonal prismatic structure with an octa-coordination metal center and hydrogen bonding between the oxygen atom (O9) of todH and the oxygen atom (O2) of tmhd (bond length = 2.807 Å). In complex **8**, the Sr–O (todH oxygen) lengths are in the range of 2.697–2.803 Å, which is slightly shorter than the Sr–O (todH oxygen) lengths in **9** (2.601–2.788 Å) (Figures 3 and 4, Table 2). This might be attributed to the higher steric

hindrance in **9** because of using the sterically bulky tmhd ligands. The average O–Sr–O chelate angles between the metal and todH ligands were 61.41° in **8** and 61.32° in **9**, which were smaller than that of complex **3**.

Complexes **10** and **12** displayed monomeric structures with strontium atoms bonded to two hfac and one silyl etheral group ligand, where the hydroxyl groups of tmgeH or todH ligands were substituted with trimethyl silyl groups from bis(trimethylsilyl)amine (Figures 5 and 7). In complex **10**, the molecular geometry, structure, and coordination pattern were similar to those of complex **3** as a distorted square antiprismatic geometry and eight-coordinate statements. The Sr–O (hfac oxygen) distances are in the range of 2.516–2.552 Å (average 2.535 Å), which are longer than those of complex **3** (Table 2). These bond length differences might be attributed to the higher steric hindrance than **3** due to the silyl group of the dmts ligand. The O–Sr–O chelate angle between the metal and tmge ligand is 62.15°, which is similar to the O–Sr–O chelate angle of **1**. The crystal structure of **12** displayed tricapped noncoordination trigonal prismatic geometry, where one DME ligand from Sr(btsa)₂·2DME coordinated to the strontium atom to saturate the coordination sphere. The Sr–O (meeH oxygen) distances are 2.531–2.798 Å (average 2.647 Å), which are longer than those of complex **10**.

Complex **11** showed a dimeric structure with strontium atoms bonded to two tmhd and one meeH ligand, where the oxygen atoms from tmhd bridged the two metal centers by μ₂-O bonding, similar to [Sr(bdeamp)(hfac)]₃ and [Sr(dadamb)(hfac)]₃ as μ₂-O of the diketonato ligand. In this complex, the crystal structure showed a highly distorted square antiprismatic molecular geometry, where the metal nonbonding distance of 4.1798 (4) is longer than those of other strontium metal complexes, such as [Sr(bdmp)(btsa)]₂·2THF, [Sr(demamp)(btsa)]₂, and [Sr(dmamp)(btsa)]₂·DME (Figure 6 and Table 2). The bridging angle between the two metal centers is 104.43 (5), which is similar to that of [Sr(demamp)(btsa)]₂.^{9,34,35}

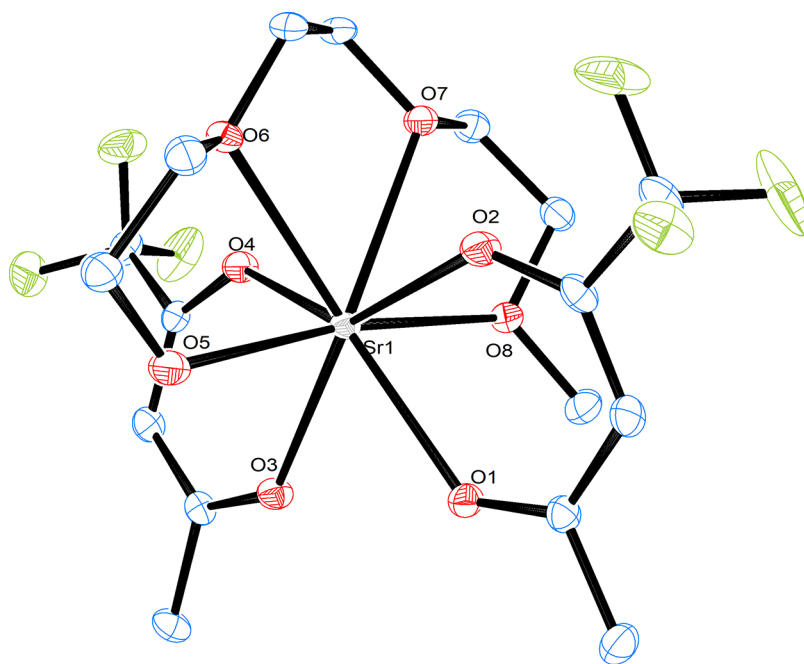
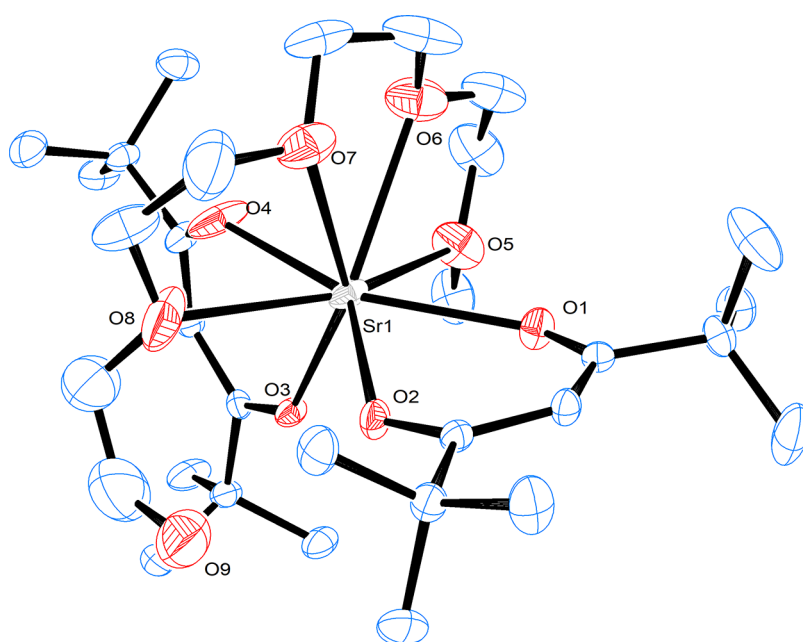
**Figure 2.** ORTEP drawing of the crystal structure of Sr(tmge)(tfac)₂ (**3**). The ellipsoids represent a probability 30%.

