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A study on the development of CVD precursors V – syntheses and characterization of new *N*-alkoxy-β-ketoiminate complexes of titanium ☆

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Abstract

The synthesis and characterization of various new titanium *N*-alkoxy-β-ketoiminate complexes are reported. Reactions between *N*-alkoxy-β-ketoimine ligands and Ti(O-*i*Pr)$_4$ resulted in dimeric [Ti(O-*i*Pr)$_2$(*N*-alkoxy-β-ketoiminate)]$_2$ complexes or monomeric [Ti(*N*-alkoxy-β-ketoiminate)$_2$] ones depending on the amount of ligands. Terdentate *N*-alkoxy-β-ketoiminate ligands do not prevent dimer complexes from undergoing disproportional rearrangement to produce Ti(O-*i*Pr)$_4$ and [Ti(*N*-alkoxy-β-ketoiminate)$_2$]. The mechanism of this behavior is too complicated but it may include the dissociation and recoordination of ligands. Crystal structures of [Ti(*N*-alkoxy-β-ketoiminate)$_2$] (MeC(O)CHC(Me)NC(Et)CH$_2$O (**3f**) and *t*-BuC(O)CHC(Me)NCH$_2$CH(Me)O (**3k**)) show that these are distorted octahedron and β-ketoiminate ligands appear to coordinate as a β-imino enolate. Two terdentate β-ketoiminate ligands coordinate meridionally and they are perpendicular to each other. Thermal characteristics of monomeric and dimeric titanium complexes were determined by TGA and DSC and these are reasonably volatile as potential precursors of TiO_2 thin films.

1. Introduction

Titanium oxide, TiO_2, is an important component in many ternary perovskites, the best known of which are ferroelectrics, such as $BaTiO_3$ (BT) and $SrTiO_3$ (ST) [1]. The closely related materials [Pb(Zr,Ti)O_3] (PZT) and [(Pb,La)(Zr,Ti)O_3] (PLZT) have also drawn much interests due to their pyroelectric and ferroelectric properties, which have promising applications as infrared detectors and next generation non-volatile ferroelectric-based memory devices (FeRAMs) [2]. Recent report on much increased dielectric constant of the material with the addition of a small percentage of TiO_2 to Ta_2O_5 offers the potential of improved performance DRAMs [3]. Moreover, (Ba,Sr)TiO_3 (BST) has drawn interests due to its high dielectric constant and low leakage current density, which can be applicable to a capacitor in giga-bit dynamic random access memories (DRAMs) [4].

For the successful fabrication of thin films containing titanium oxides, suitable precursors with high volatility, enhanced thermal and chemical stability and easy decomposition are required. For BST thin film fabrication by liquid source (LS) metalloorganic chemical vapor deposition (MOCVD) method, enhanced compatibility of titanium precursors with barium and strontium complexes such as Ba(thd)$_2$ and Sr(thd)$_2$ (thd = 2,2,6,6-tetramethyl-2,5-heptanedionate) is another important requirement [5]. However, the precursor chemistry of titanium is far from well development.

Up to date, several precursors such as $TiCl_4$ [6] and Ti(OR)$_4$ (R = Et, *i*Pr) [7] have been used but some drawbacks such as halide contamination of the films, high

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fabrication temperature, and high reactivity towards air and moisture, respectively. Several mixed ligand complexes, such as $[Ti(O\text{-}iPr)_2(thd)_2]$ [8], $[Ti(O\text{-}iPr)_x(dmae)_{4-x}]$ $(x = 2, 3)$ (dmae = dimethylaminoethoxide) [9], $[TiO(thd)_2]$ [10], and $[Ti(mpd)(thd)_2]$ (mpd = 2-methyl-2,4-pentanedioxy) [5], have been recently adopted as a titanium precursor in the liquid injection MOCVD processes.

Recently, β-ketoiminate, β-diketiminate, and *N*-alkoxy-β-ketoiminate, a terdentate dianionic ligand, have drawn interests and have been adopted successfully for the preparation of MOCVD precursors [11] and catalysts [12].

In this study, new titanium complexes containing *N*-alkoxy-β-ketoiminate ligands have been prepared and characterized.

2. Results and discussion

2.1. Synthesis of ligands and complexes

As shown in Scheme 1, various *N*-alkoxy-β-ketoimine ligands can be prepared by the simple dehydration reaction between β-diketone and amino alcohols, sometimes in the presence of acid catalysts such as formic acid or *p*-toluenesulfonic acid (*p*-TsOH). Yields are generally high but rather low in the cases of bulky substituents as expected.

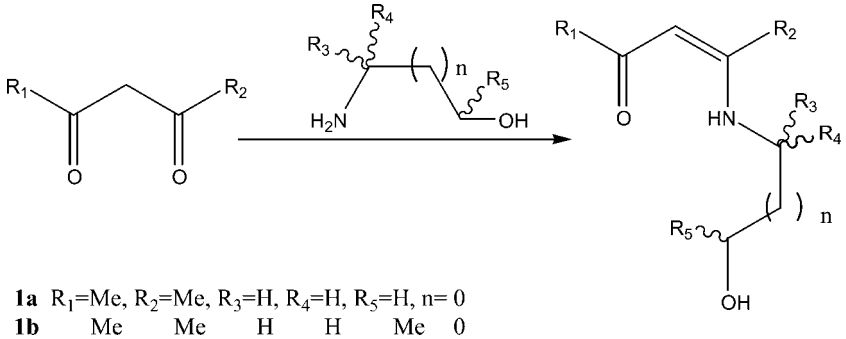
Prepared *N*-alkoxy-β-ketoimine ligands react with $Ti(O\text{-}iPr)_4$ to produce dimeric $[Ti(O\text{-}iPr)_2$(*N*-alkoxy-β-ketoiminate)$]_2$ complexes or monomeric [Ti(*N*-alkoxy-β-ketoiminate)$_2$] ones depending on the amount of ligands (Schemes 2 and 3).

It was reported that $Ti(OR)_4$ reacted with β-diketone to produce $[Ti(OR)_3$(β-diketonate)$]_2$ or $[Ti(OR)_2$(β-diketonate)$_2]$ depending on the reaction conditions and $[Ti(OR)_3$(β-diketonate)$]_2$ was fluxional [13]. Disproportionation of $[Ti(OR)_3$(β-diketonate)$]_2$ into $Ti(OR)_4$ and $[Ti(OR)_2$(β-diketonate)$_2]$ was also reported [14]. Fluxionality of $[Ti(OR)_3$(β-diketonate)$]_2$ may induce chemical instability and transformation, which should be avoided during storage or delivery in the MOCVD process. It is expected that this type of disproportionation reaction can be freezed by *N*-alkoxy-β-ketoiminates, terdentate ligands, due to enhanced chelate effect and limited allowed conformations. Enhanced chemical and thermal stability of $[M(OR)_3$(*N*-alkoxy-β-ketoiminate)] (M = Nb, Ta) and much higher deposition rate with reduced carbon residue in the MOCVD process [11i] is another reason to prepare titanium complexes with alkoxide and *N*-alkoxy-β-ketoiminate ligands. Contrary to this expectation, $[Ti(O\text{-}iPr)_2$(*N*-alkoxy-β-ketoiminate)$]_2$ is disproportionated to produce $Ti(O\text{-}iPr)_4$ and [Ti(*N*-alkoxy-β-ketoiminate)$_2$].

2.2. Structures and disproportional rearrangements of [Ti(N-alkoxy-β-ketoiminate)(OR)$_2$]$_2$

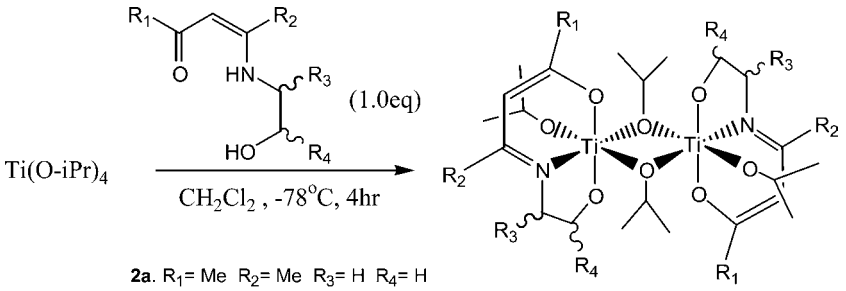
In order to investigate the mechanism of the disproportional rearrangement, several experiments shown in Scheme 4 have been done.

Driving force of this disproportional rearrangements may be thermodynamic stabilities of one of or both homoleptic titanium complexes such as $Ti(OR)_4$ and [Ti(*N*-alkoxy-β-ketoiminate)$_2$]. [Ti(*N*-alkoxy-β-ketoiminate)$_2$] was found to be stable toward the addition of $Ti(OR)_4$ up to 10 equivalents. However, [Ti(*N*-alkoxy-β-



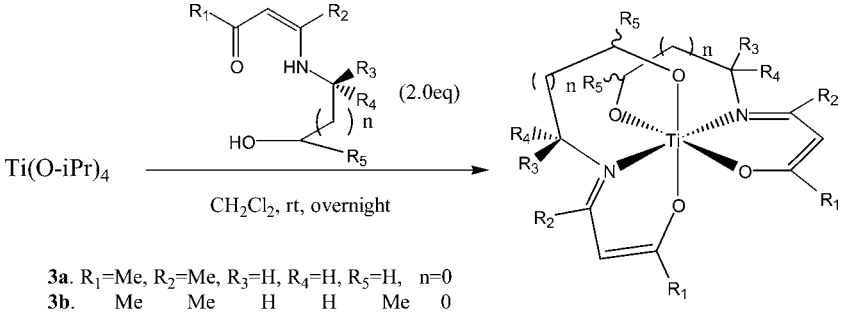
1a	R_1=Me,	R_2=Me,	R_3=H,	R_4=H,	R_5=H,	n= 0
1b	Me	Me	H	H	Me	0
1c	Me	Me	Me	H	H	0
1d	Me	Me	Me	Me	H	0
1e	Me	Me	H	H	H	1
1f	Me	Me	Et	H	H	0
1g	i-Pr	i-Pr	H	H	H	0
1h	i-Pr	i-Pr	H	H	Me	0
1i	i-Pr	i-Pr	Me	H	H	0
1j	t-Bu	Me	H	H	H	0
1k	t-Bu	Me	H	H	Me	0

Scheme 1.



	R_1	R_2	R_3	R_4
2a	Me	Me	H	H
2b	Me	Me	Me	H
2c	Me	Me	H	Me
2d	i-Pr	i-Pr	H	H
2h	i-Pr	i-Pr	H	Me

Scheme 2.



