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Synthesis and investigation of the stability of Ti(III) β-diketiminato complexes. Structure of the tetrameric non-metallocene titanium fluoride complex $(L2)_4Ti_4F_6O_2 \cdot 2toluene$ supported by the β-diketiminato ligand

Grigori B. Nikiforov, Herbert W. Roesky*, Jörg Magull, Thomas Labahn, Denis Vidovic, Mathias Noltemeyer, Hans-Georg Schmidt, Narayan S. Hosmane

Institut für Anorganische Chemie, Universität Göttingen, Tammannstrasse 4, D-37077 Göttingen, Germany

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Dedicated to Professor Hans Bock on the occasion of his 75th birthday

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Abstract

The titanium β-diketiminato complexes $(L1)TiCl_2$ (**1**), $(L1)TiCl(N2,6\text{-}{}^iPr_2C_6H_3)$ (**2**), and $(L2)_2TiCl$ (**3**) [$L1 = (2,6\text{-}{}^iPr_2C_6H_3)NC(Me)CHC(Me)N(2,6\text{-}{}^iPr_2C_6H_3)$, $L2 = {}^iPrNC(Me)CHC(Me)N{}^iPr$] have been prepared by the reaction of the lithium salt of the ligand, L, with titanium trichloride. Complex **2** was isolated from supernatant solutions of **1** containing excess of the (L1)Li salt. The monochloride complex $[(L2)TiCl(N{}^iPr)]_2$ (**4**) was prepared by reduction of $(L2)_2TiCl_2$ with the excess of Na/K alloy. Fluorination of the monochloride complex **3** with Me_3SnF affords polymeric $[(L2)TiF_2]_n$ (**5**). Oxidation of **5** gives the tetrameric complex, $(L2)_4Ti_4F_6O_2 \cdot 2toluene$ (**6**). Compounds **1**–**6** were characterized by single crystal X-ray structural analyses, elemental analyses, NMR and mass spectra. The bulky ligand (L1) stabilizes the Ti(III) complex **1** with an unusual distorted square-planar pyramidal geometry around the titanium atom, by sigma bonding to the metal. The less bulky ligand (L2) in complexes **3**, **4** and **6** has mixed σ and π coordination to the titanium center. Investigation of the C–C, N–C distances in the NCCCN unit of the coordinated β-diketiminato ligands (L1) and (L2) demonstrated the localization of the double bonds in the ligand in complexes **1**–**3** and **6**. The stability of the complexes in solution was studied by means of NMR spectroscopy. Complexes **2** and **4** are stable in solution, the polymeric and the tetrameric nature of complexes **5** and **6** is not evident in C_6D_6 solution. The $(L2)_2TiCl$ stoichiometry of the complex is unstable.

Keywords: Coordination chemistry; β-Diketiminato ligand; Titanium(III); Chloride; Fluoride

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1. Introduction

The area of metal β-diketiminato complexes was intensively developed in recent years. The β-diketiminates play a useful role as monoanionic spectator ligands by virtue of their tuneable and extensive steric demands and their diversity of bonding modes [1]. They can stabilize low metal oxidation states [2] and form complexes with unusual coordination numbers [3,4]. The β-diketiminates usually give stable complexes with the metal cations in an oxidation state of +3 [5]. During the last decade, a considerable attention was focused on titanium complexes [5f,6]. It was found that the β-diketiminato complexes of Ti(III) with the general formula $LTiCl_2$ in the presence of excess methylaluminoxane [5f] or $B(C_6F_5)_3$ [6] catalyze the homopolymerization of ethylene and the copolymerization of ethylene with α-olefins. Several compounds of general formula $LTiX_2$ ($X = Cl$, Me, $L =$ β-diketiminato ligands) were prepared and complexes $LTiCl_2 \cdot 2THF$ ($L = (PhNC(Me))_2CH$) [5f], $LTiCl_2$ ($L = ((2,4,6\text{-}Me_3C_6H_2)NC(Me))_2CH$, $((2,4,6\text{-}Me_3C_6H_2)NC({}^tBu))_2CH$) and

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* Corresponding author. Tel.: +49-551-39-3001; fax: +49-551-39-3373.

E-mail address: hroesky@gwdg.de (H.W. Roesky).

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LTiMe$_2$ (L = ((2,4,6-Me$_3$C$_6$H$_2$)NC(Me))$_2$CH) [6] were structurally characterized.

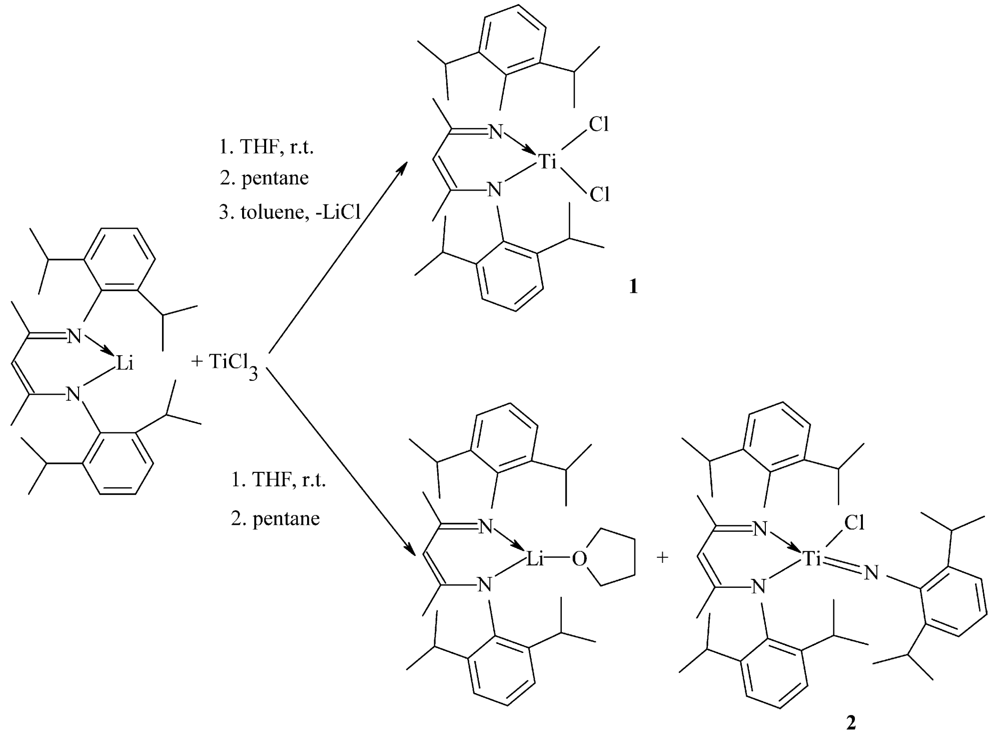
There is a general interest in the chemistry of the titanium β-diketiminato complexes from several perspectives including practical, synthetic and theoretical implications. Our interest in the chemistry of titanium β-diketiminato complexes stems from their potential use as novel olefin polymerization catalysts. Also, the β-diketiminato complexes of Ti(III) with bulky ligands can be considered as versatile starting materials for preparing low valent titanium species and for stabilization of titanium fluoride complexes. Herein we report the synthesis and characterization, including the stability, of the Ti(III) β-diketiminato complexes (L1)TiCl$_2$ (**1**), (L2)$_2$TiCl (**2**), (L1 = (2,6-^{i}Pr$_2$C$_6$H$_3$)NC(Me)CHC-(Me)N(2,6-^{i}Pr$_2$C$_6$H$_3$); L2 = ^{i}PrNC(Me)CHC(Me)N^{i}Pr, along with the first Ti(IV) complexes with the β-diketiminato ligand (L1)TiCl(N2,6-^{i}Pr$_2$C$_6$H$_3$) (**3**), [(L2)TiCl(^{i}PrN)]$_2$ (**4**) and the titanium fluoride complexes [(L2)TiF$_2$]$_n$ (**5**) and (L2)$_4$Ti$_4$F$_6$O$_2$·2toluene (**6**).

2. Results and discussion

The Ti(III) dichloride complex, (L1)TiCl$_2$, was prepared by the reaction of LLi and TiCl$_3$ in THF, followed by washing with pentane and recrystallization from toluene (Scheme 1). There were no observable reactions in solutions of Et$_2$O, toluene and hexane. It is important to note that TiCl$_3$ does not dissolve completely in THF during the reaction. Even after 10 days of the reaction some amount of TiCl$_3$ suspension was found in the supernatant liquid. The interaction of TiCl$_3$ with less bulky ligands, (PhNC(Me))$_2$CH [5f], or ((2,4,6-Me$_3$C$_6$H$_2$)NC(Me))$_2$CH [6], proceeds quickly and gives high yields of products. Complex LTiCl$_2$ (deep red/brown crystals) with the same ligand (L1) was prepared by Budzelaar et al. [6] and characterized by elemental analysis. Green colored single crystals of (L1)TiCl$_2$ (**1**), suitable for X-ray diffraction analysis, were obtained by crystallization from its toluene solution.