Table 2. Selected Bond Lengths (Å) and Bond Angles (°) for 3 and 8–12

bond lengths (Å)	3	8	9	10	11	12
Sr1–O1	2.545(15)	2.502(4)	2.648(3)	2.541(18)	2.677(18)	2.531(4)
Sr1–O2	2.521(15)	2.520(4)	2.535(3)	2.552(18)	2.548(16)	2.597(4)
Sr1–O3	2.477(14)	2.485(3)	2.566(3)	2.516(19)	2.473(14)	2.557(4)
Sr1–O4	2.511(14)	2.461(4)	2.528(3)	2.530(19)	2.484(15)	2.534(4)
Sr1–O5	2.543(16)	2.803(6)	2.601(3)	2.632(19)	2.761(15)	2.680(4)
Sr1–O6	2.675(15)	2.740(6)	2.694(3)	2.634(18)	2.755(15)	2.651(4)
Sr1–O7	2.641(14)	2.650(5)	2.744(3)	2.628(18)	2.587(15)	2.798(4)
Sr1–O8	2.618(15)	2.697(7)	2.692(3)	2.620(19)		2.786(4)
Sr1–O9			2.788(3)			2.702(4)
bond angles (°)	3	8	9	10	11	12
O1–Sr1–O2	70.04(5)	69.29(12)	67.95(8)	68.26(6)	65.16(4)	67.31(13)
O3–Sr1–O4	70.31(5)	69.86(13)	61.68(9)	69.39(6)	69.23(5)	68.69(13)
O5–Sr1–O6	61.75(5)	59.99(19)	61.67(8)	62.52(6)	61.78(5)	62.31(12)
O6–Sr1–O7	63.72(5)	60.08(2)	59.70(9)	62.57(6)	62.15(5)	62.60(12)
O7–Sr1–O8	62.90(5)	64.17(2)	62.46(8)	63.72(6)		
O8–Sr1–O9			61.42(8)			60.82(13)
Sr1–O1–Sr1 ⁱ					104.43(5)	

Figure 3. ORTEP drawing of the crystal structure of Sr(tod)(tmhd)₂ (8). The ellipsoids represent a probability 30%.

Thermogravimetric Analyses. Thermogravimetric analysis (TGA) of complexes 3–12 was conducted from room temperature to 600 °C under a constant flow of nitrogen to avoid air contact (Figures 8 and 9). Complexes 3, 5, 8, and 11 showed two-step mass loss patterns in their TGA curves. In the first step, the TGA plots of complexes 3, 5, 8, and 11 showed 52, 25, 31, and 25% mass losses, respectively, from 110 to 260 °C. In the second step, the observed mass losses were 12, 63, 51, and 67%, respectively, for 3, 5, 8, and 11 in the 260–400 °C temperature range, where the residual masses of 36, 12, 18, and 8% were observed, respectively. The first mass losses of 3, 5, 8, and 11 are comparable to the mass of 2tfacH, tmgeH, todH, meeH (calcd. 55, 26, 30, and 64%, respectively). The TGA plots of complexes 4, 7, and 12 showed multistep weight loss, where compounds 4, 7, and 12 displayed 41, 53, and 88% mass loss in the 25–450 °C temperature range and displayed residual masses of 59, 47, and 12%. In DSC analysis, complex 4 showed exotherm at 203 and 329 °C and endotherm at 108

and 275 °C (Figure S1). Complexes 6, 9, and 10 exhibited relatively sharp TGA curves with single-step weight losses of 91, 80, and 88%, respectively, between 100 and 330 °C, where residual masses of 9, 20, and 12% were observed. The residual masses of 8 and 9 are comparable to the mass of SrO and SrCO₃ (calcd. 15 and 18%), where residual masses of 10 and 12 are comparable to the masses of Sr (calcd. 12 and 12%). The complexes 3, 4, and 6 showed nonvolatile residual masses of 36, 41, and 51%, respectively, reflecting the decomposition of the compounds during the experiments and, thus, the thermally unstable property.

EXPERIMENTAL SECTION

General Remarks. NMR spectra were recorded with a Bruker 500 MHz spectrometer (¹H) and a Bruker 500 MHz spectrometer (¹³C) with C₆D₆ as the solvent and reference. IR spectra were obtained using a Nicolet Nexus FT-IR spectrophotometer. Elemental analyses were carried out

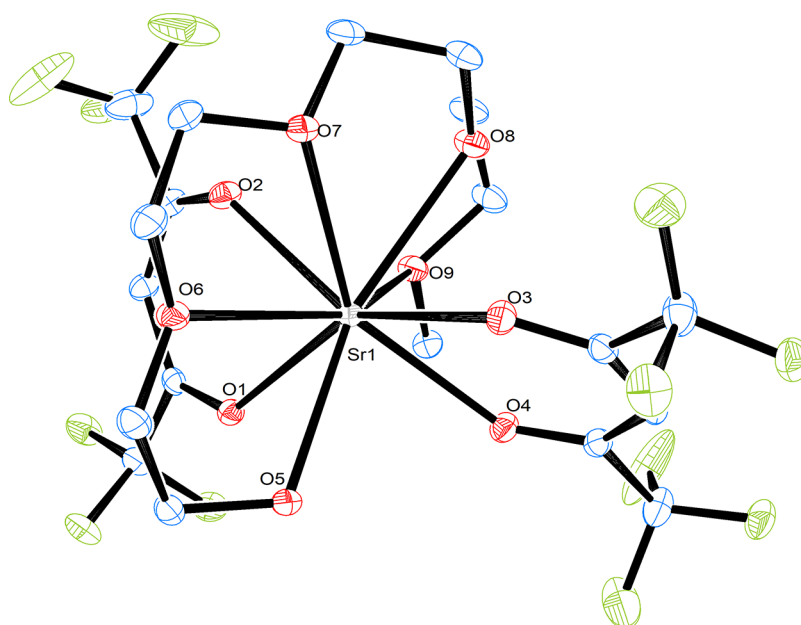


Figure 4. ORTEP drawing of the crystal structure of $\text{Sr}(\text{tod})(\text{hfac})_2$ (9). The ellipsoids represent a probability 30%.

