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Isomers and Conformers of Complexes of Ti(O*i*Pr)$_4$ with Cyclopentane-1,2-Dione: NMR Study and DFT Calculations

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^{1}H and ^{13}C NMR spectra of Ti(O*i*Pr)$_4$ complexes with 3-methyl-1,2-cyclopentanedione in deuterochloroform solution reveal formation of different compounds, depending on the molar ratio of diketone and Ti-isopropoxide. The obtained results were compared with the DFT calculations of these complexes. Both NMR study and theoretical calculations show that the most stable complex is formed with two dione and one single isopropoxide molecules. Detailed conformational analysis was required to find the relative energies of the isomers and conformers of the systems. A possibility of presence of multiple isomeric complexes, some of which come in enantiomeric pairs, was revealed. Possible abundances of the isomers were estimated on the basis of Boltzmann distribution. © 2014 Wiley Periodicals, Inc.

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Introduction

Chiral titanium complexes have been found to be efficient catalysts for asymmetric chemical transformations. From these, asymmetric epoxidation of allylic alcohols[1,2] and sulfoxidation[3,4] are of the most widely used. Additionally, a number of different other Ti-catalyzed asymmetric transformations is introduced in synthetic organic chemistry (e.g., Refs. [5–10]). We have found that Ti(O*i*Pr)$_4$/tartaric ester complex serves as an asymmetric inducer for the asymmetric Baeyer–Villiger oxidation of cyclobutanones,[11] α-hydroxylation of β-hydroxyketones,[12] and a cascade oxidation of 1,2-diketones to γ-lactone carboxylic acids.[13,14]

The structure of titanium/substrate/ligand complexes is a key factor determining the activity and selectivity of the catalytic processes. There have been several experimental and computational investigations dealing with the structure of titanium/ligand complexes[15–20] and titanium/substrate/ligand clusters.[21–27] Much less attention is paid to titanium/substrate complexes.[28,29]

The complexes of 1,2-cyclopentanedione **1** (Scheme 1) with $VOCl_3$ have been studied.[30] The findings indicate that a large variability exists among the structures, depending on the components of the complex. Ligand position and orientation plays also a significant role in energy distribution and complex stability.[31–33]

We have investigated the mechanism of a Ti-based asymmetric oxidation cascade reaction of 3-alkyl-1,2-cyclopentanedione.[34] To establish the possible structure of 3-alkyl-1,2-cyclopentanedione titanium complexes that form together with the asymmetric ligand a catalytic intermediate cluster, we investigated the structure of complexes between 3-methyl-1,2-cyclopentanedione **1** and Ti(O*i*Pr)$_4$ **2** using the ^{1}H and ^{13}C NMR spectra of the solutions at different component ratios. However, the chemical and spectral data were not sufficient to establish the structure of the complexes. Therefore, possible structures of the complexes were modeled using DFT methodology and structures of possible isomers and conformers of the systems with various degrees of substitution were established. Relative energies of the structures were used to explain the equilibria observed in the NMR experiments.

The systematic conformational analysis of penta- and hexacoordinated complexes involved creation of a list of all possible relative positions and orientations of the ligands involved. Systematic studies of complexes with bidentate asymmetric ligands are rare in the literature. We used a classification system analogous to the one used in [31]. We believe that the systematic enumeration of possible relative orientations of the mix of axially symmetric and nonaxially symmetric ligands, as presented in this study, has a value of its own in further studies of systems of analogous compositions.

