Study on the Development of CVD Precursors II-Synthesis and Properties of New Lathanum β-diketonates

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A new synthetic route for the lanthanum β-diketonate compounds *via in-situ* formed lanthanum alkyl complexes was developed in the process for the development of suitable MOCVD (metal-organic chemical vapor deposition) precursors of PLT, one of the promising material for the ferroelectric film. A series of lanthanum -diketonate compounds were successfully synthesized by this method. This new method is found to have some merits; versatile method for almost every β-diketone, β-hydroxyketone, and β-hydroxyaldehyde, short reaction time, easy purification for high purity, moderate to high yield, and easy access to anhydrous compounds. In some cases, anhydrous oligomeric products fail to show the higher volatility. On the other hand, some lanthanum β-diketonates with aromatic groups such as La(1,3-biphenyl-1,3-propandione)3 are found to have favorable properties for a precursor of lanthanum oxide, one of major components of PLT, such as low melting point, and much higher decomposition temperature. A plausible pyrolysis mechanism is proposed by the TGA, where consecutive dissociation of R, CO, CH, C, and O fragments occurs.

Introduction

Considerable interests in thin films of the perovskite-type ferroelectric materials such as lead titanate ($PbTiO_3$) based ceramics (PT, PZT, PLZT, PLT) with pyroelectric and piezoelectric properties have been shown for the possible application as memory capacitors, microactuators, piezoelectric devices, and pyroelectric sensors.[1] Lanthanide-doped lead titanate thin films by using MOCVD (Metal Organic Chemical Vapor Deposition) technique produced smoother surface morphology and structural change from tetragonal to cubic with the increase of lanthanum content from 0-15%.[2] The success of this technique requires reliable precursors of high volatility, low toxicity and high thermal and chemical stability. Several precursors such as metal alkyls and alkoxides have been used for their volatility but their toxicity and instability toward temperature, moisture and other chemicals limited wider uses. On the other hand, metal β-diketonates are stable toward hydrolysis and temperature, moderately volatile and nontoxic. However, well-developed synthetic methods for metal β-diketonates are not yet established for their long history.[3] Recently, other organometallic compounds with cyclopentadienyl ligands have been developed and were used as CVD precursors with some success.[4] Also, in order to develop the optimal precursors and design the optimal apparatus for the CVD process, the effect of the substituents and reaction conditions on the properties of the precursors should be understood. Up to date, fluoroalkyl or bulky groups in the β-diketones are known to induce the higher volatility and stability. However, fluoroalkyl β-diketonates may cause contamination of the film by the residual fluorine. Another strategy to the higher volatility of the precursor, the preparation of polydentate base adducts of metal β-diketonates, has been employed and examined. This strategy can be applied in the cases of complexes whose central metal atoms are large. These complexes are coordinatively unsaturated if the number of β-diketonates is determined only to neutralize the charge of the metal. Therefore, these complexes tend to form the oligomeric compounds or hydrated ones, which decreases the volatility significantly. Therefore, it is expected that Lewis acid/base adducts with neutral compounds having electron donor atoms such as oxygen or nitrogen atoms would be free of vacant sites and show higher stability and volatility. Fujinaga[5] reported that the vaporization rate of β-diketonate compounds could be stabilized when free β-diketones were present in the carrier gas in a study of separation of β-diketonate compounds by gas chromatography. Collman[6] also reported the same trend in the case of barium β-diketonate compounds. Recently this strategy has showed recognizable success in the preparation of some metal complexes, especially barium ones which showed very low volatility. Spee[7] reported that polyether, $CH_3O(CH_2CH_2O)_nCH_3$ ($n=1$-4) adducts of $Ba(hfa)_2$ (hfa: hexafluoroacetylacetonate) were synthesized and these complexes showed much higher volatilities than the parent complexes. Barron[8] also showed that dramatically increased volatility and stability of barium β-diketonate compounds could be achieved by adding nitrogen base such as amines instead of polyethers in the carrier gas (some barium β-diketonate compounds melt in the range of 70 and 100 ℃ and vaporize at 130-230 ℃ without decomposition) but the amine adduct complexes were not isolated. Other similar reports[9] have followed but the dissociation of bases before the vaporization of the compounds were observed and extensive studies have been employed to improve this behavior. In our group, new precursors for PLT thin films have been searched and an improved preparative method was developed. In this study, a new synthetic pathway (equation (1)) for the lathanum β-diketonate complex, which can be applicable as a precursor for the La_2O_3 that is, in turn, an important component of the PLT thin film was inve-

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stigated and properties of newly prepared lathanum β-diketonate complexes were characterized by spectroscopic methods and thermal analysis.

$$LaCl_3 + 3\ MeLi \xrightarrow[THF,\ -78\ ℃ \rightarrow RT]{} LaMe_3 + 3\ LiCl$$

$$LaMe_3 + 3\ acacH \xrightarrow{THF} La(acac)_3 + 3\ methane \quad (1)$$

Experiment

All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques unless stated otherwise. Solvents were reagent grade and were distilled over nitrogen from appropriate drying agents prior to use.[10] Reagent grade chemicals including β-diketones were purchased from Aldrich Chemical Co., Inc. and used without further purification unless stated otherwise. Infrared spectra were recorded on a Nicolet MX-IE, Shimadzu IR-435 and Bruker IFS-66 and the IR samples were prepared as KBr pellets. ^{1}H NMR spectra were recorded by using 5 mm tube on a Bruker AC-250 FT NMR spectrometer operating at 250.133 MHz and were referenced to tetramethylsilane (TMS). Thermal analyses were performed on a TA Instruments, DSC 2010 (DSC) and a TA Instruments, SDT 2960 (TGA, DTA). Elemental analyses were performed in the research center of Oriental Chemical Industries. Mass spectral analyses were carried out employing a HP5890A GC/HP 5917A MS detector equipped with a 30 m-long capillary column packed with liquid methyl silicon.