A brown solution was obtained after washing of the reaction product of (L1)Li and TiCl$_3$ with pentane. From this solution the red crystalline substance was obtained that appeared to be complex (L1)TiCl(N2,6-^{i}Pr$_2$C$_6$H$_3$) (**2**). The monochloride complex (L1)$_2$TiCl was not isolated even with excess of (L1)Li salt and after evaporation of pentane; instead, a dark-brown viscous oil was collected. The EI MS spectrum of a small red crystal covered with this oil exhibited the heaviest fragment that can be assigned to the [(L1)$_2$TiCl$^+$–C$_{12}$H$_{17}$] cation.

Complexes (L1)TiCl$_2$ **1** and (L1)TiCl(N2,6-^{i}Pr$_2$C$_6$H$_3$) (**2**) crystallize in the monoclinic space group $P2_1/n$. Selected bond lengths and angles of **1** and **2** are listed in Table 1; a summary of the crystallographic data and refinement parameters for the structures of **1** and **2** are given in Table 3.



Scheme 1. Synthesis of the complexes **1** and **2**.

Table 1
Selected bond lengths (Å) and angles (°) for **1** and **2**

Bond lengths		Bond angles	
Complex **1**			
Ti–N(1)	2.068(2)	N(1)–Ti–N(2)	87.14(10)
Ti–N(2)	2.093(2)	N(1)–Ti–Cl(2)	144.08(7)
Ti–Cl(2)	2.439(1)	N(1)–Ti–Cl(3)	104.38(7)
Ti–Cl(3)	2.254(1)	Cl(2)–Ti–Cl(1)	111.19(4)
N(1)–C(2)	1.338(4)	Cl(2)–Ti–N(2)	89.83(7)
N(2)–C(4)	1.331(4)	Cl(3)–Ti–N(2)	102.67(7)
C(2)–C(3)	1.396(4)		
C(3)–C(4)	1.407(4)		
Complex **2**			
Ti–N(1)	2.020(7)	N(1)–Ti–N(2)	95.1(3)
Ti–N(2)	2.026(7)	N(1)–Ti–N(3)	113.3(3)
Ti–N(3)	1.710(8)	N(1)–Ti–Cl(1)	114.9(2)
Ti–Cl(1)	2.315(2)	N(3)–Ti–Cl(1)	116.0(2)
N(1)–C(13)	1.367(14)	N(2)–Ti–Cl(1)	108.03(17)
N(2)–C(15)	1.316(12)	N(3)–Ti–N(2)	106.8(3)
C(13)–C(14)	1.424(10)		
C(14)–C(15)	1.390(12)		

X-ray structural analysis proved that compound **1** is dimeric in the solid state (Fig. 1), while other known Ti(III) β-diketiminato complexes with less bulky ligands L = $(PhNC(Me))_2CH$, $((2,4,6\text{-}Me_3C_6H_2)NC(Me))_2CH$, $((2,4,6\text{-}Me_3C_6H_2)NC({}^tBu))_2CH$ are monomeric [5f,6]. Compound **2** is solvent-free and monomeric (Fig. 2).

In both complexes **1** and **2** the β-diketiminato ligand coordinates to the metal center through the two nitrogen atoms. The NCCCN unsaturated back bone of the ligand is almost planar, with 0.031 (3) Å deviation from planarity in **1**, 0.037 (15) Å in **2**. The titanium atom is out of plane of the diimine ligand framework by 0.79 (3) Å in **1** and 1.030 (5) Å in **2**. The geometries of each (L1)$TiCl_2$ unit of the complex **1** and (L1)Ti fragment in **2** are similar to that of the titanium(III) complex, $LTiX_2$ (X = Cl, Me) [6], containing the β-diketiminato ligands (L = $((2,4,6\text{-}Me_3C_6H_2)NC(Me))_2CH$, $((2,4,6\text{-}Me_3C_6H_2)NC({}^tBu))_2CH$). Comparison of the C–C, C–N distances in the NCCCN unit of **1** and **2** (Table 1) demonstrates the localization of double bonds, like in compound (L1)H [7] (Scheme 2).

The titanium–nitrogen distances in **1** are comparable with those in complex $LTiCl_2$ (2.087 Å (L = $(PhNC(Me))_2CH$) [5f]), where the titanium center has a coordination number 6 and longer than those in $LTiCl_2$ (1.983(3), 1.964(3) Å, L = $((2,4,6\text{-}Me_3C_6H_2)NC(Me))_2CH$; 1.986(1) Å, L = $((2,4,6\text{-}Me_3C_6H_2)NC({}^tBu))_2CH$ [6]), where the Ti atom is four coordinated.

While the titanium–terminal chlorine bond length in **1** is short, the titanium–bridging chlorine distance is longer (Table 1) than those in known β-diketiminato complexes of Ti(III), $LTiCl_2$ (Ti–Cl 2.395 Å [5f], 2.295(1), 2.297 (6) Å [6]), in which two terminal chlorine atoms are bonded to Ti. The titanium–bridging chlorine distances are similar to those found for Ti(III) complexes with two bridging chlorine atoms $[Ti(\mu\text{-}Cl)Cl_2(Me_2P(CH_2)_2PMe_2)]_2$ [8] (Ti–Cl 2.437(2) Å) and slightly shorter than those for $\{[\eta^8\text{-}1,4\text{-}(SiMe_3)_2C_8H_6]Ti(\mu\text{-}Cl)\}_2(THF)$ [9], $[Cp_2Ti(\mu\text{-}Cl)]_2$, $[(C_5H_4Me)Ti(\mu\text{-}Cl)]_2$ [10] (Ti–Cl 2.480(2); 2.536(2); 2.566(2) Å, respectively). The terminal Cl(3) in **1** is almost perpendicular to the equatorial plane, as evidenced from the angle [N(2)–Ti–Cl(3) = 102.67(7)°] (Table 1). The titanium atom is penta-coordinated. The two nitrogen atoms and the chlorine atoms on titanium are involved in a distorted square-planar pyramidal geometry around the metal center.

The bond lengths between titanium and nitrogen atoms of diimine in complex **2** are nearly the same, but shorter than those in Ti(IV) α-iminato complex $LTiCl_2(N2,6\text{-}{}^iPr_2C_6H_3)\cdot Py$ (Ti–N 2.200(5) and 2.317(4) Å, L = PhNC(Me)C(Me)NPh) [11]. However, they are similar to those in several titanium complexes with Ti–N single bonds (Ti–N 2.025(2) [15], 2.195(3) [13], 2.006(2) [12] Å).

The Ti–N(3) distance is considerably shorter than the other two Ti–N(1) and Ti–N(2) in the complex and is comparable with titanium nitrogen double bond length in Ti(IV) complexes $[Ti(NSiMe_3)(L^1)Cl]$, $[Ti(N{}^tBu)(L^2)Cl]Cl$ (L^1, L^2 = triazacyclononane ligands) [13], $[TiCl_2(NC_6H_4Me\text{-}2)(Py)_2]_2$ [14], $\{\kappa^3N\text{-}(2\text{-}C_5H_4N)C(Me)(CH_2NSiMe_3)_2\}Ti(N{}^tBu)\cdot Py$ [15] $Ti(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(\{({}^tBuN)CH_2\}_3)Cl_2$ [16] (Ti–N 1.718(2); 1.699(2); 1.711(2); 1.701(2); 1.713(3) Å, respectively). The Ti bound to three nitrogen atoms and a chlorine atom are involved in a distorted tetrahedral geometry around the metal center indicating its coordination number as four.

Elemental analysis confirms the anticipated formula as (L1)$TiCl_2$ and shows that compound **1** is solvent-free and contains no lithium chloride impurity. The composition of the unanticipated formula (L1)$TiCl(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)$, that resulted from the X-ray structural analysis, is also consistent with the elemental analysis of the red crystals of **2**.

Complexes **1** and **2** were studied by means of mass spectrometry. In the EI MS of **1** is detected the molecular ion [M^+] and several fragments. Complex **2** exhibits the molecular ion [M^+] as well as an intensive peak of the [$M^+\text{-}NC_{12}H_{17}$] cation in the EI MS spectrum. Proton NMR spectra of **1** contain a set of broad resonances ($\Delta\nu_{1/2}$ ranging from 50 to 1000 Hz) and a number of sharp resonances that are assigned to the coordinated ligand. Nonetheless, the fine structures of the resonances due to the paramagnetic nature of Ti(III) complex could not be observed even at low temperatures. The proton NMR spectra of **2** in C_6D_6 showed only a set of resonances. The two Me groups of the backbone of the ligand are magnetically non-

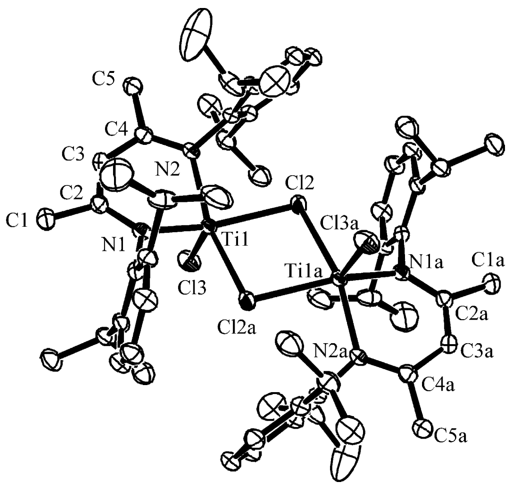


Fig. 1. Molecular structure of $[(L1)TiCl_2]_2$ (**1**), hydrogen atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms: $-x$, $-y+2$, $-z$.

