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## Study on the Development of CVD Precursors I-Synthesis and Properties of New Titanium $\beta$ -Diketonates

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*Received March 25, 1996*

Preparation and properties of potential CVD (Chemical Vapor Deposition) precursors for the  $\text{TiO}_2$ , a major component of the perovskite materials such as PT, PLT, PZT, and PLZT were investigated. Reactions between  $\beta$ -diketonates and  $\text{TiMe}_3$ , formed in situ failed to produce stable  $\text{Ti}(\beta\text{-diketonate})_3$  complexes but a stable purple solid, characterized as  $(\text{OTi}(\text{BPP})_2)_2$  (BPP=1,3-biphenyl-1,3-propanedione) was obtained when BPP was used. Several new  $\text{Ti}(\text{Oi-Pr})_2(\beta\text{-diketonate})_2$  complexes with aromatic or ring substituents were synthesized by the substitution reaction of  $\text{Ti}(\text{Oi-Pr})_4$  by  $\beta$ -diketonates and characterized with  $^1\text{H}$  NMR, IR, ICP, and TGA. Solid complexes such as  $\text{Ti}(\text{Oi-Pr})_2(\text{BAC})_2$  (BAC=1-phenyl-2,4-pentanedione),  $\text{Ti}(\text{Oi-Pr})_2(\text{BPP})_2$ ,  $\text{Ti}(\text{Oi-Pr})_2(\text{1-HAN})_2$  (1-HAN=2-hydroxy-1-acetonaphthone),  $\text{Ti}(\text{Oi-Pr})_2(\text{2-HAN})_2$  (2-HAN=1-hydroxy-2-acetonaphthone),  $\text{Ti}(\text{Oi-Pr})_2(\text{ACCP})_2$  (ACCP=2-acetylcyclopentanone), and  $\text{Ti}(\text{Oi-Pr})_2(\text{HBP})_2$  (HBP=2-hydroxybenzophenone) were found to be stable toward moisture and air.  $\text{Ti}(\text{Oi-Pr})_2(\text{ACCP})_2$  and  $\text{Ti}(\text{Oi-Pr})_2(\text{HBP})_2$  were proved to have lower melting points and higher decomposition temperatures. However, these complexes are thermally stable and pyrolysis under an inert atmosphere resulted in incomplete decomposition.  $\text{Ti}(\text{Oi-Pr})_2(\text{DPM})_2$  (DPM=dipivaloylmethane) and  $\text{Ti}(\text{Oi-Pr})_2(\text{HFAA})_2$  (HFAA=hexafluoroacetylacetone) were sublimed substantially during the thermal decomposition. Pyrolysis mechanism of these complexes are dependent on type of  $\beta$ -diketonate but removal of Oi-Pr ligands occurs before the decomposition of  $\beta$ -diketonate ligands.

### Introduction

Recent development in the information and communication industries demands higher density of dynamic random access memory (DRAM) than ever and it is becoming a consensus that this goal can be achieved only by introducing higher dielectric materials such as  $\text{SrTiO}_3$  or  $(\text{Ba}, \text{Sr})\text{TiO}_3$ .<sup>1</sup> Moreover, Lead titanate ( $\text{PbTiO}_3$ ) based ceramics such as PT, PZT, PLZT and PLT were found to have interesting piezoelectric, pyroelectric, ferroelectric, and electrooptic properties which can be applicable to nonvolatile ferroelectric RAMs, optoelectronic devices, sensors, and transducers.<sup>2</sup> Metal organic chemical vapor deposition (MOCVD) has been investigated as a promising technique for the commercial production of thin films of these ceramics, especially for the better step coverage, easy scale-up, easy control of composition and thickness, and limited diffusion of substrate while many processing techniques are available.<sup>3</sup> The success of this technique requires reliable precursors of high volatility, low toxicity

and high 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  $\beta$ -diketonates are stable toward hydrolysis and temperature, moderately volatile and nontoxic. In the above perovskite structure materials,  $\text{TiO}_2$  is a major component and several alkoxide-based precursors such as  $\text{Ti}(\text{OEt})_4$ ,<sup>2b,4</sup>  $\text{Ti}(\text{Oi-Pr})_4$ ,<sup>1b,5</sup> and  $\text{Ti}(\text{Ot-Bu})_4$ ,<sup>5a</sup> have been used as a thin film precursor but some disadvantages such as moisture sensitivity, step coverage, and possible intermolecular reactions amongst several precursors in the process of transportation in the CVD chamber were pointed out even though these are quite volatile. For the purpose of improving these properties of the precursors, new precursors such as  $\text{Ti}(\text{DPM})_2\text{Cl}_2$ ,  $\text{Ti}(\text{Oi-Pr})_2(\text{DPM})_2$ ,<sup>6</sup> and  $\text{TiO}(\text{DPM})_2$ <sup>1b</sup> were employed. These compounds were chosen for all source materials to have a similar reaction velocity and diffusion coefficient. This may help to have even distribution of composition along the carrier gas flow direction. However, no systematic investigation on the effect of substituents of  $\beta$ -diketonates on the physical properties

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of precursors has been reported. In our group, new precursors for PLT thin films have been investigated and an improved preparative method and properties of new titanium  $\beta$ -diketonates are presented in this paper.