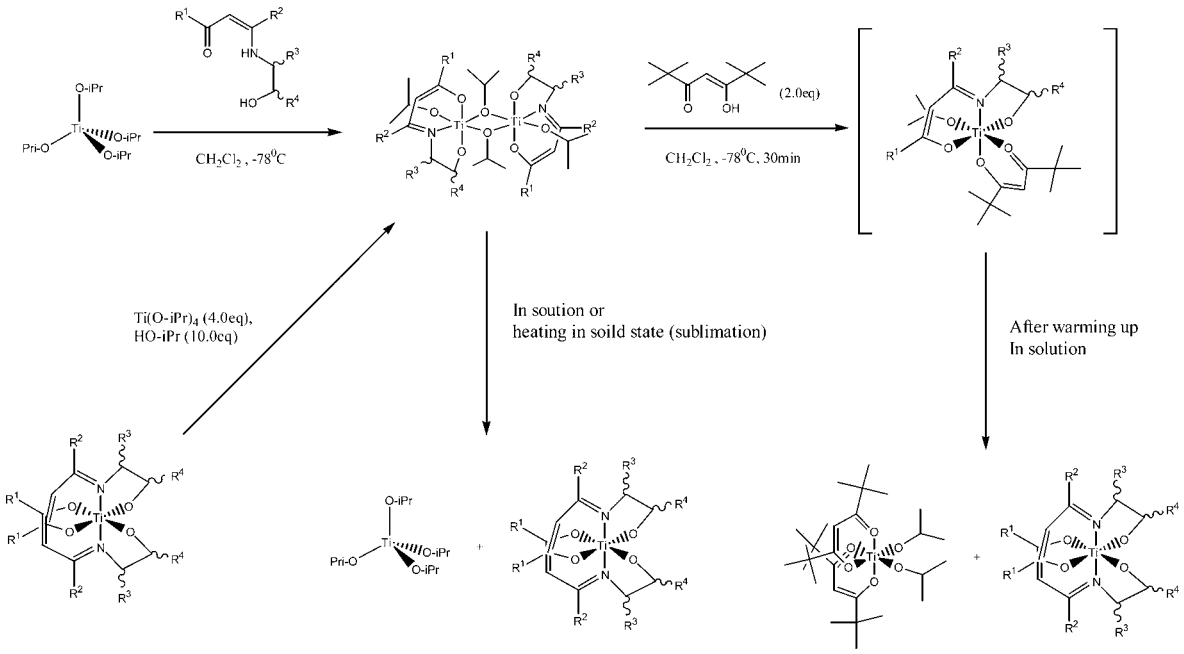
	R_1	R_2	R_3	R_4	R_5	n
3a	Me	Me	H	H	H	0
3b	Me	Me	H	H	Me	0
3c	Me	Me	Me	H	H	0
3d	Me	Me	Me	Me	H	0
3e	Me	Me	H	H	H	1
3f	Me	Me	Et	H	H	0
3h	i-Pr	i-Pr	H	H	Me	0
3i	i-Pr	i-Pr	Me	H	H	0
3j	t-Bu	Me	H	H	H	0
3k	t-Bu	Me	H	H	Me	0

Scheme 3.

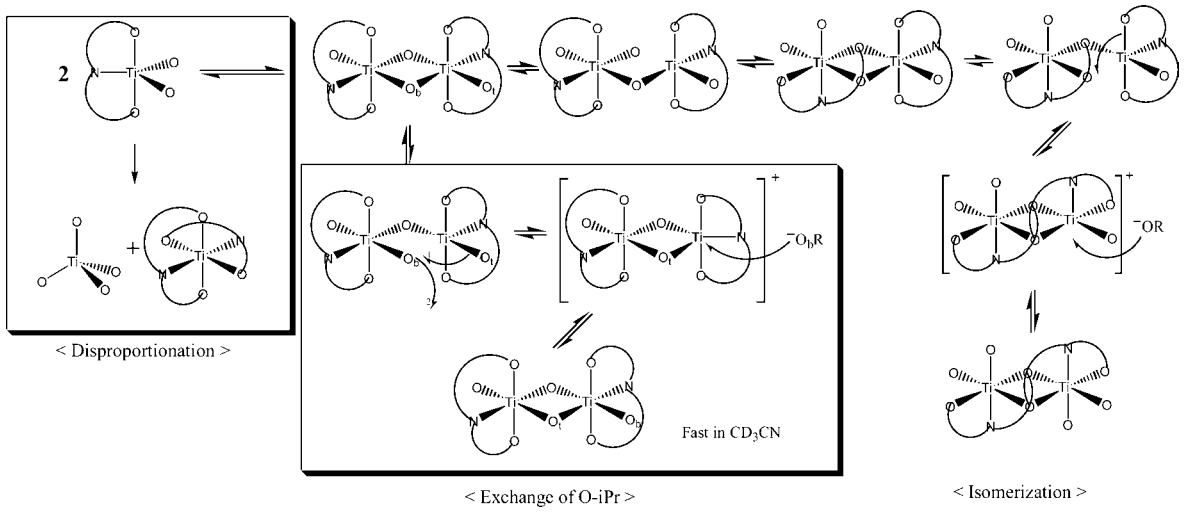
ketoiminate)$_2$] produced dimer complexes in an hour in the presence of 4 equivalents of Ti(OR)$_4$ and 10 equivalents of isopropanol. It is also found that sublimation of these dimeric complexes under reduced pressure (around 10^{-2} Torr) induces disproportional rearrangement to produce Ti(O-*i*Pr)$_4$ and [Ti(*N*-alkoxy-β-ketoiminate)$_2$]. From these experiments, it indicates that free isopropanol or isoproxide ion may involve in this disproportional process. In order to find some supporting evidences, variable temperature (VT) NMR (^{1}H and ^{13}C) experiments of **2a** and **2d** have been done. The spectra were too complicated to be interpreted reasonably (supplementary information) but many peaks for C(O)CHC(N) of *N*-alkoxy-β-ketoiminate ligands (~5 ppm in ^{1}H, 160–180 ppm in ^{13}C) and for Me's of *N*-alkoxy-β-ketoiminate and isoproxide ligands (1–2 ppm in ^{1}H and 20–70 ppm in ^{13}C) indicate that more than 2 isomers must be involved in this rearrangement. Also addition of Ti(OR)$_4$ (1 equivalent) to this solution retards the exchange rate possibly due to formation of starting dimeric complex by the reaction between dissociated *N*-alkoxy-β-ketoiminate ligands and Ti(OR)$_4$. Based on these observations, the possible pathways involving isomerization and exchange of isopropoxides are described in Scheme 5. Even though [Ti(OR)$_3$(β-diketonate)]$_2$ is reported to undergo disproportional rearrangement via a nondissociative pathway where exchange of bridging OR and β-diketonate ligands occurs [14], the dissocitation of isopropoxide and/or possibly *N*-alkoxy-β-ketoiminate ligands is proposed due to faster exchange rates in polar solvents (toluene < $CHCl_3$ < CH_3CN). Possible involvement of a 5-coordinate monomeric complex can be effectively excluded by no change in the presence of pyridine, THF and CH_3CN.

2.3. Crystal structures of [Ti(*N*-alkoxy-β-ketoiminate)$_2$]

Crystal structures of Ti($CH_3C(O)CHC(NCH(CH_2CH_3)CH_2O)CH_3)_2$ (**3f**) and Ti($(CH_3)_3CC(O)CHC(NCH_2CH(Me)O)CH_3)_2$ (**3k**) are determined by single crystal X-ray crystallography and these structures are shown in Figs. 1 and 2, respectively. Selected bond



Scheme 4.



Scheme 5.

lengths and angles are also given in Tables 1 and 2, respectively and summary of crystal data is shown in Table 3.

The crystal structure of **3f** contains two ligands and one metal center in an asymmetric unit. Two tridentate NO_2 donor units occupy an approximately meridional arrangement around titanium, with its overall coordination number 6 to yield a distorted octahedral TiN_2O_4 coordination sphere (Fig. 1). The four oxygens of two different ligands form an equatorial plane with maximum deviation of 0.345 Å and two N atoms occupy the axial positions (Ti–N(1) 2.185 Å, Ti–N(2) 2.173 Å, N(1)–Ti–N(2) 176.6°). A similar coordinating behavior has been observed by Doherty et al. [12] for the related ligand, $MeC(O)CHC(Me)N(CH_2CH_2O)$. The potential symmetry of **3f** may be broken by the arrangement of two coordinating ligands which are arrayed in the same direction.

In unit-cell of the corresponding dissymmetric β-ketoiminate compound, **3k**, it contains a pair of unusual crystallographcally independent molecules (A and B), which are structural isomers to each other (Fig. 2). In both complexes (A and B), the four oxygens of two different ligands form equatorial plane with the maximum

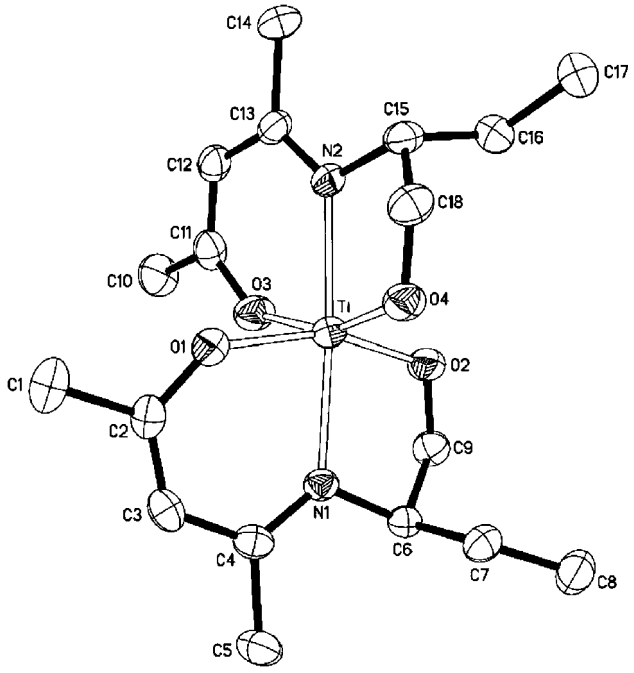


Fig. 1. Crystal structure of **3f** with atom-numbering scheme. Displacement ellipsoids are drawn at 30% probability level and H atoms have been omitted for clarity.

deviation of 0.353 and 0.348 Å, and two N atoms occupy the axial positions [molecule A: Ti(1)–N(1) 2.155 Å, Ti(1)–N(2) 2.168 Å, N(1)–Ti(1)–N(2) 172.6°; molecule B: Ti(2)–N(3) 2.154 Å, N(1)–Ti(2)–N(2) 177.4°], respectively. A remarkable conformational difference of two molecules in **3k** is an arrangement of two coordinating ligands. In molecule A, the two ligands around metal center array in the same direction similar to that of **3f**. However, molecule B has a crystallographic 2-fold axis. As a consequence of this symmetry, each *t*-butyl group separates as far as possible. This effect is related to the greater distortion of the molecule A than that of molecule B, which is coordinated fairly symmetrically to the ligands.