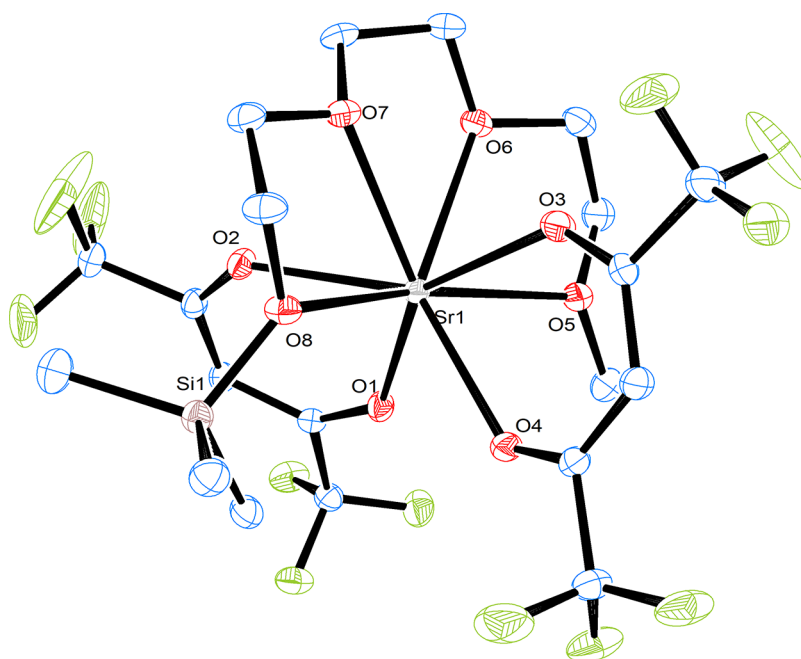


Figure 5. ORTEP drawing of the crystal structure of $\text{Sr}(\text{dmts})(\text{hfac})_2$ (10). The ellipsoids represent a probability 30%.

using a Thermo Scientific OEA Flash 2000 Analyzer. Thermogravimetric analyses were conducted using a SETAR-AM 92–18 TG-DTA instrument with a constant flow of nitrogen (500 mL/min) throughout the experiment. All reactions were carried out under inert dry conditions in an argon-filled glovebox. Hexane and toluene were purified using an Innovative Technology PS-MD-4 solvent purification system. All other chemicals were purchased from Aldrich and Alfa Aesar without further purification. Melting points were measured by a StuartTM SMP40 automatic melting point apparatus.

General Procedure for the Synthesis of $[\text{Sr}(\text{tmge})(\text{btsa})_2]$ and $[\text{Sr}(\text{tod})(\text{btsa})_2]$. A hexane solution (10 mL) of tmgeH (or todH) was added dropwise to a solution of

$\text{Sr}(\text{btsa})_2 \cdot 2\text{DME}$ in hexane (20 mL) at room temperature with constant stirring and was stirred for 15 h. After the completion of the reaction, the reaction mixture was filtered and volatiles were removed *in vacuo* to obtain the product as a white solid. X-Ray-quality crystals were grown from a saturated solution in toluene upon cooling.

$[\text{Sr}(\text{tmge})(\text{btsa})_2]$ (1). $\text{Sr}(\text{btsa})_2 \cdot 2\text{DME}$ (0.59 g, 1.0 mmol) and tmgeH (0.16 g, 1.0 mmol) were used. Yield: 0.34 g (85%). ^1H NMR (500 MHz, C_6D_6): δ = 0.44 [s, 18H, $\text{Si}(\text{CH}_3)_3$], 2.82 [t, 2H, CH_2OCH_3], 2.98 [t, 2H, OCH_2CH_2], 3.13 [t, 2H, $\text{CH}_2\text{CH}_2\text{O}$], 3.15 [t, 2H, OCH_2CH_2], 3.37 [s, 3H, CH_3OCH_2], 3.50 [t, 2H, $\text{CH}_2\text{CH}_2\text{O}$], 4.14 [t, 2H, OCH_2CH_2] ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 6.34 [$\text{Si}(\text{CH}_3)_3$], 59.93 [CH_3OCH_2], 63.03 [OCH_2CH_2], 66.89

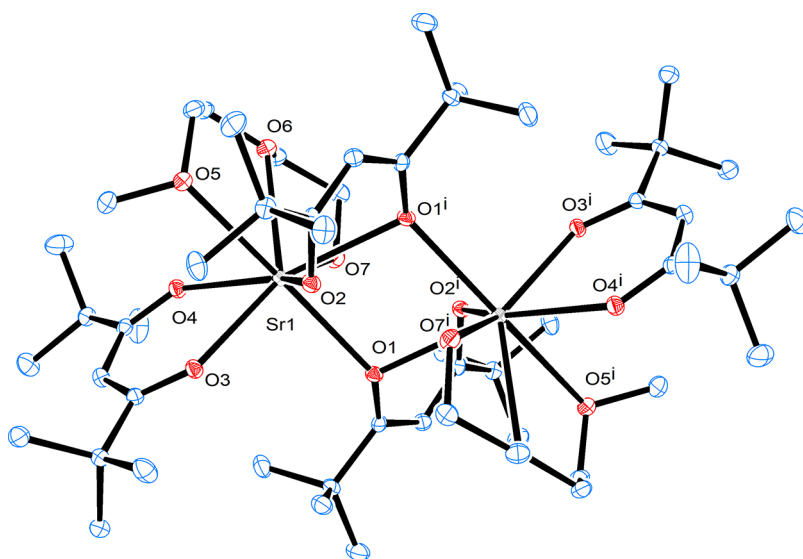


Figure 6. ORTEP drawing of the crystal structure of $[\text{Sr}(\text{mee})(\text{tmhd})]_2$ (**11**). The ellipsoids represent a probability 30%.

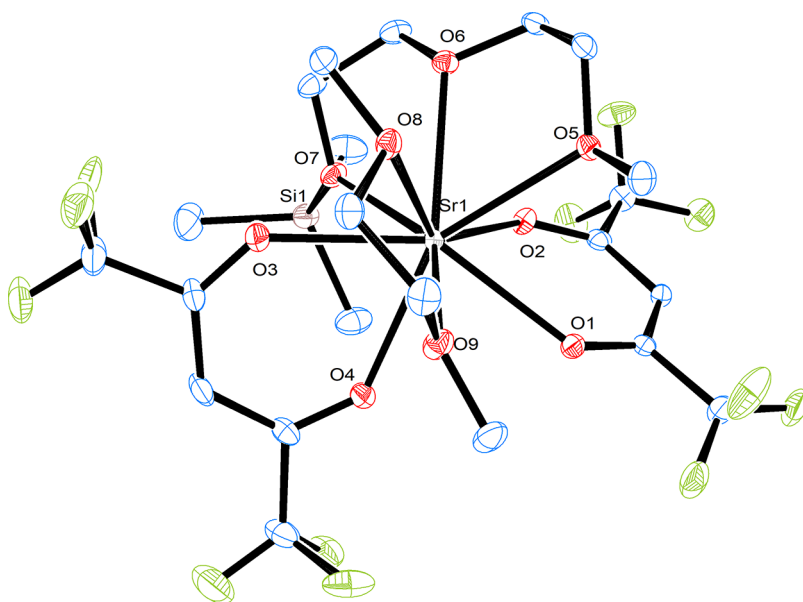


Figure 7. ORTEP drawing of the crystal structure of $\text{Sr}(\text{dts})(\text{hfac})_2 \cdot \text{DME}$ (**12**). The ellipsoids represent a probability 30%.

