Chelate Ring Folding in Titanocene Complexes with Bidentate Sulfur- and Oxygen-Containing Ligands: A Theoretical Study

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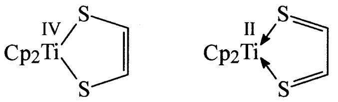
The characteristic folding of the chelate ring in mono- and binuclear titanocene complexes with dithiolene-like ligands is studied by means of density functional theory (DFT). The structures resulting from geometry optimization (42.3° folding for $Cp_2TiS_2C_2H_2$) reflect the experimental situation well (46.1° for this complex) and are in accordance with the specific orbital interactions known to be responsible for the stabilizing effect of the folding. The significantly different folding obtained for the complexes with sulfur and oxygen donor atoms is the subject of a qualitative molecular orbital analysis. The calculations show that the tendency to fold appears for only one of the two possible formal bonding situations of the systems under study, the one with a Ti(IV) center and a dianionic ligand in the mononuclear cases and a tetraanionic ligand in the binuclear ones. The conclusion is derived that the tendency to fold is principally determined by the formal bonding situation, but the amount of folding is dependent on the specific donor atoms, sulfur or oxygen.

Introduction

In contrast to iron, the early transition metal titanium cannot reach a favorable electron count by formation of a homoleptic titanocene, i.e. by binding just two cyclopentadienyl (Cp) rings. Because of the tendency to bind additional ligands of rather different types, the chemistry of metallocenes of the electron-poor transition metals is especially rich and interesting. Consequently, their technical importance is manifold reaching from homogeneous catalysts for polymerization reactions[1] to potential cancerostatics.[2] One popular class of ligands, in this connection, are the 1,2-dithiolenes, which form chelate complexes with a great variety of metallocenes[3,4] including also differently substituted titanocenes.[5,6] They open up the field of potential applications toward sulfur-involving processes, such as vulcanization.[7]

The titanocene complexes and related systems with dithiolene-like ligands show some peculiarities concerning structure and bonding by a typical chelate ring folding. Especially, the formal bonding situation and the oxidation state in these systems are subjects of an ongoing discussion.[8] The dithiolene is a prototype of a "noninnocent" ligand. These specific ligands form complexes that can easily be oxidized or reduced at the metal and at the ligand. There are two alternatives to define the formal oxidation state of the dithiolene-like ligand and the metal center, which are displayed in Scheme 1 for the mononuclear complex. The bidentate ligand corresponds in one case to a dianionic ethendithiolate containing a C=C double bond, and in the other one to a neutral ethanditHione with a C−C single bond. Consequently, the first alternative includes a formal Ti(IV)-d^0 center with 16 valence electrons (VE) and the other one a Ti(II)-d^2 center (18 VE). An analogous consideration applies to the binuclear species leading to the two formal bonding situations two Ti(IV)-d^0 (16 VE) with a tetraanionic ethentetrathiolate and two Ti(III)-d^1 (17 VE) with a dianionic tetrathiooxalate (Scheme 2).

Scheme 1



The synthetic routes utilized to obtain the experimentally characterized complexes treated in this study refer, in each case, to one of the specific bonding

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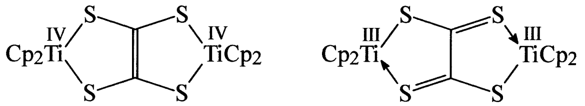
Scheme 2



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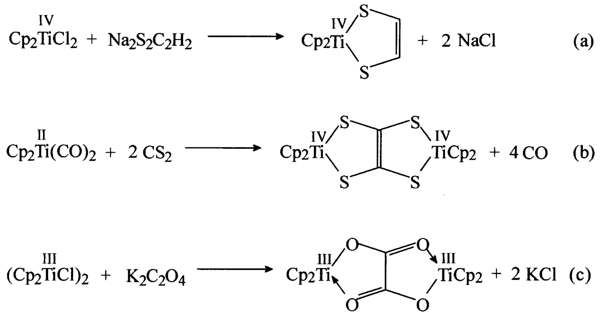
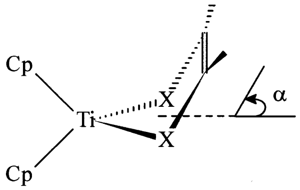