The distortions from regular octahedral symmetry are reflected by the considerable variation of bond lengths and angles, which occur about the titanium atom in each complex. The repulsive interaction between two *t*-butyl groups of molecule B in **3k** produces a marked distortion from the regular geometry: the O(4)–Ti(1)–N(2) angle is increased to 97.02(9)°. In each complex (Figs. 1 and 2), the axial positions are likely occupied by two nitrogen donors, but the distances of Ti–N bonds are quite different. For examples, each of the titanium to nitrogen bonds (2.154–2.168 Å) in **3k** is marginally shorter than the mean (2.185 Å, with stan-

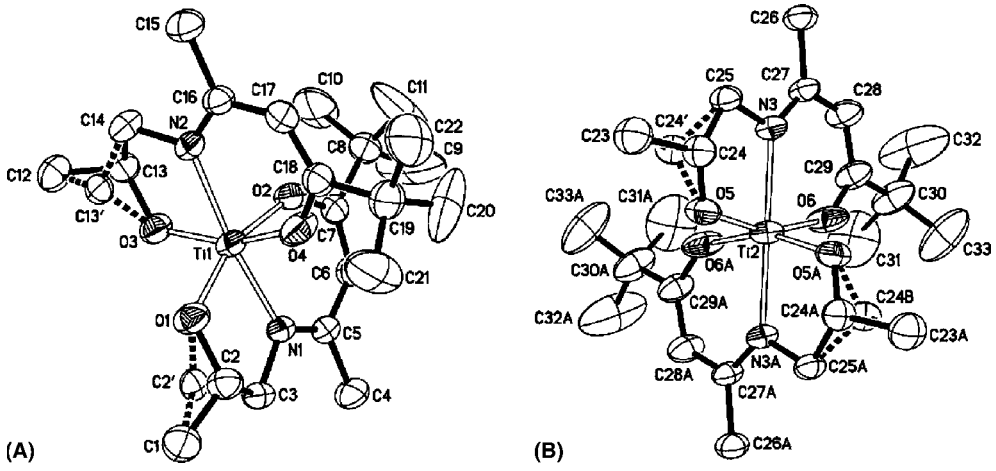


Fig. 2. Crystal structures of two isomer forms (A and B) of **3k** with atom-numbering scheme. Displacement ellipsoids are drawn at 30% probability level and H atoms have been omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for **3f**

Ti–O(1)	1.950(2)	Ti–O(2)	1.851(2)	Ti–O(3)	1.962(2)
Ti–O(4)	1.848(2)	Ti–N(1)	2.185(2)	Ti–N(2)	2.173(2)
N(1)–C(4)	1.300(3)	N(2)–C(13)	1.315(3)	C(11)–C(12)	1.370(5)
C(12)–C(13)	1.403(4)	C(2)–C(3)	1.350(5)	C(3)–C(4)	1.426(4)
O(4)–Ti–O(2)	95.31(10)	O(4)–Ti–O(1)	93.42(10)	O(2)–Ti–O(1)	158.68(8)
O(4)–Ti–O(3)	158.77(9)	O(2)–Ti–O(3)	91.17(10)	O(1)–Ti–O(3)	87.63(10)
O(4)–Ti–N(2)	77.31(8)	O(2)–Ti–N(2)	105.24(8)	O(1)–Ti–N(2)	95.63(8)
O(3)–Ti–N(2)	81.48(9)	O(4)–Ti–N(1)	104.89(8)	O(2)–Ti–N(1)	77.29(8)
O(1)–Ti–N(1)	81.69(8)	O(3)–Ti–N(1)	96.25(9)	N(2)–Ti–N(1)	176.58(9)

Table 2
Selected bond lengths (Å) and angles (°) for **3k**

Ti(1)–O(1)	1.842(2)	Ti(1)–O(3)	1.843(2)	Ti(1)–O(4)	1.934(2)
Ti(1)–O(2)	1.936(2)	Ti(1)–N(1)	2.155(2)	Ti(1)–N(2)	2.168(2)
Ti(2)–O(5)	1.842(2)	Ti(2)–O(5A)	1.842(2)	Ti(2)–O(6A)	1.939(3)
Ti(2)–O(6)	1.939(2)	Ti(2)–N(3A)	2.154(2)	Ti(2)–N(3)	2.154(2)
N(1)–C(5)	1.305(4)	N(2)–C(16)	1.294(4)	N(3)–C(27)	1.302(4)
C(5)–C(6)	1.416(5)	C(6)–C(7)	1.356(5)	C(16)–C(17)	1.417(4)
C(17)–C(18)	1.342(5)	C(27)–C(28)	1.413(4)	C(28)–C(29)	1.352(5)
O(1)–Ti(1)–O(3)	94.72(11)	O(1)–Ti(1)–O(4)	90.44(12)	O(3)–Ti(1)–O(4)	158.08(10)
O(1)–Ti(1)–O(2)	158.36(10)	O(3)–Ti(1)–O(2)	93.40(11)	O(4)–Ti(1)–O(2)	89.45(12)
O(1)–Ti(1)–N(1)	77.54(10)	O(3)–Ti(1)–N(1)	104.90(10)	O(4)–Ti(1)–N(1)	97.02(9)
O(2)–Ti(1)–N(1)	81.00(9)	O(1)–Ti(1)–N(2)	109.47(10)	O(3)–Ti(1)–N(2)	77.40(9)
O(4)–Ti(1)–N(2)	80.79(9)	O(2)–Ti(1)–N(2)	91.87(9)	N(1)–Ti(1)–N(2)	172.58(10)
O(5)–Ti(2)–O(5A)	96.82(16)	O(5)–Ti(2)–O(6A)	91.59(12)	O(5A)–Ti(2)–O(6A)	158.28(9)
O(5)–Ti(2)–O(6)	158.28(9)	O(5A)–Ti(2)–O(6)	91.59(12)	O(6A)–Ti(2)–O(6)	87.77(19)
O(5)–Ti(2)–N(3A)	100.88(10)	O(5A)–Ti(2)–N(3A)	77.54(9)	O(6A)–Ti(2)–N(3A)	81.23(9)
O(6)–Ti(2)–N(3A)	100.48(10)	O(5)–Ti(2)–N(3)	77.54(9)	O(5A)–Ti(2)–N(3)	100.88(10)
O(6A)–Ti(2)–N(3)	100.48(10)	O(6)–Ti(2)–N(3)	81.23(9)	N(3A)–Ti(2)–N(3)	177.66(13)

Table 3
Summary of crystal data and structure refinement for compounds **3f** and **3k**

	3f	**3k**
Emperical formula	$C_{18}H_{30}N_2O_4Ti$	$C_{22}H_{38}N_2O_4Ti$
Formula weight	386.34	442.44
Temperature (K)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2/n$
Unit cell dimensions		
a (Å)	10.2436(7)	12.9406(10)
b (Å)	12.4074(9)	13.4335(10)
c (Å)	15.7268(11)	22.6426(16)
α (°)	90	90
β (°)	90	99.105(2)
γ (°)	90	90
Volume (Å^3)	1998.8(2)	3886.5(5)
Z	4	6
Density (calculated) (Mg/m^3)	1.284	1.134
Absorption coefficient (mm^{-1})	0.451	0.356
$F(000)$	824	1428
Crystal size (mm^3)	$0.30 \times 0.40 \times 0.50$	$0.30 \times 0.40 \times 0.50$
Theta range for data collection (°)	2.09–28.28	1.52–28.30
Max index range h, k, l	13, 8, 20	16, 17, 30
Reflections collected	13219	24917
Independent reflections	4858 [$R_{int} = 0.0445$]	9373 [$R_{int} = 0.0551$]
Completeness to theta	28.28 °C, 99.6%	28.30°C, 96.9%
Absorption correction	None	None
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	4858/0/227	9373/0/423
Goodness-of-fit on F^2	1.042	1.058
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0434$, $wR2 = 0.1126$	$R1 = 0.0614$, $wR2 = 0.1799$
R indices (all data)	$R1 = 0.0641$, $wR2 = 0.1235$	$R1 = 0.1267$, $wR2 = 0.2107$
Absolute structure parameter	0.55(3)	
Largest diff. peak and hole	0.291 and −0.231 e Å^{-3}	0.356 and −0.292e Å^{-3}

dards deviation 0.015 Å) of 13 such bonds taken from the X-ray literature, while those (2.185 and 2.173 Å) of **3f** are comparable to the literature values [15].

It is interesting that steric bulkiness of alkyl groups in the five-membered ring does not affect the bite angles of the chelate rings. The six-membered chleate rings are nearly planar and two rings are close to perpendicular with diheral angles of 89.31(8) (**3f**), 89.64(8) (**3k**, Ti(1)), and 89.86(8)° (**3k**, Ti(2)), respectively. The bonding in the six-membered rings is localized and can be described

as a *N*-hydroxyalkylimine-enolate. The C–N bond distances (1.294–1.315 Å) in each complex are comparable to the distances of such bonds in the ketoiminate complexes taken from the X-ray literature [12,16].

The locality of bonding within the ketoiminate ligand is supported by the differences in the two C–C bond lengths in the six-membered ring of 0.033 (**3f**), 0.075, 0.060 (**3k**, Ti(1)), and 0.061 Å (**3k**, Ti(2)), which are substantially larger than the comparable differences in the bis(iminate) ([Zr{MeC(NPh)CH(NPh)Me}$_2$Cl$_2$], 0.005 Å) [16] and β-diketonate complexes ([Ti{MeC(O)CH(O)Me}(O-*i*Pr$_2$)$_3$]$_2$, 0.003 Å) [13], respectively.

In addition, the titanium ketoiminate bond length is considerably longer than its alkoxide counterparts (**3f**: 1.950(2), 1.962(2) vs. 1.848(2), 1.851(2); **3k**: Ti(1) 1.934(2), 1.936(2) vs. 1.842(2), 1.843(2), Ti(2) 1.939(2) vs. 1.842(2)). However, these values are not as marked as those observed in the β-diketonate complex ([Ti{MeC(O)CH(O)Me}(O-*i*Pr$_2$)$_3$]$_2$, 2.073(4) vs. 1.782(4) Å) [13]. These results clearly reflect the different π-donor ability of OR compared with NR$_2$ [12,17]. In each structure, two terdentate β-ketoiminate ligands occupy a meridional coordination environment.

In **3k**, thermal disorder of carbon atoms in five-membered rings are monitored [C(2):C(2′) = 69:31, C(13):C(13′) = 59:41, C(24):C(24′) = 55:45] and these prevent meaningful discussion of the ligand conformation.