Experimental: NMR Studies at Different Ratios of Ti(O*i*Pr)$_4$ and 3-Methyl-1,2-Cyclopentanedione

We prepared mixtures of 3-methyl-1,2-cyclopentanedione **1**, 2-methoxy-3-methylcyclopent-2-en-1-one, and 3-methylcyclo pent-2-en-1-one with Ti-tetraisopropoxide **2** at component ratios from 1:1 to 4:1. From the ^{1}H and ^{13}C NMR spectra of these compounds in deuterochloroform solution, we found

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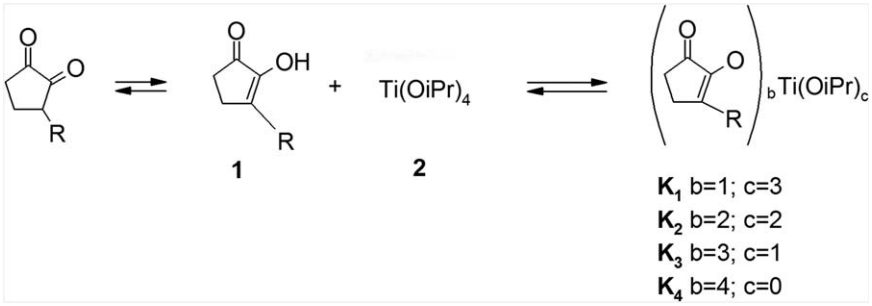


Scheme 1. Possible formal complexes of diketone **1** and Ti(*i*Pr)$_4$ **2**.

that only 3-methyl-1,2-cyclopentanedione in enolic form (presented in Scheme 1) yields complexes with titanium tetraisopropoxide. In this work, the possible enolates are denoted $\mathbf{K_1}$–$\mathbf{K_4}$ according to the number of 3-methyl-1,2-cyclopentanedienyl ligands in the complex.

The compounds **1** and **2** were mixed at different molar ratios from 1:1 to 4:1 in $CDCl_3$ solution at −20°C under argon atmosphere. NMR spectra of the reaction products reveal the formation of different Ti-enolates as well as the existence of the free initial components and isopropanol (formed in the reaction). These multicomponent multisite exchange broadened-lined spectra (clearly distinguishable) were analyzed by observing individual signals from different complexes due to relatively slow exchange rates between the complexes. Details of the analysis and a sample spectrum are available in the electronic Supplementary Information.

Enol **1**, when mixed with titanium alcoholate **2**, may form at least four different titanium enolates $\mathbf{K_1}$–$\mathbf{K_4}$ (Scheme 1). However, only three of them — $\mathbf{K_2}$ to $\mathbf{K_4}$ — were observed. In the 1:1 mixture of the components only a single new compound (determined as enolate $\mathbf{K_2}$) was detected, together with isopropanol and unreacted titanium tetraisopropoxide. In the spectrum of 2:1 mixture of the components, (ketone **1** to **2**) the same product $\mathbf{K_2}$ was observed (enolate $\mathbf{K_2}$; Scheme 2).

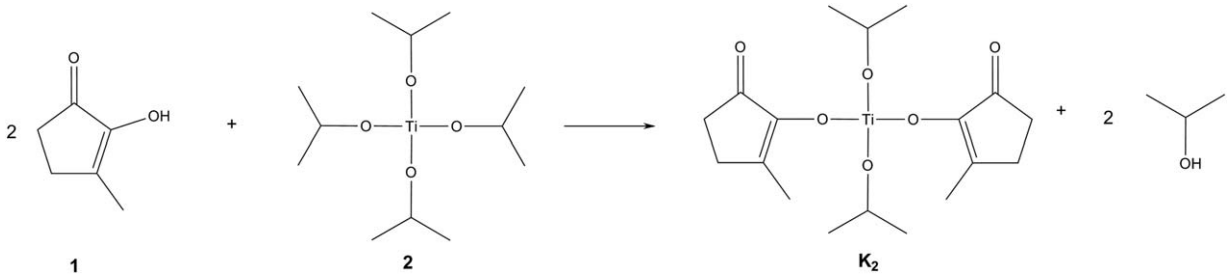
Formation of the same complex $\mathbf{K_2}$ was also observed at the 3:1 ratio of **1** and **2**. Additionally, in the 3:1 mixture the formation of a new complex $\mathbf{K_3}$ in considerable amount, with three molecules of ketone **1**, was observed. The presence of a complex $\mathbf{K_4}$ in the mixture was also detected. It is noteworthy that in this case considerable amount of free uncomplexed ketone remained in the solution. Increasing the ratio of **1** to **2** further to 4:1 results in additional increase of uncomplexed ketone. Summary of changes in relative amounts of different complexes and free ketone are given in Table 1. These data were obtained from the integration of NMR spectra.