[La(acacH)(acac)$_3$]$_n$. $LaCl_3$ (1.00 g, 4.08 mmol) was suspended in 20 mL of THF, and this solution was cooled to −78 ℃. Then, 8.8 mL of MeLi (1.4 M in diethylether, 12.3 mmol) was added dropwise to this solution while stirring and light yellow solution and oilish red compound was observed when the solution was warmed up to room temperature. This mixture solution was transferred by a filtered cannula to the 15 mL of THF solution containing 1.30 mL (12.5 mmol) of acetylacetone (acacH) and precooled at 0 ℃. The white solid was produced slowly as the solution was warmed up to room temperature. The solution was stirred for 2 hrs and the white solid was obtained by filtration and washed by 5 mL of hexane three times and dried under vacuum overnight. Yield: 1.37 g (62.8%), Anal. Calcd. for $LaC_{20}H_{29}O_8$: C, 44.87; H, 5.23; Found: C, 44.18; H, 6.25, ^{1}H NMR ($CDCl_3$, 250.133 MHz): 1.54 (br s, 18H) (acac); 5.50(s), 2.05 (s) (acacH, enol form), 3.72 (s), 2.24 (s) (acacH, keto form) (3 : 2, total 6H) (CD_3OD) 1.83 (s) MS (EI) 773 (M+La(acac)-1), 590 (M+CH_3COCH-2), 436 (M-acacH), 337 (M-2 acac-1), 238 (La(acac)), 100 (acacH), 85 (acacH-Me) (FAB) 1496 (3 M-2CH_3COCH), 1453 (3 M-acac-CH_3COCH), 1410 (3 M-2 acac), 1254 (2M+La(CH_3CO)), 1128 (2 M+CH_3COCH), 1072 (2 M), 1016 (2 M-CH_3COCH), 893 (2 M-La(CH_3CO)+3), 793 (2 M-La(acac)(CH_3CO)+2), 523 (M-Me+2), 481 (M-CH_3COCH+1), 311 (M-2acac-CO), 99 (acac) IR (KBr pellet): 1590, 1510, 1460, 1390, 1255, 1010, 920, 800, 770, 640, 525 DSC: 145 (endothermic), 281.7, 303.1 (exothermic).

La(bpp)$_3$. $LaCl_3$ (0.50 g, 2.04 mmol), 4.4 mL of MeLi (1.4 M in diethylether, 6.16 mmol) and 1.38 g (6.15 mmol) of 1,3-biphenyl-1,3-propanedione(bppH) were used in the same procedure as described above. The yellow oil product was obtained by removing solvent under reduced pressure. The product was redissolved by adding 15 mL of toluene and LiCl was filtered off. Solvent was removed under reduced pressure again and 15 mL of hexane was added to precipitate a yellow solid. The yellow solid was obtained by filtration and washed by 5 mL of hexane three times and dried under vacuum overnight. Yield: 1.13 g (68.5%), Anal. Calcd. for $LaC_{45}H_{33}O_6+2H_2O$: C, 64.01; H, 4.73; Found: C, 63.55; H, 5.22, ^{1}H NMR ($CDCl_3$, 250.133 MHz): 7.65 (br, 6H), 6.8-7.1 (br, 9H), 6.37 (br s, 3H) (CD_3OD) 8.00 (d, 6H), 7.36 (m, 9H), 6.74 (s, 3H) MS (EI) 718.18 (M-Ph-CH), 479.31 (La+2PhCO-CCO+COC_2), 428.29 (La+2PhCOCCO-1), 324.3 (La+PhCO-CCO+C2O), 207.23 (La+COCHCO), 120.19 (PhCOCH+2), 105.18 (PhCO), 77.22 (Ph) IR (KBr pellet): 1590, 1545, 1510, 1475, 1450, 1390, 1295, 1275, 1215, 1170, 1050, 1015, 930, 800, 740, 710, 680, 600, 490 DSC: 39, 127.0, 137.5, 188.5, 192.5 (endothermic), 309, 325, 335, 355, 360, 370 (exothermic).

La(tfa)$_3$. $LaCl_3$ (1.00 g, 4.08 mmol), 8.8 mL of MeLi (1.4 M in diethylether, 12.3 mmol) and 1.50 mL (12.1 mmol) of 1,1,1-trifluoroacetylacetone(tfaH) were used in the same procedure as described above. The white solid was obtained by filtration and washed by 5 mL of hexane three times and dried under vacuum overnight. Yield: 2.02 g (68.2%), Anal. Calcd. for $LaC_{15}F_9H_{12}O_6+C_6H_{14}$: C, 36.85; H, 3.80; Found: C, 36.60; H, 4.20, ^{1}H NMR ($CDCl_3$, 250.133 MHz): 5.63 (br s, 3H); 1.99 (s), 1.75 (s) (1 : 2, total 9H) (CD_3OD) 5.60 (s), 2.01 (s) MS (EI) 597.85 (M^+), 528.89 (M-CF_3), 444.95 (M-tfa), 336.91 (M-2tfa+CO+O), 310.91 (M-2tfa+O), 154.04 (tfa), 85.13 (tfa-CF_3), 69.10 (tfa-CF_3O) IR (KBr pellet): 1615, 1585, 1530, 1460, 1415, 1360, 1220, 1195, 1130, 1000, 850, 785, 720, 605, 550 DSC: 216.5, 234.5 (endothermic), 255.2, 264.5, 304.2 (exothermic).

[La(dpm)$_3$]$_2$. $LaCl_3$ (2.00 g, 8.16 mmol), 17.5 mL of MeLi (1.4 M in diethylether, 24.5 mmol) and 5.40 mL (24.6 mmol) of dipivaloylmethane (dpmH) were used in the same procedure as described above. The yellowish white solid was obtained by removal of solvent under reduced pressure. This solid was dissoved in hot benzene again and LiCl was filtered off. The solvent was removed under reduced pressure and the yellowish white solid was produced by addition of 30 mL of hexane. The solid was obtained by filtration and washed by 5 mL of hexane three times and dried under vacuum overnight. Yield: 1.80 g (32.0%), Anal. Calcd. for $La_2C_{66}H_{114}O_{12}+11\ C_6H_{14}+23\ H_2O$: C, 57.86; H, 11.47; Found: C, 57.90; H, 11.50, ^{1}H NMR ($CDCl_3$, 250.133 MHz): 5.64 (br s, 3H), 1.09 (br s, 54H), 1.13 (s) (CD_3OD) 1.08 (s) MS (EI) 1379.86 (M+2), 688.38 (M/2, monomer), 505.42 (monomer-L), 322.18 (monomer-2L) IR (KBr pellet): 1570, 1545, 1500, 1455, 1400, 1380, 1360, 1280, 1220, 1175, 1020, 960, 920, 865, 790, 760, 730, 600, 470 DSC: 146.5, 193.6, 269.5, 289.2, 317.1, 331.4 (endothermic), 390 (exothermic).