2.4. Thermal properties of [Ti(N-alkoxy-β-ketoiminate)(O-iPr)$_2$]$_2$ and [Ti(N-alkoxy-β-ketoiminate)$_2$]

Thermal properties of [Ti(*N*-alkoxy-β-ketoiminate)(O-*i*Pr)$_2$]$_2$ and [Ti(*N*-alkoxy-β-ketoiminate)$_2$] are characterized by dynamic and isothermal TGA. In Fig. 3, **2b** shows two different regions in the dynamic TGA and constant decrease of weight is observed in the isothermal TGA (200 °C). Considering that dimer complexes undergo disproportional rearrangement (vide supra), this behavior can be explained as follows; as temperature goes up, dimer disproportionally rearranges to Ti(O-*i*Pr)$_4$ and [Ti(*N*-alkoxy-β-ketoiminate)$_2$] at first and then evaporation of Ti(O-*i*Pr)$_4$ occurs at the lower temperature while [Ti(*N*-alkoxy-β-ketoiminate)$_2$] vaporizes at the higher temperature. In the isothermal TGA experiment, a constant slope after 20 min is maintained, which indicates only one compound, possibly [Ti(*N*-alkoxy-β-ketoiminate)$_2$], vaporizes. Even though the volatility of **2b** is not very good (in dynamic TGA, the amount of residue at 550 °C is 23%), constant vapor pressure at 200 °C leads to the LS MOCVD experiments using laboratory-made MOCVD apparatus. Detailed description of this apparatus can be obtained elsewhere [11j]. As shown in Fig. 4, **2c** shows higher deposition rate than commercially available Ti(mpd)(thd)$_2$ (Ashai Denka Chemical Co.). Since this may be due to high volatility of Ti(O-*i*Pr)$_4$, thermal characteristics of [Ti(*N*-alkoxy-β-ketoiminate)$_2$] were investigated. The results are summarized in Table 4. Melting points of these complexes are generally high around 200 °C and introduction of alkyl substituents on the alkoxy backbones tends to lower vaporization temperature and

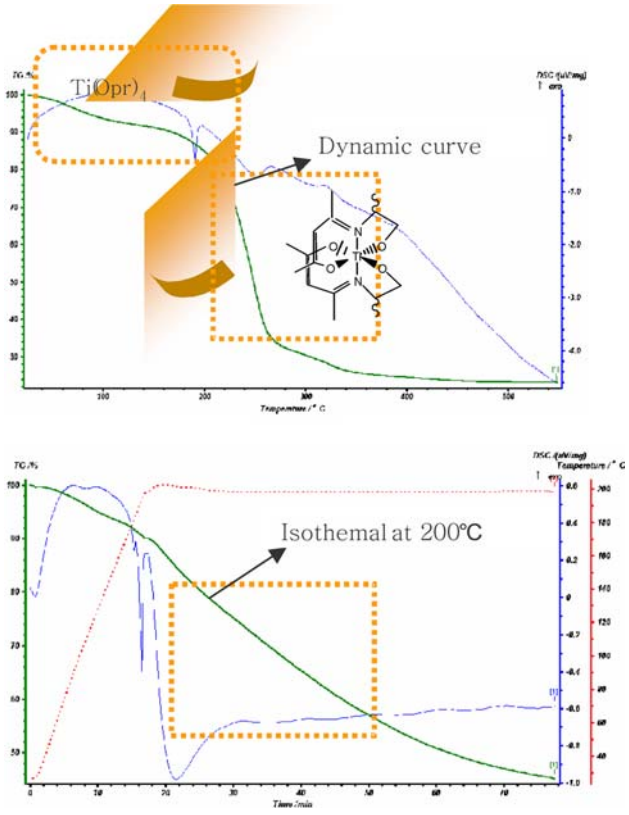


Fig. 3. Dynamic and isothermal (200 °C) TGA thermodiagrams of **2b**.

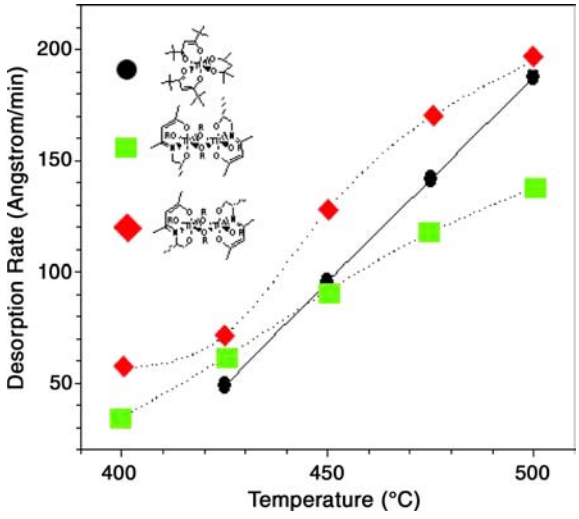


Fig. 4. Deposition rate of TiO_2 layer with several Ti precursors as a function of deposition temperature (deposition conditions(**2b**, **2c**, Ti(mpd)(thd)$_2$) solvent: *n*-butyl acetate (0.05 M, 5 ml), *n*-butyl acetate (0.05 M, 3 ml), MeOH (0.05 M, 5 ml); temperature of evaporation: 260, 230, 260 °C; temperature of substrate: 400–500 °C).

Table 4
Thermal characteristics of [Ti(*N*-alkoxy-β-ketoiminate)$_2$]

Complex	Melting point (°C)	Evaporation temperature (°C)	Residue (%)
3a	199	323	8
3b	199	290	0.5
3c	60	295	3.3
3d	218	290	13.7
3e	178	270	26.6
3h	185	285	8.3
3i	175	295	3.6
3k	220	290	0.5

amount of residue. Methyl group on the carbon next to N leads to higher vaporization temperature and residue amount than methyl group on the carbon next to O. Residue of **3a** is much less than that of **3e** while melting point and vaporization temperature of **3a** are lower than those of **3e**. This indicates that 6,5 chelate rings (**3a**) lead to better thermal stability and higher volatility than 6,6 ones (**3e**). Weight decrease rates of **3a** and **3b** were measured by isothermal TGA at 150, 200, and 250 °C and it is found that these are less than that of commercially available Ti(mpd)(thd)$_2$. This represents enhanced compatibility with not much volatile precursors of barium and strontium in the fabrication of BST thin films. Performance of these complexes as precursors of LSMOCVD was already reported elsewhere [5].

2.5. Other properties of [Ti(N-alkoxy-β-ketoiminate)$_2$]

These complexes showed much improved chemical stability toward hydrolysis. After the exposure to air for 3 months, these complexes do not show any extra peaks in NMR spectra. **3a** is slightly soluble in *n*-butyl acetate, while **3b** shows much higher solubility in the same solvent (0.08 M in *n*-butyl acetate and 0.4 M in THF). However, **3b** shows ligand dissociation in MeOH, which should be improved for the application to LSMOCVD.

3. Conclusions

Various *N*-alkoxy-β-ketoimine ligands have been prepared with high yields and reactions between these ligands and Ti(O-*i*Pr)$_4$ resulted in dimeric [Ti(O-*i*Pr)$_2$(*N*-alkoxy-β-ketoiminate)]$_2$ complexes or monomeric [Ti(*N*-alkoxy-β-ketoiminate)$_2$] ones depending on the amount of ligands. Dimer complexes undergo disproportional rearrangement to produce Ti(O-*i*Pr)$_4$ and [Ti(*N*-alkoxy-β-ketoiminate)$_2$]. The mechanism of this behavior is too complicated but it may include the dissociation and recoordination of ligands. Crystal structures of **3f** and **3k** show that β-ketoiminate ligands appear to coordinate as a β-imino enolate, rather than as its β-ketoamide tautomer. Two terdentate β-ketoiminate ligands coordinate meridianally and they are perpendicular to each other. Thermal characteristics determined by TGA and DSC show that dimeric complexes undergo disproportionation, evaporation of Ti(O-*i*Pr)$_4$ and [Ti(*N*-alkoxy-β-ketoiminate)$_2$] successively and volatility of monomeric ones depends on the substituents on the backbone of alkoxy part.

4. Experimental

All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques unless stated otherwise. The solvents were reagent grade and were distilled under nitrogen over appropriate drying agents prior to use. Reagent grade chemicals were purchased from Aldrich Chemical Co., Inc. and Strem Chemicals Inc. and used without further purification unless stated otherwise. *N*-hydroxyalkyl-β-ketoimines, $CH_3C(O)CH_2C(NCH_2CHR'OH)CH_3$ ($R' = H$, **1a**; $R' = Me$, **1b**) and Ti[$CH_3C(O)CH_2C(NCH_2CHR'OH)CH_3$]$_2$ ($R' = H$, **3a**; $R' = Me$, **3b**) were prepared according to published procedures [12]. ^1H and ^{13}C NMR spectra were recorded by using 5 mm tube on a Bruker AC-250 (VT NMR experiments, 250.133 and 62.896 MHz, respectively) or Varian Gemini 2000 (RT NMR experiments, 199.976 and 50.289 MHz, respectively) FT NMR spectrometer and were referenced to tetramethylsilane (TMS). Variable temperature NMR spectra were obtained using toluene-d_8 as a solvent in the range of 213–353 K. Elemental analyses were performed with EA-1110 (CE Instruments) in the Inha University.

Thermal analysis (TGA and DSC) was done with NETZSCH STA 449C (1 atm and 1.3 mbar, heating rate = 10 °C/min, N_2 flow rate = 20 ml/min) in Samsung Advanced Institute of Technology.

A laboratory-made liquid delivery MOCVD apparatus was employed for the testing of the synthesized Ti precursors in the deposition of TiO_2 thin films. The detailed description of apparatus and experimental conditions were given elsewhere [11j].

4.1. X-ray data collection, structure determination and refinement

Crystals suitable for X-ray diffraction were mounted on a Siemens SMART diffractometer equipped with a graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation source and a CCD detector and 45 frames of two-dimensional diffraction images were collected and processed to deduce the cell parameter and orientation matrix. A total of 1271 frames of two-dimensional diffraction images were collected, each of which was measured for 10 s. The frame data were

processed to give structure factors by the program SAINT [18]. The intensity data were corrected for Lorentz and polarization effects. The structures were solved by a combination of the direct method and the difference Fourier methods provided by the program package SHELXTL [19], and refined using a full-matrix least-square against F^2 for all data. All the non-H atoms were refined anisotropically. All hydrogen atoms were included in calculated positions with isotropic thermal parameters 1.2 times those of attached atoms.

5. Ligand synthesis

5.1. 2-N-(2-Hydroxyethylimino)-4-pentanone (**1a**), $CH_3C(O)CHC(HNCH_2CH_2OH)CH_3$

Yield: 12.88 g (90%).

5.2. 2-N-(2-Hydroxy-2-methylethylimino)-4-pentanone (**1b**), $CH_3C(O)CHC(HNCH_2CH(CH_3)OH)CH_3$

Yield: 29.83 g (95%).

5.3. 2-N-(2-Hydroxy-1-methylethylimino)-4-pentanone (**1c**), $CH_3C(O)CHC(HNCH(CH_3)CH_2OH)CH_3$

D/L-2-Amino-1-propanol (10.0 g, 13.31 mmol) and 2,4-pentanedione (11.11 g, 111.0 mmol) were dissolved in 100 ml of CH_3OH with 0.51 g of HCOOH and the mixture was refluxed for a day while stirring vigorously. After cooling down to room temperature, the solvent was removed under reduced pressure. The product was extracted to the organic layer with H_2O/CH_2Cl_2 (20/150 ml) mixture. The product remained in the aqueous layer was extracted with 100 ml of CH_2Cl_2 three times. After the solution was dried with $MgSO_4$, the solvent was removed under reduced pressure. The product was purified with a silica column, eluting with ethylacetate. Yield: 15.52 g (89%).