$[\text{CH}_2\text{CH}_2\text{O}]$, 68.02 $[\text{OCH}_2\text{CH}_2]$, 69.10 $[\text{CH}_2\text{CH}_2\text{O}]$, 70.23 $[\text{OCH}_2\text{CH}_2]$, 77.63 $[\text{CH}_2\text{CH}_2\text{O}]$ ppm. FT-IR (KBr, cm^{-1}): 2937 (s), 2798 (w), 1243 (m), 1100 (s), 1072 (s), 886 (m), 820 (m). $\text{C}_{26}\text{H}_{66}\text{N}_2\text{O}_8\text{Si}_4\text{Sr}_2$ (822.40): calcd. C, 37.97; H, 8.09; N, 3.41. Found: C, 37.49; H, 8.09; N, 3.10.

$[\text{Sr}(\text{tod})(\text{btsa})]_2$ (**2**). $\text{Sr}(\text{btsa})_2 \cdot 2\text{DME}$ (0.59 g, 1.0 mmol) and todH (0.20 g, 1.0 mmol) were used. Yield: 0.36 g (80%). ^1H NMR (500 MHz, C_6D_6): δ = 0.45 [s, 18H, $\text{Si}(\text{CH}_3)_3$], 2.99 [t, 2H, OCH_2CH_3], 3.13 [t, 2H, $\text{CH}_2\text{CH}_2\text{O}$], 3.29 [t, 2H, OCH_2CH_2], 3.34 [t, 2H, $\text{CH}_2\text{CH}_2\text{O}$], 3.36 [s, 3H, CH_3OCH_2], 3.37 [t, 2H, OCH_2CH_2], 3.54 [t, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$], 3.78 [t, 2H, OCH_2CH_2], 4.12 [t, 2H, $\text{CH}_2\text{CH}_2\text{O}$] ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 6.08 [$\text{Si}(\text{CH}_3)_3$], 59.48 [CH_3OCH_2], 52.07 [$\text{CH}_2\text{CH}_2\text{O}$], 65.59 [OCH_2CH_2], 68.92 [$\text{CH}_2\text{CH}_2\text{O}$], 69.21 [OCH_2CH_2], 70.12 [OCH_2CH_2], 71.68 [$\text{CH}_2\text{CH}_2\text{O}$], 75.71 [OCH_2CH_2] ppm. FT-IR (KBr, cm^{-1}): 2935 (s), 2796 (w), 1472 (w), 1363 (w), 1241 (m), 1097 (s), 1077 (s), 821 (m).

$\text{C}_{30}\text{H}_{74}\text{N}_2\text{O}_{10}\text{Si}_4\text{Sr}_2$ (900.50): calcd. C, 39.57; H, 8.19; N, 3.08. Found: C, 39.14; H, 7.97; N, 2.93.

General Procedure for the Synthesis of $\text{Sr}(\text{tmgeH})(\beta\text{-diketonate})_2$ and $\text{Sr}(\text{todH})(\beta\text{-diketonate})_2$ Complexes. A hexane solution (10 mL) of β -diketone was added dropwise to a solution of $[\text{Sr}(\text{tmge})(\text{btsa})]_2$ or $[\text{Sr}(\text{tod})(\text{btsa})]_2$ in hexane (30 mL) at room temperature with constant stirring and was stirred for 15 h. After the completion of the reaction, the reaction mixture was filtered and volatiles were removed *in vacuo* to obtain the product as a white solid. X-Ray-quality crystals were grown from a saturated solution in hexane upon cooling.

$\text{Sr}(\text{tmgeH})(\text{tfac})_2$ (**3**). $[\text{Sr}(\text{tmge})(\text{btsa})]_2$ (**1**) (0.41 g, 0.5 mmol) and tfacH (0.308 g, 2 mmol) were used. Yield: 0.44 g (80%), m.p. 115 °C. ^1H NMR (500 MHz, C_6D_6): δ = 1.86 [s, 6H, CHCOCH_3], 2.95–3.42 [br. t, 10 H, $\text{CH}_2\text{CH}_2\text{O}$, OCH_2CH_2 , $\text{CH}_2\text{CH}_2\text{O}$, OCH_2CH_2 , $\text{CH}_2\text{CH}_2\text{O}$], 3.19 [s, 3H, CH_3OCH_2], 3.72 [br. t, 2H, OCH_2CH_2], 4.88 [s, 1H,

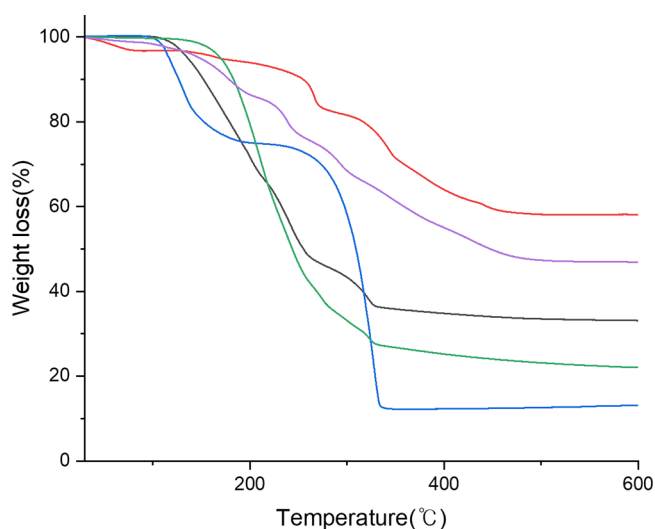


Figure 8. TGA plot of complexes 3 (black), 4 (red), 5 (blue), 6 (green), and 7 (purple).