Comparison of ^{13}C NMR spectra of initial free substrate **1** and its complexes $\mathbf{K_2}$ to $\mathbf{K_4}$ with Ti(O*i*Pr)$_4$ clearly point to the formation of Ti—O bond via the hydroxyl group (see details in the electronic Supplementary Information).

The experimental NMR results reveal that the relative abundances of the complexes of **1** with **2** come in the sequence $\mathbf{K_2} > \mathbf{K_3} > \mathbf{K_4} > \mathbf{K_1}$. The $\mathbf{K_2}$ is formed first, and it is the single complex observed at low **1** to **2** ratios. Upon increasing ratios to 3:1 and 4:1, two new complexes $\mathbf{K_3}$ and $\mathbf{K_4}$ appear in the NMR spectra. The lines of $\mathbf{K_1}$ are not observed in NMR spectra at all. It was impossible to obtain quantitative data about the relative stability of these complexes from the measured mixtures, because in these multicomponent mixtures free **1** is present in significant amounts, as is also free isopropanol, which forms in the course of the reaction. Its presence results in remarkable broadening of signals in NMR spectra of measured samples. To get more information about the relative stability of complexes $\mathbf{K_1}$–$\mathbf{K_4}$ and to verify conclusions made on the basis of the NMR spectra, a computational study was undertaken.

Computations: DFT Modeling of the Complex Structures

Calculations of the structure of the complexes were carried out using DFT approach according to standard computational chemistry methodology. Initially, relative location and orientations of the ligands were set up by following simple chemical



Scheme 2. Formation of complex $\mathbf{K_2}$.

Table 1. Distribution of diketone **1** molecules between different solute molecules in the deuterochloroform at different diketone **1** and $Ti(OiPr)_4$ **2** ratios.

No	Ratio 1:2	Free ketone	$Ti(OiPr)_4$	K_2	K_3	K_4
1	1:1	–	0.5	0.5	–	–
2	2:1	–	–	2	–	–
3	3:1	0.80	–	0.75	1.15	0.30
4	4:1[a]	2.40	–	0.15	1.15	0.30

[a] some insoluble precipitate also formed.

intuition. However, the relative energies of the complexes did not correlate with the experimental findings reported above. Therefore, a careful and systematic search for lowest energy isomers and conformers of the complexes was required to reach an understanding of the experimental findings.

The original optimizations and conformational searches were performed with the BP86 functional and the SV(P) basis set. The selected lowest-energy geometries were refined with the def2-TZVP basis set.[35] Solvent effects ($CDCl_3$ solvent, $\varepsilon = 4.81$ at 293 K[36]) were accounted for with the COSMO continuum model. Geometries of the structures were fully optimized, and minima were verified with vibrational analysis. Gas-phase zero-point vibrational energies were added to the solvent-optimized electronic energies.[37] Turbomole version 5.10[38] software was used. Final geometries and original energies in Hartree are available in the electronic Supplementary Information.

Titanium tetraisopropoxide

Conformational analysis of this molecule was performed by changing the eight torsional angles corresponding to the rotation around Ti—O and O—C bonds. In the lowest energy conformers, the hydrogen atom at the tertiary carbon is directed toward the oxygen atom of a neighboring isopropoxy group. The lowest energy conformer (Fig. 1) has S_4 symmetry, and each hydrogen at the tertiary carbons is pointed at an oxygen of another O—*i*Pr group in such arrangement that no oxygen has more than one hydrogen pointing at it. Excluding possible rotations and reflections of the whole molecule, such arrangement is unique.