^{1}H NMR ($CDCl_3$): 10.8(br s, 1H, C(O)CH=C(N*H*)), 4.93(s, 1H, C(O)C*H*=C(NH)), 3.72(m, 1H, HNC*H*(Me)CH_2OH), 3.62(dd, 1H, NCHMeC*H*aHbOH), 3.52 (dd, 1H, NCHMeCHa*H*bOH), 3.35(br s, 1H, NCH(Me)CH_2O*H*), 1.98(s, 3H, CH=C(NH)CH_3), 1.97(s, 3H, CH_3C(O)CH), 1.18(d, 3H, HNCH(CH_3)CH_2OH). ^{13}C NMR ($CDCl_3$): 192.45(s, CH_3C(O)CH), 160.69(s, CH=*C*(NH)CH_3), 93.19(s, C(O)*C*H=C(NH)), 64.57(s, HNCH(Me)*C*H_2OH), 48.45(s, HN*C*H(Me)CH_2OH), 26.19(s, *C*H_3C(O)CH), 16.69(s, CH=C(NH)*C*H_3), 15.7 (s, NHCH(*C*H_3)CH_2OH). *Anal.* Calc. for $C_8H_{15}NO_2$: C, 61.12; H, 9.62; N, 8.92. Found: C, 61.15; H, 10.76; N, 9.07%.

5.4. 2-N-(1,1-dimethyl-2-Hydroxyethylimino)-4-pentanone (**1d**), $CH_3C(O)CHC(HNC(CH_3)_2CH_2OH)CH_3$

2-Amino-2-methyl-1-propanol (13.35 g, 149.8 mmol) and 2,4-pentanedione (10.0 g, 99.88 mmol) were dissolved in 100 ml of CH_3OH with 0.51 g of HCOOH and the mixture was refluxed for a day while stirring vigorously. The solvent was removed under reduced pressure and the solid was purified with recrystallization using 200 ml of ethylether at room temperature. Yield: 10.95 g (64%).

^{1}H NMR ($CDCl_3$): 11.32(br s, 1H, C(O)CH=C(N*H*)), 4.88(s, 1H, C(O)C*H*=C(NH)), 4.35(br s, 1H, HNC(Me)$_2$$CH_2$O*H*), 3.53(s, 2H, NC(Me)$_2$CH_2OH), 2.04(s, 3H, CH=C(N)CH_3), 1.94(s, 3H, CH_3C(O)), 1.33(s, 6H, (HNC(CH_3)$_2$$CH_2$OH). ^{13}C NMR ($CDCl_3$): 194.24(s, CH_3C(O)CH), 163.88(s, CH=*C*(NH)CH_3), 97.07(s, C(O)*C*H=(NH)), 70.93(s, NHC(Me)$_2$*C*H_2OH), 56.44(s, HN*C*(Me)$_2$$CH_2$OH), 28.67(s, CH=C(NH) *C*H_3), 25.72(s, HNC(*C*H_3)$_2$$CH_2$OH), 20.96(s, *C*$H_3$ C(O)CH). *Anal.* Calc. for $C_9H_{17}NO_2$: C, 63.13; H, 10.01; N, 8.18. Found: C, 63.38; H, 10.57; N, 8.23%.

5.5. 2-N-(3-Hydroxypropylimino)-4-pentanone (**1e**), $CH_3C(O)CHC(HNCH_2CH_2CH_2OH)CH_3$

The same procedure as described in Section 5.3 was adopted except 3-amino-1-propanol (9.0 g, 119.8 mmol) and 2,4-pentanedione (10.0 g, 99.88 mmol). The product was purified with a silica column, eluting with ethylacetate/hexane (80%). Yield: 14.00 g (93%).

^{1}H NMR ($CDCl_3$): 10.86(br s, 1H, C(O)CH=C(N*H*)), 4.96(s, 1H, C(O)C*H*=C(NH)), 3.74 (t, 2H, NCH_2CH_2C*H*$_2$OH), 3.38(dt, 2H, NC*H*$_2$ CH_2CH_2OH), 2.67(br s, 1H, $NCH_2CH_2CH_2$O*H*), 1.98 (s, 3H, CH=C(NH)CH_3), 1.94(s, 3H, CH_3C(O)CH), 1.83(m, 2H, NCH_2C*H*$_2$$CH_2$OH). ^{13}C NMR ($CDCl_3$): 194.94(s, CH_3 *C*(O)CH), 163.80(s, CH=*C*(NH)CH_3), 95.46(s, C(O) *C*H=C(NH)), 59.62(s, $HNCH_2CH_2$ *C*H_2OH), 39.92(s, HN*C*$H_2CH_2CH_2$OH), 32.85(s, HN CH_2*C*H_2CH_2OH), 28.85(s, *C*H_3C(O)CH), 18.99(s, CH=C(NH)*C*H_3). *Anal.* Calc. for $C_8H_{15}NO_2$: C, 61.12; H, 9.62; N, 8.91. Found: C, 60.90; H, 9.94; N, 9.09%.

5.6. 2-N-(2-Hydroxy-1-ethylethylimino)-4-pentanone (**1f**), $CH_3C(O)CHC(HNCH(CH_2CH_3)CH_2OH)CH_3$

The same procedure as described in Section 5.3 was adopted except 2-amino-1-butanol (11.0 g, 119.8 mmol) and 2,4-pentanedione (10.0 g, 99.88 mmol). The product was purified with a silica column, eluting with ethylacetate/hexane (80%). Yield: 14.71 g (86%).

^{1}H NMR ($CDCl_3$): 10.85(br d, 1H, C(O)CH=C(N*H*)), 4.96(s, 1H, C(O)C*H*=C(NH)), 3.66–3.55 (m, 1H, HNC*H*(Et)CH_2OH), 3.66–3.55(m, 1H, NCH(Et) C*H*aHbOH), 3.25(br s, 1H, NCH(Et) CH_2O*H*), 2.06(s,

3H, CH=C(NH)CH_3), 1.99(s, 3H, CH_3C(O)CH), 1.56(m, 3H, HNCH(CH_2CH$_3$)CH$_2$OH), 0.95(t, 7.4 Hz, HNCH(CH$_2$CH_3)CH$_2$OH). ^{13}C NMR ($CDCl_3$): 195.15 (s, CH$_3$*C*(O)CH), 163.86(s, CH=*C*(NH)CH$_3$), 95.87(s, C(O)*C*H=C(NH)), 65.91(s, HNCH(Et)*C*H$_2$ OH), 57.23 (s, HN*C*H(Et)CH$_2$OH), 28.90(s, *C*H$_3$C (O)CH), 25.54(s, CH=C(NH)*C*H$_3$), 19.66(s, NHCH (*C*H$_2$CH$_3$)CH$_2$OH), 10.56(s, NHCH(CH$_2$*C*H$_3$)CH$_2$ OH). *Anal.* Calc. for $C_9H_{17}NO_2$: C, 63.13; H, 10.01; N, 8.18. Found: C, 63.41; H, 10.23; N, 8.12%.

5.7. 2,6-Dimethyl-3-N-(2-hydroxyethylimino)-5-heptanone (**1g**), $(CH_3)_2CHC(O)CHC(HNCH_2CH_2OH)CH(CH_3)_2$

Ethanolamine(4.30 g, 70.4 mmol) and 2,6-dimethyl-3,5-heptanedione (10.0 g, 64.0 mmol) were dissolved in 180 ml of benzene with 0.63 g of H_2SO_4 0.63 g (1 drop). The mixture in a Dean and Stark apparatus was refluxed for 6 h while stirring vigorously. After cooling down to room temperature, the solvent was removed under reduced pressure. The product was extracted to the organic layer with H_2O/benzene (20/200 ml) mixture. The product remained in the aqueous layer was extracted with 100 ml of benzene three times. After the solution was dried with $MgSO_4$, the solvent was removed under reduced pressure. The product was purified by recrystallization in 100 ml of *n*-hexane at −20 °C. Yield: 10.72 g (84%).

^{1}H NMR ($CDCl_3$): 11.20(br s, 1H, C(O)CH=CN*H*), 5.05(s, 1H, C(O)C*H*=CNH), 3.79 (t, $^3J_{HH} = 5.60$ Hz, 2H, HNCH$_2$C*H*$_2$OH), 3.44 (dt, $^3J_{HH} = 5.60$ Hz, 5.40 Hz, 2H, HNC*H*$_2$CH$_2$OH), 2.73 (h, $^3J_{HH} = 7.00$ Hz, 1H, HNCC*H* Me$_2$), 2.45 (h, $^3J_{HH} = 7.00$ Hz, 1H, Me$_2$C*H*C(O)CH), 2.35(br s, 1H, NCH$_2$CH$_2$O*H*), 1.14 (d, $^3J_{HH} = 7.00$ Hz, 6H, HNCCH(CH_3)$_2$), 1.08 (d, $^3J_{HH} = 7.00$ Hz, 6H, (CH_3)$_2$CHC(O)CH). ^{13}C NMR ($CDCl_3$): 200.86(s, Me$_2$CH*C*(O)CH), 172.13(s, HN*C* CHMe$_2$), 86.45(s, C(O)*C*H=CNH), 59.91(s, NCH$_2$ *C*H$_2$OH), 42.75(s, N*C*H$_2$CH$_2$OH), 38.09(s, Me$_2$*C*H-C(O)CH), 26.91(s, HNC*C*HMe$_2$), 19.52(s, HNCCH(*C* H$_3$)$_2$), 18.27(s, (*C*H$_3$)$_2$CHC(O)CH). *Anal.* Calc. for $C_{11}H_{21}NO_2$: C, 66.29; H, 10.62; N, 7.03. Found: C, 66.10; H, 10.84; N, 7.09%.

5.8. 2,6-Dimethyl-3-N-(2-hydroxy-2-methylethylimino)-5-heptanone (**1h**), $(CH_3)_2CHC(O)CHC(HNCH_2CH(CH_3)OH)(CH(CH_3)_2)$

The same procedure as described in Section 5.6 was adopted except 1-amino-2-propanol (5.77 g, 76.8 mmol) and 2,6-dimethyl-3,5-heptanedione (10.0 g, 64.0 mmol). The product was purified with a silica column, eluting with ethylacetate/hexane (80%). Yield: 11.61 g (85%).

^{1}H NMR ($CDCl_3$): 11.21(br s, 1H, C(O)CH = CN*H*), 5.01(s, 1H, C(O)C*H*=CNH), 3.95 (q, $^3J_{HH} = 6.00$ Hz, 1H, HNCH$_2$C*H*MeOH), 3.42(br s, 1H, NCH$_2$CH$_2$O*H*), 3.22(m, 2H, HNC*H*$_2$CHMeOH), 2.70 (h, $^3J_{HH} = 7.00$ Hz, 1H, HNCC*H*Me$_2$), 2.42 (h, $^3J_{HH} = 7.00$ Hz, 1H, Me$_2$C*H*C(O)CH), 1.23 (d, $^3J_{HH} = 6.00$ Hz,, 3H, NCH$_2$ CH(CH_3)OH), 1.10 (d, $^3J_{HH} = 7.00$ Hz, 6H, HNCCH (CH_3)$_2$), 1.05 (d, $^3J_{HH} = 7.00$ Hz, 6H, (CH_3)$_2$CHC(O) CH). ^{13}C NMR ($CDCl_3$): 200.82(s, Me$_2$CH*C*(O)CH), 171.90(s, HN*C*CHMe$_2$), 86.42(s, C(O)*C*H=CN), 65.13 (s, NCH$_2$*C*HMeOH), 47.92(s, HN*C*H$_2$CHMeOH), 38.12 (s, Me$_2$*C*HC(O)CH), 26.85(s, HNC*C*HMe$_2$), 19.56(s, HNCCH(*Ca*H$_3$)(CbH$_3$)), 19.47(s, HNCCH(CaH$_3$)(*Cb*H$_3$)), 19.20(s, NCH$_2$ CH(*H*H$_3$)OH), 18.27(s, (*C*H$_3$)$_2$CHC(O) CH). *Anal.* Calc. for $C_{12}H_{23}NO_2$: C, 67.57; H, 10.87; N, 6.56. Found: C, 67.44; H, 11.33; N, 6.48%.