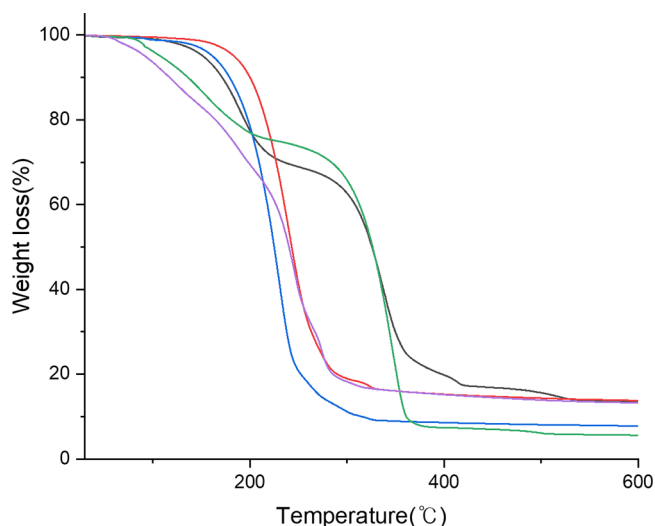


Figure 9. TGA plot of complexes 8 (black), 9 (red), 10 (blue), 11 (green), and 12 (purple).

OHCH_2CH_2], 5.75 [s, 2H, β -CH (tfac)] ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 28.72 [CH_3COCH], 58.54 [CH_3OCH_2], 60.51 [OCH_2CH_2], 68.93 [$\text{CH}_2\text{CH}_2\text{O}$], 69.46 [OCH_2CH_2], 69.73 [$\text{CH}_2\text{CH}_2\text{O}$], 70.55 [OCH_2CH_2], 71.56 [$\text{CH}_2\text{CH}_2\text{O}$], 93.94 [CCHC], 118.62 [CF_3CCH], 121.49 [CH_3CCH], 169.17 [CF_3CCH] ppm. ^{19}F NMR (470.54 MHz, C_6D_6): δ = -76.85 [$\text{C}(\text{CF}_3)$] ppm. FT-IR (KBr, cm^{-1}): 3272(m), 2922(m), 1638(s), 1503(s), 1354(m), 1285(s), 1212(m), 1180(m), 1135(s), 1080(s), 946(m), 857(m). $\text{C}_{17}\text{H}_{24}\text{F}_6\text{O}_8\text{Sr}_1$ (557.98): calcd. C, 36.59; H, 4.34. Found: C, 36.93; H, 4.04.

Sr(tmgeH)(acac)₂ (4). [Sr(tmge)(btsa)]₂ (1) (0.41 g, 0.5 mmol) and acacH (0.200 g, 2 mmol) were used. Yield: 0.36 g (82%), m.p. 90 °C. ^1H NMR (500 MHz, C_6D_6): δ = 2.01 [s, 12H, CH_3CCH], 3.13 [s, 3H, CH_2OCH_3], 3.25 [t, 2H, $\text{CH}_2\text{CH}_2\text{O}$], 3.31 [t, 2H, OCH_2CH_2], 3.34 [t, 2H, $\text{CH}_2\text{CH}_2\text{O}$], 3.35 [t, 2H, $\text{CH}_2\text{CH}_2\text{O}$], 3.37 [t, 2H, $\text{CH}_2\text{CH}_2\text{O}$], 3.64 [t, 2H, OCH_2CH_2], 4.32 [s, 1H, OHCH_2CH_2], 5.34 [s, 2H, β -CH (acac)] ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 28.25 [CH_3CCH], 58.37 [CH_3OCH_2],

61.12 [OCH_2CH_2], 70.02 [$\text{CH}_2\text{CH}_2\text{O}$], 70.21 [OCH_2CH_2], 70.31 [$\text{CH}_2\text{CH}_2\text{O}$], 71.69 [OCH_2CH_2], 72.42 [$\text{CH}_2\text{CH}_2\text{O}$], 99.81 [CCHC], 189.00 [CH_3CCH] ppm. FT-IR (KBr, cm^{-1}): 3336(m), 2970(s), 2913(s), 1652(m), 1455(m), 1199(m), 1146(s), 976(m), 930(m), 886(m), 837(m), 673(m). $\text{C}_{17}\text{H}_{30}\text{O}_8\text{Sr}_1$ (450.03): calcd. C, 45.37; H, 6.72. Found: C, 44.36; H, 6.30.

Sr(tmgeH)(tmhd)₂ (5). [Sr(tmge)(btsa)]₂ (1) (0.41 g, 0.5 mmol) and tmhdH (0.368 g, 2 mmol) were used. Yield: 0.52 g (85%), m.p. 107 °C. ^1H NMR (500 MHz, C_6D_6): δ = 1.35 [s, 36H, (CH_3)₃CC], 3.13 [t, 2H, CH_2OCH_3], 3.15 [s, 3H, CH_3OCH_2], 3.25 [t, 2H, $\text{CH}_2\text{CH}_2\text{O}$], 3.26 [t, 2H, OCH_2CH_2], 3.27 [t, 2H, OCH_2CH_2], 3.28 [t, 2H, $\text{CH}_2\text{CH}_2\text{O}$], 3.51 [t, 2H, $\text{CH}_2\text{CH}_2\text{O}$], 4.38 [s, 1H, OHCH_2CH_2], 5.86 [s, 2H, β -CH (tmhd)] ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 28.92 [(CH_3)₃CC], 40.86 [(CH_3)₃CC], 58.88 [CH_3OCH_2], 60.67 [OCH_2CH_2], 69.09 [$\text{CH}_2\text{CH}_2\text{O}$], 69.31 [OCH_2CH_2], 69.50 [$\text{CH}_2\text{CH}_2\text{O}$], 70.65 [OCH_2CH_2], 71.86 [$\text{CH}_2\text{CH}_2\text{O}$] ppm. FT-IR (KBr, cm^{-1}): 3321(m), 2948(s), 1606(s), 1503(m), 1532(s), 1403(s), 1386(m), 1243(m), 1120(s), 1182(s), 1087(s), 1061(s), 863(m). $\text{C}_{29}\text{H}_{54}\text{O}_8\text{Sr}_1$ (618.35): calcd. C, 56.33; H, 8.80. Found: C, 56.19; H, 9.03.

