

Synthesis and Thermal Behavior of Heteroleptic γ -Substituted Acetylacetonate-Alkoxides of Titanium

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A series of heteroleptic titanium derivatives of general formula $[Ti(OiPr)_2(R-acac)_2]$ with acetylacetonate ligands modified in the internal (γ - or 3-) position by different substituents (R=OAc, NO_2 , Me, Et, Cl, Br) has been synthesized and completely characterized by liquid multinuclear NMR and FTIR. The influence of the nature of the group on the thermal stability of the different complexes was studied by thermogravimetric analysis (TGA) and gave the following decreasing stability

Introduction

Titanium tetraisopropoxide [Ti(OiPr)₄]_m (TTIP) is one of the most widely used titanium alkoxide as a starting reagent for gas phase TiO₂ deposition processes due to its high volatility.^[1] However, it is a thermally unstable and extremely reactive compound that generates a lot of handling difficulties. In order to have a monomer structure and increase the thermal stability, complexes based on disubstituted-diketonates of the general formula $[Ti(OiPr)_2(\beta-dik)_2]$ (β -dik = acac, 2,4-pentanedione; thd, 2,2,6,6-tetramethyl-3,5-heptanedione) have been extensively investigated as precursors for the production of TiO₂ thin films in the gas phase (over 200 patents mention their uses).^[2,3] Mono-substituted β -diketonate dimer complexes of the general formula $[Ti(OiPr)_3(\beta-dik)]_2$ are little employed because they are generally converted into di-substituted derivatives by a redistribution reaction of the ligand.^[4] Such derivatives presented as common features high thermal stability for good transportation but lower volatility and mainly low reactivity. Their use are generally accompanied by a high level of carbon in the final layer requiring the use of a reactive gas (O₂, H₂O ...) or even an

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ranking: $H < NO_2 < CI < Me < Br < Et < OAc$. DFT calculations showed that this ranking followed the same order as the stability of the keto-enolate form compared to the β -diketonate form. Other DFT calculations also confirmed that for these molecules the ligands degraded sequentially and that the singular high reactivity of the Et-acac based complex could be due to the rupture of the C–C bond to lead to a CH₂°-acac radical, which triggers the decomposition.

inhibition of the growth of the layer due to a very low degradation of the precursor. Improving the quality of deposits therefore implies the design of more reactive precursors, especially for deposition techniques such as Chemical Beam vapor Deposition (CBVD),^[5] which does not allow the additional addition of a reactive gas.

Few studies have been reported in the literature on the volatility and thermal behavior of $[Ti(OiPr)_2(\beta-dik)_2]$ compounds by varying the nature of the group at the outer position of the β -diketonate.^[6] Hence, [Ti(OiPr)₂(thd)₂] exhibited a better degradation than [Ti(OiPr)₂(acac)₂] while being less volatile. Mass spectrometry studies have shown that [Ti(OiPr)₂(thd)₂] thermally degraded to Ti(thd)₃ or TiO(thd)₂ species demonstrating that the nature of the β -diketonate played a major role in the complete decomposition of the precursor^[3] and that one of the starting point of the decomposition pathway was the cleavage of the external alkyl group (i.e. by β -elimination).^[7] The internal (γ - or 3-) position of the acac ligand has often been modified to allow the grafting of metal alkoxide complexes onto oxide surfaces^[8,9] but data exploiting this modification to study the thermal degradation of such complexes were scarce and dealt only with homoleptic systems $M(\beta-dik)_3$.^[10-14]

Herein, we report the syntheses of a series of heteroleptic titanium derivatives [Ti(OiPr)₂(R-acac)₂] with acac ligands modified with different substituents (R=OAc, NO₂, Me, Et, Cl, Br) at the γ -position and the impact on their thermal stability by thermogravimetric analysis (TGA) and Density Functional Theory (DFT) calculation in order to reach optimal thermal degradation of acac-based titanium complexes. DFT has become the theoretical quantum approach of choice to calculate structure and properties of molecular systems, thanks to its reasonable computational effort required. We used it for a) estimating the keto-enol forms ratio for the differently γ -modified β -diketones ligands, and b) performing an energy decomposition analysis which provides the interaction energy of e.g. a ligand with respect to the remaining part of the complex. The energy decomposition analysis, first introduced by Ziegler and Rauk in

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Scheme 1. Synthesis of heteroleptic Ti(IV) γ -modified β -diketonatealkoxides.

1979,^[15] has been generalized by Bickelhaupt and Baerends,^[16] but, to our knowledge, has never been applied before to interpret the thermal behavior of precursors.