### Experimental

All manipulation were performed under an 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. Reagent grade chemicals including  $\beta$ -diketonates 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.  $^1\text{H}$  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). Metal contents were analyzed by ICP (Lactam 8440) and 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.

**(OTi(BPP)<sub>2</sub>)<sub>2</sub>.** Anhydrous  $\text{TiCl}_3$  (0.48 g, 3.1 mmol) was suspended in 20 mL of  $\text{CH}_2\text{Cl}_2$  and the solution was cooled to  $-78^\circ\text{C}$ . 6.6 mL of 1.4 M MeLi solution was added dropwise to this solution and the solution was warmed up to room temperature and then stirred for 1 hr. This black brown solution was cooled down to  $-78^\circ\text{C}$  again and 15 mL of  $\text{CH}_2\text{Cl}_2$  solution containing 2.09 g of 1,3-biphenyl-1,3-propanedione (BPP, 9.3 mmol) was added to this solution dropwise. (color changes to dark green solution) This solution was warmed up to room temperature again and stirred for 2 hrs. (color changes to green solution) This solution was filtered to remove LiCl with a celite column and the solvent was removed under reduced pressure to obtain a red gel. Brick-red solid was obtained after addition of 40 mL of *n*-hexane and the solid was filtered by a schlenk frit and washed with 5 mL of *n*-hexane three times and dried under vacuum overnight. Yield: 1.20 g (76.9%). mp  $280^\circ\text{C}$  (decomp.). ICP: Ti content 8.34 (theory: 8.62). Anal. Calcd. for  $\text{Ti}_2\text{C}_{60}\text{H}_{44}\text{O}_{10} + 5\text{H}_2\text{O}$ : C, 64.88; H, 4.90; Found: C, 64.30; H, 4.40.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 7.92 (m, 4H), 7.47 (m, 6H), 6.79 (s, 1H). MS (EI) 790 (M-3Ph+1), 742 (M-BPP-2CO+1), 636 (M-2BPP+Ph-O+1), 510 (OTi(BPP)<sub>2</sub>)

\*The product (3 samples) was spread over a weighing paper in air for one day and weighed. Then the product was dried in an oven maintained at  $125^\circ\text{C}$  for 3 hrs and cooled in a desiccator for 30 min and weighed again. The average reduced mass was found to be 8.5%, which corresponds to the 5 molecules of water (theory: 8.1%).

**Ti(Oi-Pr)<sub>2</sub>(BAC)<sub>2</sub>.**  $\text{Ti}(\text{Oi-Pr})_4$  (1.80 mL, 6.10 mmol) was suspended in 20 mL of THF and 0.94 mL (12.3 mmol) of isopropanol and the solution was cooled down to  $-78^\circ\text{C}$ . 15 mL of THF solution containing 1-phenyl-2,4-pentanedione (BAC) (2.05 g, 12.7 mmol) was added to this solution by cannula dropwise and the solution was warmed up to room

temperature and stirred for 2 hrs. Scarlet solution was resulted and the solvent was removed under reduced pressure to obtain dark orange solid. This solid was recrystallized by THF and *n*-hexane and filtered and washed with 5 mL of *n*-hexane three times and dried under reduced pressure for 3 hrs. to obtain pale orange solid. Yield: 2.24 g (75.2%) mp  $107^\circ\text{C}$ ,  $194^\circ\text{C}$  (decomp.). ICP: Ti content 9.28 (theory: 9.81).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 8.01 (br d, 2H), 7.77 (br d, 2H), 7.47-7.33 (m, 6H), 6.24 (br s, 2H), 4.88 (br h, 2H), 2.24 (s), 2.07 (s), 2.02 (s) (total 6H), 1.26 (br s, 12H). MS (EI) 488 (M+), 429 (M- (Oi-Pr)), 370 (M- 2(Oi-Pr)), 327 (M-BAC)

\*The same procedures as above were adopted in the syntheses of the following compounds.