Scheme 4



situations (Scheme 3). The mononuclear titanocene-ethenedithiolate, $Cp_2Ti(S_2C_2H_2)$, is directly accessible via the reaction of titanocenedichloride, Cp_2TiCl_2, formally a Ti(IV) species and a standard educt in this field of chemistry, with the sodium salt of the ligand $Na_2S_2C_2H_2$.[9] The binuclear sulfur-containing complex μ-$C_2S_4(Cp_2Ti)_2$ is obtained by the reductive dimerization of CS_2 with $Cp_2Ti(CO)_2$, a Ti(II) compound.[10] A still different route leads to the oxygen-containing complex μ-$C_2O_4(Cp_2Ti)_2$ using as educts the Ti(III) species $(Cp_2TiCl)_2$ and potassium oxalate, the salt of the ligand.[11]

A conspicuous structural characteristic observed for the 1,2-dithiolene complexes of group 4 metallocenes is the folding along the S−S axis leading to an envelope-like conformation of the five-membered chelate ring. The fold angle is defined between the X−Ti−X plane (X = S, O) and the plane of the chelate ligand (see Scheme 4). For example, the mononuclear complex $Cp_2Ti(S_2C_2H_2)$ exhibits a fold angle of 46.1°.[12] In solution, at a certain temperature, the chelate ring conformation is inverted via a planar transition state. By means of temperature-dependent ^1H NMR spectroscopy, the corresponding chelate ring inversion barrier was found to be 62 kJ/mol.[13] A considerable amount of similar data is available also for derived titanocenes with substituents at the cyclopentadienyl rings or at the chelate ligand.[5,14] The binuclear complex μ-$C_2S_4(Cp_2Ti)_2$ shows a *trans* folding of the same magnitude (46.5°).[10] Surprisingly, the corresponding complex with oxygen donor atoms, μ-$C_2O_4(Cp_2Ti)_2$, shows a very small *cis* folding, for which experimental indications exist that it is caused by intermolecular interactions in the crystal.[11] Moreover, this complex is paramagnetic,[15] in contrast to the strongly folded diamagnetic sulfur systems.

Only a few theoretical studies dealing with the folding problem have been published, which are based on purely qualitative analyses or semiempirical computational schemes.[16−18] In the present paper, we consider the phenomenon of the chelate ring folding in a systematic approach involving mono- and binuclear systems with both sulfur and oxygen donor atoms. On the basis of complete geometry optimizations performed using density functional theory, we examine the former analyses, give reasons for the structural features of the complexes, and make predictions for systems that have not been observed experimentally up to now.

Computational Details

We carried out B3LYP-DFT[19,20] calculations for the following eight systems: the four mononuclear complexes $Cp_2Ti(IV,II)(X_2C_2H_2)$ (X = S, O) and the four binuclear systems μ-$C_2X_4(Cp_2Ti(IV,III))_2$. The different oxidation states of the titanium center correspond to different occupation numbers of the orbitals of a given symmetry representation. The appropriate orbital occupations can be determined by a group theoretical analysis based on the valence bond picture, which is shown below together with the results. The calculations were performed applying the GAUSSIAN98 package.[21] Effective core potentials of the type ecp-10-mdf with the corresponding valence basis set were used for titanium.[22] The standard 6-31G* basis set was used for the atoms of the chelate ligands. For the atoms of the Cp rings, it is sufficient to use the 3-21G basis set. This reduces the computational effort without any noticeable influence on the resulting structures as test calculations have shown. The minimum structures and transition states presented in this paper were characterized by vibrational analyses. Calculations based on the extended Hückel theory (EHT) were carried out with the CACAO package[23] using the default atom parameters of the software.