Results and Discussion

Syntheses and structures

Titanium diisopropoxide bis (γ-modified-acetylacetonate) complexes of the general formula $[Ti(OiPr)_2(R-acac)_2]$ $[R=NO_2$ (1), OAc (2), Me (3), Et (4), Cl (5)] have been synthesized by reacting two equivalents of γ -modified diketone ligands and one equivalent of [Ti(OiPr)₄]_m in n-hexane at room temperature and were obtained in quantitative yield. The compound [Ti-(OiPr)₂(Br-acac)₂] (6) was obtained through direct bromination of compound [Ti(OiPr)2(acac)2] (A) in 82% yield, using Nbromosuccinimide (NBS). (Scheme 1) All were soluble in most organic solvents. The liquid ¹H and ¹³C NMR spectra of all compounds were in perfect agreement with their raw formula and high purity. Compounds A, 2 and 4 were yellow-orange liquids or oils while compounds 1, 3, 5 and 6 were in yellow solid form. The liquid compounds could not be purified by vacuum distillation but some of the solid compounds could be purified by crystallization in hexane or hexane/isopropanol mixture and characterized by single crystal X-ray diffraction.

[Ti(OiPr)₂(NO₂-acac)₂] (1) and [Ti(OiPr)₂(Me-acac)₂] (3) crystallized in the triclinic space group P-1 and [Ti(OiPr)₂(Br-acac)₂] (6) in the monoclinic space group $P2_1/n$. They all adopted a mononuclear structure, where the 6-coordinated titanium atom was surrounded by two isopropoxyde ligands and two bidentate β -diketonate ligands in *cis* position (Figure 1) as generally observed.^[6] The angles between two neighboring oxygen atoms lied in the range 80-102°, indicating distorted octahedral geometries around metal center. The average Ti-O bond distances of iso-propoxide ligands [av. 1.775 (3) Å] was shorter than those of β -diketonate ones [av. 2.044 (3) Å]. (Table 1) Overall, these bond lengths and bond angles

Table 1. Selected bond lengths (Å) and angles (°) of derivatives 1, 3, and 6.					
	NO ₂ -acac (1)	Me-acac (3)	Br-acac (6)		
Ti–O5 (OR)	1.777 (3)	1.785 (2)	1.796 (3)		
Ti-06 (OR)	1.772 (3)	1.814 (2)	1.792 (3)		
Ti–O1 (acac)	2.016 (3)	1.981 (2)	2.016 (3)		
Ti–O2 (acac)	2.083 (3)	2.090 (2)	2.067 (3)		
Ti–O3 (acac)	2.002 (3)	2.023 (2)	2.059 (3)		
Ti–O4 (acac)	2.076 (2)	2.001 (2)	2.006 (3)		
01-Ti–O2	81.18 (11)	80.76 (9)	81.08 (12)		
03-Ti–04	81.83 (10)	81.38 (9)	81.30 (12)		
05-Ti–06	101.54 (13)	98.55 (11)	101.76 (15)		

compared well with the literature values reported for related compounds.^[4,6,17] Concerning the nitro group in γ -position of the diketone, C-NO₂ bond lengths [1.442 (3) and 1.454 (3) Å] was in the normal range for this type of compound.^[16] However, the presence of nitro group in the γ -position of the β diketonate moiety brought in significant intermolecular Hbonding (3.47–3.59 Å) between oxygen atoms of NO₂ group and hydrogen atoms in α -position of β -diketonate ligand. There was also weak interaction present between oxygen atoms of β diketonate moieties and central methine hydrogen atoms on isopropoxide ligands. Compared to the plane of β -diketonate moiety, the NO₂ group was slightly tilted with the torsion angle varying in the range 47.5–51.6°. For compound 3, the C–C bond length involving the methyl group in the γ -position of the β diketone was consistent with usual C-C bond length. For compound 6, the C-Br bond lengths [av. 1.910 Å] was in the usual range.^[11-13] Similar to [Ti(OiPr)₂(Me-acac)₂] (3), [Ti(OiPr)₂(Bracac)₂] (6) discrete mononuclear molecules were rather loosely packed, and no significant intermolecular interaction was found.

Thermal behavior

All compounds were tested in TGA under argon atmosphere between 20 and 600 °C with a temperature ramp of 5 °C min⁻¹. The curves are summarized in Figure 2 and compared to

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Figure 1. ORTEP drawings of (A) $[Ti(OiPr)_2(NO_2-acac)_2]$ (1), (B) $[Ti(OiPr)_2(Me-acac)_2]$ (3) and (C) $[Ti(OiPr)_2(Br-acac)_2]$ (6) with 50% probability ellipsoids (Hydrogen atoms are omitted for clarity).

compound **A**. All these compounds were found to be nonvolatile under reduced pressure, so the weight losses observed can be considered as resulting only from thermal degradation and therefore dependent from the stability of the compounds. In general, all the new compounds showed an onset of weight loss at lower temperatures than the reference compound suggesting lower thermal stability induced by the functionalization of the internal position of the acac ligand. Based on the temperature of onset of weight loss, the following decreasing stability ranking was established: H (A) 172 °C > NO₂ (1) 162 °C > Cl (5) 159 °C > Me (3) 151 °C > Br (6) 141 °C > Et (4) 108 °C > OAc (2) 92 °C (Table 3).