**Ti(Oi-Pr)<sub>2</sub>(BPP)<sub>2</sub>.**  $\text{Ti}(\text{Oi-Pr})_4$  (1.45 mL, 4.90 mmol), isopropanol (0.75 mL, 9.80 mmol) and 1,3-biphenyl-1,3-propanedione (BPP) (0.50 g, 11.7 mmol) were used to produce light yellow solid. Yield: 2.94 g (98.0%) mp  $172^\circ\text{C}$ ,  $273^\circ\text{C}$  (decomp.). ICP: Ti content 7.80 (theory: 7.83).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 8.10 (d, 2H), 7.95 (d, 2H), 7.78-7.17 (m, 12H), 6.86 (s, 2H), 4.89 (h, 2H), 1.27-1.17 (m, 12H),  $J_{\text{H-H}}=6.2$  Hz. MS (EI) 612 (M+), 553 (M- (Oi-Pr)), 494 (M- 2(Oi-Pr)), 389 (M-BPP), 165 (M- 2BPP-1).

**Ti(Oi-Pr)<sub>2</sub>(1-HAN)<sub>2</sub>.**  $\text{Ti}(\text{Oi-Pr})_4$  (1.65 mL, 5.60 mmol), isopropanol (0.86 mL, 11.2 mmol), and 2-hydroxy-1-acetophenone (1-HAN) (2.20 g, 11.8 mmol) were used to produce light yellow solid. Yield: 2.66 g (88.6%) mp  $154^\circ\text{C}$ ,  $165^\circ\text{C}$  (decomp.). ICP: Ti content 8.43 (theory: 8.97).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 8.72 (d, 2H), 7.76-7.04 (m, 10H), 5.72 (br, 2H), 2.25 (s), 1.25 (br s, 12H). MS (EI) 536 (M+), 477 (M- (Oi-Pr)), 418 (M- 2(Oi-Pr)), 351 (M- (1-HAN)).

**Ti(Oi-Pr)<sub>2</sub>(2-HAN)<sub>2</sub>.**  $\text{Ti}(\text{Oi-Pr})_4$  (1.65 mL, 5.60 mmol), isopropanol (0.86 mL, 11.2 mmol), and 2-hydroxy-1-acetophenone (2-HAN) (2.20 g, 11.8 mmol) were used to produce dark yellow solid. Yield: 2.43 g (80.9%) mp  $110^\circ\text{C}$ ,  $114^\circ\text{C}$  (decomp.). ICP: Ti content 9.01 (theory: 8.97).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 7.84-7.29 (m, 12H), 4.90 (h), 4.86 (h) (1 : 4, total 2H), 2.58 (s), 2.53 (s) (1 : 4, total 12H), 1.25 (d), 1.21 (d) (1 : 4, total 12H). MS (EI) 536 (M+), 477 (M- (Oi-Pr)), 418 (M- 2(Oi-Pr)), 351 (M- (2-HAN)).

**Ti(Oi-Pr)<sub>2</sub>(ACCP)<sub>2</sub>.**  $\text{Ti}(\text{Oi-Pr})_4$  (2.13 mL, 7.20 mmol), isopropanol (1.10 mL, 14.4 mmol), and 2-acetylcyclopentanone (ACCP) (2.0 mL, 16.5 mmol) were used to produce pale yellow solid. Yield: 2.60 g (86.7%) mp  $74^\circ\text{C}$ ,  $171^\circ\text{C}$  (decomp.). ICP: Ti content 10.6 (theory: 11.51).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 4.75 (slightly br, h, 2H), 2.60-1.80 (m, 12H), 2.01 (s), 1.92 (s) (5 : 4, total 6H), 1.19-1.12 (two d, 5 : 4, total 12H). MS (EI) 415 (M-1), 357 (M- (Oi-Pr)), 298 (M- 2(Oi-Pr)), 291 (M- ACCP).

**Ti(Oi-Pr)<sub>2</sub>(HBP)<sub>2</sub>.**  $\text{Ti}(\text{Oi-Pr})_4$  (1.20 mL, 3.95 mmol), isopropanol (0.61 mL, 7.91 mmol), and 2-hydroxybenzophenone (HBP) (1.57 g, 7.91 mmol) were used to produce bright yellow solid. Yield: 2.18 g (98.6%) mp  $80^\circ\text{C}$ ,  $147^\circ\text{C}$  (decomp.). ICP: Ti content 8.52 (theory: 8.55).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 7.57-6.67 (m, 18H), 4.90 (h, 2H), 1.20 (d, 12H),  $J_{\text{H-H}}=6.2$  Hz. MS (EI) 560 (M+), 501 (M- (Oi-Pr)), 442 (M- 2(Oi-Pr)), 363 (M-HAP).