Results and Discussion

Theoretical analyses of the class of complexes under study usually start with the consideration of bent metallocenes, where the cyclopentadienyl rings leave the axial positions they occupy, for instance, in ferrocene.[16] On this basis, three empty metal hybrid orbitals stretch-

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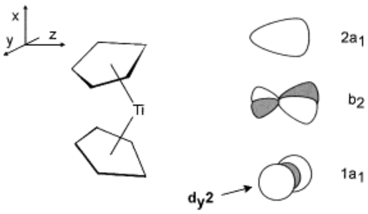
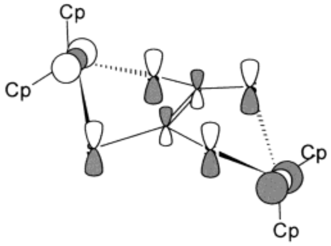
Scheme 5



Scheme 6



ing in the plane perpendicular to the bonds to the Cp rings were determined, which can act as acceptor orbitals to bind additional ligands (Scheme 5).

In a subsequent EHT study, the problem of the chelate ring folding in 1,2-dithiolene metallocenes was addressed and the main orbital interactions responsible for the tendency to fold have been identified.[17] The folding was attributed to a stabilizing interaction of the π-system of the chelate ligand with one of the hybrid orbitals at the titanium center, the so-called d_{y^2} orbital. In Scheme 6, we choose to show this interaction for the binuclear Ti(IV) complex. At the EHT level of theory, it has been concluded that the tendency to fold should be independent of the formal bonding situation (Ti(IV) vs Ti(II)). Merely, donor and acceptor orbitals should switch their roles. The resulting structures were expected to be the same.

Another previous study was dedicated to the differences occurring with the exchange of the sulfur donor atoms by oxygen.[18] The two corresponding systems for which experimental structures are available are the binuclear complexes. On the basis of a Fenske−Hall MO analysis assuming for both complexes the formal bonding situation of a dianionic bridging ligand, the different tendency to fold was traced back to the different energetic position of the lowest unoccupied MO (LUMO) in the two cases.

The computational facilities nowadays available allow the folding problem to be studied at a more sophisticated level of theory. Molecular orbital analyses on the basis of geometry-optimized complex structures should provide a deeper insight into the bonding properties.

I. DFT Results for the Mononuclear Systems $Cp_2Ti(X_2C_2H_2)$. In Table 1, we present optimized parameters of the minimum structures obtained for the mononuclear complexes. Only one of the four systems considered is known experimentally, the titanocene-dithiolene complex with a formal Ti(IV) center. Its experimental data are very well reflected by the calculation.[24] Above all, the observed folding angle (46.1°) is well reproduced (42.3°). This implies that the observed characteristic folding of the chelate ring in the complex must indeed be essentially of intramolecular origin. It can be concluded that intermolecular interactions in the crystal, which might have a similar effect, are of low importance. In complete agreement with the experiment, the calculated bond lengths in the chelate ligand indicate a rather typical C═C double bond (136 pm) and C−S single bonds (175 pm), showing that, for this complex, the formal bonding situation described by a dianionic ethendithiolate coordinated to a Ti(IV) center (see Scheme 1) does indeed apply. As a side effect of the folding, one Ti−Cp distance, the one on the side toward which the folding occurs, is slightly longer than the other one on the sterically less demanded side.

Table 1. Minimum Structures (parameters in pm and deg) of the Mononuclear Complexes $Cp_2Ti(IV,II)X_2C_2H_2$ (X = S, O), Experimental Values[1] in Parentheses

	Ti(IV), X = S[a]	Ti(II), X = S[b]	Ti(IV), X = O[c]	Ti(II), X = O[d]
folding	42.3 *(46.1)*	0.0	31.7	0.0
Ti−Cp	211.1 *(208.0)* [e]	204.4	213.7	202.6
	209.4 *(205.6)* [f]		211.6	
Ti-X	242.1 *(241.7)*	247.4	193.7	228.9
C−X	174.7 *(173.9)*	167.8	134.6	123.3
C−C	136.3 *(134.2)*	141.5	136.3	148.2
Cp−Ti−Cp	130.2 *(130.9)*	143.0	131.5	147.2
X−Ti-X	84.3 *(83.2)*	80.1	83.0	69.2
Ti−X−C	95.7 *(94.6)*	108.1	105.9	118.4