Another relevant parameter to check was the difference between the experimental weight loss and the theoretical one to obtain TiO₂. The results are summarized in Table 2 and showed that the smallest differences were observed for the alkyl groups. In particular, the presence of the ethyl group in compound $[Ti(OiPr)_2(Et-acac)_2]$ (4) was accompanied by a degradation rate very close to that of TiO₂, making it possible to envisage a more complete degradation than for the other precursors. In comparison, the compound $[Ti(OiPr)_2(OAc-acac)_2]$ (2), which started to degrade at the lowest temperature, yielded one of the highest residues far from the theoretical one to obtain TiO₂.

Theoretical calculations

In order to explain the evolution of the thermal stability of the precursors observed by the TGA, we sought to correlate the effect of the different substituents of the acac ligand on thermodynamic stability by theoretical calculations. The Brønsted acid-base reactions between Ti(OR)₄ and 2 equivalents of γ -modified β -diketone can be summarized as below.

In this case, Brønsted acidities of γ -modified β -diketone ligands are key thermodynamic parameters to obtain stable final [Ti(OiPr)₂(R-acac)₂] complexes. Considering the pKa of 16.5 isopropanol in water, the more acidic the R-acacH ligand, the more thermodynamically favorable the reaction will be. β -Diketones can exhibit two forms (β -diketone and keto-enol) and only this latter form can undergo a Brønsted acid-base reaction. It was therefore crucial to evaluate the proportion between these two forms before determining their Brønsted acidity. The

Table 2. TGA data vs acac functionalization.							
R group	H (A)	NO ₂ (1)	CI (5)	Me (3)	Br (6)	Et (4)	OAc (2)
Onset temperature weight loss [°C] Residues [%] Theoretical loss for TiO ₂ [%] Δ (Exp-Theo)	172 30.4 22.0 8.4	162 34.7 17.5 17.2	159 37.7 18.0 19.7	151 30.6 20.4 10.2	141 37.6 15.3 22.3	108 20.6 19.0 1.6%	92 37.7 16.5 21.2



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+ Ti(OiPr)₄ \longrightarrow [Ti(OiPr)₂(R-acac)₂] + 2 HOiPr

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Figure 2. TGA Patterns (20-600 °C) of derivatives A and 1-6.

ratio between the diketone and keto-enol forms was estimated by DFT calculations to better understand β -diketones stability and to anticipate their reactivity. DFT calculations by B3LYP functional were performed and have consisted first of optimizing the structure of the β -diketones and keto-enol forms and then of calculating the Gibbs free enthalpy $\triangle G_r^\circ$ between both forms (Figure S1). For this tautomeric equilibrium, we did not try to find an intermediate state or activation energy, we simply

Table 3. Ranking of $\gamma\text{-modified}\ \beta\text{-diketones}$ ligands and keto-enol/diketone ratio versus $\Delta G_r^{\circ}.$					
		ΔG° [kcal/mol]	Ratio [%] Ketoenol	Diketone	
NO ₂ -acacH		4.87	100	-	
H-acacH		2.81	99.1	0.9	
Cl-acacH		2.71	99.0	1.0	
Me-acacH		1.65	94.1	5.9	
Br-acacH		1.25	89.1	10.9	
Et-acacH		0.46	68.5	31.5	
	Normal	3.30	99.6	0.4	
OAc-acacH	+H bond	-2.94	0.7	99.3	

compared the $riangle G_r^{\circ}$ values to deduce which form was predominant. Table 3 summarizes results obtained for the calculations on the acacH ligand and γ -modified analogues and classified according to decreasing ΔG_r° values.

For the ligand OAc-acacH, an optimized structure comprising a hydrogen bond (oxygen-hydrogen distance = 2.28 Å < 2.5 Å) between the hydrogen in the γ -position and the oxygen of the ketone of the -OAc group (Figure 3) has been calculated and has demonstrated a strong stabilization of the β -diketone form to the detriment of the keto-enol one.

Except for compounds **A** and **6**, it should be noted that the order of the Gibbs free enthalpy of the ligands follows the same order as that of the onset degradation temperatures and therefore thermal stability. The more the equilibrium is shifted towards the keto-enol form the more thermally stable the compound $[Ti(OiPr)_2(R-acac)_2]$ is. This observation suggests that DFT calculations on β -diketone ligands could predict the thermal stability of such heteroleptic complexes. Indeed, the ligands in the major diketone form (OAc, Et) being less acidic, the ligand-metal bonds are weaker, resulting in less stable molecular complexes. On the other hand, although the two



Figure 3. Optimized structures of OAc-acacH ligand with hydrogen bond (Grey ball = carbon, red ball = oxygen, white ball = hydrogen).