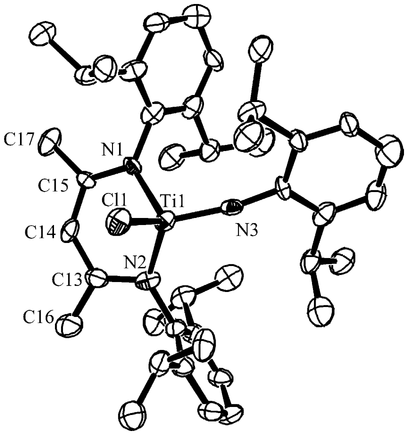


Fig. 2. Molecular structure of (L1)TiCl(N2,6-$^{i}Pr_2C_6H_3$) (**2**), hydrogen atoms are omitted for clarity.

equivalent and have different chemical shifts. This indicates that **2** is a rigid complex and stable in solution.

Compounds **1** and **2** are soluble in all common organic solvents, except in pentane and hexane they are slightly soluble. Solutions of **1** and **2** in toluene, THF, Et_2O are stable at room temperature and even at reflux temperature. However, these solutions are sensitive to air and moisture and, therefore, the crystals of **1** and **2** were stored in a glove box.

The isolation of complex **2** confirms the cleavage of the C=N double bond in the β-diketiminato unit. This phenomenon can be explained based on the following facts. The monochloride complex, $\{(L1)_2TiCl\}$, cannot be recovered from the solution containing $TiCl_3(THF)_X$–$(L1)Li(THF)_X$ with the excess (L1)Li salt, but the cation $[(L1)_2TiCl^+ - C_{12}H_{17}]$ was found in the EI MS. It is therefore possible that the $\{(L1)_2TiCl\}$ moiety could exist in solution but this unit is unstable due to the presence of two bulky β-diketiminato ligands in the internal sphere and slowly decomposed to give **2** as a final product. Thus, coordination of the β-diketiminato molecule to the titanium center plays an important role in the cleavage of C=N double bond in the molecule.

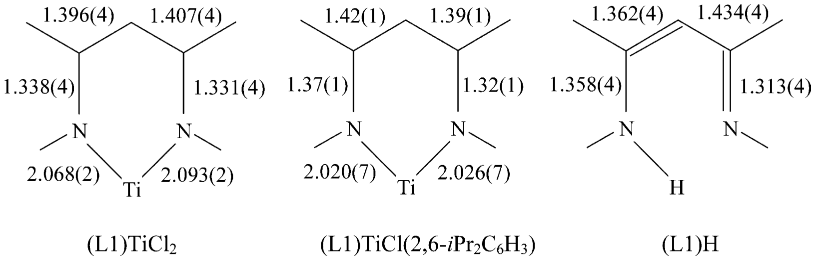
To investigate the stability of the titanium(III) β-diketiminato complex L_2TiCl, the reaction between the (L2)Li salt (L2 is less bulky ligand ($^{i}PrNC(Me))_2CH$) and $TiCl_3$ in 2:1 molar ratio was studied. The reaction product, $(L2)_2TiCl$ (**3**), was obtained in one step synthesis involving the titanium trichloride and stoichiometric amounts of the lithium salt of the ligand in THF (Scheme 3), followed by crystallization from pentane.

The C, H, N analysis confirms that the resulting compound is free from solvent and the lithium salt and contains two molecules of the ligand only. The melting point of **3** is in the range of 82–84 °C. Complex **3** exhibits a signal of the molecular ion $[M^+]$ with the relative intensity 76%, as well as several intensive peaks due to the decomposition of the titanium complex during the EI MS experimental measurements.

Compound **3** is highly soluble in all organic solvents and is paramagnetic showing strong broadened proton NMR resonances ($\Delta\nu_{1/2}$ ranged from 50 to 1000 Hz) that could not be fully interpreted. Compound **3** is sensitive to air and moisture in the solid state and in solutions. However, the crystals of **3** can be stored in a glove box for a long period of time.

A summary of the crystallographic data and refinement parameters for the structure of **3** is given in Table 3. Selected bond lengths and angles are listed in Table 2.

Complex **3** is the first crystallographically determined Ti(III) β-diketiminato complex with stoichiometry L_2TiCl. Complex **3** crystallizes in the monoclinic space group $P2_1/c$. The X-ray structural analysis revealed that



Scheme 2.

compound **3** is monomeric and free from solvent and lithium salt. In the unit cell are located 2 non-equiv. molecules of $(L2)_2TiCl$ with slightly different geometry (Table 2; Fig. 3).

In **3** the N(1)C(1)C(2)C(3)N(2) skeletal atoms are nearly planar with the deviation of 0.04 Å and coordinated to the titanium center through the two nitrogen atoms. The titanium atom is 0.98 Å out of this plane. The second ligand has a more distorted N(3)C(6)C(7)C(8)N(4) unit and the deviation from planarity is 0.104 Å. The angle between the two planes is 19.5°. In the second molecule the N(1a)C(1a)C(2a)C(3a)N(2a) skeletal atoms are also nearly planar with the deviation of 0.05 Å, the titanium atom is 0.93 Å out of this plane. The second N(3a)C(6a)C(7a)C(8a)N(4a) unit is more distorted and the deviation from planarity is 0.102 Å. The angle between the two planes is 19.2°. The β-diketiminato ligands coordinate to the metal center through the two nitrogen atoms. (Ti(1)–C(6) 2.441(5), Ti(1)–C(7) 2.520(5), Ti(1a)–C(8a) 2.439(5), Ti(1a)–C(7a) 2.536(5) Å). Although these general features resemble those of $LZrCl_3$ [1], $LSnMe_2Cl$ [1,17] (L = β-diketiminato ligands) and $[Cp_2TiCl]_2$ [10], the Ti–C distances of the latter complexes are significantly shorter (2.332(8)–2.373(6) Å). The titanium atom is 1.6305 Å out of the N(3)C(6)C(7)C(8)N(4) plane. Two planes of each β-diketiminato ligand are not parallel, as the angle between these planes is 19.5°.

The C–C and C–N bond lengths in the NCCCN units are comparable with those in the stable β-diketiminato complexes, $L_2Zr(NMe_2)_2$, L_2ZrCl_2 [5], $\{[(L)UCl(NR)(\mu\text{-}Cl)]_2\}\{(L)UCl_2(N(R)C(Ph)\text{-}NC(Ph)CHR)\}_2$, $(R = SiMe_3)$[18] and $LSnMe_2Cl$ [17,1].

The Ti–N bond lengths are not equal due to different bonding modes of the nitrogen to titanium atom, but are comparable with those in the Ti (III) β-diketiminato complex, $LTiCl_2\cdot 2THF$ (2.087 Å; $L = (PhNC(Me))_2CH$), where the Ti is six coordinated. However these bonds are longer than those in $LTiCl_2$ (1.983(3), 1.986 Å) with $L = ((2,4,6\text{-}Me_3C_6H_2)NC(Me))_2CH$, $((2,4,6\text{-}Me_3C_6H_2)NC(^tBu))_2CH$ in which the titanium atom is four coordinated. Also, the Ti–N bond lengths are similar to those found for titanium(III) complexes, $[L_2TiCl]_2$ (Ti–N 2.043 and 2.027 Å, L = pyrazolato ligand [19]; 2.080–2.12 Å, $L = C_7H_5(NMe_2)$ *N*,*N′*-dimethylaminotroponiminato ligand [13]).

All Ti-bound nitrogen and chlorine atoms are involved in a distorted square pyramidal geometry around the metal center.

The proton NMR spectrum of the solution of **3** showed a set of relatively sharp resonances in the region of 1–5 ppm due to the decomposition of complex **3** in solution over a period of 3 months. The yellow crystals of $[(L2)TiCl(N^iPr)]_2$ (**4**), contaminated with viscous oily material, were obtained from the pentane solution of **3** over a period of 3 months at 2 °C. Later it was found that complex **4** can be obtained with a better yield by reduction of $TiCl_4$ in the presence of (L2)Li salt with Na/K alloy in THF, followed by crystallization from pentane (Scheme 3; Fig. 4).

The proton NMR spectrum of **4**, in C_6D_6 showed a set of resonances with a fine structure. The two Me groups of the back bone and the two ^{i}Pr groups on the nitrogen atoms are magnetically non-equivalent and have different chemical shifts. This indicates that **4**, like **2**, is a rigid complex and stable in solution.

A summary of the crystallographic data and refinement parameters for the structure of **4** is given in Table 3. Selected bond lengths and angles are listed in Table 2. Complex **4** crystallizes in the triclinic $P\bar{1}$ space group; X-ray structural analysis revealed that compound **4** is dimeric in the solid state (Fig. 4).