**Ti(Oi-Pr)<sub>2</sub>(ACAC)<sub>2</sub>.**  $\text{Ti}(\text{Oi-Pr})_4$  (2.44 mL, 8.20 mmol), isopropanol (1.27 mL, 16.4 mmol), and 2,4-pentanedione (ACAC) (2.02 mL, 16.4 mmol) were used to produce scarlet oil. Yield: 2.83 g (94.7%) mp  $159^\circ\text{C}$  (decomp.). ICP: Ti content 13.0 (theory: 13.15).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 5.51 (s, 2H), 4.78 (h, 2H), 2.05 (s), 2.00 (s) (ratio: 3 : 2, total 12H), 1.20 (d,

12H),  $^3J_{H-H}=6.2$  Hz. MS (EI) 366 (M+2), 305 (M- (O*i*-Pr)), 246 (M- 2(O*i*-Pr)), 265 (M- ACAC), 163 (M- 2ACAC -3).

**Ti(O*i*-Pr)<sub>2</sub>(DPM)<sub>2</sub>.** Ti(O*i*-Pr)<sub>4</sub> (1.66 mL, 5.63 mmol), isopropanol (0.86 mL, 12.3 mmol), and 2,2,6,6-tetramethyl-3,5-heptanedione (DPM) (2.50 mL, 12.0 mmol) were used to produce red solid. Yield: 2.94 g (98.3%) mp 60 °C, 198 °C (decomp.). ICP: Ti content 8.45 (theory: 9.00). <sup>1</sup>H NMR (CDCl<sub>3</sub>) 5.67 (s, 2H), 4.55 (h, 2H), 1.10 (d, 12H)  $^3J_{H-H}=6.2$  Hz, 1.14 (s, 9H), 0.91 (s, 9H). MS (EI) 532 (M+), 473 (M- (O*i*-Pr)), 414 (M- 2(O*i*-Pr)), 349 (M-(DPM)), 166 (M- 2(DPM)).

**Ti(O*i*-Pr)<sub>2</sub>(TFAA)<sub>2</sub>.** Ti(O*i*-Pr)<sub>4</sub> (1.90 mL, 6.36 mmol), isopropanol (1.00 mL, 12.7 mmol), and 1,1,1-trifluoro-2,4-pentanedione (TFAA) (1.85 mL, 15.2 mmol) were used to produce scarlet oil. Yield: 2.92 g (97.3%) mp 113 °C (decomp.). ICP: Ti content 10.1 (theory: 10.15). <sup>1</sup>H NMR (CDCl<sub>3</sub>) 5.87 (br s, 2H), 4.69 (br s, 2H), 2.16 (br s), 2.04 (br s) (ratio 1:2, total 6H), 1.12 (br, d, 12H),  $^3J_{H-H}=6.2$  Hz. MS (EI) 471 (M-1), 413 (M-(O*i*-Pr)), 354 (M- 2(O*i*-Pr)), 319 (M-TFAA), 167 (M- 2TFAA +1).

**Ti(O*i*-Pr)<sub>2</sub>(HFAA)<sub>2</sub>.** Ti(O*i*-Pr)<sub>4</sub> (1.77 mL, 6.00 mmol), isopropanol (0.93 mL, 12.1 mmol), and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (HFAA) (2.00 mL, 14.1 mmol) were used to produce yellow oil. Yield: 3.15 g (90.5%) mp 115 °C (decomp.). ICP: Ti content 8.01 (theory: 8.26). <sup>1</sup>H NMR (CDCl<sub>3</sub>) 6.28 (s, 2H), 4.77 (h, 2H), 1.19 (d, 6H),  $^3J_{H-H}=6.2$  Hz. MS (EI) 581 (M+1), 521 (M- (O*i*-Pr)), 479 (M- 2(O*i*-Pr) + O), 373 (M- HFAA).