La(acch)$_3$. $LaCl_3$ (0.50 g, 2.04 mmol), 4.4 mL of MeLi (1.4 M in diethylether, 6.16 mmol) and 0.80 mL (5.97 mmol) of acetylcyclohexanone (acchH) were used in the same procedure as described above. The viscous yellow liquid was obtained by removing the solvent under reduced pressure and this liquid was dissolved in 30 mL of benzene to obtain the yellow suspension solution. LiCl was filtered off. Benzene was removed under reduced pressure and 30 mL of hexaned was added to precipitate the yellow solid. The solid was obtained by filtration and washed by 5 mL of hexane three times and dried under vacuum overnight. Yield: 1.12 g (98.2

%), Anal. Calcd. for $LaC_{24}H_{33}O_6+1.3\ C_6H_{14}+5\ H_2O$; C, 51.04; H, 8.19; Found: C, 50.20; H, 8.20, ^1H NMR ($CDCl_3$, 250.133 MHz): 2.30 (br s, 4H), 2.11 (s, 3H), 1.67 (br s, 4H) (CD_3OD) 2.36 (s, 2H), 2.15 (s, 2H), 1.98 (s, 3H), 1.63 (s, 4H) MS (EI): 556.0 (M^+), 417.1 (M-L), 140.1 (L+1), 125.1 (L-Me) IR (KBr pellet): 1600, 1470, 1390, 1355, 1340, 1270, 1170, 1020, 960, 780 DSC: 63.2, 107.5, 153.6, 160.7 (endothermic).

[La(bacH)(bac)$_3$]$_n$. $LaCl_3$ (0.52 g, 2.12 mmol), 4.4 mL of MeLi (1.4 M in diethylether, 6.16 mmol) and 1.00 g (6.16 mmol) of 1-benzoylacetone (bacH) were used in the same procedure as described above. The pale yellow solid was obtained by filtration and washed by 5 mL of cold THF and hexane three times, respectively and the resulting white solid was dried under vacuum overnight. Yield: 0.85 g (51.1%), Anal. Calcd. for $LaC_{40}H_{37}O_8+10\ H_2O$; C, 49.80; H, 5.91; Found: C, 49.45; H, 4.99, ^1H NMR ($CDCl_3$, 250.133 MHz): 7.85 (br d, 4H), 7.46 (br d, 6H), 6.17 (s, 2H), 2.29 (s, 6H); 7.73 (br s, 4H), 7.15 (br s, 4H), 5.87 (s, 2H), 2.19 (s, 6H) (total 1 : 1) (CD_3OD) 7.88 (d), 7.33 (m), 2.00 (s) MS (EI) 782.5 (M^+-1), 460.97 (M-2 bac), 301.0 (M-3 bac), 162.09 (bacH), 105.12 (bac-CH_3COCH) IR (KBr pellet): 1580, 1555, 1475, 1440, 1390, 1370, 1295, 1265, 1190, 1165, 1015, 990, 945, 830, 790, 750, 700, 660, 490 DSC: 78, 259.3, 273.8, 292.2, 335.7 (endothermic), 238.2 (exothermic).

[La(accpH)(accp)$_3$]. $LaCl_3$ (1.00 g, 4.08 mmol), 8.8 mL of MeLi (1.4 M in diethylether, 12.3 mmol) and 1.50 mL (12.1 mmol) of 2-acetylcyclopentanone (accpH) were used in the same procedure as described above. The yellow viscous liquid was obtained by removing the solvent under reduced pressure. The liquid was dissolved in 30 mL of benzene again and LiCl was filtered off. Benzene was removed under reduced pressure and 30 mL of hexane was added to produce yellow suspension solution. The yellow solid was obtained by filtration and washed by 5 mL of hexane three times and dried under vacuum overnight. Yield: 1.92 g (73.7%), Anal. Calcd. for $LaC_{28}H_{36}O_8+0.3\ C_6H_{14}+4\ H_2O$: C, 48.54; H, 6.68; Found: C, 47.80; H, 6.58, ^1H NMR ($CDCl_3$, 250.133 MHz): 2.60-2.30 (br m, 16H), 2.31 (s, 1H), 1.97 (s, 6H), 1.86 (s, 6H), 1.69 (br m, 8H) (CD_3OD) 5.60 (s), 2.00 (s) MS (EI): 636.74 (M-2), 620.8 (M-Me-3), 604.88 (M-Me-O-3), 470.9 (M-L-3Me+2), 444.9 (M-L-3Me-C_2H_3), 394.93 (M-L-3Me-C_2H_2-2C), 336.94 (M-2L-2C+2), 310.9 (M-2L-2C_2H_2), 85.15 (C_5H_8O+1), 69.14 (C_4H_5O) (FAB) 1485 (2M+2 accp-MeCO), 1403 (2 M+accp), 1323 (2 M+MeCO+3), 1277 (2 M), 1163 (2 M-accp+Me-4), 1029 (2 M-2 accp+2), 765 (M+accpH), 639 (M) IR (KBr pellet): 1610, 1580, 1530, 1460, 1420, 1360, 1290, 1220, 1190, 1130, 1000, 950, 785, 720, 550 DSC: 90.5 (endothermic), 160, 215, 264.1 (exothermic).

La(abl)$_3$. $LaCl_3$ (1.00 g, 4.08 mmol), 8.8 mL of MeLi (1.4 M in diethylether, 12.3 mmol) and 1.35 mL (12.4 mmol) of 2-acetylbutyrolactone (ablH) were used in the same procedure as described above. The off-white solid was obtained by filtration and washed by 5 mL of THF three times and dried under vacuum overnight. Yield: 1.53 g (72.0%), Anal. Calcd. for $LaC_{18}H_{21}O_9+C_4H_8O+H_2O$: C, 43.26; H, 5.08; Found: C, 43.80; H, 4.90, ^1H NMR ($CDCl_3$, 250.133 MHz): 4.27 (m, 6H), 3.67 (m, 3H), 2.70 (m, 3H), 2.38 (s, 9H), 2.25 (m, 3H) (CD_3OD) 4.24 (t, 6H), 2.87 (t, 6H), 1.12 (m, 3H), 1.85 (br s, 9H) MS (EI) 519.6 (M^+), 489.1 (M-2Me), 355.1 (M-3CH_3COC), 281.1 (M-L-2MeCOCH), 267.1 (M-L-2MeCOCH-CH_2), 207.1 (La+CO_2C_2), 127.2 (L), 71.3 (CO_2CHCH_2) IR (KBr pellet): 1650, 1520, 1370, 1250, 1140, 1020, 940, 750, 630, 460 DSC: 80 (endothermic), 252.1 (exothermic).