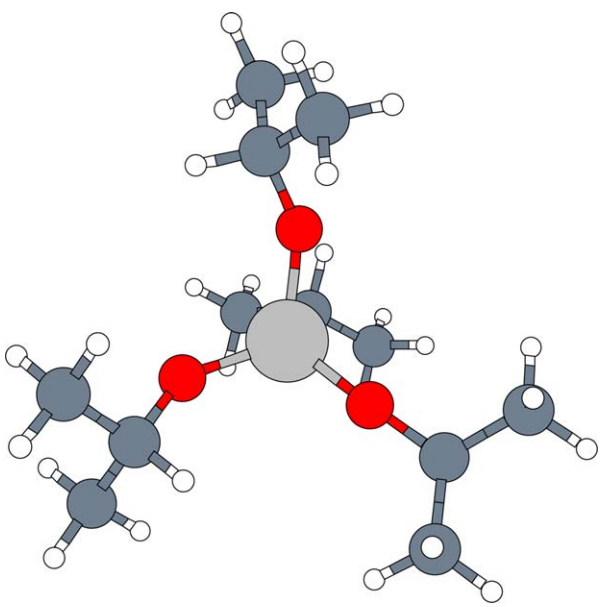


Figure 1. The lowest-energy conformer of titanium tetraisopropoxide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Complex K_1

In the conformational analysis, rotation about five torsional angles (three defining the position of each O—*i*Pr groups and two defining the position of the cyclopentanedione [C(2)—O(3)—Ti(4)—O(4) and C(1)—C(2)—O(3)—Ti(4)] were considered (Fig. 2). The bend angles C(2)—O(3)—Ti(4) in the starting geometries were set to 110 and 170 degrees to test for presence or absence of a Ti—O bond.

In this text, we shall use the terms "conformer" and "isomer" interchangeably, because the barriers for interconversion between the structures are unknown. The NMR data did not reveal presence of distinct isomers, so we are inclined to favor rapid interconversion and, consequently, do not distinguish between isomers at room temperature.

In all conformers, the orientation of the five-membered cycle is coplanar with the titanium atom as well as one of the

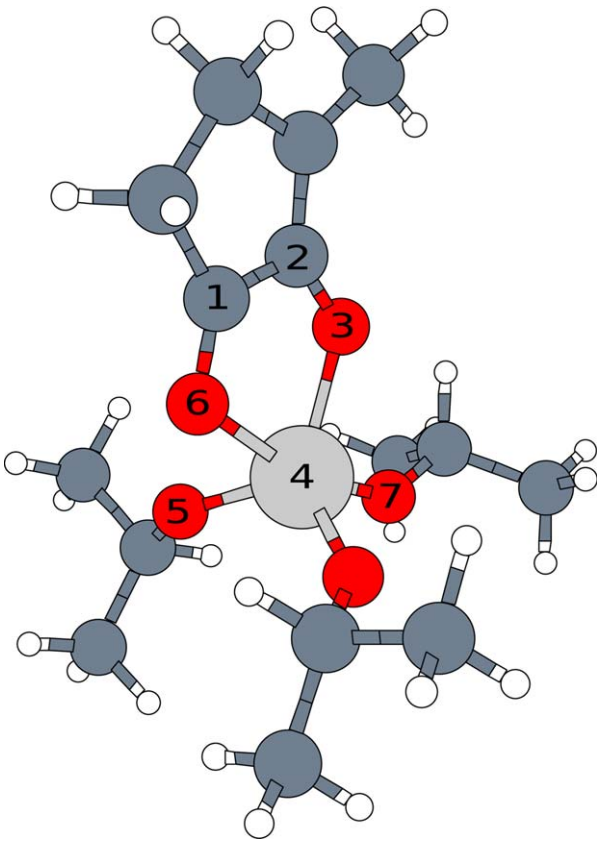


Figure 2. The lowest-energy conformer of the complex K_1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 2. Conformers of the complex $\mathbf{K_1}$. [Color table can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Conformer	1a, 1b	2	3	4a, 4b	5a, 5b
ΔE (kJ/mol)	0.00	0.00	0.60	1.14	2.25
%	43.5 (2×21.7)	17.4	14.9	25.3 (2×12.6)	14.9 (2×7.5)

isopropoxy oxygens (atom 7 in Fig. 2). The distance between substrate carbonyl oxygen atom and titanium atom was quite small: 2.27. . .2.63 Å in all converged calculations. This suggests that a weak chemical bond forms between Ti(4) and O(6).