## Results and Discussion

Initially, by using a new developed synthetic pathway *via* metal alkyl complexes formed *in-situ* we tried to prepare stable Ti(III)  $\beta$ -diketonates which are known to be very sensitive to air and moisture. Due to the charge and the preference for the six coordination of the Ti(III)  $\beta$ -diketonates, neutral Ti( $\beta$ -diketonate)<sub>3</sub> were expected. However, only one complex was found to be stable and characterized as (OTi(BPP)<sub>2</sub>)<sub>2</sub> instead of Ti(BPP)<sub>3</sub> and other  $\beta$ -diketonates produce uncharacterizable yellow solids, possibly mixture of Ti(III) and Ti(IV) complexes such as O(Ti( $\beta$ -diketonate)<sub>2</sub>)<sub>2</sub> and (OTi( $\beta$ -diketonate)<sub>2</sub>)<sub>2</sub>. In spite of failure to isolate pure Ti(III) complexes, purple, dark green or blue solution, which was characteristic to Ti(III) complexes,<sup>7</sup> were observed during the reaction in every cases. This indicates that new synthetic method is also effective for the preparation of Ti( $\beta$ -diketonate)<sub>3</sub>. In the case of BPP, ambiguity in the formulation of the product raised from the closeness of theoretical elemental analysis data of (OTi(BPP)<sub>2</sub>)<sub>2</sub> and O(Ti(BPP)<sub>2</sub>)<sub>2</sub> was resolved based on the spectroscopic data and chemical properties. The former is preferred due to sharp peaks in the <sup>1</sup>H NMR spectrum and stability in the air and water. Ti(III) complexes are paramagnetic and very sensitive to water and air. Dimeric formulation is based on the reported structure of (TiO(ACAC)<sub>2</sub>)<sub>2</sub><sup>8</sup> where oxo ligands are bridging ligands and overall geometry is octahedron. Failure to isolation of Ti( $\beta$ -diketonate)<sub>3</sub> inevitably induced to the search for the new class of titanium  $\beta$ -diketonates, Ti(OR)<sub>2</sub>( $\beta$ -diketonate)<sub>2</sub>. Some of these compounds are reported as liquids<sup>9</sup> and volatile enough to be used as a CVD precursor. However, effect of substituents of  $\beta$ -diketonates on the physical properties of the comp-

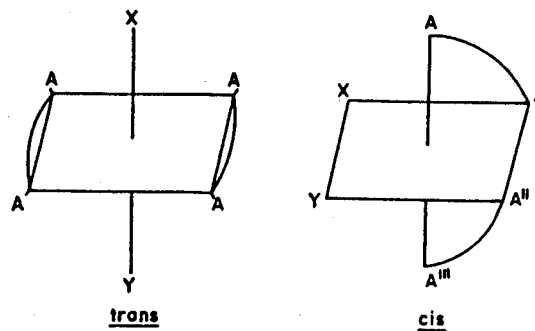


Figure 1. Possible Isomers of  $M(AA)_2X_2$ .

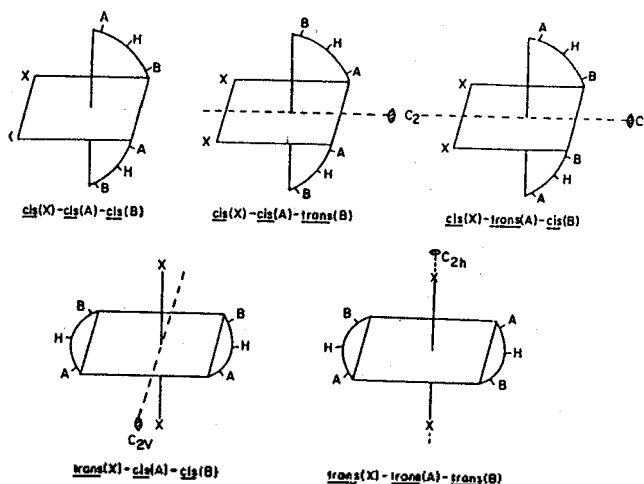


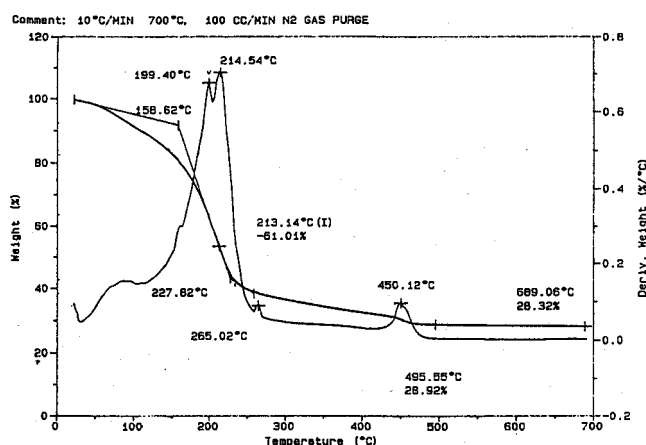
Figure 2. Possible Isomers of  $M(AB)_2X_2$ .