[a] Orbital occ.: $38a'^2\ 26a''^2$. [b] Orbital occ.: $24a_1^2\ 9a_2^2\ 14b_1^2\ 17b_2$. [c] Orbital occ.: $34a'^2\ 22a''^2$. [d] Orbital occ.: $21a_1^2\ 8a_2^2\ 13b_1^2\ 14b_2^2$. [e] Cp on the side on which the folding occurs. [f] Cp on the opposite side.

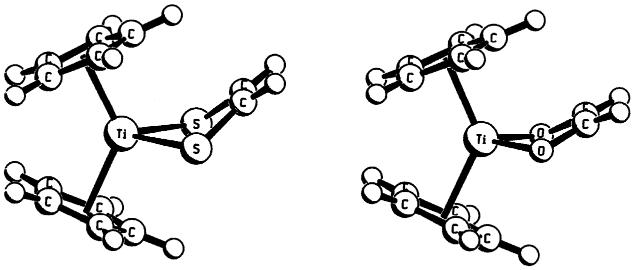


Figure 1. Optimized structures of the mononuclear complexes $Cp_2Ti(IV)S_2C_2H_2$ and $Cp_2Ti(IV)O_2C_2H_2$.

The structure of the analogous Ti(IV) complex with oxygen instead of sulfur donor atoms differs, of course, in those bond lengths (Ti−O, C−O) and bond angles (Ti−O−C) that are affected by the smaller atomic size of oxygen, leading to accordingly different proportions of the two complexes (Figure 1). However, more subtle differences between the donor atoms sulfur and oxygen should be responsible for the significantly smaller chelate ring folding of 32° in the case of oxygen. Notice that the DFT results indicate definitely for both donors the tendency to fold.

Optimizations of the mononuclear complexes in the alternative bonding situation, with a neutral chelate ligand coordinated to a Ti(II) center, lead, for both types of donor atoms, to nonfolded structures (see Table 1). The bond lengths in the chelate ligands lie between typical values for double and single bonds, which is in correspondence with the butadiene-like bonding pattern

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[24] We have obtained, in C_1 symmetry, the almost ideally staggered arrangement of the two Cp rings relative to each other. This conformation is specified by the angle between the vector running through the centroid and the vertex of one ring and the corresponding vector of the other ring. Experimentally, this angle is 33° (ideally staggered: 36°). We obtain 27°. Because the energy difference between the conformations is very small (~1 kJ/mol), we consider our structures in the following in the eclipsed conformation.

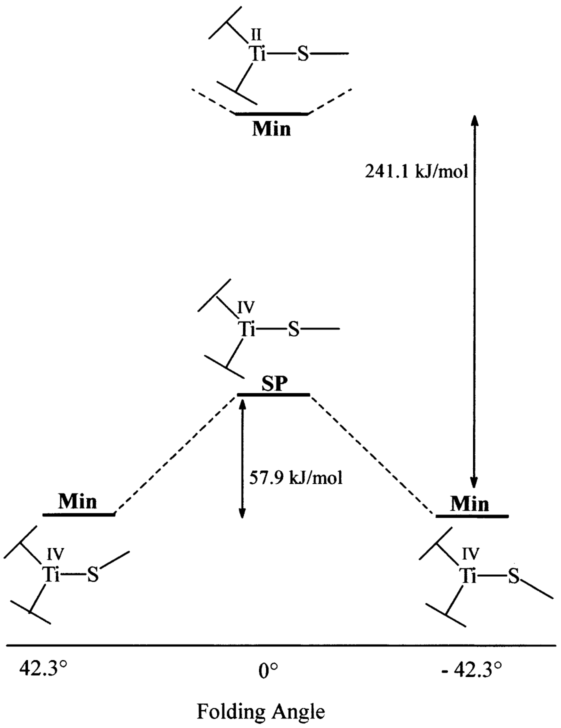


Figure 2. Energy relations between the optimized minima and saddle points (SP) for the mononuclear systems. Energy profile depicted for $Cp_2Ti(IV,II)S_2C_2H_2$, corresponding values for O-containing systems: chelate ring inversion barrier $\Delta E(SP_{Ti(IV)} - Min_{Ti(IV)})$ 16.2 kJ/mol, $\Delta E(Min_{Ti(II)} - Min_{Ti(IV)})$ 229.2 kJ/mol.