In complex **4**, the almost planar NCCCN units with the deviation of 0.044 Å from planarity are nearly perpendicular to the $Ti(\mu\text{-}Cl)_2Ti$ plane that is tilted to the titanium center with an angle of 103.35(18)°. The β-diketiminato ligands have some π character (Ti(1)–C(1) 2.675(4), Ti(1)–C(3) 2.680(3) Å). This feature resembles that of complex **3**, as well as those of the Zr(IV) and Sn(IV) β-diketiminato complexes $LZrCl_3$ [5] and $LSnMe_2Cl$ [1,18]. However, Ti–C(1) (2.675(4) Å) and Ti–C(3) (2.680(3) Å) distances in **4** are significantly longer than those in Cp_2TiCl_2 (2.354–2.358 Å) [20] or $Cp_2^*TiCl_2$ (2.346–2.352) Å [21]. The C–C bond lengths in the NCCCN unit and those between the titanium atom and the nitrogen atoms in the β-diketiminato ligand are almost equal. On the other hand, the C–N bond lengths are not equal. Thus, mixed σ and π coordination of the β-diketiminato ligand affects the C–C and C–N bonds. The Ti–Cl distances in **4** are comparable with those in Ti(IV) dimeric complexes with two bridging chlorine atoms $[LTiCl_2(\mu\text{-}Cl)]_2$ (Ti-(μ-Cl) 2.420; 2.537 Å, L = benzamidinato ligand $(NSiMe_3)_2CPh$ [22]), $[LTiCl_2(\mu\text{-}Cl)]_2$ (Ti-(μ-Cl) 2.459; 2.564 Å, $L = NH_2SiMe_2NSiMe_2Cl$ [23]). The (N^iPr) unit is almost perpendicular to the $Ti(\mu\text{-}Cl)_2Ti$ plane, the N(3)–Ti(1)–Cl(1) angle is 102.94(11)° and tilted toward the bridging chlorine atoms. The Ti=N bond length resembles that in complex **2**, but is slightly shorter due to less bulky substituents on the nitrogen atom.

All evidences indicate that the low valent titanium center plays an important role in the cleavage of the C=N bond of the coordinated diimine ligand. The Ti(III) oxidized to Ti(IV) and the N(R) group of the ligand coordinates to the titanium center leading to a Ti=N double bond. Nevertheless, it is possible to handle the solutions of **3** at low temperatures over a short period (several days) without appreciable decomposition. Moreover, the titanium center is deshielded with the two diimine ligands that are responsible for the solubility of **3** in all organic solvents. Obviously, the two β-

Table 2
Selected bond lengths (Å) and angles (°) for **3**, **4** and **6**

Bond lengths		Bond angles	
Complex **3**			
Ti(1)–N(3)	2.047(4)	N(3)–Ti(1)–N(1)	141.55(17)
Ti(1)–N(1)	2.057(4)	N(3)–Ti(1)–N(2)	90.81(16)
Ti(1)–N(2)	2.132(4)	N(1)–Ti(1)–N(2)	84.24(17)
Ti(1)–N(4)	2.179(4)	N(3)–Ti(1)–N(4)	80.88(16)
Ti(1)–Cl(1)	2.3604(2)	N(1)–Ti(1)–N(4)	95.23(17)
Ti(1)–C(6)	2.441(5)	N(2)–Ti(1)–N(4)	165.99(15)
Ti(1)–C(7)	2.520(5)	N(3)–Ti(1)–Cl(1)	116.72(14)
Ti(1)–C(8)	2.698(5)	N(1)–Ti(1)–Cl(1)	101.72(12)
Ti(1a)–N(4a)	2.034(4)	N(2)–Ti(1)–Cl(1)	95.61(12)
Ti(1a)–N(2a)	2.055(5)	N(4)–Ti(1)–Cl(1)	98.20(11)
Ti(1a)–N(1a)	2.139(4)	N(4a)–Ti(1a)–N(2a)	139.99(17)
Ti(1a)–N(3a)	2.187(4)	N(4a)–Ti(1a)–N(1a)	91.24(16)
Ti(1a)–Cl(1a)	2.363(2)	N(2a)–Ti(1a)–N(1a)	84.00(17)
Ti(1a)–C(8a)	2.439(5)	N(4a)–Ti(1a)–N(3a)	80.82(16)
Ti(1a)–C(7a)	2.536(5)	N(2a)–Ti(1a)–N(3a)	95.22(17)
		N(1a)–Ti(1a)–N(3a)	166.73(15)
		N(4a)–Ti(1a)–Cl(1a)	116.98(13)
		N(2a)–Ti(1a)–Cl(1a)	103.03(12)
		N(1a)–Ti(1a)–Cl(1a)	95.49(11)
		N(3a)–Ti(1a)–Cl(1a)	97.59(11)
Complex **4**			
Ti(1)–N(3)	1.690(3)	N(3)–Ti(1)–N(1)	108.40(14)
Ti(1)–N(1)	2.046(3)	N(3)–Ti(1)–N(2)	109.07(11)
Ti(1)–N(2)	2.052(2)	N(1)–Ti(1)–N(2)	86.39(9)
Ti(1)–Cl(1)	2.496(2)	N(3)–Ti(1)–Cl(1)	102.94(11)
Ti(1)–Cl(1a)	2.516(3)	N(1)–Ti(1)–Cl(1)	88.95(10)
Ti(1)–C(1)	2.675(4)	N(2)–Ti(1)–Cl(1)	147.47(6)
Ti(1)–C(3)	2.680(3)	N(3)–Ti(1)–Cl(1a)	102.00(13)
		Cl(1)–Ti(1)–Cl(1a)	80.62(10)
		Ti(1)–Cl(1)–Ti(1a)	99.38(10)
Complex **6**			
Ti(1)–O(1)	1.631(2)	O(1)–Ti(1)–F(1)	110.21(9)
Ti(1)–F(1)	2.017(1)	O(1)–Ti(1)–F(3)	102.44(8)
Ti(1)–F(3)	2.025(1)	F(1)–Ti(1)–F(3)	83.42(5)
Ti(1)–N(2)	2.031(2)	O(1)–Ti(1)–N(2)	104.95(8)
Ti(1)–N(1)	2.049(2)	F(1)–Ti(1)–N(2)	84.71(7)
Ti(1)–C(3)	2.717(2)	F(1)–Ti(1)–N(1)	142.06(7)
Ti(2)–F(1a)	1.966(1)	N(2)–Ti(1)–N(1)	85.12(8)
Ti(2)–F(3)	1.986(1)	F(1a)–Ti(2)–F(3)	165.27(5)
Ti(2)–F(2a)	2.030(1)	F(3)–Ti(2)–F(2)	87.38(6)
Ti(2)–F(2)	2.047(1)	F(2a)–Ti(2)–F(2)	77.75(6)
Ti(2)–N(3)	2.071(2)	F(1a)–Ti(2)–N(3)	99.31(7)
Ti(2)–N(4)	2.097(2)	F(3)–Ti(2)–N(3)	92.98(7)
Ti(2)–Ti(2a)	3.174(1)	F(2a)–Ti(2)–N(3)	170.20(7)
		F(2)–Ti(2)–N(3)	92.85(7)
		F(3)–Ti(2)–N(4)	99.12(7)
		F(2)–Ti(2)–N(4)	172.94(7)
		N(3)–Ti(2)–N(4)	89.61(8)
		F(1a)–Ti(2)–Ti(2a)	81.36(4)
		Ti(2a)–F(1)–Ti(1)	147.47(7)
		Ti(2a)–F(2)–Ti(2)	102.25(6)

diketiminato ligands (L2) stabilize the titanium(III) chloride complex.

Interaction of **3** with 1 equiv. of Me_3SnF in THF affords a clear solution. After evaporation of the solvent, the residue was extracted with pentane and the resulting pentane solution gave the dark green powder of **5**.

$$(L2)_2\underset{\mathbf{3}}{T}iCl + Me_3SnF \xrightarrow[\text{2. pentane}]{\text{1. THF r.t.}} \underset{\mathbf{5}}{((L2)TiF_2)_X}$$

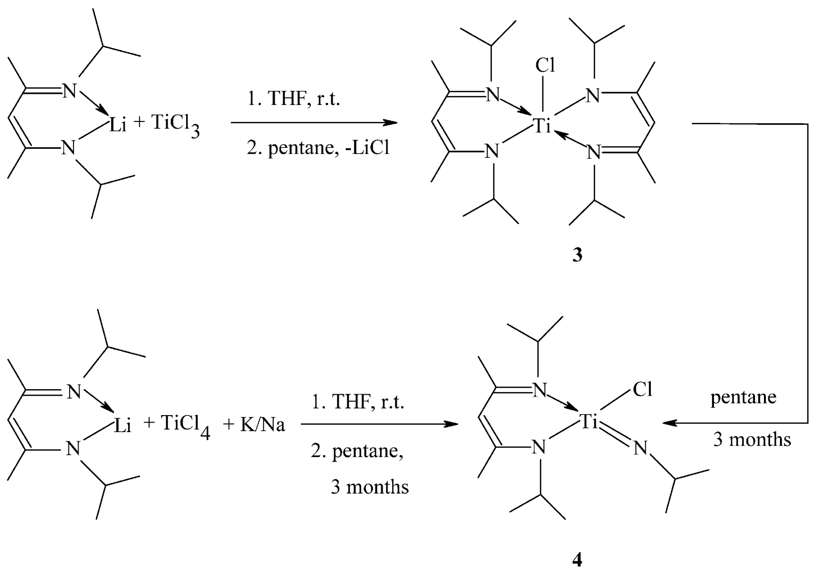
$$\mathbf{5} \xrightarrow[\text{2. toluene}]{\text{1. } CH_2Cl_2,\ [O_2]} \underset{\mathbf{6}}{(L2)_4Ti_4F_6O_2}\cdot 2\text{toluene}$$

The reaction product **5** is thermally stable with a melting point in the range of 205–207 °C. The identity of this compound containing one ligand with nearly $(L2)TiF_2$ stoichiometry was determined by its elemental analysis. Complex **5** exhibits a strong $[(L2)TiF_2{}^+]$ ion, as well as fragments of $[M^+\text{-}C_3H_7F]$ and $[M^+\text{-}C_5H_{10}N]$ in the EI MS spectrum. All attempts to crystallise **5** using different solvents have failed due to the polymeric nature of the fluoride complex **5**. Solid **5** does not dissolve at room temperature in toluene, THF and acetonitrile, but completely dissolves in hot toluene and benzene. The proton NMR spectrum of **5**, in C_6D_6, contains resonances that can be assigned to the β-diketiminato ligand L2 [1e,2c,38]. Four resonances in the range from 4.6 to 4.2 ppm were assigned to the protons connected with the central carbon atoms of the NCCCN units. Four magnetically non-equivalent ligands can be present in one complex. Obviously the polymeric compound **5** decomposes in C_6D_6 giving several species. Although **5** dissolves in acetonitrile upon heating, it produced an amorphous precipitate whose proton NMR spectrum contained resonances that can be assigned only to those of the β-diketiminato ligand L2. We were not able to observe fluorine resonances of **5** even at low temperature due to the paramagnetic nature of **5**.