La(at)$_3$. $LaCl_3$ (0.50 g, 2.04 mmol), 4.4 mL of MeLi (1.4 M in diethylether, 6.16 mmol) and 1.15 g (6.11 mmol) of 2-acetyl-1-tetranone (atH) were used in the same procedure as described above. The solvent was removed under reduced pressure to obtain the yellow solid. The yellow solid was suspended by addition of 20 mL of MeOH and isolated by filtration and washed by 5 mL of MeOH three times and dried under vacuum overnight. Yield: 0.95 g (66.4%), Anal. Calcd. for $LaC_{36}H_{33}O_6+C_6H_{14}+1.5\ H_2O$: C, 61.95; H, 6.15; Found: C, 62.15; H, 6.28, ^1H NMR ($CDCl_3$, 250.133 MHz): 7.96 (br d, 3H), 7.26 (m, 9H), 2.88 (br m, 6H), 2.66 (br m, 6H), 2.24 (s, 9H) (C_4D_8O) 8.16 (d, 3H), 7.29 (m, 9H), 2.87 (d, 6H), 2.77 (d, 6H), 2.19 (s, 9H) MS (EI) 700.2 (M^+), 212.3 (La+$CO_2CH_2CH_3$), 186.2 (L-1), 146.2 ($COPhCH_2CH_2CH_2$), 118.2 ($COPhCH_2$), 90.2 (PhCH), 77.2 (Ph) IR (KBr pellet): 1610, 1590, 1560, 1460, 1420, 1380, 1350, 1320, 1290, 1260, 1195, 1030, 990, 900, 840, 740, 540.

La(hbp)$_3$. $LaCl_3$ (0.50 g, 2.04 mmol), 4.4 mL of MeLi (1.4 M in diethylether, 6.16 mmol) and 1.21 g (6.10 mmol) of 2-hydroxybenzophenone(hbpH) were use in the same procedure as described above. The solvent was removed under reduced pressure to produce the yellow solid. The solid was dissolved in 30 mL of benzene again and LiCl was filtered off. The yellow solid was obtained by removing the solvent under reduced pressure. Hexane (30 mL) was added and the yellow solid was obtained by filtration and washed by 5 mL of hexane three times and dried under vacuum overnight. Yield: 1.24 g (83.2%), Anal. Calcd. for $LaC_{39}H_{27}O_6+1.2\ C_6H_{14}+H_2O$: C, 65.14; H, 5.38; Found: C, 65.68; H, 5.54, ^1H NMR ($CDCl_3$, 250.133 MHz): 7.36 (br s), 7.26 (br s) (total 21H), 6.85 (br s, 6H) MS (EI) 729.0 (M-1), 195.1 (L-2), 181.1 (L-OH), 121.1 (L-Ph), 105.1 (PhCO), 89.1 (PhC), 77.1 (Ph) IR (KBr pellet): 1605, 1570, 1525, 1465, 1435, 1330, 1230, 1140, 1110, 1005, 920, 830, 695, 640, 590.

La(hba)$_3$. $LaCl_3$ (1.00 g, 4.08 mmol), 8.8 mL of MeLi (1.4 M in diethylether, 12.3 mmol) and 1.30 mL (12.0 mmol) of 2-hydroxybenzaldehyde(hbaH) were used in the same procedure as described as above. The yellow viscous liquid was obtained by removing the solvent under reduced pressure. The compound was dissolved in 20mL of benzene and LiCl was filtered off. Benzene was removed under reduced pressure and the yellow solid was suspended in 30 mL of hexane and the solid was obtained by filtration and washed by 5 mL of hexane three times and dried under vacuum overnight. Yield: 1.61 g (78.5%), Anal. Calcd. for $LaC_{21}H_{15}O_6+0.6\ C_6H_{14}$: C, 53.33; H, 4.23; Found: C, 53.30; H, 4.20, ^1H NMR ($CDCl_3$, 250.133 MHz): 7.50 (br m, 6H), 6.96 (br m, 6H), 9.90 (br s, 3H) (CD_3OD) 9.91 (s, 2H), 7.20 (dd, 4H), 6.64 (dd, 4H); 7.41 (d, 2H), 7.32 (s, 2H), 7.00 (t, 2H), 6.52 (t, 2H) MS (EI) 620.9 (M-2), 595.4 (M-CO), 409.2 (M-L-PhO+2) IR (KBr pellet): 1650, 1600, 1525, 1545, 1530, 1410, 1310, 1240, 1170, 1140, 1015, 885, 750, 730, 650.

[La(hnaH)(hna)$_3$]$_n$. $LaCl_3$ (0.53 g, 2.05 mmol), 4.4 mL of MeLi (1.4 M in diethylether, 6.16 mmol) and 1.08 mL (6.29 mmol) of 2-hydroxy-1-naphthaldehyde(hnaH) were used in the same procedure as described above. The pale green solid was obtained by removing the solvent under reduced pressure and the yellow solid was produced by removing the unreacted ligand from vacuum distillation in the range

of 50 and 135 ℃. Yield: 0.98 g (58.0%), mp: 257-260 ℃ (air) (decomp. temp.) Anal. Calcd. for $LaC_{44}H_{29}O_8$: C, 63.60; H, 4.24; Found: C, 64.04; H, 3.85, ^1H NMR ($CDCl_3$, 250.133 MHz): 13.14 (s), 10.80 (s), 8.35-7.12 (m) IR (KBr pellet): 1620, 1590, 1535, 1460, 1425, 1390, 1365, 1305, 1250, 1180, 975, 835, 740.

La(1-han)$_3$. $LaCl_3$ (0.50 g, 2.04 mmol), 4.4 mL of MeLi (1.4 M in diethylether, 6.16 mmol) and 1.13 g (6.07 mmol) of 1-hydroxy-2-acetonaphthone(1-hanH) were used in the same procedure as described above. The yellow viscous liquid was obtained by removing the solvent under reduced pressure. The liquid was dissolved in 20 mL of benzene again and LiCl was filtered off. Benzene was removed under reduced pressure and 30 mL of hexane was added to produce yellow suspension solution. The yellow solid was obtained by filtration and washed by 5 mL of hexane three times and dried under vacuum overnight. Yield: 1.28 g (90.1%), Anal. Calcd. for $LaC_{36}H_{27}O_6+0.6\ C_6H_{14}+6\ H_2O$: C, 55.64; H, 5.55; Found: C, 55.70; H, 5.60, ^1H NMR (CD_3OD, 250.133 MHz) 8.44 (d, 3H), 7.60 (d, 3H), 7.53 (d, 3H), 7.42 (m, 3H), 7.20 (m, 3H), 6.69 (d, 3H), 1.59 (s, 9H) MS (EI): 695.65 (M+1), 655.48 (M-2Me-C+3), 509.52 (M-L), 262.06 ($La+C_{10}H_4$), 281.06 ($La+C_{10}H_4O$), 186.09 (L+1), 171.06 (L-Me+1), 144.07 (L-MeCO+1), 115.12 (L-MeCO-CO+1), 89.13 (C_7H_5) IR (KBr pellet): 1620, 1590, 1520, 1495, 1440, 1420, 1380, 1340, 1245, 1200, 1140, 1080, 1020, 980, 890, 780, 730, 680, 570.