represented in Scheme 1. We point out that the resulting nonfolded structures are minima on the potential surface with C_{2v} symmetry. The alternative bonding situation is realized by populating an a_1 orbital and depopulating a b_1 orbital (see Table 1). This occupation scheme forces the system into a relatively high-lying minimum state.

Figure 2 shows the relative energies of the obtained stationary points on the potential surface. The nonfolded minimum for the complex with the Ti(II) center is considerably higher in energy than the folded minimum structures for the Ti(IV) case and even higher than the nonfolded transition state of the interconversion between the latter. Note that the transition state is obtained by chosing the a_1 orbital empty and the b_1 orbital occupied. The calculated chelate ring inversion barrier of 58 kJ/mol for the sulfur-containing complex is in good accordance with the experimental value (62 kJ/mol).[13] In the case of the oxygen-containing complex, the energetic effect of the folding is calculated to be considerably weaker (16 kJ/mol).

The structural parameters of the transition states for the chelate ring inversion are summarized in Table 2. The vibration analysis leads, for these systems, to one imaginary frequency, which indicates the folding. Notice the clear structural difference to the nonfolded minimum systems in the alternative bonding situation, which is most evident for the carbon−carbon bond lengths (compare with Table 1).

Table 2. Structures of the Nonfolded Transition States for the Chelate Ring Inversion of the Mononuclear Complexes $Cp_2Ti(IV)X_2C_2H_2$ (X = S, O) (parameters in pm and deg)

	X = S[a]	X = O[b]
Ti−Cp	211.0	213.0
Ti-X	246.1	190.1
C−X	176.6	135.8
C−C	134.3	134.9
Cp−Ti−Cp	131.3	132.8
X−Ti-X	86.6	81.8

[a] Orbital occ. X = S: $23a_1^2\ 9a_2^2\ 15b_1^2\ 17b_2^2$ [b] Orbital occ. X = O: $20a_1^2\ 8a_2^2\ 14b_1^2\ 14b_2^2$

Table 3. Minimum Structures (parameters in pm and deg) of the Binuclear Complexes μ-$C_2X_4(Cp_2Ti(IV,III))_2$ (X = S, O), Experimental Values[2,3] in Parentheses

	Ti(IV), X = S[a]	Ti(III), X = S[b]	Ti(IV), X = O[c]	Ti(III), X = O[d]
folding	45.7 *(46.5)*	0.0	37.9	0 *(7.6, cis)*
Ti−Cp	210.9 *(208.3)*[e] 209.2 *(204.9)*[f]	209.0	211.2 209.4	209.3*(205.8)*
Ti−X	241.4 *(241.4)*	254.2	201.0	214.4 *(215.7)*
C−X	175.6 *(173.7)*	170.3	130.4	126.0 *(125.6)*
C−C	140.7 *(141.3)*	150.0	144.4	153.7 *(152.3)*
Cp−Ti−Cp	131.0 *(132.8)*	136.8	133.2	137.9 *(135.4)*
X−Ti-X	82.9 *(82.1)*	78.9	82.0	76.4 *(75.8)*
Ti−X−C	96.1 *(95.8)*	110.0	103.2	115.6 *(114.7)*

[a] Orbital occ.: $36a_g^2\ 24b_g^2\ 25a_u^2\ 35b_u^2$. [b] Orbital occ.: $22a_g^2\ 15b_{1g}^2\ 14b_{2g}^2\ 9b_{3g}^2\ 9a_u^2\ 14b_{1u}^2\ 16b_{2u}^2\ 20b_{3u}^2\ 23a_g^1\ 21b_{3u}^1$. [c] Orbital occ.: $32a_g^2\ 20b_g^2\ 21a_u^2\ 31b_u^2$. [d] Orbital occ.: $19a_g^2\ 12b_{1g}^2\ 13b_{2g}^2\ 8b_{3g}^2\ 8a_u^2\ 13b_{1u}^2\ 13b_{2u}^2\ 17b_{3u}^2\ 20a_g^1\ 18b_{3u}^1$. [e] Cp on the side on which the folding occurs. [f] Cp on the opposite side.