Sr(todH)(tfac)₂ (6). [Sr(tod)(btsa)]₂ (1) (0.45 g, 0.5 mmol) and tfacH (0.308 g, 2 mmol) were used. Yield: 0.51 g (85%), m.p. 134 °C. ^1H NMR (500 MHz, C_6D_6): δ = 1.87 [s, 6H, CHCOCH_3], 3.04 [br. d, 2H, $\text{CH}_2\text{CH}_2\text{O}$], 3.08 [t, 4H, OCH_2CH_2 , $\text{CH}_2\text{CH}_2\text{O}$], 3.17 [t, 2H, OCH_2CH_2], 3.19 [s, 3H, CH_2OCH_3], 3.25 [t, 2H, $\text{CH}_2\text{CH}_2\text{O}$], 3.28 [t, 2H, OCH_2CH_2], 3.32 [t, 2H, $\text{CH}_2\text{CH}_2\text{OH}$], 3.44 [t, 2H, OCH_2CH_2], 4.10 [br. s, 1H, $\text{CH}_2\text{CH}_2\text{OH}$], 5.80 [s, 2H, β -CH (tfac)] ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 29.01 [CH_3COCH], 58.58 [CH_3OCH_2], 60.32 [OCH_2CH_2], 68.93 [$\text{CH}_2\text{CH}_2\text{O}$], 69.01 [OCH_2CH_2], 69.18 [$\text{CH}_2\text{CH}_2\text{O}$], 69.71 [OCH_2CH_2], 69.92 [$\text{CH}_2\text{CH}_2\text{O}$], 70.53 [OCH_2CH_2], 71.95 [OCH_2CH_2], 93.36 [CCHC], 121.62 [CF_3CCH], 169.30 [CCCH], 195.03 [CHCCF_3] ppm. ^{19}F NMR (470.54 MHz, C_6D_6): δ = -76.65 [$\text{C}(\text{CF}_3)$] ppm. FT-IR (KBr, cm^{-1}): 3280(m), 2927(m), 1643(s), 1517(s), 1469(m), 1279(s), 1179(m), 1133(m), 842(m), 765(m). $\text{C}_{19}\text{H}_{28}\text{F}_6\text{O}_9\text{Sr}_1$ (602.03): calcd. C, 37.91; H, 4.69. Found: C, 37.48; H, 4.66.

Sr(todH)(acac)₂ (7). [Sr(tod)(btsa)]₂ (2) (0.45 g, 0.5 mmol) and acacH (0.200 g, 2 mmol) were used. Yield: 0.37 g (74%), m.p. 128 °C. ^1H NMR (500 MHz, C_6D_6): δ = 2.01 [s, 12H, CHCOCH_3], 3.29–3.37 [br. 16 H, OCH_2CH_2 , $\text{CH}_2\text{CH}_2\text{O}$, OCH_2CH_2 , $\text{CH}_2\text{CH}_2\text{O}$, OCH_2CH_2 , $\text{CH}_2\text{CH}_2\text{O}$, OCH_2CH_2 , $\text{CH}_2\text{CH}_2\text{O}$], 3.34 [s, 3H, CH_2OCH_3], 3.59 [s, 1H, OHCH_2CH_2], 5.36 [s, 2H, β -CH (acac)] ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 28.66 [CH_3CCH], 60.81 [CH_3OCH_2], 67.83 [OCH_2CH_2], 69.78 [$\text{CH}_2\text{CH}_2\text{O}$], 70.00 [OCH_2CH_2], 70.44 [$\text{CH}_2\text{CH}_2\text{O}$], 71.51 [OCH_2CH_2], 99.88 [CCHC], 189.08 [CH_3CCH] ppm. FT-IR (KBr, cm^{-1}): 3067(w), 2918(m), 1613(s), 1513(s), 1398(s), 1241(m), 1197(w), 1105(w), 1012(m), 912(m). $\text{C}_{19}\text{H}_{34}\text{O}_9\text{Sr}_1$ (494.09): calcd. C, 46.19; H, 6.94. Found: C, 45.96; H, 6.35.

Sr(todH)(tmhd)₂ (8). [Sr(tod)(btsa)]₂ (1) (0.45 g, 0.5 mmol) and tmhdH (0.368 g, 2 mmol) were used. Yield: 0.59 g (90%), m.p. 103 °C. ^1H NMR (500 MHz, C_6D_6): δ = 1.38 [s, 36H, (CH_3)₃CC], 3.05 [t, 2H, $\text{CH}_2\text{CH}_2\text{O}$], 3.14 [t, 2H, OCH_2CH_2], 3.20 [t, 2H, $\text{CH}_2\text{CH}_2\text{O}$], 3.21 [t, 2H, OCH_2CH_2], 3.28 [s, 3H, CH_3OCH_2], 3.36 [t, 2H, $\text{CH}_2\text{CH}_2\text{O}$], 3.36 [t, 2H, OCH_2CH_2], 3.46 [t, 2H,

$\text{CH}_2\text{CH}_2\text{O}$], 3.66 [t, 2H, OCH_2CH_2], 4.87 [s, 1H, OHCH_2CH_2], 5.85 [s, 2H, $\beta\text{-CH}$ (tmhd)] ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 29.02 [(CH_3) $_3\text{CC}$], 40.86 [(CH_3) $_3\text{CC}$], 58.95 [CH_3OCH_2], 60.33 [CH_3OCH_2], 69.25 [$\text{CH}_2\text{CH}_2\text{O}$], 69.27 [$\text{CH}_2\text{CH}_2\text{O}$], 69.38 [$\text{CH}_2\text{CH}_2\text{O}$], 69.85 [OCH_2CH_2], 70.54 [OCH_2CH_2], 87.54 [CCHC], 197.40 [CCCH] ppm. FT-IR (KBr, cm^{-1}): 3335(m), 2949(s), 1591(s), 1532(m), 1455(m), 1432(m), 1356(m), 1124(m), 1088(s), 863(w), 788(w). $\text{C}_{31}\text{H}_{38}\text{O}_9\text{Sr}_1$ (662.40): calcd. C, 56.21; H, 8.83. Found: C, 55.82; H, 8.84.