lexes has not been reported and these liquid complexes are still unstable toward hydrolysis. Therefore, a series of Ti(O*i*-Pr)<sub>2</sub>( $\beta$ -diketonate)<sub>2</sub> were synthesized by a slightly modified method of literature<sup>9</sup> with high yields.  $\alpha$ -Hydroxyaldehydes such as 1- and 2-HAN also produce the same product of  $\beta$ -diketonates as expected. Two kinds of products, gel-like liquids (ACAC, TFAC, HFAC) and solids (other  $\beta$ -diketonates), were obtained. Interestingly, every liquid reacts with water but other solid products do not show any reactivity toward water at all. At this point, it cannot be concluded whether this typical reactivity is only related with the phase of the products or not. These Ti(O*i*-Pr)<sub>2</sub>( $\beta$ -diketonate)<sub>2</sub>-type complexes have several isomers as shown in Figures 1 and 2. In the cases of the symmetrical  $\beta$ -diketonate complexes such as Ti(O*i*-Pr)<sub>2</sub>(ACAC)<sub>2</sub>, Ti(O*i*-Pr)<sub>2</sub>(DPM)<sub>2</sub>, Ti(O*i*-Pr)<sub>2</sub>(BPP)<sub>2</sub>, and Ti(O*i*-Pr)<sub>2</sub>(HFAC)<sub>2</sub> *trans* isomer is expected to have one alkyl peak of  $\beta$ -diketonate while *cis* isomer has two different alkyl peaks. From the <sup>1</sup>H NMR spectra with two different alkyl peaks the structure of three complexes except Ti(O*i*-Pr)<sub>2</sub>(HFAC)<sub>2</sub> is interpreted to be *cis* isomer. In the spectrum of Ti(O*i*-Pr)<sub>2</sub>(HFAC)<sub>2</sub> one methine peaks of both  $\beta$ -diketonate and isopropoxide, and one methyl peak of isopropoxide were observed and this cannot distinguish *cis* isomer from *trans* one. However, since most of the Ti(O*i*-Pr)<sub>2</sub>( $\beta$ -diketonate)<sub>2</sub> are *cis* isomers<sup>10</sup> this complex is also assigned as a *cis* one. In the cases of the unsymmetrical  $\beta$ -diketonate complexes, 5 isomers are possible. Based on the literature,<sup>11</sup> *cis* (isopropo-

**Table 1.** IR Absorption Bands of  $Ti(OiPr)_2(\beta\text{-diketonate})_2$  ( $cm^{-1}$ )

$\beta$ -diketone	ACAC	DPM	TFAA	HFAA	BAC	BPP	1-HAN	2-HAN	ACCP	HBP
IR frequency	1585	1574	1624	1651	1597	1597	1585	1616	1601	1605
	1524	1531	1535	1562	1547	1551	1531	1528	1489	1531
	1431	1501	1454	1539	1524	1520	1493	1447	1377	1458
	1385	1381	1366	1450	1450	1373	1420	1369	1288	1339
	1327	1358	1296	1366	1362	1315	1288	1281	1126	1246
	1277	1292	1142	1258	1312	1227	1211	1207	991	1138
	1126	1227	1015	1215	1126	1123	1130	1161	945	995
	1011	1138	860	1161	999	1072	988	1022	849	849
	930	999	771	1111	852	991	899	829	729	760
	852	872	725	1015	779	852	810	756	625	702
	768	849	679	860	714	756	741	687	463	613
	663	791	575	810	621	721	621	621	450	505
	617	625	486	663	575	621	517	494		436
	548	501	460	594	460	586	428	436		
	440			509		455				

xide) isomers are preferred. TFAC, BAC, and 1-HAN complexes are fluxional, where there may be equilibria amongst three *cis* isomers as  $Ti(BAC)_2F_2$ . On the other hand, 2-HAN, ACCP, and HBP complexes are nonfluxional; former two complexes have two isomers, possibly *cis-cis-trans* and *cis-trans-cis* ones, and latter one have one isomer but distinction between *cis-cis-trans* and *cis-trans-cis* cannot be made. Since chelating ligands are known to stop fluxional behavior by reducing the rate of intramolecular exchange and by limiting the number of chemically reasonable pathways for the rearrangement,<sup>12</sup> the behavior of 1-HAN draws attention while a 2-HAN complex is not fluxional. More detailed study on the fluxional mechanism is under progress. Mass spectra of these complexes shows easy rupture of a M-O(i-Pr) bond and these fragments resulted from the removal of iso-propoxide moieties were monitored in most of the cases. This pattern is consistent with the observation of easier replacement of an OR ligand than  $\beta$ -diketonate ones from the  $Ti(Oi-Pr)_2(\beta\text{-diketonate})_2$ .<sup>13</sup> IR spectra were not quite helpful to assign structures of the prepared complexes. IR absorption peaks are summarized in Table 1. No significant shift of IR bands with the change of substituents of  $\beta$ -diketonates were observed in the various complexes investigated in this study. However, shift to the lower wave number of CO stretching frequencies of  $\beta$ -diketonates on coordination were observed as reported in the literature.<sup>14</sup> Melting point analysis shows that ACCP, HBP, and BAC complexes among the newly synthesized solid ones are promising precursors for the  $TiO_2$  from the view point of lower mp (74, 80, 107 °C) and higher decomposition temperature. (171, 147, 194 °C) Moreover, these complexes are stable toward moisture and oxygen. All three liquid complexes and  $Ti(Oi-Pr)_2(DPM)_2$  are also proved as useful precursors in this criteria. However, these are unstable toward moisture and oxygen. The effect of substituents on the property of the complexes cannot be described in a definite way. However, aromatic substituents of  $\beta$ -diketonates tend to increase the mp and decomposition temperatures, which follows the general trend found by Mehrotra.<sup>15</sup> Ring substituents spanning from the carbonyl carbon to the me-