La(2-han)$_3$. $LaCl_3$ (0.50 g, 2.04 mmol), 4.4 mL of MeLi (1.4 M in diethylether, 6.16 mmol) and 1.05 g (5.64 mmol) of 2-hydroxy-1-acetonaphthone(2-hanH) were used in the same procedure as described above. The yellow solid was obtained by filtration and washed by 5 mL of THF, cooled at 0 ℃, three times and dried under vacuum overnight. Yield: 0.82 g (57.7%), Anal. Calcd. for $LaC_{36}H_{27}O_6+0.6\ C_4H_8O+2\ H_2O$: C, 59.56; H, 4.63; Found: C, 60.00; H, 4.60, ^1H NMR (CD_3OD, 250.133 MHz): 8.0 (d, 3H), 7.60 (m, 6H), 7.25 (m, 3H), 7.05 (d, 3H), 1.86 (s, 9H) MS (EI): 675.7 (M-OH-2), 650.7 (M-MeCO-1), 511.2 (M-L+2), 478.2 (M-L-2Me-1), 186.09 (L+1), 171.06 (L-Me+1), 144.07 (L-MeCO+1), 115.12 (L-MeCO-CO+1), 89.13 (C_7H_5) IR (KBr pellet): 1620, 1530, 1500, 1450, 1420, 1370, 1340, 1300, 1245, 1200, 1020, 820, 730.

La(hap)$_3$. $LaCl_3$ (1.00 g, 4.08 mmol), 8.8 mL of MeLi (1.4 M in diethylether, 12.3 mmol) and 1.50 mL (12.3 mmol) of 2-hydroxyacetophenone(hapH) were used in the same procedure as described above. Half of the solvent was removed under reduced pressure. 10 mL of ether was added to this solution and the yellow solid was obtained by filtration and washed by 1 : 1 solution of ether/THF three times and dried under vacuum overnight. Yield: 1.63 (73.4%), Anal. Calcd. for $LaC_{24}H_{21}O_6+2\ H_2O$: C, 49.66; H, 4.31; Found: C, 50.30; H, 4.00, ^1H NMR (CD_3OD, 250.133 MHz): 7.80 (br d, 3H), 7.48 (br d, 3H), 6.91 (br m, 6H), 2.60 (s, 9H) MS (EI): 527.4 (M-Me), 480.6 (M-2MeC-C+2), 429.1 (M-2MeCO-MeC+2), 355.2 (M-L-2MeC), 341.1 (M-L-MeCO-MeC+2), 194.3 (La+2CO-1), 165.3 (La+CO-2), 136.2 (L+1), 121.2 (L-Me), 93.2 (L-MeCO), 77.3 (Ph), 65.3 (C_5H_5) IR (KBr pellet): 1630, 1590, 1530, 1460, 1435, 1350, 1320, 1255, 1220, 1150, 1120, 1020, 950, 840, 750, 730, 705, 605, 575.

La(hfa)$_3$. $LaCl_3$ (0.50 g, 2.04 mmol), 8.8 mL of MeLi (1.4 M in diethylether, 12.3 mmol) and 1.80 mL (6.29 mmol) of 1,1,1,5,5,5-hexafluoroacetylacetone(hfaH) were used in the same procedure as described above. The yellow viscous liquid was obtained by removing the solvent under reduced pressure. The liquid was dissolved in 30 mL of hexane again and the white solid (1.42 g) was obtained by filtration and washed with 5 mL of hexane three times. This solid was dissolved in the boiling ethylacetate again and LiCl was filtered off. The solvent was removed under reduced pressure and the white solid was dried under vacuum overnight. Yield: 0.71 g (45.8%), Anal. Calcd. for $LaC_{15}F_{18}H_3O_6+C_4H_8O_2$: C, 26.89; H, 1.30; Found: C, 27.10; H, 0.70, ^1H NMR (CD_3OD, 250.133 MHz) 5.73 (s, 3H) MS (EI): 707.36 (M-OF2-1), 667.36 (M-CF_3CC), 558.64 (M-2CF_3-C_2F_2+2), 469.83 (M-3CF_3CO+1), 427.95 (La+3CF_3+2CHCO), 358.97 (La+2CF_3+2CHCO), 286.95 (La+CF_3+2CCO-1), 221.01 (La+2CHCO), 145.04 ($CF_3C_2HFO_2$), 138.9 (La), 119.05 ($CF_2C_3HO_2$), 69.16 (C_3HO_2) IR (KBr pellet): 1655, 1610, 1565, 1530, 1485, 1255, 1205, 1185, 1145, 800, 660, 585.

La(hbta)$_3$. $LaCl_3$ (0.50 g, 2.04 mmol), 4.4 mL of MeLi (1.4 M in diethylether, 12.3 mmol) and 1.00 g (6.13 mmol) of 3-hydroxy-1,2,3-benzotriazine(hbtaH) were used in the same procedure as described above. The greenish yellow solid was obtained by filtration and washed by 5 mL of cold THF three times and dried under vacuum overnight. Yield: 0.95 g (74.2%), Anal. Calcd. for $LaC_{21}H_{12}N_9O_6+3\ H_2O$: C, 37.10; H, 2.65; Found: C, 37.30; H, 2.60, ^1H NMR (CD_3OD, 250.133 MHz) IR (KBr pellet): 1615, 1485, 1465, 1365, 1290, 1245, 1190, 1070, 980, 900, 765, 700, 695, 500.