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compounds, [Ti(OiPr)₂(OAc-acac)₂] (2) and [Ti(OiPr)₂(Et-acac)₂] (4), had close onset degradation temperatures, their weight losses were very different from the theoretical percentage to have TiO_2 , far for 2 and very close for 4 (Table 1). We were therefore interested in the influence of the fragmentation of these heteroleptic compounds in order to identify a key parameter allowing near-complete degradation.

To investigate the decomposition mechanism involved in the TGA experiment, DFT calculations have been performed on several $[Ti(OiPr)_2(R-acac)_2]$ complexes $[R=NO_2$ (1), OAc (2), Et (4)]. When the complex dissociated, the expected fragments that were eliminated may be isopropoxyl (OiPr) and γ -modified acetylacetonate (R-acac). If a decomposition into neutral fragments was considered, the binding energy of Ti with the four fragments was -21.66 eV (499 kcal/mol), whereas if ionic fragments (Ti⁴⁺ and negatively charged ligand fragments) were considered, the binding energy of Ti⁴⁺ with the four fragments was -102.0 eV. This clearly indicated that due to the electrostatic contributions, decomposition of the complex did not lead to charged fragments. The calculation energies are shown in Table 4 for $[Ti(OiPr)_2(R-acac)_2]$ complexes $[R=NO_2$ (1), OAc (2), Et (4)].

The results summarized in Table 4 demonstrated that the differences were minimal, so that the two fragments OiPr and R-acac could be expected to be removed with the same ease. Moreover, for the three complexes, the fragmentation energies were very close, which did not explain the differences in thermal stability observed in the TGA, or even contradicted them, as it was lower for the complex 1 based on the NO₂-acac ligand. Complete fragmentation scheme and DFT calculations of $[Ti(OiPr)_2(R-acac)_2]$ complexes $[R=NO_2$ (1), OAc (2)] are shown in Figure S1 and Table S2. It should be mentioned that such calculations assumed that the experiments involved rapid degradation of the complex, i.e. not without significant time between the removal of the first and second ligand. Consequently, all calculations were made against a geometry of the initial neutral complex. If the experiment assumed that the degradation of the complex was a slow process, it would be necessary to re-optimize the eliminated fragments, a process that would lead to modified energies, but not to significantly modified trends.

Table 4. Energies (eV) for the first fragmentations of $[Ti(OiPr)_2(R-acac)_2]$ complexes $[R=NO_2$ (1), OAc (2), Et (4)].					
Fragmentation reaction	$R = NO_2$	R=OAc	R=Et		
	[eV]	[eV]	[eV]		
Loss of R-acac	4.96	5.06	5.46		
Loss of OiPr	5.23	5.14	5.23		

Table 5. Energies (eV) for the partial fragmentations of $[Ti(OiPr)_2(R-acac)_2]$ complexes [R=OAc (3), Et (5)].						
	R = OAc		R = Et			
Fragments Energy (eV)	Ac 4.23	OAc 1.20	Me 5.23	Et 5.90		

In addition, the fact that the $[Ti(OiPr)_2(R-acac)_2]$ [R=OAc (2), Et (4)] complexes behaved singularly by yielding the lowest onset degradation temperatures would indicate that these complexes probably did not decompose by overall removal of ligands, but probably by partial decomposition of ligands. Calculations of the binding energy of different fragments in relation to the rest of the complex showed that the departures of the OAc and Me groups were favoured (Table 5). However, producing an acac-CH₂° radical more reactive/less stable than acac° one, could be at the origin of the almost complete degradation of [Ti(OiPr)₂(Et-acac)₂] (lowest residue content) compared to others complexes of this study.

Conclusions

Six new titanium alkoxide complexes di-substituted with γ modified β -diketonates were synthesized and thoroughly characterized. None of them showed volatility, and TGA demonstrated that thermal stability was modulated by the nature of the γ -position group. These results were consistent with DFT calculations, which demonstrated that improved thermal stability of the Ti(OR)₂(R-acac)₂ complexes could be correlated with the greater stability of the γ -modified ketoenolate isomer compared to that of β -diketonates. DFT calculations also showed that thermal decomposition should occur by sequential fragmentation. An alkyl group at the γ -position such as ethyl was found to enhance the reactivity of this type of molecule, giving the lowest residue content close to TiO₂. It could be envisaged that this reactivity (and hence degradation) could be improved by the introduction of a group that could allow a primary degradation step such as C-C cleavage to give a reactive radical.