Evaporation of CH_2Cl_2 solution of **5** gave a viscous residue. Recrystallization of this residue from toluene afforded green crystals of the tetranuclear complex $(L2)_4Ti_4F_6O_2\cdot 2$toluene (**6**) with two terminal oxygen atoms coordinated to the two titanium atoms. Although the nature of the oxygen is not exactly known (H_2O, air), **6** has been characterized thoroughly, including X-ray analysis.

A summary of the crystallographic data and refinement parameters for **6** are given in Table 3. Selected bond lengths and angles are listed in Table 2.

Complex **6** crystallizes in the monoclinic space group $P2_1/n$. The crystal structure of **6** (Fig. 5) shows a tetranuclear complex $(L2)_4Ti_4F_6O_2\cdot 2$toluene that contains two (L2)Ti and two (L2)TiO units connected via bridging fluorine atoms. This complex can formally be described as a mixed Ti(III)/Ti(IV) fluoride complex. A part of the inorganic core, Ti(1){μ-F}$_2$Ti(2)Ti(2a){μ-F}$_2$Ti(1a), is almost planar with two terminal oxygen atoms and two bridging fluorine atoms F(2) and F(2a) that are out of this plane (Fig. 5). While the angle between F(1)–Ti–O(1) is 110.21(9)°, the two bridging fluorine atoms F(2) and F(2a) are located between the Ti(2) and Ti(2a) atoms above and below the plane so



Scheme 3. Synthesis of complexes **3** and **4**.

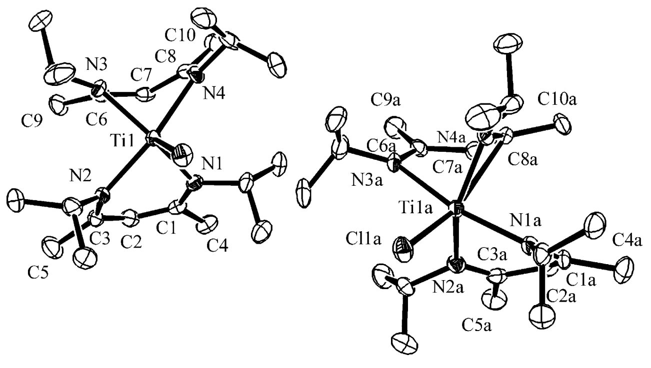


Fig. 3. Molecular structure of (L2)$_2$TiCl (**3**), hydrogen atoms are omitted for clarity.

that the F(2)–F(2a) line is perpendicular to this plane. The geometry of the inorganic core in **6** differs from those in known tetranuclear Ti(III) complexes

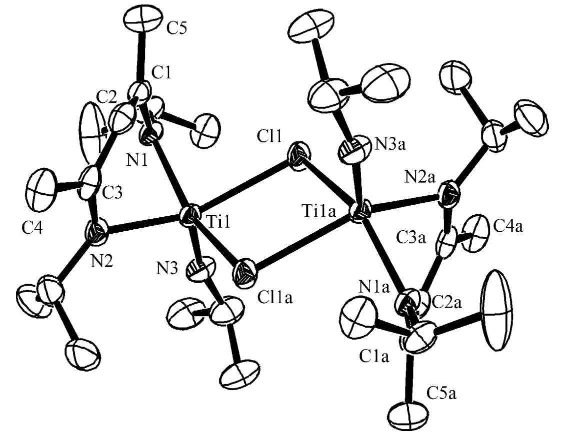
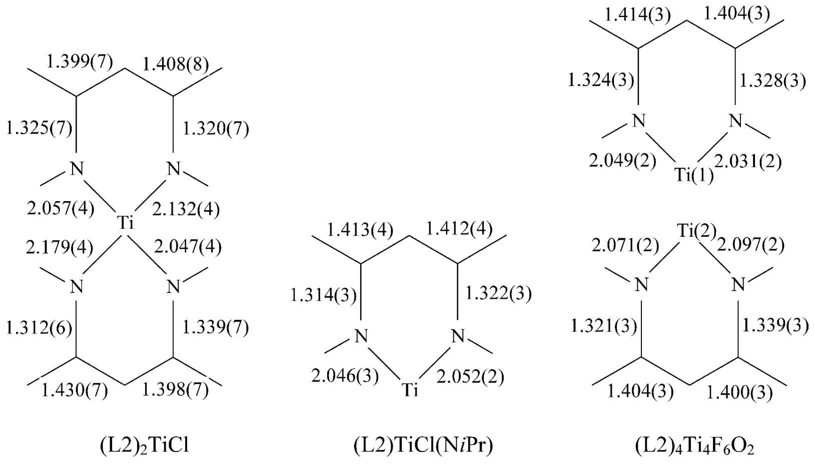


Fig. 4. Molecular structure of [(L2)TiCl(N^{i}Pr)]$_2$ (**4**), hydrogen atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms: $-x+1$, $-y$, $-z$.



Scheme 4.

Table 3
Crystallographic data of the X-ray diffraction studies of compounds **1**, **4** and **6**

	1	**2**	**3**	**4**	**6**
Empirical formula	$C_{29}H_{41}Cl_2N_2Ti$	$C_{41}H_{58}ClN_3Ti$	$C_{22}H_{42}ClN_4Ti$	$C_{14}H_{28}ClN_3Ti$	$C_{29}H_{50}F_3N_4OTi_2$
M_r	536.44	676.25	445.95	321.74	623.53
Temp (K)	133(2)	133(2)	270(2)	153(2)	133(2)
Radiation used (λ(Å))	Mo K_α (0.71073)	Mo K_α (0.71073)	Mo K_α (0.71073)	Mo K_α (0.71073)	Mo K_α (0.71073)
Crystal description	green plates	red needles	dark green blocks	yellow blocks	green plates
Crystal size (mm)	0.8 × 0.8 × 0.2	1.00 × 0.10 × 0.10	1.00 × 0.60 × 0.50	0.80 × 0.80 × 0.70	0.8 × 0.8 × 0.10
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a (Å)	13.792(3)	8.9426(18)	9.4490(2)	9.302(9)	15.307(3)
b (Å)	13.584(3)	24.116(5)	15.045(3)	9.504(11)	13.094(3)
c (Å)	15.693(3)	17.949	35.357(7)	11.124(11)	16.856(3)
α (°)	90	90	90	98.96(11)	90
β (°)	105.42(3)	92.02(3)	93.84(3)	107.07(4)	105.06(3)
γ (°)	90	90	90	104.94(4)	90
V (Å^3)	2834.4(10)	3868.5(13)	5015.0(17)	879.40(15)	3262.3(11)
Z	4	4	8	1	4
F (0 0 0)	1140	1456	1928	344	1324
ρ_{calc} (g cm^{-3})	1.257	1.161	1.181	1.215	1.270
μ (mm^{-1})	0.510	0.321	0.462	0.631	0.533
Total reflections	15 516	9155	15 219	3228	52 241
Unique reflections	4827	4179	8728	3062	5634
R_{int}	0.0663	0.1331	0.0942	0.0572	0.0739
Scan range θ (°)	1.75–24.86	1.41–22.23	3.54–25.02	3.54–25.00	1.60–24.88
Completeness to θ_{max} (%)	98.2	85.5	98.6	98.8	99.5
Index ranges	$-16 \leq h \leq 16$, $-12 = k = 15$, $-18 = l = 18$	$-8 = h = 9$, $-25 = k = 25$, $-18 = l = 12$	$-11 = h = 11$, $-17 = k = 17$, $-42 = l = 42$	$-11 = h = 11$, $-11 = k = 11$, $-10 = l = 13$	$-18 = h = 18$, $-15 = k = 15$, $-19 = l = 19$
Data/restraints/parameters	4827/0/317	4179/1/415	8728/0/530	3062/0/184	5634/0/365
R_1 [a] [b], wR_2 [$I > 2\sigma(I)$] [c]	0.0476, 0.1119	0.0654, 0.1264	0.0736, 0.1805	0.0445, 0.1232	0.0375, 0.0958
R_1 [a] [d], wR_2 (all data) [c] [d]	0.0679, 0.1172	0.1629, 0.1548	0.0962, 0.1936	0.0468, 0.1262	0.0520, 0.0993
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Goodness-of-fit on F^2 [e]	0.919	0.810	1.197	1.003	0.893
Max./min. el. dens. (e Å^{-3})	0.812, −0.721	0.373, −0.224	0.742, −0.517	0.988, −0.500	1.291, −0.331

[a] $R_1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$.