5.9. 2,6-Dimethyl-3-N-(2-hydroxy-1-methylethylimino)-5-heptanone (**1i**), $(CH_3)_2CHC(O)CHC(HNCH(CH_3)CH_2OH)(CH(CH_3)_2)$

The same procedure as described in Section 5.6 was adopted except D/L-2-amino-1-propanol (7.21 g, 95.99 mmol) and 2,6-dimethyl-3,5-heptanedione (10.0 g, 64.0 mmol). The product was purified with a silica column, eluting with ethylacetate/hexane (80%). Yield: 11.65 g (81%).

^{1}H NMR ($CDCl_3$): 11.12(br d, 1H, C(O)CH = C(N*H*CH(Me))), 5.03(s, 1H, C(O)C*H*=C(NH)), 3.79(m, 1H, HNC*H*(Me)CH$_2$OH), 3.59(br m, 2H, NCHMeC*H*$_2$ OH) 2.89(br s, 1H, NCH(Me)CH$_2$O*H*), 2.78(m, 1H, CH=C(NH)C*H* (CH$_3$)$_2$), 2.45(m, 1H, (CH$_3$)$_2$ C*H* C(O)CH), 1.22(d, 3H, NCH(CH_3)CH$_2$OH), 1.15(d, 6H, CH=C(N)CH(CH_3)$_2$), 1.07(dd, 6H(CH_3)$_2$CHC (O)). ^{13}C NMR ($CDCl_3$): 202.57 (s, Me$_2$CH *C*(O)CH), 173.73(s, HN*C*CHMe$_2$), 88.24(s, C(O) *C*H=CN), 67.28 (s, HNCHMe*C*H$_2$OH), 50.00(s, N*C*H MeCH$_2$OH), 39.93(s, Me$_2$*C*HC(O)CH), 28.75(s, HNC *C*HMe$_2$), 22.03(s, HNCCH(*Ca*H$_3$)(CbH$_3$)), 21.72(s, HN CCH (CaH$_3$)(*Cb*H$_3$)), 20.16(s, (*C*H$_3$)$_2$CHC (O)CH), 18.90(s, NCH(*C*H$_3$)CH$_2$OH). *Anal.* Calc. for $C_{12}H_{23}NO_2$: C, 67.57; H, 10.87; N, 6.56. Found: C, 67.44; H, 11.70; N, 6.52%.

5.10. 5,5-Dimethyl-2-N-(2-hydroxyethylimino)-4-hexanone (**1j**), $(CH_3)_3CC(O)CHC(HNCH_2CH_2OH)CH_3$

The same procedure as described in Section 5.3 was adopted except ethanolamine(1.30 g, 21.3 mmol) and 2,2-dimethyl-3,5-hexanedione (2.02 g, 14.2 mmol). The product was purified with a silica column, eluting with ethylacetate/hexane (80%). Yield: 1.56 g (59%).

^{1}H NMR ($CDCl_3$): 11.04(br s, 1H, C(O)CH=CN*H*), 5.14(s, 1H, C(O)C*H*=CNH), 3.76 (t, $^3J_{HH} = 5.60$ Hz, 2H, HNCH$_2$C*H*$_2$OH), 3.39 (dt, $^3J_{HH} = 5.60$, 5.40 Hz, 2H, HNC*H*$_2$CH$_2$OH), 3.11(br s, 1H, HNCH$_2$CH$_2$O*H*), 1.97(s, 3H, HNCCH_3), 1.11(s, 9H, (CH_3)$_3$CC(O)CH).

^{13}C NMR ($CDCl_3$): 202.39(s, Me_3CC(O)CH), 162.54(s, HNCCH$_3$), 89.32(s, C(O)CH=CNH), 60.02(s, NCH$_2$ CH$_2$OH), 43.63(s, HNCH$_2$CH$_2$OH), 39.58(s, (CH$_3$)$_3$ CC(O)CH), 26.25(s, (CH$_3$)$_3$CC(O)CH), 17.82(s, HNC CH$_3$). *Anal.* Calc. for $C_{10}H_{19}NO_2$: C, 64.83; H, 10.34; N, 7.56. Found: C, 64.76; H, 10.82; N, 7.60%.

*5.11. 5,5-Dimethyl-2-N-(2-hydroxy-2-methylethylimino)-4-hexanone (**1k**), $(CH_3)_3CC(O)CHC(HNCH_2CH(CH_3)OH)CH_3$*

The same procedure as described in Section 5.3 was adopted except 1-amino-2-propanol (6.34 g, 84.38 mmol) and 2,2-dimethyl-3,5-hexanedione (2.02 g, 14.2 mmol). Ethanol was employed as a solvent. The product was purified with recrystallization in 80 ml of *n*-hexane at −20 °C. Yield: 10.93 g (78%).

^{1}H NMR ($CDCl_3$): 11.04(br s, 1H, C(O)CH=CNH), 5.13(s, 1H, C(O)CH=CNH), 3.96(m, 1H, HNCH$_2$ CH(Me)OH), 3.26 (dd, 1H, HNCHaHbCH(Me)OH), 3.20(dd, 1H, HNCHaHbCH(Me)OH), 3.19 (br s, 1H, HNCH$_2$CH(Me)OH), 1.96(s, 3H, HNCCH_3), 1.23(d, 3H, HNCH$_2$CH(CH_3)OH), 1.11(s, 9H, (CH_3)$_3$CC(O) CH). ^{13}C NMR ($CDCl_3$): 204.16(s, Me$_3$CC(O)CH), 164.20(s, HNCCH$_3$), 91.18(s, C(O)CH=CNH), 67.11(s, NCH$_2$$C$H(Me)OH), 50.71(s, HN$CH_2$CH(Me)OH), 41.46(s, (CH$_3$)$_3$$C$C(O)CH), 28.16(s, ($CH_3$)$_3$CC(O)CH), 21.00(s, HNC$CH_3$), 19.77(s, HNCH$_2$CH($CH_3$)OH). *Anal.* Calc. for $C_{11}H_{21}NO_2$: C, 66.29; H, 10.62; N, 7.03. Found: C, 65.72; H, 11.08; N, 7.12%.

6. Preparation of metal complexes

6.1. Dimeric N-alkoxy-β-ketoiminato titanium diisopropoxide complexes

*6.1.1. [Ti(CH$_3$C(O)CHC(NCH$_2$CH$_2$O)CH$_3$)(O-iPr)$_2$]$_2$ (**2a**)*

Ligand **1a** (2.52 g, 17.59 mmol) in 25 ml of CH_2Cl_2 was added dropwise to the solution containing Ti(O-*i*Pr)$_4$ (5.0 g, 17.59 mmol) in 20 ml of CH_2Cl_2 over 4 h via cannular at −78 °C. After the addition was completed, the solution turned to yellow. The solution was stirred for one more hour and the solvent was removed at −20 °C. Recrystallization in 40 ml of *n*-hexane at −20 °C produced yellow solid. Yield: 4.88 g (90%).

^{1}H NMR ($CDCl_3$): 5.27(s, 2H, C(O)CHC(N)), 4.65(br m, 4H, OCH), 4.43(t, 4H, NCH$_2$CH_2O), 3.84(t, 4H, NCH_2CH$_2$O), 1.99(s, 12H, C(N)CH_3), 1.95(s, 12H, CH_3C(O)), 1.18(d, 24H, OCH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$): 173.17(s, CH$_3$$C$(O)CH), 167.18(s, CH$C$(N) CH$_3$), 100.15(s, C(O)$C$HC(N)), 75.24(s, O$C$H(Me)$_2$), 67.49(s, NCH$_2$$CH_2$O), 56.35(s, N$CH_2CH_2$O), 23.36(s, OCH($CH_3$)$_2$), 21.88(s, C(N)$CH_3$), 20.12(s, CH$_3$C(O)). *Anal*. Calc. for $C_{26}H_{50}N_2O_8Ti_2$: C, 50.86; H, 8.21; N, 4.56. Found: C, 50.54; H, 8.24; N, 4.65%.

*6.1.2. [Ti(CH$_3$C(O)CHC(NCH$_2$CH(Me)O)CH$_3$)(O-iPr)$_2$]$_2$ (**2b**)*

The same procedure as described in Section 6.1.1 was adopted except ligand **1b** (2.76 g, 17.59 mmol). Recrystallization in mixed solvents (40 ml of *n*-hexane/5 ml of CH_2Cl_2) at −20 °C produced yellow solid. Yield: 5.42 g (96%).

^{1}H NMR ($CDCl_3$): 5.24(s, 2H, CH), 4.72(m, 2H, NCH$_2$CH(Me)O), 4.60(br m, 4H, OCH(Me)$_2$), 3.96(dd, 2H, NCHaHbCH(Me)O), 3.43(dd, 2H, NCHaHbCH(-Me)O), 1.98(s, 6H, C(N)CH_3), 1.96(s, 6H, CH_3C(O)), 1.20(d, 24H, OCH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$): 176.30(s, CH$_3$$C$(O), 169.80(s, C(N)CH$_3$)), 102.89(s, C(O)CHC (N)), 77.86(s, NCH$_2$$C$H(Me)O), 75.86(s, O$C$H(CH$_3$)$_2$), 65.65(s, N$CH_2$CH(Me)O), 26.06(s, OCH($CH_3$)$_2$), 24.41 (s, C(N)$CH_3$), 22.66(s, CH$_3$C(O)), 22.10(s, NCH$_2$CH (CH$_3$)O).

*6.1.3. [Ti(CH$_3$C(O)CHC(NCH(Me)CH$_2$O)CH$_3$)(O-iPr)$_2$]$_2$ (**2c**)*

The same procedure as described in Section 6.1.1 was adopted except ligand **1c** (1.66 g, 10.55 mmol) and Ti(O-*i*Pr)$_4$ (3.0 g, 10.55 mmol). Removal of solvent under reduced pressure at −40 °C produced viscous red liquid. Yield: 3.18 g (94%).

^{1}H NMR ($CDCl_3$): 5.21(s, 2H, C(O)CHC(N)), 4.62(m, 4H, OCH(Me)$_2$), 4.60(dd, 2H, NCH(Me)CHa HbO), 4.23(m, 2H, NCH(Me)CH$_2$O), 3.91(dd, 2H, NCH(Me)CHaHbO), 2.05(s, 6H, C(N)CH_3), 1.96(s, 6H, CH_3C(O)), 1.30(d, 6H, NCH(CH_3)CH$_2$O), 1.20(d, 24H, OCH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$): 173.6(s, CH$_3$$C$(O)), 166.1(s, C(N)CH$_3$), 100.6(s, C(O)CHC(N)), 73.9(s, OCH(Me)$_2$), 73.81(s, NCH(Me)CH$_2$O), 61.89(s, NCH (Me)CH$_2$O), 23.44(s, OCH(CH$_3$)$_2$), 21.85(s, CH$_3$C(O)), 19.1(s, C(N)CH$_3$), 18.2(s, NCH(CH$_3$)CH$_2$O).