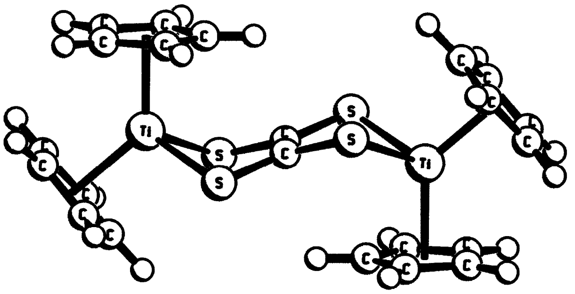


Figure 3. Optimized structure of the binuclear complex μ-$C_2S_4(Cp_2Ti(IV))_2$.

II. DFT Results for the Binuclear Systems μ-$C_2X_4(Cp_2Ti)_2$. In Table 3, we present optimized parametersof the minimum structures obtained for the binuclear complexes. The calculation reproduces remarkably well the experimental structure of the sulfur-containing complex with formal Ti(IV) centers. This holds, especially, for the folding angle. In general, the folding in the binuclear systems is of the same order of magnitude as in the mononuclear ones (compare with Table 1 and see Figure 3), which points toward a similar origin of the folding. Again, we obtain a much smaller folding for the complex with oxygen donor atoms. In the bridging ligands, the formal C=C double bond is significantly longer than in the unsubstituted 1,2-dithiolene, indicating a noticeable conjugation through the bridging ligand.

The chelate ring inversion barriers for the Ti(IV) systems with oxygen and sulfur donor atoms are summarized in Figure 4. Because the systems contain now two chelate rings, it is not surprising that the magnitude of the inversion barrier is higher than in the mononuclear cases. (Unfortunately, for the experimentally known sulfur system, the inversion barrier has not been measured to the best of our knowledge.) Again, we

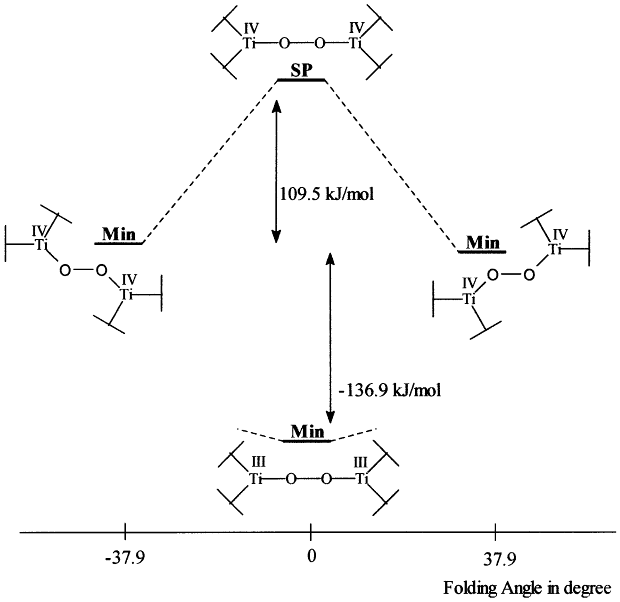


Figure 4. Energy relations between the optimized minima and saddle points (SP) for the binuclear systems. Energy profile depicted for μ-$C_2O_4(Cp_2Ti(IV,III))_2$, corresponding values for S-containing systems: chelate ring inversion barrier $\Delta E(SP_{Ti(IV)} - Min_{Ti(IV)})$ 146.4 kJ/mol, $\Delta E(Min_{Ti(III)} - Min_{Ti(IV)})$ 15.4 kJ/mol.