La(hnq)$_3$. $LaCl_3$ (1.00 g, 4.08 mmol), 8.8 mL of MeLi (1.4 M in diethylether, 12.3 mmol) and 2.13 g (12.2 mmol) of 2-hydroxy-1,4-naphthoquinone(hnqH) were used in the procedure as described above. The red solid was obtained by filtration and washed by 5 mL of cold THF three times and dried under vacuum overnight. Yield: 1.75 g (65.1%), Anal. Calcd. for $LaC_{30}H_{15}O_9+7\ H_2O$: C, 45.90; H, 3.70; Found: C, 45.70; H, 3.40, ^1H NMR (CD_3OD, 250.133 MHz) 7.96 (m, 6H), 7.74 (t, 3H), 7.56 (m, 6H) MS (EI): 523.7 (M-Ph$C_2O_2H_2$-1), 409.5 (M-L-Ph), 368.5 (M-L-PhCOC-1), 313.4 (M-2L+1), 279.3 (La+2$C_3O_2H_2$+1), 256.4 (La+2$C_2O_2H_2$+1), 171.2 (L-2), 155.3 (L-O-2), 115.2 (PhCOC-1), 97.3 (C_4O_3H), 69.3 (C_3O_2H), 57.3 (C_2O_2H) IR (KBr pellet): 1650, 1580, 1555, 1475, 1380, 1340, 1270, 1120, 985, 840, 780, 750.

Results and Discussion

Historically, the syntheses of volatile lanthanum β-diketonate compounds were initially investigated for the purpose of separation of rare earth metals but the same studies are required for the preparation of precursors of the modern electronic materials in these days. Berg reported that lathanum acetylacetonate did not sublime and this was attributed to the higher polarity of the hydrates. Therefore, he expected that anhydrous complexes would sublime significantly. However, every try to remove coordinated water molecules in the presence of desiccants have failed and this was explained by the fact that initial removal of water and β-diketone induces the formation of a basic compounds followed by the formation of polynuclear species by the reaction among these basic compounds.[11] It also reported that lanthanum β-diketonates with fluorinated alkyl groups such as La(hfa)$_3$ or bulky alkyl groups such as La(dpm)$_3$ showed increased thermal stability and volatility as mentioned above. Lanthanum com-

pounds generally show the lower volatility than other lanthanide metal complexes. In the lanthanide series, it is well known that the volatility of metal β-diketonates increases with the increase of atomic weight and this is due to the decrease of ionic radius (lanthanide contraction). The structure of $La(acac)_3(H_2O)_2$ was determined to have a distorted square antiprism[12] and it is assumed that molecules have hydrogen bonds among zigzag chains in the [101] orientation. (between H atom of Me of acetylacetonate and O atom of coordinated water) Based on this structure, it is expected that increased volatility would be achieved with the structure where the hydrogen bond is unfavorable. One strategy for this structure is to the sysnthesis of anhydrous complexes and the other one is the change of substituents of β-diketone to decrease the partial positive charge of hydrogen of a carbonyl group. In this study, a general preparative method for the lanthanum β-diketonate compounds (equation 1) with high yield, easiness of purification and short reaction time were designed under these strategies. Synthesis of anhydrous complexes can be achieved by employing the extensive anhydrous reaction conditions. (anhydrous $LaCl_3$, solvents, dry glasswares and dry nitrogen atmosphere) However, in some cases, these reaction conditions induced the oligomeric compounds instead of anhydrous monomeric ones. Table 1 shows the m.p.'s and yields of lanthanum β-diketonate compounds prepared in this study and available reported data are included for comparison. Yields of these compounds are moderate to high except dpm, tfa, and hfa complexes. Crude product yields of these compounds are rather high but optimal purification processes were not found yet. Compounds were classified by the number of ligands per metal. Class I compounds are believed to have 4 ligands per metal atom, while class II ones have 3 ligands. Class III is assigned to the compounds that are not able to be classified as a conven-

Table 1. Characteristic Temperatures of Lathanum β-diketonates

Class		β-diketones		yield	m.p.	decomp.	m.p.(℃)
		R1	R2	(%)	(℃)	temp.(℃)	(literature)[14]
I		Me (acac)	Me	62.8		274-275	150-152(dihydrate)
						276-278*	142-143(tri ∻)
		Me (bac)	Ph	51.1	227-228		
					244-245*		
		Me (accp)	$CH_2CH_2CH_2$	73.7	186-188		
					188-189*		
		H (hna)	$CHCH\text{-}C_6H_4$	58.0		257-260	
II	1	Me (acch)	$(CH_2)_4$	98.2	175	350	
					180*		
		Me (abl)	$O\text{-}CH_2CH_2$	72.0		253-256	
						257-258*	
		Me (at)	$CH_2CH_2\text{-}C_6H_4$	66.4	218-220		
					220-221*		
		Me (1-han)	$CHCH\text{-}C_6H_4$	90.1		279-282	
						269-271*	
		Me (2-han)	$CHCH\text{-}C_6H_4$	57.7		328-330	
						318-320*	
		Me (hap)	CHCHCHCH	73.4		299-302*	
		H (hba)	CHCHCHCH	78.5		180	
						170*	
		Ph (bpp)	Ph	68.5	99-102	230	142-143(monomer)
					96-99*		
		Ph (hbp)	CHCHCHCH	83.2		155-159*	
	2	Me (tfa)	CF_3	27.5 (68.2)[1]		232-235	142-144(dihydrate)
						243-246*	
		CF_3 (hfa)	CF_3	45.8 (78.7)[1]		300	143-146(dihydrate)
		t-Bu (dpm)	t-Bu	32.1 (87.9)[1]	229-230		238-248(dimer)
					238-241*		148-149(monomer)
III		$CHCHCHCN_3$	74.2		200		
		(hbta)			200*		
		C_6H_4CO	65.1		230		
		(hnq)			240*		

1 yield of crude products. *measured in a N_2 atmosphere. m.p. without *: measured in air.