**Figure 3.** A TGA-DTA Diagram of  $Ti(Oi-Pr)_2(ACAC)_2$ .

thine carbon between carbonyl groups (ACCP, HBP and HAN) decrease the mp even though it is well-recognized that substituents of methine carbon lower the volatilities of the complexes. In these compounds, an aryl substituent (HBP) also induces higher mp as mentioned above but lower thermal stability. 1-HAN and 2-HAN show higher mp as expected but decomposition temperatures are very close to the mp's. Comparison between HBP and 1-HAN complexes indicates that even distribution of aryl substituents (HBP) might induce the higher volatility (lower mp). The reason of this phenomenon is not clear right now but it may relate with the geometry of the complex, if any. A typical TGA-DTA diagram is shown in Figure 3. From the TGA diagrams of the complexes prepared in this study, TGA data were analyzed in Table 2. Residue portions at the end point of 700 °C are usually higher than the theoretical ones of  $TiO_2$ . Generally, complexes containing  $\beta$ -diketonates with aromatic substituents are resistant to the thermal decomposition and an oxygen atmosphere should be applied to guarantee the complete thermal decomposition of complexes to  $TiO_2$ . Only exceptional complexes are DPM and HFAA ones. This indi-

**Table 2.** TGA Data of  $Ti(OiPr)_2(\beta\text{-diketonate})_2$

Class	$\beta$ -diketone	-Oi-Pr		-2 Oi-Pr		-4 R		-2 CH		-CO		-C		-O		
		Exp.	theo.	Exp.	theo.	Exp.	theo.	Exp.	theo.	Exp.	theo.	Exp.	theo.	Exp.	theo.	
I	ACAC	158.6		199.4		214.5		227.8		265.0		450.1		689.1		
		82.80	83.79	63.60	67.58	53.20	51.10	42.80	43.96	38.40	36.26	34.40	32.97	28.32	28.57	
	DPM	260.0		284.4		330.0								691.6		
		53.60	88.91	36.40	77.82	16.80	34.96							7.93	19.55	
	HFAA	161.2		178.3		309.3								691.3		
		58.00	89.83	49.00	79.66	20.00	32.07							11.17	17.93	
	BPP	170.0		279.3		307.9	-Ph							691.6		
		94.40	90.36	82.00	80.72	68.80	68.14							18.46	16.99	
						356.7	-3Ph									
						44.80	42.97									
				393.3	-4Ph											
				29.40	30.39											
		-Oi-Pr		-2 Oi-Pr		-2 Me		-2 R		-2CH		-CHCO-CH		-CO		
		Exp.	theo.	Exp.	theo.	Exp.	theo.	Exp.	theo.	Exp.	theo.	Exp.	theo.	Exp.	theo.	
II	TFAA	130.0		170.7		224.2	-Me	237.5	-R			396.7		691.6		
		88.40	87.5	77.60	75.0	70.40	71.82	52.93	54.03			28.00	27.96	22.50	22.03	
						-2Me	273.3	-2R								
						68.64	42.87	39.41								
BAC	185.0		237.3		471.2		691.6									
	87.70	87.91	75.82	65.30	69.67	39.00	38.11	32.41	32.79							
		-Oi-Pr		-2 Oi-Pr		-2 Me		-(ring-O)		-CO		-CO				
		Exp.	theo.	Exp.	theo.	Exp.	theo.	Exp.	theo.	Exp.	theo.	Exp.	theo.			
III	ACCP	186.7		211.6		222.3	-Me	461.5		691.3						
		86.80	85.82	72.16	71.63	68.03	47.50	48.56	43.05	41.83						
						-2Me	64.42									
	1-HAN	204.3		306.9		330.0				683.8						
		86.70	88.99	75.70	77.99	72.30	72.39			42.52	43.66					
	2-HAN	113.9		260.0		286.7				497.9		689.8				
		92.30	88.99	75.80	77.99	74.00	72.39			43.30	43.66	38.10	38.43			
	HBP	161.7		213.3		371.6	-Ph			471.3		690.1	-Ph			
91.83		89.46	80.00	78.93	67.00	65.18			47.30	46.61	36.84	32.86				