Table 4. Structures of the Nonfolded Transition States for the Chelate Ring Inversion of the Binuclear Complexes μ-$C_2X_4(Cp_2Ti(IV))_2$ (X = S, O) (parameters in pm and deg)

	X = S[a]	X = O[b]
Ti−Cp	211.2	212.0
Ti-X	251.4	199.1
C−X	174.2	137.0
C−C	142.9	142.1
Ti−Cp−Cp	131.1	132.6
X−Ti−X	85.9	83.3

[a] Orbital occ.: $22a_g^2\ 15b_{1g}^2\ 14b_{2g}^2\ 9b_{3g}^2\ 9a_u^2\ 15b_{1u}^2\ 16b_{2u}^2\ 20b_{3u}^2$.
[a] Orbital occ.: $19a_g^2\ 12b_{1g}^2\ 13b_{2g}^2\ 8b_{3g}^2\ 8a_u^2\ 14b_{1u}^2\ 13b_{2u}^2\ 17b_{3u}^2$.

realize that the energetic effect of the folding is considerably smaller for the oxygen-containing system. The structural parameters of the transition states (D_{2h} symmetry) are summarized in Table 4.

For the alternative bonding picture, with a dianionic oxalate-type bridging ligand coordinated to two Ti(III) centers, again nonfolded structures (D_{2h} symmetry) result from the optimizations (see Table 3). We point out that the alternative formal bonding situation for all of our complexes arises from the redistribution of two electrons from the double bond of the ligand toward the titanium. In the case of the binuclear complexes each Ti center obtains formally one electron. We, therefore, have to consider open-shell d^1 centers. For these triplet systems, a fairly typical C−C single bond results.

The binuclear Ti(III) systems are energetically not as unfavorable as their mononuclear analogues, the Ti(II) complexes (see Figure 4). In the oxygen case, the nonfolded Ti(III) triplet complex turns out to be energetically clearly preferred over the folded Ti(IV) singlet system. This should be the reason that the only experimentally observed complex of this class with oxygen donor atoms is binuclear, almost nonfolded (compare Table 3), and paramagnetic. Notice that, in the sulfur case, the folded Ti(IV) complex, which is found experimentally, is calculated to lie only around 15 kJ/mol below its nonfolded paramagnetic Ti(III) counterpart. We conclude for the binuclear complexes that a tendency to fold appears only for complexes with Ti(IV) centers. This tendency is considerably stronger in the case of sulfur donor atoms, in correspondence to what has been found for the mononuclear systems.

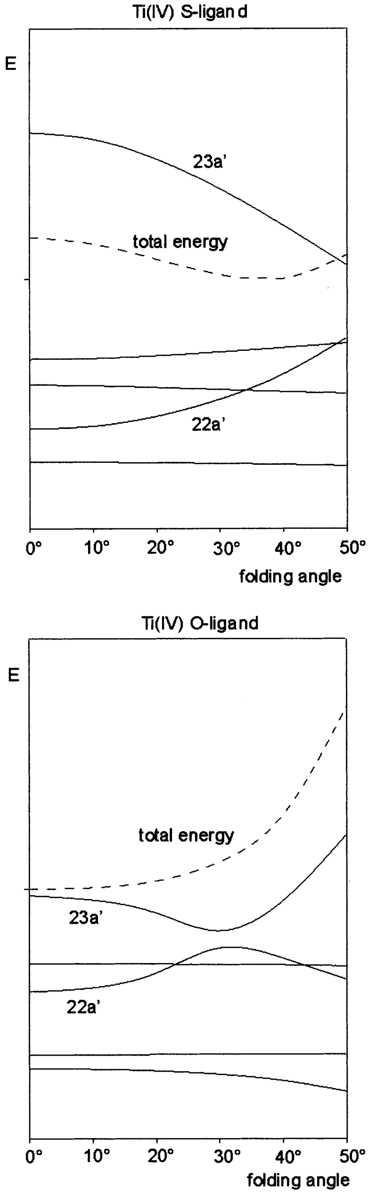
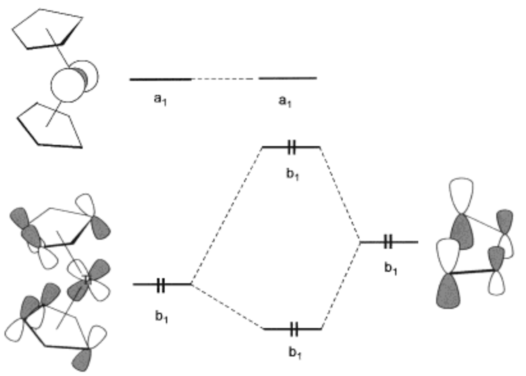