The presence of a chemical bond was tested by performing an atoms-in-molecules[39] (AIM) analysis with the AIMAll[41] software. A bond critical point exists along the Ti(4)—O(6) path, but the bond delocalization index (DI, interpreted as bond order) as calculated in the AIM model is only 0.22, suggesting the presence of a weak chemical bond. For comparison, the Ti(4)—O(3) bond has a DI 0.51, the other three Ti—O bonds are 0.81–0.86, and the carbon–carbon single bonds in the system are all very close to 1.0. If we take the bond with DI = 0.22 into account, the coordination number of titanium in this compound becomes five. This coordination is reflected in the figures, by drawing a bond between the corresponding atoms.

We also checked whether further increase of coordination number would be favorable by adding a sixth ligand, an isopropanol molecule. Performed calculations showed that six-coordinated $\mathbf{K_1}$ complex is higher in energy relative to the products: the lowest-energy conformer was 14.5 kJ/mol higher in energy than isolated reactants.

Eight conformers of the complex $\mathbf{K_1}$ with five-coordinated titanium were found. In all cases the position of the five-membered cyclic ligand remains the same and conformers differ from each other only by the position of isopropoxy groups. These positions can be uniquely described in all eight conformers by the directions of the hydrogen atoms at the tertiary carbons (shown in magenta color in Table 2). The prevalences of conformers were calculated as Boltzmann distribution and are given in Table 2. Enantiomeric structures are marked with the same number, distinguished by the letter in the designation. Detailed geometries and energies of the systems are available in the electronic Supplementary Information.

Complex K_2

Conformational analysis of this complex involved rotation of both the isopropoxy ligands along the Ti—O and O—C bonds, as well as altering the relative positions of the two pentanedione ligands. The results indicate that both pentanedione ligands are bidentate (Fig. 3), like in the complex $\mathbf{K_1}$. In the majority of the optimized structures, the distance between the pentanedione carbonyl oxygen atom and titanium atom was between 2.22 and 2.37 Å. AIM bond DIs for the two Ti—O bonds of each ligand are near 0.2 and 0.5, just like in $\mathbf{K_1}$. We presume that a similar weak bond is formed as in the previous case. The titanium atom therefore has coordination number six (Fig. 3).

In a near-octahedral complex with two similar monodentate and two similar asymmetric bidentate ligands, eight ways to position the substrate cycles exist. Six of them form three enantiomeric pairs (mirror images of each other), whereas two are C_s-symmetric if rotations of the monodentate ligands are ignored. The latter differ from each other by the orientation of the methyl groups of the pentanedione. As noted above, in the absence of information about isomerization barriers, we cannot distinguish between conformers and isomers of the system. We assume a Boltzmann distribution of the systems with differing energies, corresponding to free rapid interconversion of the isomers.

We denote the asymmetric isomers by three prefixes (e.g., *cis-cis-trans*), where the first one indicates the relative positioning of the isopropoxy ligands, the second one denotes the

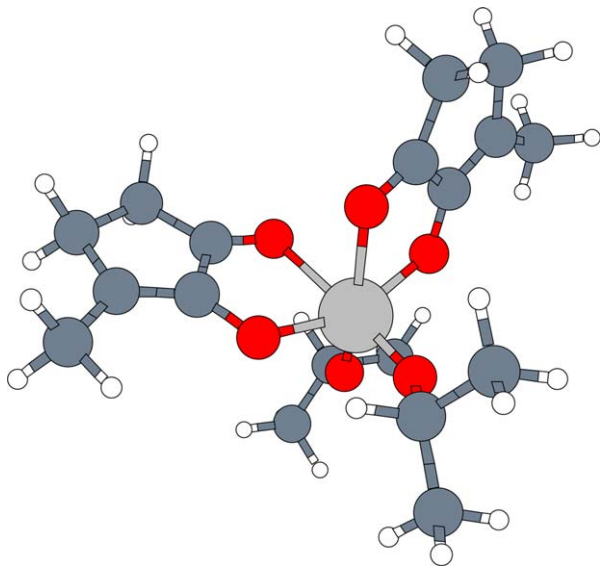
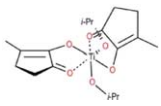
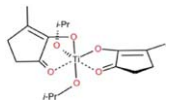
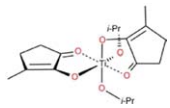
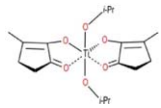
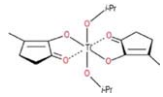