\*upper figure in the box: temperature (°C) determined by the DTA down figure in the box: Wt % at the temperature

cates that sublimation rates of these complexes are faster than the decomposition ones under the experimental conditions. However, at the point of 250 °C, only HFAA, ACAC, and TFAC are thermally decomposed over 50%. This property represents that these complexes cannot be utilized as precursors on the thermally unstable substrates. Preparation of PLT thin films by using these complexes and characterization of these films are under progress. Table 2 indicates that pyrolysis of the complexes may proceed as follows;

symmetric  $\beta$ -diketonates, complex  $\rightarrow$  (complex-Oi-Pr)  $\rightarrow$  (fragment 1 - Oi-Pr)  $\rightarrow$  (fragment 2 -  $nR(n=1-4)$ )  $\rightarrow$  (fragment 3 -  $n(CHCO)(n=1-2)$ )

unsymmetric  $\beta$ -diketonates without a ring spanning from methine carbon to carbonyl carbon, complex  $\rightarrow$  (complex-Oi-Pr)  $\rightarrow$  (fragment 1 - Oi-Pr)  $\rightarrow$  (fragment 2 - 2 Me)  $\rightarrow$  (fragment

3 - 2 R)  $\rightarrow$  (fragment 4 - 2 CH)  $\rightarrow$  (fragment 5 - 2 CO)

unsymmetric  $\beta$ -diketonates with a ring spanning from methine carbon to carbonyl carbon, complex  $\rightarrow$  (complex - Oi-Pr)  $\rightarrow$  (fragment 1 - Oi-Pr)  $\rightarrow$  (fragment 2 - 2 R)  $\rightarrow$  (fragment 3 - (ring-O))  $\rightarrow$  (fragment 4 - CO)

Initial removal of two Oi-Pr fragments may represent the tendency of easier replacement of these functional group as mentioned above.<sup>4</sup> In the third case, methyl fragments dissociate before ring fragments but phenyls were removed after the ring dissociation. This may result from the stronger C-C bond of  $sp^2$  than that of  $sp^3$ . Moreover, It is worth to note that small change of the position of the substituents may induce the significant change of decomposition temperature as shown in cases of 1- and 2-HAN complexes. In the cases of DPM and HFAA complexes, fewer residue portion

**Table 3.** Modified TGA Data of  $Ti(OiPr)_2(\beta\text{-diketonate})_2$ 

Class	$\beta$ -diketone	-Oi-Pr		-2 Oi-Pr		-4 R		-2 CHCO	
		Exp.	theory	Exp.	theory	Exp.	theory	Exp.	theory
I	DPM	260.0		284.4		313.0	-2 t-Bu	691.6	
		53.60	36.05	36.40	31.55	23.80	22.86	7.93	7.93
						330.0	-4 t-Bu		
						16.80	14.17		
	HFAA	161.2		178.3		309.3		691.3	
		58.00	55.96	49.00	49.63	20.00	19.98	11.17	11.27

than the expected one due to the concurring sublimation of the parent complexes were observed and the experimental data were modified and listed in Table 3 assuming the final residue portion represented the fragment obtained in the final stage as shown above. These results indicate that the same pyrolysis mechanism can be applied but sublimation might occur after the removal of 1 equivalent Oi-Pr in the DPM complex and the loss of HFAA complex occurs before the pyrolysis.

### Conclusion

Preparation of  $Ti(BPP)_3$  by the reaction between BPP and  $TiMe_3$  formed in situ lead only to the formation of  $(OTi(BPP))_2$ , a stable solid toward moisture and air. Synthesis of  $Ti(Oi-Pr)_2(\beta\text{-diketonate})_2$  by the substitution reaction of  $Ti(Oi-Pr)_4$  proceeds with a good yield and complexes of  $\beta$ -diketonates containing aromatic substituents or a ring spanning from a methine carbon to a carbonyl carbon showed the much improved stability toward moisture and air and lower mp and higher decomposition temperature, which are the required properties for the potential CVD precursors. Pyrolysis of these complexes proceeds the initial dissociation of Oi-Pr's followed by removal of the substituents, and CHCO fragments of the  $\beta$ -diketonate successively.

**Acknowledgment.** This work was supported by the Korea Ministry of Education Research Fund for advanced materials in 1994-1995 and Xue wishes to express her appreciation to Inha University and Korea Ministry of Education Research Fund for the allowance of the post doctoral fellowship.

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