Experimental Section

Synthesis

All manipulations using metal alkoxides were carried out under inert gas using a glove box (N₂) or standard Schlenk techniques (Ar). [Ti(OiPr)₄]_m was purchased from STREM Chemicals and distillated under vacuum prior being used. N-bromosuccinimide $(C_4H_4NO_2Br, NBS)$ and acetylacetone (2,4-pentadione, acacH) were purchased from Acros organics. 3-ethyl-2,4-pentanedione (Et-acacH) and 3-chloroacetylacetone (Cl-acacH) were supplied from Merck and used as received. γ -modified acacH ligands (NO₂-acacH, CH₃COO-acacH, Me-acacH) were synthesized through modified procedures reported in the literature and thoroughly characterized by multinuclear NMR and FTIR (See Supplementary Materials). Anhydrous n-hexane was obtained using a solvent drier, SPS (solvent purification system) from MBRAUN and stored under argon over 4 Å molecular sieves. Dichloromethane (CH₂Cl₂) was dried over MgSO₄, filtered and stored under argon over 4 Å molecular sieves. Isopropanol was refluxed and distillated on [Al(OiPr)₃]₄ and then stored under argon over 4 Å molecular sieves. Deuterated chloroform was stored in a Rotaflow flask over 4 Å molecular sieves.

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Preparation of [Ti(OiPr)₂(acac)₂] (A)

The synthesis was done by a modified protocol based on reference.^[18] 3.9 g of [Ti(OiPr)₄]_m (13.7 mmol) were diluted in n-hexane (65 mL) then 2.75 g of acacH (27.5 mmol) was added slowly. The mixture was let under stirring overnight. All volatiles were removed under vacuum, the brown-orange liquid obtained was then purified by vacuum distillation (1 mbar, oil bath at 150 °C) and gave a bright orange liquid (**A**). Yield: 80% (m=4.00 g) . ¹**H NMR** (**CDCl**₃, **\delta ppm**) 1.12–1.18 [d, ³J=6.4 Hz, 12H, OCH(CH₃)₂], 1.88, 1.99 [s, 12H, COCH₃], 4.74 [m, 2H, OCH(CH₃)₂], 5.47 [s, 2H, COCHCO]. ¹³**C NMR** (**CDCl**₃, **\delta ppm**) 25.3 [OCH(CH₃)₂], 26.1, 27.1 [COCH₃], 78.3 [OCH (CH₃)₂], 102.8 [COCHCO], 187.3, 191.4 [CH₃COCH]. **FT-IR** (**Nujol**, **cm**⁻¹) 2964, 2925, 2859 [v C–H]; 1608, 1587, 1524 [v C=O], 1383, 1359; 1326, 1125, 1012 [v C–O], 993, 929; 665, 619 [v Ti–O].

Preparation of [Ti(OiPr)₂(NO₂-acac)₂] (1)

The same protocol as described above with 1.51 g (10.4 mmol) of NO₂-acacacH and 1.48 g of $[Ti(OiPr)_4]_m$ (5.2 mmol) gave, after removal of all volatiles, an orange-yellow viscous liquid. Purification by vacuum distillation was attempted, but the product completely decomposed. The product crystallized in an isopropanol/n-hexane mixture at about 2 °C to give light yellow needle crystals. MP (ATG-DSC) = 57 °C. Yield > 99% (m = 2.35 g). ¹H NMR (CDCl₃, δ ppm) 1.17–1.26 [d, ³J = 6.4 Hz, 12H, OCH(CH₃)₂], 2.23 [s, 6H, COCH₃], 2.36 [s, 6H, COCH₃], 4.76 [m, 2H, OCH(CH₃)₂]. ¹³C NMR (CDCl₃, δ ppm) 24.9, 25.1 [OCH(CH₃)₂], 25.6, 25.9, 26.6, 29.9 [COCH₃], 82.2, 83.9 [OCH (CH₃)₂], 139.4 [COC(NO₂)CO], 187.3, 189.6 [CH₃CO]. FT-IR (Nujol, cm⁻¹) 2967, 2927, 2861 [v C–H]; 1608, 1588, 1528 [v C=O], 1415, 1346 [v C-NO₂]; 1287, 1161, 1117[v C–O]; 926, 824; 684, 667, 624 [vTi–O].