Figure 3. The lowest-energy conformer of the complex $\mathbf{K_2}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 3. Conformers of complex $\mathbf{K_2}$. [Color table can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

					
Conformer	Λ, Δ-*cis-cis-trans*	Λ, Δ-*cis-cis-cis*	Λ, Δ-*cis-trans-cis*	*trans-syn*	*trans-anti*
ΔE (kJ/mol)	0.00	5.78	25.72	28.61	54.54
%	94.0 (2×47.1)	6.0 (2×2.9)	0.0 (2×0.0)	0.0	0.0

relative position of the carbonyl oxygens (weaker/longer chemical bonds) of the pentanedione, and the third prefix determines the locations of the stronger/shorter titanium–oxygen bonds with pentanediones. The positions of the methyl substituents of the substrate are uniquely determined, being *anti* in the *cis-cis-trans* and *cis-trans-cis* complexes and *syn* in the *cis-cis-cis* case. Λ and Δ describe the chirality of enantiomeric complexes.

In the symmetric isomers, the cyclic ligands lie on the same plane, and we only need to indicate the relative positions of the isopropoxy ligands (*trans* in both cases) and the methyl substituents of the pentanediones (*syn* or *anti*). Structures and relative energies of the eight isomers are listed in Table 3.

Positions of the pentanedione ligands have significant influence on the energy of complex $\mathbf{K_2}$. Boltzmann probabilities of the last four conformers (Λ-*cis-trans-cis,* Δ-*cis-trans-cis, trans-syn, and trans-anti*) are very low, practically equal to zero, because difference in energies between those conformers and the lowest-energy conformer (*cis-cis-trans*) is more than 25 kJ/mol. The energy of the complex is also influenced by the rotation of isopropoxy ligand, although the effects have smaller magnitude than the energy differences associated with position of pentanediones. The lowest-energy minima with respect to this rotation are reported in all cases.

We conclude that the *cis-cis-trans* isomer is the prevalent one in the solution, with a small (∼3%) presence of the cis-*cis-cis* isomers. Assuming rapid interconversion, the probability of the remaining isomers is close to zero.

Complex K_3

Initial geometries of the conformers of $\mathbf{K_3}$ were generated by fixing the positions of the two bidentate ligands, whereas the positions of the remaining pentanedione ligand and isopropoxy ligand were changed by altering torsional angles corresponding to rotation of the five-membered ring around Ti—O bond and Ti—O*i*Pr in the case of isopropoxy ligand. The titanium atom prefers to remain six-coordinate, not forming the seventh bond with the other oxygen of the additional cyclopentanedione ligand. The ligand remains monodentate.

Ten different ways to situate the bidentate pentanedione cycles exist in the complex $\mathbf{K_3}$. The two additional conformers, when compared to those of $\mathbf{K_2}$, arise from different relative positions of the monodentate ligands, which are now distinguishable (O*i*Pr and the substrate), unlike in $\mathbf{K_2}$, where they were chemically identical (O*i*Pr). The two variants of the *cis-cis-cis* isomer will be denoted with prime (′) and second (″) symbols (Table 4). In this table, the lowest relative energies of different spatial structures of complexes $\mathbf{K_3}$ are given.

The most preferable pentanedione position in $\mathbf{K_3}$ again appears to be *cis-cis-trans*, with smaller but relevant probability of the *cis-cis-cis′* and *cis-cis-cis″* isomers. Prevalence of the remaining isomers is close to zero.