$\text{Sr}(\text{todH})(\text{hfac})_2$ (**9**). $[\text{Sr}(\text{tod})(\text{btsa})_2]$ (**1**) (0.45 g, 0.5 mmol) and hfacH (0.406 g, 2 mmol) were used. Yield: 0.58 g (82%), m.p. 104 °C. ^1H NMR (500 MHz, C_6D_6): δ = 2.76 [t, 2H, $\text{CH}_2\text{CH}_2\text{O}$], 2.83 [t, 2H, OCH_2CH_2], 2.86 [t, 2H, OCH_2CH_2], 2.99 [t, 2H, $\text{CH}_2\text{CH}_2\text{O}$], 2.99 [t, 2H, OCH_2CH_2], 3.12 [t, 2H, OCH_2CH_2], 3.14 [$\text{CH}_2\text{CH}_2\text{O}$], 3.18 [s, 3H, CH_3OCH_2], 3.20 [t, 2H, OCH_2CH_2], 6.28 [s, 2H, $\beta\text{-CH}$ (tmhd)] ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 58.63 [CH_3OCH_2], 60.36 [$\text{CH}_2\text{CH}_2\text{O}$], 68.40 [$\text{CH}_2\text{CH}_2\text{O}$], 69.31 [OCH_2CH_2], 69.73 [$\text{CH}_2\text{CH}_2\text{O}$], 70.10 [OCH_2CH_2], 70.25 [$\text{CH}_2\text{CH}_2\text{O}$], 70.86 [OCH_2CH_2], 87.25 [CCHC], 120.02 [CF_3CCH], 175.37 [CHCCF_3] ppm. ^1F NMR (470.54 MHz, C_6D_6): δ = -76.78 [$\text{C}(\text{CF}_3)$] ppm. FT-IR (KBr, cm^{-1}): 3509(m), 2933(m), 1673(s), 1533(s), 1472(m), 1256(s), 1189(s), 1133(s), 1079(s), 955(m). $\text{F}_{12}\text{C}_{19}\text{H}_{22}\text{O}_9\text{Sr}_1$ (709.97): calcd. C, 32.14; H, 3.12. Found: C, 31.63; H, 3.04.

General Procedure for the Synthesis of the $\text{Sr}(\text{dmts})(\text{hfac})_2$ Complex. A hexane solution (10 mL) of hfacH was added dropwise to a solution of $[\text{Sr}(\text{tmge})(\text{btsa})_2]$ in hexane (30 mL) at room temperature with constant stirring and was stirred for 15 h. After the completion of the reaction, the reaction mixture was filtered and volatiles were removed *in vacuo* to obtain the product as a white solid. X-Ray-quality crystals were grown from a saturated solution in hexane upon cooling.

$\text{Sr}(\text{dmts})(\text{hfac})_2$ (**10**). $[\text{Sr}(\text{tmge})(\text{btsa})_2]$ (**1**) (0.41 g, 0.5 mmol) and hfacH (0.406 g, 2 mmol) were used. Yield: 0.59 g (80%), m.p. 95 °C. ^1H NMR (500 MHz, C_6D_6): δ = 0.01 [s, 9H, (CH_3) $_3\text{SiO}$], 2.68 [t, 2H, SiOCH_2], 2.84 [t, 2H, OCH_2CH_2], 3.06 [t, 2H, $\text{CH}_2\text{CH}_2\text{O}$], 3.06 [s, 3H, CH_3OCH_2], 3.07 [t, 2H, OCH_2CH_2], 3.21 [m, 2H, $\text{CH}_2\text{CH}_2\text{O}$], 3.21 [t, 2H, OCH_2CH_2], 6.33 [s, 2H, $\beta\text{-CH}$ (hfac)] ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = -1.65 [(CH_3) $_3\text{SiO}$], 59.33 [(CH_3) $_3\text{OC}$], 62.34 [$\text{CH}_2\text{CH}_2\text{O}$], 69.02 [$\text{CH}_2\text{CH}_2\text{O}$], 69.77 [OCH_2CH_2], 70.30 [$\text{CH}_2\text{CH}_2\text{O}$], 70.54 [OCH_2CH_2], 71.69 [OCH_2CH_2], 88.27 [CCHC], 120.27 [CF_3CCH], 176.73 [CF_3CCH] ppm. ^1F NMR (470.54 MHz, C_6D_6): δ = -76.75 [$\text{C}(\text{CF}_3)$] ppm. FT-IR (KBr, cm^{-1}): 2943(m), 1670(m), 1527(m), 1472(w), 1259(m), 1191(m), 1143(m), 1085(m), 953(w), 851(m), 792(m), 765(w), 659(m). $\text{C}_{20}\text{H}_{26}\text{O}_8\text{Sr}_1\text{Si}_1\text{F}_{12}$ (738.10): calcd. C, 32.54; H, 3.55. Found: C, 32.59; H, 3.53.

General Procedure for the Synthesis of and $\text{Sr}(\text{dts})(\text{hfac})_2\cdot\text{DME}$ and $[\text{Sr}(\text{meeH})(\text{tmhd})_2]$ Complexes. A hexane solution (10 mL) of β -diketone was added dropwise to a solution of $\text{Sr}(\text{btsa})_2\cdot\text{DME}$ in hexane (30 mL) at room temperature with constant stirring and was stirred for 15 h. After the completion of the reaction, the reaction mixture was filtered and volatiles were removed *in vacuo* to obtain the product as a white solid. X-Ray-quality crystals were grown from a saturated solution in hexane upon cooling.

$[\text{Sr}(\text{meeH})(\text{tmhd})_2]$ (**11**). $\text{Sr}(\text{btsa})_2\cdot\text{DME}$ (0.59 g, 1 mmol), meeH (0.12 g, 1 mmol), and tmhdH (0.368 g, 2

mmol) were used. Yield: 0.46 g (80%), m.p. 85 °C. ^1H NMR (500 MHz, C_6D_6): δ = 1.31 [s, 36H, (CH_3) $_3\text{CC}$], 3.10 [t, 2H, CH_2CH_2], 3.10 [s, 3H, CH_3OCH_2], 3.22 [t, 2H, $\text{CH}_2\text{CH}_2\text{O}$], 3.49 [t, 2H, OCH_2CH_2], 3.89 [t, 2H, $\text{CH}_2\text{CH}_2\text{O}$], 5.81 [s, 2H, $\beta\text{-CH}$ (tmhd)] ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 29.21 [(CH_3) $_3\text{CCO}$], 41.18 [(CH_3) $_3\text{CC}$], 59.26 [CH_3OCH_2], 61.32 [$\text{CH}_2\text{CH}_2\text{O}$], 69.43 [$\text{CH}_2\text{CH}_2\text{O}$], 61.55 [OCH_2CH_2], 72.90 [OCH_2CH_2], 89.82 [CCHC], 199.24 [CCCH] ppm. FT-IR (KBr, cm^{-1}): 3177(w), 2953(m), 2866(w), 1593(m), 1533(m), 1454(m), 1128(w), 1065(w), 864(w). $\text{C}_{54}\text{H}_{100}\text{O}_{14}\text{Sr}_2$ (1148.60): calcd. C, 56.47; H, 8.78. Found: C, 56.51; H, 8.73.