Preparation of [Ti(OiPr)₂(OAc-acac)₂] (2)

The same protocol as described above with 1.02 g of OAc-acacH (6.5 mmol) and 0.89 g of $[Ti(OiPr)_4]_m$ (3.1 mmol) gave, after removal of all volatiles, an orange-brown viscous oil. Purification by vacuum distillation was attempted but product entirely decomposed. Yield: 99% (m = 1.48 g). ¹H NMR (CDCl₃, δ ppm) 1.18 [d, ³J = 6.5 Hz, 12H, OCH(CH₃)₂], 1.90 [s, 6H, COCH₃], 1.97 [s, 6H, COCH₃], 2.20 [s, 3H, OOCCH₃], 4.77 [m, 2H, OCH(CH₃)₂]. ¹³C NMR (CDCl₃, δ ppm) 24.7, 25.3 [OCH(CH₃)₂], 27.7 [COCH₃], 30.1 [OOCCH₃], 82.5, 83.6 [OCH (CH₃)₂], 129.5 [COC(OAc)CO], 187.3, 189.6 [CH₃CO], 199.5 [OOCCH₃]. FT-IR (Nujol, cm⁻¹) 2962, 2922, 2857 [v C–H]; 1756, 1720 [v COO], 1599, 1585, 1525 [v C=O]; 1415, 1346, 1287, 1161, 1117, 1001 [v C–O]; 926, 824; 684, 667, 624 [v Ti–O].

Preparation of [Ti(OiPr)₂(Me-acac)₂] (3)

The same protocol as described above with 1.05g of Me-acacH (9.2 mmol) and 1.31g of $[Ti(OiPr)_4]_m$ (4.6 mmol) gave, after removal of all volatiles, an orange powder. Product crystallized in n-hexane at around 2 °C to give square light-yellow crystals. MP (ATG-DSC) = 71 °C. Yield: 99% (m = 1.80 g). ¹H NMR (CDCl₃, δ ppm) 1.14–1.15 [d, ³J = 6.4 Hz, 12H, OCH(CH₃)₂], 1.86 [s, 6H, CCH₃], 1.99 [s, 6H, COCH₃], 2.06 [s, 6H, COCH₃], 4.73 [m, 2H, OCH(CH₃)₂]. ¹³C NMR (CDCl₃, δ ppm) 24.9, 25.1 [OCH(CH₃)₂], 25.6, 25.9, 26.6, 29.9 [COCH₃], 82.2, 83.9 [OCH (CH₃)₂], 139.4 [COC(NO₂)CO], 187.3, 189.6 [CH₃CO]. FT-IR (Nujol, cm⁻¹) 2959, 2922, 2855 [v C–H]; 1605, 1582, 1527 [v C=O], 1380, 1359; 1325, 1122, 1011 [v C–O], 993, 928; 664, 623 [v Ti–O].

Preparation of [Ti(OiPr)₂(Et-acac)₂] (4)

The same protocol as described above with 1.06 g of Et-acacH (8.3 mmol) and 1.18 g of $[Ti(OiPr)_4]_m$ (4.2 mmol) gave, after removal of all volatiles, a viscous orange-brown liquid. Purification by vacuum distillation was attempted but product entirely decomposed. Yield: 93 % (m = 1.65 g). ¹H NMR (CDCl₃, δ ppm) 0.99 [t, ³J = 6.5 Hz, 6H, CH₂CH₃], 1.11 [d, ³J = 6.3 Hz, 6H, OCH(CH₃)₂], 1.19 [d, ³J = 6.3 Hz, 6H, OCH(CH₃)₂], 1.19 [d, ³J = 6.3 Hz, 6H, OCH(CH₃)₂], 1.96 [s, 6H, COCH₃], 2.04 [s, 6H, COCH₃], 2.22–2.28 [q, 4H, CH₂CH₃], 4.69 [m, 2H, OCH(CH₃)₂]. ¹³C NMR (CDCl₃, δ ppm) 15.2 [CH₂CH₃], 2.24 [OCH(CH₃)₂], 2.5.3, 26.6 [COCH₃], 76.3 [OCH(CH₃)₂], 114.4 [COC(Me)CO], 185.4, 190.6 [CH₃CO]. FT-IR (Nujol, cm⁻¹) 2959, 2922, 2855 [v C–H]; 1605, 1582, 1527 [v C=O], 1380, 1359; 1325, 1122, 1011 [v C–O], 993, 928; 664, 623 [v Ti–O].

Preparation of [Ti(OiPr)₂(Cl-acac)₂] (5)

The same protocol as described above with 1.79 g of Cl-acacH (13.3 mmol) and 1.78 g of [Ti(OiPr)_4]_m (6.3 mmol) gave, after removal of all volatiles, a yellow powder. MP (ATG-DSC) = 65.5° C. Yield > 99% (m = 2.71 g). ¹H NMR (CDCl₃, δ ppm) 1.17 [d, ³J = 6.3 Hz, 12H, OCH(CH₃)_2], 2.18 [s, 6H, COCH₃], 2.27 [s, 6H, COCH₃], 4.74 [m, 2H, OCH(CH₃)_2]. ¹³C NMR (CDCl₃, δ ppm) 25.3 [OCH(CH₃)_2], 26.1 [COCH₃], 79.9 [OCH(CH₃)_2], 110.5 [COC(Cl)CO], 186.3, 188.6 [CH₃CO]. FT-IR (Nujol, cm⁻¹) 2955, 2921, 2851 [v C–H]; 1603, 1579, 1524 [v C=O], 1449, 1362; 1331, 1162, 1126, 1003 [v C–O], 851 [v C–Cl]; 620, 559 [v Ti–O].