[b] Denotes the value of the residual considering only the reflections with $I > 2\sigma(I)$.

[c] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\Sigma^2(F_o^2)^2 + (aP)^2 + bP]$, $P = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)/3]$.

[d] Denotes the value of the residual considering all the reflections.

[e] $S = [\Sigma[w(F_o^2 - F_c^2)^2]/[(n-p)^{1/2}]$, n, number of data; p, parameters used.

$\{[C_5H_4(SiMe_3)]_2TiF_2\}_3M$ (M = Ti [24], Ga [24], Al [25]). However, no tetranuclear Ti(IV) fluoride complexes are known for comparison. Nonetheless, trinuclear and hexanuclear Ti(IV) fluoride complexes, $[TiF_3(\mu\text{-}Ph_2PO_2)_3Ti(\mu\text{-}Ph_2PO_2)_3TiF_3]\cdot 1.5CH_3CN$ [26], $Cp^*_4Ti_4Zn_2Me_2F_{14}$ [33] have been structurally characterized.

Each titanium atom of the inorganic $Ti_4F_6O_2$ unit is coordinated to the β-diketiminato ligand, thus providing its partial solubility in hydrocarbon solvents.

The Ti(1)–N distances in **6** are shorter than the Ti(2)–N distances due to smaller ionic radius of the Ti(IV) compared to that of the Ti(III) ion. The Ti–N bond lengths in **6** have different values for four coordinated ligands, similar to those in **1**–**4**, due to a different donor–acceptor bond character in the complex. The toluene molecules are not coordinated to any titanium center; they occupy vacant lattice sites.

The two titanium atoms Ti(1) and Ti(1a) are coordinated to the two bridging fluorine atoms, terminal oxygen and nitrogen atoms of the β-diketiminato ligand. The NCCCN planar moieties of this β-diketiminato ligands are almost perpendicular to the inorganic plane Ti(1){μ-F}$_2$Ti(2)Ti(2a){μ-F}$_2$Ti(1a). The short C–Ti distances (2.717(5) Å) indicate a partial π coordination of the NCCCN unsaturated system to the titanium center as in **3** and **4**. The Ti(1)-{μ-F} distances in **6** are similar to those in Ti(IV) complexes, but differ marginally from the corresponding distances in $[(C_5H_4Me)TiF_3]_2\cdot(THF)$ (Ti-{μ-F} 2.022 Å) [27]. The Ti–O bond distance in **6** is similar to the titanium–oxygen double bond length in complexes $LTi(O)(NCS)_2$ (Ti=O 1.638 [28] Å), L = 1,4,7,-trimethyl-1,4,7 triazacyclononane; $L_2Ti(O)OPy$ (1.654 [29] Å), L = benzamidinate ligand; $(L^1)(L^2)Ti(O)$ (1.657 [30] Å), L^1 = 2,6-diisopropylphenoxide, L^2 = 4-pyrrolidinopyridine.

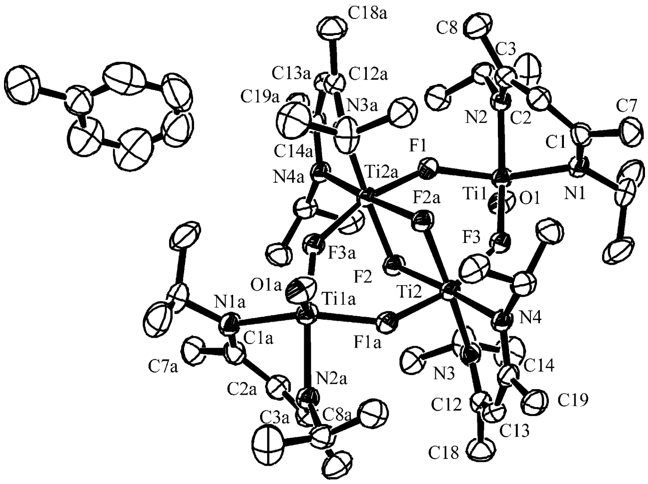


Fig. 5. Molecular structure of $(L2)_4Ti_4F_6O_2\cdot$toluene (**6**), hydrogen atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms: $-x+2$, $-y+1$, $-z$.

The Ti(2) and Ti(2a) atoms are bonded to two different kinds of bridging fluorine atoms and to the nitrogen atoms of the β-diketiminato ligand. The Ti(2)–{μ-F(2)} bond lengths are longer than Ti(2)–{μ-F(1)}, Ti(2)–{μ-F(3)} bonds. The Ti(2)–{μ-F} bond lengths are similar to Ti–{μ-F}distances in Ti(III) clusters, $Cp^*_{12}Ti_{14}Na_{18}F_{48}(THF)_6$ (short Ti–F 1.98 Å, long Ti–F 2.05 Å), $(Cp^*TiF_2)_6CaF_2(THF)_2$ (Ti–F 2.06 Å) [31] and $Cp^*_6Ti_6Na_7F_{19}\cdot 2.5(THF)$ (Ti–F 2.046 Å) [32]. The coordination number of the titanium atoms, Ti(2) and Ti(2a), in **6** is six with the four bridging fluorine atoms and two nitrogen atoms of the β-diketiminato ligand that form a distorted octahedral geometry about the metal atom.

The distance between the Ti(2) and Ti(2a) atoms in **6** is the shortest Ti–Ti contact and can be described as a bonding distance. The Ti(2)–Ti(2a) bond length is similar to the Ti–Ti distance in the Ti(IV) polynuclear fluoride complex, $Cp^*_4Ti_4(ZnMe)_2F_{14}$ (Ti–Ti 3.007 Å) [33], in the Ti(III) complexes, Cp_2LTi_2HCl (L = fulvalene), with bridging chlorine and hydrogen atoms (Ti–Ti 3.128 Å) [34] and $\{Cp(\mu\text{-}[\eta^1{:}\eta^5\text{-}C_5H_4])Ti(PMe_3)\}_2$ (Ti–Ti 3.222 Å) [35] and in the tetranuclear Ti(III) complex with bridging sulfur atoms, $(C_5H_4Me)_4Ti_4S_4$ (Ti–Ti 3.007 Å) [36].

Complex **6** is more thermally stable than **5**, with the melting point of 238–240 °C. The signals of the $[(L2)TiFO^+]$ ion and its fragments as well as those for the $[(L2)TiF_2{}^+]$ unit and its fragments were observed in the EI-mass spectra of **6**. Compound **6** is insoluble in C_6D_6 and toluene at r.t., but dissolves upon heating. The proton NMR spectrum of **6**, in C_6D_6, exhibits resonances due to different species containing the β-diketiminato ligand L2. For the interpretation of the ^1H NMR spectrum of **6**, the resonances of compound (L2)H [37] and complex **5** were also taken into account. Specifically, the proton NMR spectra of **6** exhibited resonances of $[(L2)TiF_2]$ and [(L2)TiFO] units, in addition to other resonances that do not correspond to **6**. Therefore, it is reasonable to assume that the tetrameric compound **6** decomposes in C_6D_6 leading to several species containing the β-diketiminato ligand.

3. Conclusions

We have prepared and characterized the Ti(III) complexes, $(L1)TiCl_2$ (**1**), $(L2)_2TiCl$ (**3**) and the Ti(IV) complexes, $(L1)TiCl(N2,6\text{-}^iPr_2C_6H_3)$ (**2**), $[(L2)TiCl(N^iPr)]_2$ (**4**) with the β-diketiminato ligands (L1), (L2). The titanium β-diketiminato complexes, **1**, **2** and **3**, have been obtained by the direct reaction of the lithium salt of the ligand with the titanium trichloride. The monochloride complex $\{[(L1)_2TiCl\}$ is not isolable from the supernatant solutions with the excess (L1)Li salt, but by means of the mass spectrometry, the fragment $[(L1)_2TiCl^+-C_{12}H_{17}]$ of this complex was detected; the final product of the reaction of $TiCl_3$ with excess of (L1)Li was complex **2**. With the less bulky ligand it was possible to isolate **3**, but the latter compound is unstable and slowly decomposed with the cleavage of the C–N double bond of the coordinated β-diketiminato ligand. The Ti(III) is oxidized to Ti(IV) and the N(R) group of the ligand coordinated to the titanium center giving complex **4** with Ti–N double bond. The bulky ligand L1 = $(2,6\text{-}^iPr_2C_6H_3)NC(Me)CHC(Me)N(2,6\text{-}^iPr_2C_6H_3)$ stabilizes the dimeric Ti(III) complex with the unusual coordination of the titanium atom, in which the ligand is σ-bonded to the titanium atom with the coordination number of 5. The less bulky ligand, L2 = $^iPrNC(Me)CHC(Me)N^iPr$ in the complexes **3**, **4** and **6** has mixed σ- and π-coordination to the titanium center. Comparison of the C–C, N–C distances in the NCCCN asymmetric unit of the coordinated β-diketiminato ligand demonstrated that the localization of the double bonds is significant in complexes **1**–**3** and **6**, as in (L1)H (Schemes 2 and 4). The solid state structure of Ti(IV) complexes **2** and **4** is also present in C_6D_6 solution as confirmed by their proton NMR spectra. It is shown that Me_3SnF is an appropriate fluorination reagent for the non-metallocene Ti(III) compound (**3**), but the basicity of the ligand L2 was not enough to stabilize the Ti(III) fluoride complex. Fluorination of the monochloride complex **3** afforded a polymeric substance, $[(L2)_4TiF_2]_n$ (**5**). Oxidation of **5** gave a tetrameric complex, $L_4Ti_4F_6O_2\cdot 2$toluene (**6**), which can formally be described as a mixed Ti(III)/Ti(IV) fluoride complex. Thus, this work clearly demonstrates that the solid state structures of **5** and **6** are not present in C_6D_6 solution.