*6.1.4. [Ti((CH$_3$)$_2$CH)C(O)CHC(CH(CH$_3$)$_2$)(NCH$_2$CH$_2$O)(O-iPr)$_2$]$_2$ (**2d**)*

The same procedure as described in Section 6.1.1 was adopted except ligand **1d** (2.10 g, 10.55 mmol) and Ti(O-*i*Pr)$_4$ (3.0 g, 10.55 mmol). Recrystallization in 25 ml of *n*-hexane at −20 °C produced yellow solid. Yield: 3.41 g (89%).

^{1}H NMR ($CDCl_3$): 5.23(s, 2H, C(O)CHC(N)), 4.62(br m, 4H, OCH(Me)$_2$), 4.32(br t, 4H, NCH$_2$ CH_2O), 3.84(br t, 4H, NCH_2CH$_2$O), 2.89(m, 2H, C(N) CH(Me)$_2$), 2.41(m, 2H, (Me)$_2$CHC(O)), 1.15(d, 24H, C(N)CH(CH_3)$_2$), 1.14(d, 24H, (CH_3)$_2$CHC(O)). ^{13}C NMR ($CDCl_3$): 182.60(s, (CH$_3$)$_2$CHC(O)), 177.15 (C(N)(CH(CH$_3$)$_2$)), 93.70(s, C(O)CHC(N)), 77.23(s, OCH(CH$_3$)$_2$), 70.29(s, NCH$_2$$CH_2$O), 56.48(s, NCH$_2$ CH$_2$O), 36.80(s, (CH$_3$)$_2$$C$HC(O)), 31.46(s, C(N)C($C$H (CH$_3$)$_2$)), 25.88(s, O(CH($CH_3$)$_2$)), 20.78(s, C(N)(CH ($CH_3$)$_2$)) 20.78(s, ($CH_3$)$_2$CHC(O)).

*6.1.5. [Ti((CH$_3$)$_2$CH)C(O)CHC(CH(CH$_3$)$_2$)(NCH$_2$CH(Me)O)(O-iPr)$_2$]$_2$ (**2h**)*

The same procedure as described in Section 6.1.1 was adopted except ligand **1h** (2.25 g, 10.55 mmol) and Ti(O-*i*Pr)$_4$ (3.0 g, 10.55 mmol). Recrystallization in 20 ml of *n*-hexane at −20 °C produced yellow solid. Yield: 3.65 g (95%).

^{1}H NMR ($CDCl_3$): 5.30(s, 2H, C(O)C*H*C(N)), 4.65(m, 4H, OC*H*(Me)$_2$), 4.65(m, 2H, NCH$_2$C*H*(Me)O), 4.02(dd, 2H, NC*H*aHbCH(Me)O), 3.55(dd, 2H, NCHa*H*bCH(-Me)O), 2.89(m, 2H, C(N)C*H*(Me)$_2$), 2.43(m, 2H, (Me)$_2$C*H*C(O)), 1.17(d, 24H, C(N)CH (C*H*$_3$)$_2$), 1.10(d, 24H, (C*H*$_3$)$_2$CHC(O)), 1.08(d, 6H, NCH$_2$CH(C*H*$_3$)O). ^{13}C NMR ($CDCl_3$): 181.10(s, ((CH$_3$)$_2$CH)*C*(O)), 175.37 (s, *C*(N)(CH(CH$_3$)$_2$)), 91.51(s, C(O)*C*HC(N)), 74.65(s, O(*C*H(CH$_3$)$_2$)), 73.56(s, NCH$_2$*C*H(Me)O), 60.92(s, N*C*H$_2$ CH(Me)O), 34.18(s, (CH$_3$)$_2$*C*H)C(O)), 28.89(s, C(N) (*C*H(CH$_3$)$_2$)), 23.42(s, O(CH(*C*H$_3$)$_2$)), 19.43(s, NCH$_2$CH (*C*H$_3$)O), 18.41(s, C(N)(CH(*Ca*H$_3$)(CbH$_3$)), 18.19(s, C(N)(CH(CaH$_3$) (*Cb*H$_3$)), 18.13(s, (*C*H$_3$)$_2$CHC(O)).

6.2. Monomeric bis titanium complexes

*6.2.1. Ti(CH$_3$C(O)CHC(NCH$_2$CH$_2$O)CH$_3$)$_2$ (**3a**)*

Ligand **1a** (3.67 g, 25.61 mmol) in 20 ml of CH_2Cl_2 was added dropwise to the solution containing Ti(O-*i*Pr)$_4$ (3.31 g, 11.64 mmol) in 25 ml of CH_2Cl_2 over 4 h via cannular at room temperature. After the addition was completed, the solution turned to yellow. The solution was stirred for one more hour and the solvent was removed under reduced pressure. Recrystallization in 40 ml of *n*-hexane at −20 °C produced yellow solid. Yield: 3.72 g (95%).

*6.2.2. Ti(CH$_3$C(O)CHC(NCH$_2$CHMeO)CH$_3$)$_2$ (**3b**)*

The same procedure as described in Section 6.2.1 was adopted except ligand **1b** (11.06 g, 70.36 mmol) and Ti(O-*i*Pr)$_4$ (10.0 g, 35.18 mmol). Yield: 12.18 g (96%).

*6.2.3. Ti(CH$_3$C(O)CHC(NCHMeCH$_2$O)CH$_3$)$_2$ (**3c**)*

The same procedure as described in Section 6.2.1 was adopted except ligand **1c** (8.0 g, 50.89 mmol) and Ti(O-*i*Pr)$_4$ (7.23 g, 25.44 mmol). Yield: 8.38 g (92%).

^{1}H NMR ($CDCl_3$): 5.27, 5.24, 5.08, 5.08(s, 2H, C(O)C*H*C(N)), 4.79(dd, 1H, NCH(Me)C*Ha*bHcdO), 4.58(dd, 1H, NCH(Me)C*Hb*HcdO), 4.35(m, 2H, NC*H*(Me)CH$_2$O), 4.00(dd, 1H, NCH(Me)CHab*Hc*dO), 3.83(dd, 1H, NCH(Me)CHab*Hc*dO), 2.14, 2.12, 2.11, 2.07(s, 6H, C(N)C*H*$_3$), 1.94, 1.92, 1.88, 1.80(s, 6H, C*H*$_3$C(O)), 1.51, 1.37, 1.32, 1.24, 1.17(d, 6H, NCH(C*H*$_3$)CH$_2$O). ^{13}C NMR ($CDCl_3$): 176.72, 175.83, 175.40(s, CH$_3$*C*(O)), 167.89, 167.27, 166.76(s, *C*(N)CH$_3$), 103.30, 103.20, 102.01(s, C(O)*C*HC(N)), 78.07, 78.00, 77.14(s, NCH(Me)*C*H$_2$O), 66.14, 65.73, 65.24, 64.96(s, N*C*H(Me)CH$_2$O), 24.92, 24.58, 24.40, 24.25(*H* H$_3$C(O)), 21.82, 21.59, 21.43, 20.74(C(N)*C*H$_3$), 20.35, 20.08, 19.30, 18.35(NCH(*C*H$_3$)CH$_2$O). *Anal.* Calc. for $C_{16}H_{26}N_2O_4Ti$: C, 53.64; H, 7.32; N, 7.82. Found: C, 53.32; H, 7.66; N, 7.79%.

*6.2.4. Ti(CH$_3$C(O)CHC(NC(Me)$_2$CH$_2$O)CH$_3$)$_2$ (**3d**)*

The same procedure as described in Section 6.2.1 was adopted except ligand **1d** (3.01 g, 17.58 mmol) and Ti(O-*i*Pr)$_4$ (2.50 g, 8.79 mmol). Yield: 3.19 g (94%).

^{1}H NMR ($CDCl_3$): 5.13(s, 2H, C(O)C*H*C(N)), 4.32 (d, 2H, NC(Me)$_2$C*Ha*HbO), 4.01 (d, 2H, NC(Me)$_2$-CHa*Hb*O), 2.21(s, 6H, C(N)C*H*$_3$), 1.92(s, 6H, C*H*$_3$C(O)), 1.56 (s, 6H, NC(C*H*$_3$)*a*(CH$_3$)bCH$_2$O), 1.38(s, 6H, NC(CH$_3$)a(C*H*$_3$)*b*CH$_2$O). ^{13}C NMR ($CDCl_3$): 174.70(s, CH$_3$*H*(O)), 169.31(s, *H*(N)CH$_3$), 104.71(s, C(O)*H*HC(N)), 84.79(s, N*H*(Me)$_2$CH$_2$O), 71.41(s, NC(Me)$_2$*H*H$_2$O), 25.69(s, *H* H$_3$C(O)), 25.1(s, C(N)*H*H$_3$), 24.5(s, NC*Ca* H$_3$CbH$_3$CH$_2$O), 24.4(s, NCCaH$_3$*Cb* H$_3$CH$_2$O). *Anal.* Calc. for $C_{18}H_{30}N_2O_4Ti$: C, 55.96; H, 7.83; N, 7.25. Found: C, 55.59; H, 8.22; N, 6.87%.

*6.2.5. Ti(CH$_3$C(O)CHC(NCH$_2$CH$_2$CH$_2$O)CH$_3$)$_2$ (**3e**)*

The same procedure as described in Section 6.2.1 was adopted except ligand **1e** (1.11 g, 7.04 mmol) and Ti(O-*i*Pr)$_4$ (1.0 g, 3.52 mmol). Yield: 1.20 g (95%).

^{1}H NMR ($CDCl_3$): 5.14(s, 2H, C(O)C*H*C(N)), 4.36(t, 4H, NCH$_2$CH$_2$C*H*$_2$O), 3.64(t, 4H, NC*H*$_2$CH$_2$CH$_2$O), 2.07(m, 4H, NCH$_2$C*H*$_2$CH$_2$O), 2.00(s, 6H, C(N)C*H*$_3$), 1.90(s, 6H, C*H*$_3$C(O). ^{13}C NMR ($CDCl_3$): 176.05(s, CH$_3$*C*(O)), 168.01(s, *C*(N)CH$_3$), 103.64(s, C(O)*C*HC (N)), 73.23(s, N*C*H$_2$CH$_2$CH$_2$O), 50.19(s, NCH$_2$CH$_2$ *C*H$_2$O), 32.34(s, NCH$_2$*C*H$_2$CH$_2$O), 25.33(s, *C*H$_3$C(O)), 22.41(s, C(N)*C*H$_3$). *Anal.* Calc. for $C_{16}H_{26}N_2O_4Ti$: C, 53.64; H, 7.32; N, 7.82. Found: C, 53.33; H, 7.49; N, 7.97%.