Preparation of [Ti(OiPr)₂(Br-acac)₂] (6)

The synthesis was done following a new protocol. 0.67 g of Ti(OiPr)₂(acac)₂ (1.8 mmol) was diluted in dichloromethane (56 mL) cooled at around 0°C. Then 0.72 g of dry N-bromosuccinimide (4.1 mmol) in 15 mL of dichloromethane was added very slowly (10 min addition) and at 0°C. The mixture was let under stirring overnight. After removal of all volatiles, an orange brown powder was obtained. Attempts to remove succinimide by washing with nhexane and filtering failed. Product crystallized in isopropanol/nhexane mixture at around 2°C to give square light-yellow crystals. MP (ATG-DSC) = 75 °C. Yield: 82% (m = 0.77 g). ¹H NMR (CDCl₃, δ ppm) 1.17 [d, ³J=6.3 Hz, 12H, OCH(CH₃)₂], 2.26 [s, 6H, COCH₃], 2.35 [s, 6H, COCH₃], 4.74 [m, 2H, OCH(CH₃)₂]. ¹³C NMR (CDCl₃, δ ppm) 26.2 [OCH(CH₃)₂], 26.9 [COCH₃], 81.2 [OCH(CH₃)₂], 112.2 [COC(CI)CO], 187.3, 189.1 [CH₃CO]. FT-IR (Nujol, cm⁻¹) 2954, 2920, 2856 [v C–H]; 1601, 1575, 1524 [v C=O], 1448, 1359; 1330, 1159, 1124, 1010 [v C-O], 701 [v C-Br]; 622, 562 [v Ti-O].

Characterizations

NMR spectra were recorded on Bruker AVANCE III 400 MHz with a BBFO probe (Z gradient) using Topspin software. All chemical shifts were measured relatively to the deuterated solvents in case of ^{13}C NMR (in CDCl₃: $\delta\!=\!77.23$ ppm triplet), or to the residual protic solvent for ^1H NMR (in CDCl₃: $\delta\!=\!7.24$ ppm singlet). FT-IR spectra were recorded from 4000 to 400 cm $^{-1}$ at room temperature using Bruker Vector 22 and Opus software. Operation chamber is maintained under N₂ with constant gas flow. Samples were prepared under argon flow between KBr windows with Nujol (dried over 3 Å molecular sieves).

TGA data were collected on a TGA/DSC 1 thermal analysis MX1 from Mettler Toledo, Stare system, gas controller GC200. In order to prepare samples, the following procedure was used: 100μ L aluminum crucibles (top and bottom) are weighed together on high precision balance (10^{-3} mg) then they are brought into the glovebox. Into the glovebox (under N₂), 5–10 mg of product were



placed into the crucible bottom, the cap is added and then the entire crucible is sealed using a special baler from Mettler Toledo and finally samples are brought out of the glovebox. Before analysis, samples are weighed once again on high precision balance. Sample were pierced just before analysis; the method uses as carrier gas argon with a flow of 30cc per minute with a program beginning with 4 minutes at 25 °C and then a heating rate of 5 °C per minute until reaching 600 °C.

Suitable single crystals of derivatives [Ti(OiPr)₂(NO₂-acac)₂] (1), $[Ti(OiPr)_2(CH_3-acac)_2]$ (3) and $[Ti(OiPr)_2(Br-acac)_2]$ (6) (Table 6) were mounted on a Gemini kappa-geometry diffractometer (Agilent Technologies UK Ltd) equipped with an Atlas CCD detector and using Mo radiation ($\lambda = 0.71073$ Å). Intensities were collected at 150 K by means of the CrysalisPro software. Reflection indexing, unit-cell parameters refinement, Lorentz-polarization correction, peak integration, and background determination were carried out with the CrysalisPro software.^[19] An analytical absorption correction was applied using the modeled faces of the crystal.^[20] The resulting set of hkl was used for structure solution and refinement. The structures were solved by direct methods with SIR97^[21] and the least-square refinement on F2 was achieved with the CRYSTALS software.[22] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C-H in the range 0.93-0.98, N–H in the range 0.86–0.89 and O–H = 0.82 (Å) and Uiso(H) (in the range 1.2–.5 times Ueg of the parent atom), after which the positions were refined with riding constraints.