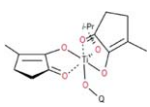
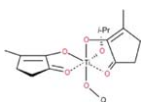
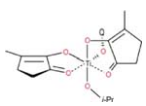
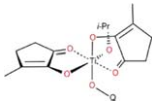
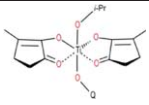
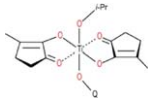
The bond DIs for the bidentate ligands are slightly higher than in the previous cases, averaging 0.25 for the weaker bond and 0.53 for the stronger one. The singly bound pentanedione has a bond index 0.69 and the O*i*Pr ligand −0.90.

Complex K_4

Initial geometries of the conformers of $\mathbf{K_4}$ were generated by fixing the positions of two bidentate cyclic ligands and the positions of the remaining two pentanediones were changed by altering torsional angles corresponding to rotation of the five-membered ring around Ti—O bond.

Exhaustive search for all conformers of this complex would have been computationally too demanding. Therefore a subset of the full conformational space was scanned. The simplifications were based on assumed similarity of relative energies of isomers of $\mathbf{K_4}$ on one hand, and $\mathbf{K_2}$ and $\mathbf{K_3}$ on the other hand. As expected (Table 5), the *cis-cis-trans* isomer turned out to be most preferable here too. The bond DIs (bond orders) of the bidentate ligands increase further being 0.27 and 0.58, respectively. The singly bound pentanediones have stronger bonds, with a DI of 0.72. Thus, we see a systematic increase of bond

Table 4. Conformers of complex $\mathbf{K_3}$.[a] [Color table can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

			
Conformer	Λ, Δ-*cis-cis-trans*	Λ, Δ-*cis-cis-cis′*	Λ, Δ-*cis-cis-cis″*
ΔE (kJ/mol)	0.00	6.44	8.37
%	93.9 (2×46.9)	4.4 (2×2.2)	1.8 (2×0.9)
			
Conformer	Λ, Δ-*cis-trans-cis*	*Trans-syn*	*Trans-anti*
ΔE (kJ/mol)	26.91	31.21	57.70
%	0.0 (2×0.9)	0.0	0.0

[a] Q = pentanedione.

Table 5. Relative energies of conformers of $\mathbf{K_4}$.

Conformer	Λ, Δ-*cis*-*cis*-*trans*	Λ, Δ-*cis*-*cis*-*cis*	Λ, Δ-*cis*-*trans*-*cis*	*trans*-*syn*	*trans*-*anti*
ΔE (kJ/mol)	0.00	5.36	25.42	32.14	53.40
%	92.8 (2×46.4)	7.2 (2×3.6)	0.0 (2×0.0)	0.0	0.0

order as the number of pentanedione ligands in the complexes is increased.

Discussion

The DFT results indicate that after two or more substitutions of isopropyl ligands at the titanium atom with 3-methyl-1,2-cyclopentanedione molecules, it is most probable that two cyclopentanedione ligands are bidentate and are situated in *cis-cis-trans* positions relative to each other. The probability that the bidentate pentanediones are situated in *cis-cis-cis* positions is significantly lower, whereas the existence probability of the other relative positions of bidentate pentanediones is practically zero. The Boltzmann probabilities of various isomers of all three complexes $\mathbf{K_2}$–$\mathbf{K_4}$ are summarized in Table 6.

Relative energies of complex formation of all complexes are depicted in Figure 4. The energy of the lowest-energy stereoisomer for each system is presented. Formation of the complexes $\mathbf{K_2}$ and $\mathbf{K_3}$ is more preferable than formation of the complex $\mathbf{K_1}$, with the formation of $\mathbf{K_2}$ being more favorable by 16 kJ/mol of Gibbs free energy than formation of $\mathbf{K_1}$. This is in good agreement with experimental findings. The NMR results presented above showed presence of complexes $\mathbf{K_2}$, $\mathbf{K_3}$, as well as small amounts of $\mathbf{K_4}$. No $\mathbf{K_1}$ was found in the experiment. Moreover, the formation of complex $\mathbf{K_2}$ is more favorable than formation of the complexes with a larger number of ligands. This is also in good agreement with experiment: in reactions with different molar ratios of reagents the complex $\mathbf{K_2}$ was always formed, the complexes $\mathbf{K_3}$ and $\mathbf{K_4}$ were formed only then the molar ratio of substrate and Ti(O*i*Pr)$_4$ was larger than 2:1.