4. Experimental

4.1. General procedures and starting materials

All operations were performed using standard Schlenk line and dry box techniques under purified nitrogen and argon atmosphere. Water-free titanium trichloride used was of commercial reagent quality (purity 99.99%). The compounds LH with the ligands $L1 = (2,6\text{-}{}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NC(Me)})_2\text{CH}$, $L2 = ({}^i\text{PrNC(Me)})_2\text{CH}$ were prepared by the known literature methods [5d,37,38]. The purity of LH was checked by the elemental analysis, ^{1}H and ^{13}C NMR spectra. Me_3SnF was prepared by the literature method [39]. The purity of Me_3SnF was checked by elemental analysis, the product contains less than 1% of chlorine. While toluene, pentane and THF were dried over Na/benzophenone and distilled under nitrogen prior to use, C_6D_6 and [D_8] THF were dried over Na and degassed and CD_2Cl_2 was dried over CaH_2 and degassed. Proton NMR spectra were recorded using Bruker AM 200 NMR spectrometer. Chemical shifts are reported in δ units downfield from Me_4Si with the solvent as the reference signal. Mass spectra were recorded using a Finnigan MAT 8230 mass spectrometer, and elemental analysis were carried out at the Analytical Laboratories of the Institute of Inorganic Chemistry at the University of Göttingen. Melting points were measured in sealed capillary tubes under nitrogen and are not corrected.

*4.2. Reaction of (L1)Li with $TiCl_3$ in THF. Synthesis of (L1)$TiCl_2$ (**1**) and (L1)TiCl(N(2,6-^{i}Pr)$_2$$C_6H_3$) (**2**)*

Dry THF (50 ml) was added to the compound (L1)H (3.75 g, 9.0 mmol) in a 100 ml Schlenk flask. The mixture was cooled to −78 °C and to this a solution of 5.62 ml (1.6 M, 9.0 mmol) LiMe in Et_2O was added dropwise. The reaction mixture was stirred for 1 h at −78 °C, allowed to warm to room temperature and stirred until methane evolution had ceased. This solution was added dropwise to a suspension of $TiCl_3$ (1.39 g, 9.0 mmol) in THF (120 ml) at r.t. in a 200 ml Schlenk flask. Subsequently, the reaction mixture was stirred for 6 days at r.t. The resulting suspension was filtered, THF removed under vacuum, and the green residue washed portion wise (15 mled by heating in toluene (150 ml) and allowed to stand 7 days at room temperature, when a white powder (LiCl) separated from a clear green solution. The solution was filtered and concentrated to 50 ml. The green crystals were separated by filtration. A second portion of crystals was obtained from this filtrate. Yield: 3.10 g (65%). $C_{29}H_{41}Cl_2N_2Ti$: Calc. C 64.93, H 7.65, N 5.22; Found: C 64.90, H 7.70, N 5.18%. M.p. 174–176 °C. EI MS: m/z (%) = 535 (100) [M^+], 521 (2) [M^+-CH_4], 500 (2) [M^+-$C_{12}H_{17}$]. ^{1}H NMR (200 MHz, C_6D_6, r.t.), $\delta = -5$ ($\Delta\omega_{1/2}$ 800 Hz), 0.81 (d,;> 24H, $J = 6.0$ Hz, CHMe_2), 0.95 (24H, CHMe_2), 1.16 (d, 24H, $J = 6.5$ Hz, CHMe_2), 1.24 (d, 24H, $J = 8.5$ Hz, CHMe_2), 1.3 ($\Delta\omega_{1/2}$ 95 Hz), 1.4 (24H, CHMe_2) 1.6 (24H, CHMe_2), 1.70 (s, 6H, Me), 2.0 (s, 6H, Me), 2.2 ($\Delta\omega_{1/2}$ 54 Hz) 2.9 ($\Delta\omega_{1/2}$ 64 Hz), 3.25 (sept, 4H, $J = 6.5$ Hz, CHMe$_2$), 4.4 ($\Delta\omega_{1/2}$ 96 Hz), 4.83 (s, 1H, γ-CH), 5.7 ($\Delta\omega_{1/2}$ 80 Hz), 6.3 ($\Delta\omega_{1/2}$ 223 Hz), 6.6–7.6 (m, 6H, C_6H_3) ppm.

The dark-brown pentane solution A was filtered and concentrated. Finally, the resulting pentane solution was left at 2 °C to produce big colorless crystals of (L1)Li·THF (0.6 g) that were separated by filtration. $C_{33}H_{51}LiN_2O$ Calc. C 79.52, H 10.24, N 5.62; Found: C 79.60, H 10.31, N 5.68%. The ^{1}H and ^{13}C NMR spectra are identical to those reported earlier for (L1)Li·THF [6]. Crystallographic data are also consistent with those in the literature [6,7]: space group monoclinic $P2_1/n$, $a = 9.54$ Å, $b = 17.91$ Å, $c = 21.71$ Å, $\beta = 95.4°$, $V = 3694$ Å^3.

The dark-brown pentane solution after removing the (L1)Li salt by filtration was left undisturbed at 2 °C. After 14 days small red crystals, covered with viscous mass, were separated from the pentane solution. EI MS: m/z (%) = 758 (44) [$(L)_2TiCl^+ - C_{12}H_{17}$], 675 (3) [$M^+$], 599 (6) [$(L1)_2TiCl^+ - (C_{12}H_{17})_2$], 564 (10) [$(L1)_2Ti^+ - (C_{12}H_{17})_2$], 535 (8) [$(L1)_2Ti^+ - (NC_{12}H_{17})_2$], 500 (100) [$M^+ - NC_{12}H_{17}$].

Red crystals that are appropriate for X-ray analysis were obtained from the pentane solution after 3 months. Yield of **2** (0.42 g, 7%). $C_{41}H_{58}ClN_3Ti$: Calc. C 72.84, H 8.59, N 6.22; Found: C 72.90, H 8.66, N 6.17%. M.p. 97–98 °C. EI MS: m/z (%) = 675 (34) [M^+], 660 (5) [$M^+ - CH_3$], 632 (1) [$M^+ - C_3H_7$], 500 (100) [$M^+ - NC_{12}H_{17}$]. ^{1}H NMR (200 MHz, C_6D_6, r.t.), $\delta = 1.17$ (d, 12H, $J = 3.0$ Hz, CHMe_2), 1.20 (d, 24H, $J = 3.9$ Hz, CHMe_2), 1.57 (s, 3H, Me), 1.68 (s, 6H, Me), 2.95 (sept, 4H, $J = 6.5$ Hz, CHMe$_2$), 3.33 (sept, 2H, $J = 6.8$ Hz, CHMe$_2$), 4.81 (s, 1H, γ-CH), 6.6–7.2 (m, 6H, C_6H_3) ppm.

*4.3. Preparation of $(L2)_2TiCl$ (**3**)*

Compound (L2)H (1.41 g, 1.57 ml, 7.8 mmol) was added to dry THF (30 ml) in a 50 ml Schlenk flask. The mixture was cooled to −78 °C and to this a solution of 4.85 ml (1.6 M, 7.8 mmol) LiMe in Et_2O was added dropwise. The reaction mixture was stirred for 1 h at −78 °C, allowed to warm to r.t. and stirred until methane evolution had ceased. The resulting solution was added dropwise to a suspension of $TiCl_3$ (0.6 g, 3.9 mmol) in THF (30 ml) at −79 °C in a 100-ml Schlenk flask, allowed to warm to room temperature and stirred at this temperature for 2 h. THF was removed in vacuo, and the residue extracted with pentane (60 ml). The green pentane solution was allowed to stand overnight at r.t., during which time a white powder (LiCl) separated out of a clear yellow solution and was removed by filtration, and the filtrate was concentrated (5–7 ml). The concentrated solution was left undisturbed for 2 days at −24 °C. Finally, dark-green crystals formed, which were separated by filtration and dried in vacuo. Yield of **3** 1.47 g (85.0%). $C_{22}H_{42}ClN_4Ti$: Calc. C 59.26, H 9.43, N 12.57; Found: C 59.31, H 9.47, N 12.51%. M.p. 82–84 °C. EI MS: m/z (%) = 445 (76) $[M^+]$, 426 (8) $[M^+ - CH_4]$, 404 (14) $[M^+ - C_3H_7]$, 383 (7) $[M^+ - C_2H_5Cl]$. ^1H NMR (200 MHz, C_6D_6, r.t.), $\delta = 0.9$ ($\Delta\omega_{1/2}$ 45 Hz), 1.1 (12H CH*Me*$_2$), 1.3 (12H, CH*Me*$_2$), 1.5 (12H, CH*Me*$_2$), 1.7 (6H, Me), 1.8 ($\Delta\omega_{1/2}$ 143 Hz), 3.5 (2H, C*H*Me$_2$) 3.8 (2H, C*H*Me$_2$), 4.2 (1H, γ-CH), 4.5 (1H, γ-CH) ppm.