DFT calculations

DFT calculations for diketone/keto-enol ratio determinations have been performed using Gaussian09 package,^[23] the hybrid B3LYP functional^[24,25] without symmetry restrictions and chloroform as solvent.^[26] An energy decomposition analysis was performed, a procedure which provided the interaction energy of a compound with respect to its constituting fragments. This technique, which was implemented in ADF code,^[27,28] has been developed by Baerends, Ziegler and Frenking.^[29,30] Calculations have been performed with TZP basis set^[28] and PBE exchange-correlation . functional.^[31] DFT calculations for fragmentation of the Ti(OR)₂(Racac), derivatives have then been performed according to the following steps:

- 1. Geometry optimization of the whole complex through Kohn-Sham calculations with PBE exchange-correlation functional and TZP basis set, with ADF software.^[28]
- 2. Calculation of the electronic structure of the (separated) four ligands in their geometry within the complex, and the free Ti atom (unrestricted calculation)
- Calculation of the electronic structure of the whole complex 3 from its fragments, namely the four ligands and the Ti atom
- 4. Calculation of the electronic structure of fragments consisting of the complex stripped from one ligand (either R-acac or OiPr) (in their geometry within the complex) (unrestricted calculation)
- 5. Calculations of the electronic structure of the entire complex from a ligand fragment and the corresponding stripped complex. These two calculations provide the binding energies of the fragments that are first eliminated in the experiment. The Gibbs free energies are not calculated but can be estimated as slightly lower due to the increase in entropy during dissociation.
- 6. The process is further pursued by a calculation of the electronic structure of fragments consisting of the complex undergoing a second fragmentation from one ligand (either R-acac or OiPr) (in their geometry within the complex).
- 7. Calculations of the electronic structure of the complex amputated with a ligand fragment and the corresponding complex amputated twice. These four calculations provide the binding energies of the second fragments that are eliminated during the experiment. These calculations are reported in the Supplementary Information file.

Supporting Information (see footnote on the first page of this article): Synthesis and ¹H, ¹³C NMR and FTIR characterizations of the synthesized ligand.

Deposition Numbers 2018641 (for 1), 2018642 (for 3), and 2018643 (for 6) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/ structures.

Table 6. Crystallographic data of derivatives 1, 3 and 6.					
[Ti(OiPr) ₂ (R-acac) ₂]	$R = NO_2$ (1)	$R = CH_3$ (3)	R = Br (6)		
Empirical formula	$C_{16}H_{26}N_2O_{10}Ti$	C ₁₈ H ₃₀ O ₆ Ti	C ₁₆ H ₂₆ Br ₂ O ₆ Ti		
Formula weight (g mol ⁻¹)	454.29	390.33	522.09		
Crystal system	Triclinic	Triclinic	Monoclinic		
Space group	P	P	P2 ₁ /n		
a (Å)	7.3757 (10)	9.3260 (12)	11.751 (2)		
b (Å)	11.1868 (16)	10.3893 (17)	14.156 (2)		
c (Å)	13.9854 (18)	11.9249 (14)	13.174 (2)		
α (°)	94.076 (11)	81.287 (12)			
β (°)	100.886 (11)	85.906 (10)	105.671 (19)		
γ (°)	108.497 (13)	70.706 (13)			
V (Å ³)	1064.0 (3)	1077.7 (3)	2110.0 (6)		
Z	2	2	4		
μ (mm ⁻¹)	0.46	0.42	4.22		
Temperature (K)	100	200	150		
Measured reflections	13917	18774	17612		
Independent reflections (R _{int})	5153 (0.056)	5398 (0.049)	5227 (0.052)		
Data/restrains/parameters	5138/12/272	5389/0/226	5216/0/227		
Goodness of fit	0.97	0.98	0.98		
$R[F^2 > 2\sigma (F^2)]$	0.061	0.059	0.048		
wR(F ²)	0.146	0.127	0.094		
Residual electron	-0.98 to 0.87	-0.72 to 0.70	-1.13 to 1.16		
density (e.Å ⁻³)					



Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Density functional calculations $\cdot \beta$ -Diketonates \cdot Ligand design \cdot Thermal behavior \cdot Titanium

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FULL PAPERS



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1 – 9

Synthesis and Thermal Behavior of Heteroleptic γ-Substituted Acetylacetonate-Alkoxides of Titanium The thermal behavior (stability and decomposition) of a series of heteroleptic titanium derivatives $[Ti(OiPr)_2(R-acac)_2]$ with acetylacetonate ligands modified in the internal (γ - or 3-) position by different substituents $(R = OAc, NO_2, Me, Et, Cl, Br)$ was studied by thermogravimetric analysis and DFT calculations.