tional β-diketone or β-hydroxyketone or β-hydroxyaldehyde but closely related. Generally, class I and II-2 compounds show higher melting points than the reported ones most probably due to formation of oligomeric products. However, exact numbers of monomer in the products cannot be determined even by the FAB techniques of MS in some compounds. The structure of these compounds cannot be clearly determined by a NMR spectroscopy due to poor solubility in the common organic solvents. However, these complexes showed 2 different Me peaks whose ratio was 3 : 1 in acac while 1 : 1 in bac and accp and 2 : 1 in tfa compounds. Therefore, it can be concluded that the structures of oligomeric products are dependent on the nature of ligand. Due to lack of high resolution mass spectra and limited ranges of mass spectra obtained in some cases, exact mass of these complexes were not obtained but other physical properties such as melting points, solubilities, fragmentation patterns of mass spectra strongly indicate the oligomeric nature of these compounds. These oligomeric complexes were not hygroscopic, which might indicate that coordinating sites are filled. Melting points of these complexes were not sharp but rather broad, which is generally reported. Effect of the substituents on the thermal properties is not clear but contrary to the reported general trends,[3(b)] introduction of phenyl groups generally leads to decrease of m.p. The melting point of bpp complex is lower than that of bac one, which is lower than that of acac one. Lathanum bpp complex showed higher decomposition temperature (230 ℃) which is higher by more than 100 ℃ than m.p. This property is desirable to transfer reliable amount of precursors to the CVD chamber without decomposition. However, high hygroscopic nature of this compound represents that these properties are not due to bulkiness of phenyl group, which might prevent water molecules from coordination. This might be explained by the decrease of partial positive charge on the hydrogen atom of phenyl group caused by the change of hybridization from sp^3 to sp^2, which induces stronger covalency. Berg[13] also reported the increase of volatility in some metal β-diketonates due to delocalization of charge through resonance with the introduction of aromatic rings. Also, ring formation by connecting the carbonyl carbon and central carbon located between carbonyl groups induced the decrease of m.p. Compounds with six member ring appears to have lower m.p. and higher thermal stability than 5-member ring ones. Lathanum acch and accp compounds showed this trend and inclusion of oxygen atom into a back bone(abl) resulted in lower thermal stability (no defined m.p.). Lathanum at and han compounds showed that thermal properties can be modified by the hybridization of backbones (sp^3 *vs.* sp^2). Relative positions of substituents also appear to change the thermal properties as shown in cases of 1- and 2-han complexes. New complexes in class III did not produce any potential precursors. The β-hydroxyketone compounds were generally more stable than β-hydroxyaldehyde ones. Higher stability toward moisture and oxygen in β-diketone complexes were observed than that in β-hydroxyketone or β-hydroxyaldehyde ones. No appreciable change in IR spectra with change of substituents of β-diketones was observed. Any generalized fragmentation patterns of the complexes in the mass spectra cannot be derived but Me groups, if presented, appears to be dissociated easier than other groups. DSC diagrams in this study were very complicated. This can be attributed to the characteristic thermal property of lanthanum β-diketonates, softening and melting in the wider range. Table 2 showed the thermal decomposition behaviors of the lanthanum β-diketonates determined by TGA diagram. Compounds were classified by residual weight % around 700 ℃. Type A showed less weight % than theoretical one while residual weight % of type B was much higher than theoretical value. Type C was assigned to the behavior of class III compounds in Table 1. Residual amount of abl, hfa, and dpm complexes were significantly less than the theoretical values and this was attributed to the concurring sublimation. Therefore, in the case of abl complexes, the data was modified assuming the final residue is only La_2O_3. Lathanum hfa and dpm compounds appeared to be sublimed significantly in the experimental conditions and this may reflect why these compounds are widely used as CVD precursors. However, this property as a potential CVD precursor may play in an adverse way from the economic point of view. In other words, ceramic yield of these compounds would be very low and most of them would be removed without deposition on the substrate because a CVD chamber is maintained in a low pressure. From this point of view, Lathanum bpp complexes are desirable because the decomposition rate appears to be much faster than the sublimation one and loss by sublimation can be minimized. However, the temperature required for the complete decomposition is rather high and the introduction of external oxidizing agents such as oxygen appears to be needed. Preparation of La_2O_3 or PLT thin films by using $La(bpp)_3$ is under progress. A plausible pyrolysis mechanism of these complexes is proposed based on the analysis of TGA diagram. As shown in Table 2, La_2O_3 was produced by the consecutive dissociation of R, CO, CH, C, and O. Despite of the diversity in the substituents, almost the same dissociation pathway to the lanthanum oxides appears to be applicable in this series of complexes. Me groups dissociate than any other ones. Ph or CF_3 are expected to be hard to be dissociated due to stronger C-C bonds. Pyrolysis pattern of the compounds with a ring is rather complicated. However, substituents on the carbonyl carbon atom dissociate earlier than one on the CH carbon. In these compounds, C-O bond dissociation may occur more easily than in other acyclic compounds probably due to the formation of more stable ring fragments. Decomposition temperatures of compounds with aromatic or cyclic group tends to be higher as mentioned above. However, for the more accurate deduction of the pyrolysis mechanism of these compounds, a TGA coupled with mass detector for the analysis of the fragments is required.

Conclusion

In this study, a new synthetic method for the lanthanum -diketonates *via in-situ* formed lanthanum alkyl complexes were developed and a series of new lanthanum β-diketonates were prepared and analyzed by spectroscopic and thermal analyses. This method was designed to synthesize anhydrous complexes, which are expected to have higher volatility than hydrated ones by eliminating the hydrogen bonds associated with coordinated water molecules. This method was found to have several advantages; short reaction time, easy purification, moderate to high yield, and easy production of anhyd-

Table 2. TGA Data of Lanthanum β-diketonates

Type	Class	Ligand	-R	-CO	-CH	-C	-O	Finalresidue Wt. %	Theory
A	II-1	bpp	250.93 9.44(9.52) (Ph) 470.00 47.20(47.61) (5 Ph)	603.33 19.20(19.66) (3CO+CH+C)	691.47 4.44(2.97)	4.44(2.97) (1.5O)		20.36	20.16
		abl	271.27 44.40(41.51) ($3CO_2CH_2CH_2$) 497.55 20.80(22.49) (C_2CH_3)			717.79 11.60(4.61) (1.5O)		23.20	31.31
		abl[1]	271.27 24.96(24.79) (3MeCO) 497.55 28.08(25.37) (3 OCH_2CH_2)			717.79 23.76 (18.45) ($3C_2$+1.5O)	31.31	31.31	
	II-2	hfa						3.06	21.43
		dpm						1.98	23.65
B	I	acac	117.0 2.67(2.80) (Me)	335.0 44.00(42.92) (7Me+4CO+CH)	557.5 6.66(7.28) (3CH)	730.0 3.67(5.22) (CO)		43.00	30.40
		bac	185.77 7.43(7.65) (4Me) 293.33 27.90(29.47) (3Ph) 353.33 9.00(9.82) (Ph)	402.69 10.67(10.72) (3CO) 509.86 4.33(3.57) (CO)		689.90 6.62(6.63) (4CH)		34.05	20.78
		accp	85.66 9.20(9.37) (4Me) 282.5 38.93(41.22) (4 c-(C_5H_8))	690.38 18.20(17.49) (4CO)				33.67	25.43
	II	acch	156.67 8.67(8.08) (3Me) 548.69 34.03(36.66) ($3C_5H_8$)	273.33 17.33(15.10) (3CO)	285.00 4.67(7.01) (3CH)	689.90 2.91(2.88) (O)		31.06	29.28
		at	199.05 5.55(6.42)(3Me) 591.67 36.72(37.68)($3PhCH_2$) 691.58 3.18(4.00)($2CH_2$)					54.55	23.25
B	II-1	1-han	236.67 7.24(6.48) (3Me) 605.83 32.23(32.83) ($3C_6H_4$) 691.18 3.67(3.74) (2CH)					56.86	23.46
		2-han	133.78 2.16(2.16) (Me) 689.06 50.55(48.38) (2Me+3PhCHCH)					47.39	23.46
		hap	175.83 3.02(2.76) (3Me) 346.67 22.79(24.61) (2Me+PhCO) 688.22 20.18(19.11) (PhCO)					54.01	29.93