$\text{Sr}(\text{dts})(\text{hfac})_2\cdot\text{DME}$ (**12**). $\text{Sr}(\text{btsa})_2\cdot\text{DME}$ (0.59 g, 1 mmol), meeH (0.12 g, 1 mmol), and hfacH (0.406 g, 2 mmol) were used. Yield: 0.51 g (75%), m.p. 60 °C. ^1H NMR (500 MHz, C_6D_6): δ = 0.08 [s, 9H, CH_3SiO], 2.86 [s, 4H, $\text{CH}_2\text{CH}_2\text{O}$], 3.01 [t, 2H, $\text{CH}_2\text{CH}_2\text{O}$], 3.06 [s, 6H, CH_3OCH_2], 3.06 [s, 3H, CH_3OCH_2], 3.19 [t, 2H, $\text{CH}_2\text{CH}_2\text{O}$], 3.24 [t, 2H, OCH_2CH_2], 3.43 [t, 2H, $\text{CH}_2\text{CH}_2\text{O}$], 6.28 [s, 2H, $\beta\text{-CH}$ (tmhd)] ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 0.22 [$\text{Si}(\text{CH}_3)\text{OCH}_2$], 59.97 [CH_3OCH_2], 60.09 [CH_3OCH_2], 63.27 [$\text{CH}_2\text{CH}_2\text{O}$], 71.19 [$\text{CH}_2\text{CH}_2\text{O}$], 72.06 [CH_3OCH_2], 72.57 [OCH_2CH_2], 73.83 [OCH_2CH_2], 89.63 [CCHC], 121.48 [CF_3CCH], 177.63 [CHCCF_3] ppm. ^1F NMR (470.54 MHz, C_6D_6): δ = -76.78 [$\text{C}(\text{CF}_3)$] ppm. FT-IR (KBr, cm^{-1}): 3523(w), 2934(w), 2889(w), 1673(s), 1533(s), 1472(m), 1255(m), 1189(m), 1133(m), 1079(m), 841(m), 577(m). $\text{F}_{12}\text{C}_{22}\text{H}_{32}\text{O}_9\text{SiSr}$ (784.17): calcd. C, 33.70; H, 4.11. Found: C, 33.24; H, 3.89.

Crystallography. Single crystals of **1**, **3**, **8**, **9**, **10**, **11**, and **12** complexes were grown from their saturated solutions in hexane and toluene at -30 °C. In a typical procedure, a specimen of suitable size and quality was obtained from the solution, coated with Paratone oil, and mounted on a glass capillary. Reflection data were collected using a Bruker SMART Apex II-CCD area detector diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). The hemisphere of the reflection data was collected as ω -scan frames with 0.3° per frame and an exposure time of 10 s per frame. Cell parameters were determined and refined using the SMART program.³⁸ Data reduction was performed using SAINT software.³⁹ The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied using the SADABS program.⁴⁰ The structures of the prepared compounds were solved by direct methods, and all nonhydrogen atoms were subjected to anisotropic refinement by the full-matrix least-squares method on F^2 using the SHELXTL/PC package.⁴¹ Hydrogen atoms were placed at their geometrically calculated positions and refined based on the corresponding carbon atoms with isotropic thermal parameters. CCDC 2242279-2242281, 2090311-2090312, and 218706-218707 for complexes **1**, **3**, **8**, **9**, **10**, **11**, and **12** contain the supplementary crystallographic data for this article.

CONCLUSIONS

New strontium β -diketonate complexes with ethereal or silyl groups were successfully synthesized and characterized. All Sr compounds were prepared via a controlled substitution reaction with $\text{Sr}(\text{btsa})_2\cdot\text{DME}$. Partially substituted compound **1** showed dimeric structures with hexa-coordination states. The compounds **3–10** and **12** displayed monomeric structures with an octa- to nona-coordination state, whereas complex **11** showed an octa-coordinated dimeric structure. In complexes

3–9 and 11, the tmge and tod ligands were reduced to tmgeH and todH, respectively. In complexes 10 and 12, the hydroxyl hydrogen of tmgeH and meeH was substituted with a trimethylsilyl group from HMDS as by-product. However, complex 9 did not precede silylation of alcohol because of the more electron rich five oxygen atoms in which all coordinated to the strontium although HMDS existed as by-product compared with tmgeH and meeH. Additionally, complexes 3 and 6 with half the number of fluorine atoms compared to complexes 10 and 12 existed as alcohol form of tmgeH and todH because of the lower electronegativity than hfac ligand. The FT-IR spectra showed –OH stretching peaks of complexes 2–9 and 11 Si–CH₃ stretching and rocking vibration peaks of complexes 9 and 10. The TGA curves for complexes 10 and 12 showed minimal nonvolatile residues and single-step weight losses.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c08020>.

- Data collection parameter for complex 1 (CIF)
- Data collection parameter for complex 3 (CIF)
- Data collection parameter for complex 8 (CIF)
- Data collection parameter for complex 9 (CIF)
- Data collection parameter for complex 10 (CIF)
- Data collection parameter for complex 11 (CIF)
- Data collection parameter for complex 12 (CIF)
- DSC data of complex 4 and NMR spectra of complexes 1–12 (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to the Center for Chemical Analysis at the Korea Research Institute of Chemical Technology (KRICT) for allowing the use of their facilities and Bruker SMART APEX II for solving the crystal structures. This work was supported by the Materials and Components Technology Development Program (20010275, Development of ALD precursors for high k thin film in logic and DRAM Flash memory devices) funded by the Ministry of Trade, Industry & Energy (MOTIE, Republic of Korea) and the Development of smart chemical materials for IoT devices Project through the Korea Research Institute of Chemical Technology (KRICT) of Republic of Korea (SS2121-10).

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