The calculations did not fully explain the absence of $\mathbf{K_1}$ in the spectra. It is computed to have slightly lower Gibbs energy than $\mathbf{K_4}$, which was observed. This discrepancy could be attributed both to the experiments, where ketone **1** to alcoholate **2** ratios less than 1:1 were not investigated, as well as to calculations, where an exhaustive conformational search of $\mathbf{K_4}$ could not be performed.

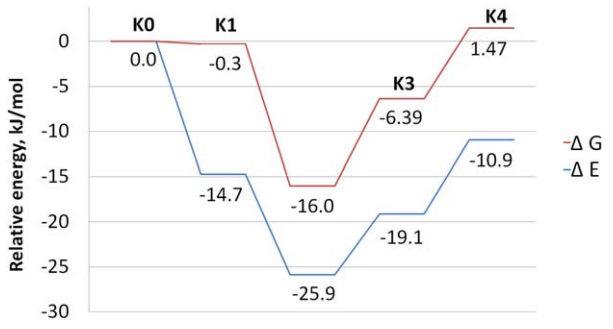


Figure 4. Relative energies of the lowest-energy isomers of the complexes $\mathbf{K_1}$–$\mathbf{K_4}$. The reactants are indicated as $\mathbf{K_0}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 6. Relative probabilities of the isomers of complex is $\mathbf{K_2}$–$\mathbf{K_4}$.

Conformer	Λ, Δ-*cis*-*cis*-*trans*	Λ, Δ-*cis*-*cis*-*cis*	Λ, Δ-*cis*-*trans*-*cis*	*trans*-*syn*	*trans*-*anti*
$\mathbf{K_2}$	94.0	6.0	0.0	0.0	0.0
$\mathbf{K_3}$	94.0	6.2	0.0	0.0	0.0
$\mathbf{K_4}$	92.8	7.2	0.0	0.0	0.0

Conclusions

The results of calculations support the experimental finding that formation of $\mathbf{K_2}$ is most favored. Also, coordination of both oxygen atoms to titanium that was suggested by the NMR spectrum is also supported by the calculations.

Formation of $\mathbf{K_3}$ is slightly unfavorable and it is in accordance with the experiment—complex $\mathbf{K_3}$ forms only in the case of excess of ketone **1**. Formation of complex $\mathbf{K_4}$ is even less favored. In our experiments, we found only traces of $\mathbf{K_4}$ in the solution, even when fourfold excess of ketone **2** was used. According to our calculations, complexes $\mathbf{K_2}$–$\mathbf{K_4}$ are six-coordinated, having two different types of ligands—the cyclopentanedione ligand can be coordinated in unidentate or bidentate manner depending on the composition of the complex and availability of free coordination sites at titanium.

The relative instability of triply substituted complex $\mathbf{K_3}$ can be justified by geometrical factors: in doubly substituted $\mathbf{K_2}$, Ti atom is six-coordinated with approximately octahedral geometry (Fig. 1). Addition of the third bidentate ligand replacing a unidentate one would lead to seven-coordination, or an unsaturated valence. Similar reasoning also applies to $\mathbf{K_4}$, where two of the four substrate ligands remain mono-coordinated.

A side-product of the present study is an enumeration and systematization of the possible relative orientations of the kinds of penta- and hexa-coordinated complexes where the bidentate ligands are not symmetric. The lists presented in Tables (2–5) of this work may be utilized in future studies of similar complexes.

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Keywords: density functional theory · NMR · conformations · isomers · complexes · titanium

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Additional Supporting Information may be found in the online version of this article.

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