4.4. *Preparation of $[(L2)TiCl(N^{i}Pr)]_2$ (4)*

Compound (L2)H (2.32 g, 2.58 ml, 12.7 mmol) was added to dry THF (30 ml) in a Schlenk flask (50 ml). The mixture was cooled to −78 °C and to this a solution of 8.0 ml (1.6 M, 12.7 mmol) LiMe in Et_2O was added dropwise. The reaction mixture was stirred for 1 h at −78 °C, allowed to warm to r.t. and stirred until methane evolution had ceased. The resulting solution was added dropwise to a solution of $TiCl_4$ (1.21 g, 0.7 ml, 6.35 mmol) in THF (30 ml) at −79 °C in a 100-ml Schlenk flask, stirred for 1 h and allowed to warm to r.t. and stirring was continued for 2 h at this temperature. Finally Na/K alloy (0.841 g, K 18.9 mmol, Na 3.6 mmol) was added via syringe and the resulting mixture was rigorously stirred for 4 days at r.t. THF was removed under vacuum, and the residue extracted with pentane (60 ml). The dark-green pentane solution was filtered and concentrated to 15 ml. The resulting solution was left undisturbed for 3 months at 2 °C. Finally, big yellow crystals formed, that were separated by filtration, washed with pentane and dried in vacuo. Yield of **4** 0.67 g (33%). $C_{14}H_{28}ClN_3Ti$: Calc. C 52.26, H 8.71, N 13.06; Found: C 52.31, H 9.76, N 13.01%. M.p. 112–114 °C. EI MS: m/z (%) = 321 (100) $[M^+]$, 306 (45) $[M^+ - CH_4]$, 278 (41) $[M^+ - C_3H_7]$. ^1H NMR (200 MHz, C_6D_6, r.t.), $\delta = 1.12$ (d, 12H, $J = 6.3$ Hz, CH*Me*$_2$), 1.41 (d, 3H, $J = 3.0$ Hz, CHMe*Me*), 1.45 (d, 3H, $J = 3.9$ Hz, CH*Me*Me), 1.71 (s, 6H, Me), 3.47 (sept, 2H, $J = 6.2$ Hz, C*H*Me$_2$), 3.6 (m, 1H, C*H*MeMe), 4.49 (s, 1H, γ-CH) ppm.

4.4.1. *Alternative method*

Solution of **3** (1 g, 2.2 mmol) in pentane (10 ml) was kept at 2 °C for 1 month. From this solution small yellow crystals, covered with a film of a viscous oil, were obtained. M.p. 112–114 °C. EI MS: m/z (%) = 831 (100) $[M_2{}^+ - C_3H_7N]$, 42 (10) $[C_3H_6]^+$. The crystals that are sufficient for characterization were grown during the 3 month period from the pentane solution of **3**. These crystals were washed with pentane and dried in vacuo. The analytical data for the colorless crystals are consistent with those of **4**.

4.5. *Reaction of $(L2)_2TiCl$ with Me_3SnF in THF, preparation of (5)*

A mixture of **3** (1.4 g, 3.1 mmol) and Me_3SnF (0.57 g, 3.1 mmol) in a 100 ml Schlenk flask in THF (40 ml) was stirred until all the solid dissolved (12 h). All volatiles were removed under vacuum, and the residue extracted with pentane (20 ml). This solution was left undisturbed for 7 days at r.t. The resulting dark-green powder was separated by filtration and washed with pentane (3 ml). Another crop of this dark-green powder was obtained from the supernatant pentane solution. Yield of $[(L2)TiF_2]$ **5** (0.38 g, 90%). $C_{11}H_{21}F_2N_2Ti$: Calc. C 49.44, H 7.87, N 10.49; Found: C 49.14, H 7.78, N 10.15%. M.p. 205–207 °C. EI MS: m/z (%) = 528 (3) $[M_2F_2{}^+ - C_3H_7]$, 508 (2) $[M_2F^+ - C_3H_7]$, 486 (1) $[M_2F_2{}^+ - C_5H_{10}N]$, 449 (1) $[M_2{}^+\text{-}C_5H_{10}N]$, 394 (8) $[M_2{}^+\text{-}C_8H_{17}N_2]$. ^1H NMR (200 MHz, C_6D_6, r.t.), $\delta =$ 1.10 (d, 12H, $J = 6.2$ Hz, CH*Me*$_2$), 1.22 (d, 12H, $J = 4.8$ Hz, CH*Me*$_2$), 1.37 (d, 12H, $J = 6.8$ Hz, CH*Me*$_2$), 1.44 (d, 12H, $J = 7.9$ Hz, CH*Me*$_2$), 1.48 (12H, CH*Me*$_2$), 1.71 (s, 6H, Me), 1.84 (12H, CH*Me*$_2$), 2.05 (s, 6H, Me), 2.21 (s, 6H, Me), 3.10 (s, 6H, Me), 3.37 (s, 6H, Me), 3.46 (2H, C*H*Me$_2$), 3.52 (2H, C*H*Me$_2$), 4.50 (s, 1H, γ-CH), 4.58 (s, 1H, γ-CH), 4.88 (s, 1H, γ-CH), 5.26 (s, 1H, γ-CH) ppm.

4.6. *Synthesis of $(L2)_4Ti_4F_6O_2 \cdot 2$toluene (6)*

Compound **5** (0.4 g) was dissolved in CH_2Cl_2 (15 ml) in a Schlenk flask (100 ml). A second Schlenk flask (100 8ml) filled with toluene (15 ml) was connected via the glass filter to the first flask containing the solution of **5**. The system was kept undisturbed at 2 °C. After 10 days all CH_2Cl_2 evaporated into the flask containing the toluene. The resulting residue is a viscous mass. To this mass fresh toluene (7 ml) was added and the solution was left at r.t. Oxygen gas for the oxidation of **5** was slowly diffused through the pinch hole in the stopper during 12 days. The green crystals, formed after 12 days, were separated by filtration, washed with pentane (3 ml) and dried in vacuo. Yield of $(L2)_4Ti_4F_6O_2$ (0.18 g, 45%). $C_{11}H_{21}F_{1.5}N_2O_{0.5}Ti$: Calc. C 49.72, H 7.91, N 10.55; Found: C 49.24, H 8.01, N 10.21%. M.p. 238–240 °C.

EI MS: m/z (%) = 589 (2) [((L2)TiFO)$_2$TiN$_2$C$_2$H$_3^+$ $-$C$_3$H$_7$], 528 (19) [((L2)TiF$_2$)$_2$F$_2^+$ $-$C$_3$H$_7$], 508 (10) [((L2)TiF$_2$)$_2$F$^+$ $-$C$_3$H$_7$], 486 (5) [((L2)TiF$_2$)$_2$F$_2^+$ $-$C$_5$H$_{10}$N], 450 (6) [((L2)TiF$_2$)$_2^+$ $-$C$_5$H$_{10}$N], 388 (2) [((L2)TiF$_2$)$_2$F$^+$ $-$C$_{11}$H$_{21}$N], 347 (38) [((L2)TiF$_2$)$_2^+$ $-$C$_{11}$H$_{21}$NF], 267 (100) [(L2)TiF$_2^+$], 264 (28) [(L2)TiFO$^+$]. ^{1}H NMR (200 MHz, C$_6$D$_6$, r.t.), δ = 1.10 (d, 12H, J = 6.3 Hz, CHMe_2), 1.20 (12H, CHMe_2), 1.23 (s, 3H, Me, toluene), 1.35 (d, 12H, J = 5.8 Hz, CHMe_2, LTiO unit), 1.50 (12H, CHMe_2), 1.71 (s, 6H, Me), 1.84 (12H, CHMe_2), 2.10 (s, 6H, Me), 3.10 (s, 6H, Me), 3.34 (s, 6H, Me), 3.36 (2H, CHMe$_2$), 3.42 (2H, CHMe$_2$), 3.47 (2H, CHMe$_2$), 4.49 (s, 1H, γ-CH), ppm.

4.7. X-ray crystallographic study

Crystal data and experimental conditions are listed in Table 3. Selected bond lengths and bond angles with standard deviations in parentheses are presented in Tables 1 and 2. Intensity data for the crystal structures of (L1)TiCl$_2$, (L1)TiCl(N2,6^{i}PrC$_6$H$_3$) and (L2)$_4$-Ti$_4$F$_6$O$_2$·2toluene were collected on a Stoe image plate IPDS II-system. Data for the crystal structure of [(L2)TiCl(N^{i}Pr)]$_2$ and (L2)$_2$TiCl were collected on a Stoe–Siemens four-circle diffractometer. All structures were solved by direct methods (SHELXS-97) and refined against F^2 using SHELXS-97 [40]. The heavy atoms were refined anisotropically. Hydrogen atoms were included using the riding model with U_{iso} tied to U_{iso} of the parent atoms.

5. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 196926-196930 Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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