Table 2. Continued

Type	Class	Ligand	-R	-CO	-CH	-C	-O	Finalresidue Wt. %	Theory
		hbp	107.40 10.48(10.54) (Ph) 270.91 11.13(10.54) (Ph) 556.68 39.05(39.01) (Ph+2PhCO)	691.59 2.44(3.83) (CO)				36.90	22.30
		hba	322.58 18.08(17.32) (PhCH) 690.97 16.58(17.32) (PhCH)					65.34	32.43
	II-2	tfa	85.80 9.00(7.53) (3Me) 293.51 25.67(23.08) ($2CF_3$)	691.45 7.90(9.37) (2CO)				57.43	27.25
C	III	hnq	225.00 10.67(11.54) (C_6H_4) 610.00 15.00(14.76) (C_4HO_3) 690.99 5.38(6.23) (C_2HO)					68.95	24.74

Data were obtained in the nitrogen flow of 10 mL/min. Numbers are represented temperature, experimental weight loss, and theoretical weight loss, respectively. Numbers and chemical formula in a parenthesis represent the fragment lost. [1]modified data assuming the final residue is $1/2La_2O_3$.

rous compounds. However, in some cases, oligomeric products with even higher melting points than the reported one were prepared. Introduction of an aromatic ring or a cyclic fragment in a ligand induced higher thermal and moisture stability and lower melting points of the lanthanum β-diketonates. Lanthanum bpp(1,3-biphenyl-1,3-propanedione) complexes were found to have desirable properties as a MOCVD precursor for the lanthanum oxides such as lower m.p., higher decomposition temperature, and thermal and moisture stability. However, rather higher temperature for the complete decomposition of this complex required the oxidizing agents. Analysis of TGA diagrams of these complexes indicates that consecutive dissociation of R, CO, CH, C, and O occurs during the pyrolysis.

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Synthesis and Characterization of Dodecanucleotides Containing the XhoI Recognition Sequence with a Phosphorothioate Group at the Cleavage Site

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The synthesis and characterization of diastreomeric dodecanucleotides, d[GATC$_{p(S)}$TCGAGATC], containing recognition sequence of the XhoI restriction endonuclease with a phosphorothioate internucleotidic linkage the cleavage site are described. R_p and S_p form of diastereomerically pure dinucleoside phosphorothioates d[C$_{p(S)}$T] were presynthesized and used for the addition to the growing oligonucleotide chain as a block. The stereochemistry of dinucleoside phosphorothioate was assigned by ^{31}P NMR spectroscopy, enzyme digestion, and reverse-phase HPLC. XhoI restriction endonuclease cut only R_p diastereomer d[GATC$_{p(S)}$TCGAGATC]. The rate of hydrolysis is slower than that of the unmodified dodecamer d[GATCTCGAGATC]. The phosphorothioate nucleotide is using for determination of the stereochemical course of the XhoI catalyzed reaction.

Introduction

Type II restriction endonucleases[1] catalyze the cleavage of double stranded DNA at sequence-specific sites typically 4-6 base pairs in length. Although these enzymes are immensely important in genetic engineering, not much mechanistic information is available.[2] Progress in understanding how these enzymes recognize and cut the sequence-specific sites of DNA has been aided by the crystal structures of both the EcoRI[3,4] and the EcoRV endonuclease.[5,6] Recent advances in the efficient synthesis of small oligonucleotides have made it possible to undertake a variety of mechanistic investigations with these enzymes. It has been known that certain restriction enzymes including EcoRI are capable of cleaving phosphorothioate internucleotidic lingkages when incorporated into the (−) strand of fd DNA, although at reduced rate. It is, therefore, possible to determine the streochemical course of the such an enzyme catalyzed reaction providing we could synthesize an oligonucleotide containing the appropriate recognition sequence with a phosphorothioate internucleotidic linkage of known absolute configuration at cleavage site. Restriction endonuclease catalyzed hydrolysis in the presence of $H_2{}^{18}O$ and subsequent nuclease P1 cleavage of the reaction products should furnish a deoxynucleoside 5′-[^{18}O]-phosphorothioate whose absolute configuration should be amenable to stereochemical analysis by ^{31}P NMR spectroscopy.[7] The knowledge of whether such an enzymatic reaction proceeds with retention or inversion of configuration at phosphorous provides evidence for or against the existence of a covalent enzyme intermediate and thus limits the number of mechanisms that can be proposed for an enzymatic reaction. Using phosphorothioate nucleotides, stereochemical course of reactions catalyzed by restriction endonucleases EcoRI[8] and EcoRV[9] were determined to be inversion of configuration at phosphorus, respectively. It is known that a structural homology between EcoRI[3], and EcoRV[10] in the vicinity of the phosphorus to be cleaved was noticed, consisting of four amino acids located in a similar steric arrangement. It was also demonstrated that the two acidic amino acids of this homologous region are important for catalysis. It was concluded, therefore, that the general mechanism of both enzymes is similar, including the same stereochemical course of reaction.[10]

We are interested whether other restriction endonucleases catalyze reactions with inversion of configuration at phosphorous as EcoRI and EcoRV did. We wish to describe here the synthesis and characterization of diastreomeric dodecanucleotides, d[GATC$_{p(S)}$TCGAGATC] (Figure 1), which con-

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**Abbreviations used are as follows: Bz, Benzoyl; DCPh, 2,5-dichlorophenyl; DMTr, 4,4′-dimethoxytrityl; DTT, dithiothreitol