*6.2.6. Ti(CH$_3$C(O)CHC(NCH(CH$_2$CH$_3$)CH$_2$O)CH$_3$)$_2$ (**3f**)*

The same procedure as described in Section 6.2.1 was adopted except ligand **1f** (2.30 g, 13.44 mmol) and Ti(O-*i*Pr)$_4$ (1.91 g, 6.72 mmol). Yield: 2.41 g (93%).

^{1}H NMR ($CDCl_3$): 5.28, 5.25, 5.09(s, 2H, C(O) C*H*C(N)), 4.69 (dd, 1H, NCH(Et)C*Ha*bHcdO), 4.65(dd, 1H, NCH(Et)C*Hab*HcdO), 4.18(dd, 1H, NCH(Et)CH-ab*Hc*dO), 4.17(dd, 1H, NCH(Et)CHab*Hc*dO), 4.03(m, 2H, NC*H*(Et)CH$_2$O), 2.21(m, 2H, NCH(C*Ha*Hb CH$_3$) CH$_2$O), 2.11, 2.06(s, 6H, C(N)C*H*$_3$), 1.92, 1.89, 1.80(s, 6H, C*H*$_3$C(O)), 1.66(m, 2H, NCH (CHa*Hb*CH$_3$)CH$_2$O), 0.97 (t, 6H, NCH(CH$_2$C*H*$_3$) CH$_2$O). ^{13}C NMR ($CDCl_3$): 175.89(s, CH$_3$*H*(O)), 167.13(s, *C*(N)CH$_3$), 102.04(s, C(O)*C*HC(N)), 74.46(s, N*C*H(Et)CH$_2$O), 72.78(s, NCH(Et)*C*H$_2$O), 27.47(s, *C*H$_3$C(O)), 24.67(s, C(N)*C*H$_3$), 21.99(s, NCH(*C*H$_2$CH$_3$) CH$_2$O), 11.77(s, NCH(CH$_2$*C*H$_3$)CH$_2$O). *Anal.* Calc. for $C_{18}H_{30}N_2O_4Ti$: C, 55.96; H, 7.83; N, 7.25. Found: C, 56.76; H, 8.30; N, 7.27%.

*6.2.7. Ti((CH$_3$)$_2$CHC(O)CHC(CH(CH$_3$)$_2$)(NCH$_2$CH(Me)O))$_2$ (**3h**)*

The same procedure as described in Section 6.2.1 was adopted except ligand **1h** (1.5 g, 7.03 mmol) and Ti(O-*i*Pr)$_4$ (1.0 g, 3.52 mmol). Yield: 1.57g (95%).

^{1}H NMR ($CDCl_3$): 5.23, 5.22, 5.20, 5.15(s, 2H, C(O)C*H*C(N)), 4.87(m, 2H, NCH$_2$C*H*MeO), 4.22(dd, 1H, NC*Ha*bHcdCH(Me)O), 4.13(dd, 1H, NC*Ha*bHcdCH(Me)O), 3.88(dd, 1H, NCHab*Hc*dCH(Me)O), 3.76(dd, 1H, NCHab*Hcd*CH(Me)O), 2.92(m, 2H, C(N)C*H*(Me)$_2$), 2.30(m, 2H, C*H*(Me)$_2$C(O)), 1.11–1.23(4d, 12H, C(N)CH(C*H*$_3$)$_2$), 1.21(3d, 6H, NCH$_2$CH(C*H*$_3$)O), 0.88–0.98 (4d, 12H, (C*H*$_3$)$_2$CHC(O)). ^{13}C NMR (CD_2Cl_2): 183.51, 183.35, 183.02(s, (CH$_3$)$_2$CH*C*(O)), 177.05, 176.49, 175.91, 175.70(s, *C*(N)(CH(CH$_3$)$_2$)), 93.46, 93.30, 93.19(s, C(O)*C*HC(N)), 76.99, 76.52, 76.40, 76.12(s, NCH$_2$*C*H(Me)O), 65.96, 65.60, 64.79(s, N*C*H$_2$CH(Me) O), 36.35, 36.27, 36.13 (s, (CH$_3$)$_2$*C*HC(O)), 31.46, 31.40, 31.24(s, C(N)(*C*H(CH$_3$)$_2$)), 21.66–20.18 (3s, (*C*H$_3$)$_2$ CHC(O)CHC(NCH$_2$CH(*C*H$_3$)O)(CH(*C*H$_3$)$_2$)). *Anal*. Calc. for $C_{24}H_{42}N_2O_4Ti$: C, 61.27; H, 9.00; N, 5.95. Found: C, 61.18; H, 9.23; N, 6.00%.

*6.2.8. Ti(CH$_3$C(O)CHC(NCH(CH$_2$CH$_3$)CH$_2$O)CH$_3$)$_2$ (**3f**)*

The same procedure as described in Section 6.2.1 was adopted except ligand **1i** (6.0 g, 28.14 mmol) and Ti(O-*i*Pr)$_4$ (4.0 g, 14.07 mmol). Yield: 6.22 g (94%).

^{1}H NMR ($CDCl_3$): 5.34, 5.17, 5.13(s, 2H, C(O)C*H*C(N)), 4.83(dd, 1H, NCH(Me)C*Ha*bHcdO), 4.79(dd, 1H, NCH(Me)C*Hab*HcdO), 4.56(m, 1H, NC*Ha*(Me)CH$_2$O), 4.38(m, 1H, NC*Hb*(Me)CH$_2$O), 4.03(dd, 1H, NCH(Me)CHab*Hc*dO), 3.95(dd, 1H, NCH(Me)CHab*Hcd*O), 3.03(m, 2H, C(N)(C*H*(CH$_3$)$_2$), 2.39(m, 1H, (CH$_3$)$_2$C*Ha* C(O)), 2.30(m, 1H, (CH$_3$)$_2$C*Hb* C(O)), 1.51, 1.41, 1.37(d, 6H, NCH(C*H*$_3$)CH$_2$O), 1.24–1.13(4d, 12H, C(N)(CH(C*H*$_3$)$_2$), 1.04–0.85(5d, 12H, (C*H*$_3$)$_2$CHC(O)). ^{13}C NMR ($CDCl_3$): 183.45, 182.98, 182.81(s, CH$_3$*C*(O)), 175.95, 175.70, 175.32(s, *C*(N) CH$_3$), 94.31, 93.84, 93.59(s, C(O)*C*HC(N)), 76.80, 76.69, 76.36(s, N*C*H(Me)CH$_2$O), 64.77, 64.36, 63.59(s, NCH (Me)*C*H$_2$O), 36.46, 36.36, 36.22(s, (CH$_3$)$_2$*C*HC(O)), 31.20, 31.00, 30.90(s, C(N)*C*H(CH$_3$)$_2$), 22.32, 22.17, 22.10, 22.05(s, NCH(*C*H$_3$)CH$_2$O), 21.87, 21.66, 21.60, 21.50(s, C(N)CH(*C*H$_3$)$_2$), 20.89, 20.78, 20.63, 20.52(s, (*C*H$_3$)$_2$CHC(O)). *Anal.* Calc. for $C_{24}H_{42}N_2O_4Ti$: C, 61.27; H, 9.00; N, 5.95. Found: C, 61.33; H, 9.48; N, 5.72%.

*6.2.9. Ti((CH$_3$)$_3$CC(O)CHC(NCH$_2$CH$_2$O)CH$_3$)$_2$ (**3j**)*

The same procedure as described in Section 6.2.1 was adopted except ligand **1j** (4.98 g, 26.88 mmol) and Ti(O-*i*Pr)$_4$ (3.82 g, 13.44 mmol). Yield: 5.05 g (91%).

^{1}H NMR ($CDCl_3$): 5.18(s, 2H, C(O)C*H*C(N)), 4.44–4.26(ddt, 4H, NCH$_2$C*H*$_2$O), 4.03–3.82 (ddt, 4H, NC*H*$_2$CH$_2$O), 2.00(s, 6H, C(N)C*H*$_3$), 0.92(s, 18H, (C*H*$_3$)$_3$CC(O)). ^{13}C NMR ($CDCl_3$): 184.48(s, (CH$_3$)$_3$ C*C*(O)), 168.87(s, *C*(N)CH$_3$), 97.01(s, C(O)*C*HC(N)), 70.89(s, NCH$_2$*C*H$_2$O), 60.18(s, N*C*H$_2$CH$_2$O), 37.84(s, (CH$_3$)$_3$*C*C(O)), 28.04(s, (*C*H$_3$)$_3$ CC(O)), 22.87(s, C(N)*C*H$_3$). *Anal*. Calc. for $C_{20}H_{34}N_2O_4Ti$: C, 57.97; H, 8.27; N, 6.76. Found: C, 57.87; H, 8.63; N, 6.70%.

*6.2.10. Ti((CH$_3$)$_3$CC(O)CHC(NCH$_2$CH(Me)O)CH$_3$)$_2$ (**3k**)*

The same procedure as described in Section 6.2.1 was adopted except ligand **1k** (4.0 g, 20.06 mmol) and Ti(O-*i*Pr)$_4$ (2.85 g, 10.03 mmol). Yield: 3.91 g (88%).

^{1}H NMR ($CDCl_3$): 5.30, 5.28, 5.23, 5.19(s, 2H, C(O)C*H*C(N)), 4.91, 4.82(m, 2H, NCH$_2$C*H*(Me)O), 4.16(dd, 1H, NC*Ha*bHcdCH(Me)O), 3.98(dd, 1H, NC*Ha*bHcdCH(Me)O), 3.77(dd, 1H, NCHab*Hc*dCH(Me)O), 3.63(dd, 1H, NCHab*Hcd*CH(Me)O), 2.07, 2.06, 2.04(s, 6H, C(N)C*H*$_3$), 1.22–1.14(d, 6H, NCH$_2$CH(C*H*$_3$)O), 1.02, 1.01, 1.00, 1.00(s, 18H, (C*H*$_3$)$_3$CC(O)). ^{13}C NMR ($CDCl_3$): 185.12(s, (CH$_3$)$_3$C*C*(O)), 168.79, 168.46, 168.17(s, *C*(N)CH$_3$), 97.47, 97.00, 96.89(s, C(O)*C*HC(N)), 77.31, 76.80, 76.36(s, NCH$_2$*C*H(Me)O), 67.53, 66.95, 66.57, 66.36(s, N*C*H$_2$CH(Me)O), 38.29, 38.22(s, C(N)*C*H$_3$), 28.50(s, (*C*H$_3$)$_3$CC(O)), 23.13, 22.02, 21.18, 20.73(s, NCH$_2$CH(*C*H$_3$)O). *Anal*. Calc. for $C_{22}H_{38}N_2O_4Ti$: C, 59.73; H, 8.66; N, 6.33. Found: C, 59.44; H, 8.78; N, 6.84%.

7. Supplementary material

Variable temperature ^{1}H NMR spectra of **2a** (250 MHz, 213–297 K, toluene-d_8), Variable temperature ^{13}C NMR spectra of **2a** (250 MHz, 215–297 K, $CDCl_3$). Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 218803 and 218804 for compound **3f** and **3k**, respectively. Copies of this information may be obtained free of the charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc. cam.ac.uk or http://www.ccdc.cam.ac.uk).

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