Figure 5. EHT Walsh diagrams for the folding of the mononuclear Ti(IV) complexes with S- and O-ligands.

III. Molecular Orbital Analysis. By means of a qualitative MO analysis, we are able to get deeper insight into the specific bonding properties of the complexes. We focus on the mononuclear systems, but it is expected from the previous discussion that the conclusions also apply for the binuclear cases. In Figure 5, Walsh diagrams at the EHT level are presented showing the dependence of the orbital energies and the total energy on the folding angle. (In the EHT method, the total energy is simply the sum of the energies of the occupied orbitals.) Remarkably, the total energy of the sulfur-containing system has a minimum at an angle of around 40°, in surprisingly good agreement with the experimental value and the DFT result. No

Scheme 7

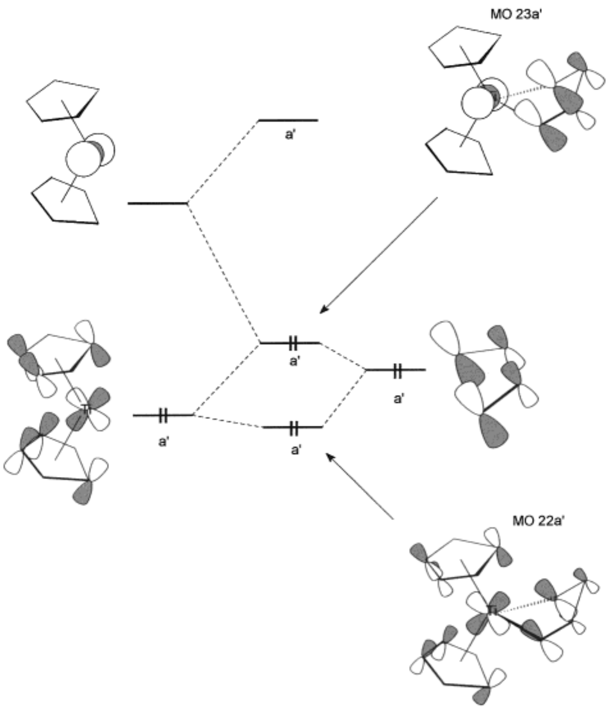


folding, however, is indicated for the oxygen-containing system in contrast to the DFT result. Obviously, the EHT level is not sufficient to describe appropriately the folding indicated for this specific system by the DFT optimization.

The Walsh diagrams show that only the two highest occupied MOs are affected by the folding, thus being mainly responsible for the curvature of the total energy. Independent of the donor atoms, sulfur or oxygen, the folding of the chelate ring causes an energetic stabilization of the HOMO 23a′ and a simultaneous destabilization of the MO 22a′. Obviously, the resulting folding angle balances these two competing effects. To analyze the orbitals 22a′ and 23a′, we develop an orbital interaction picture by dividing the complex into two characteristic fragments, a bent titanocene with a Ti(IV) center and the dianionic chelate ligand (Scheme 7). For the metal fragment, we consider the LUMO, which is the d_{y^2} type acceptor orbital (see above), and the HOMO, which represents mainly an interaction between the Cp rings and the titanium center. For the chelate ligand, we involve only the HOMO. This orbital is occupied when a dianionic species is considered instead of a neutral one. (Notice that we could generate the Ti(II) case merely by populating the LUMO of the titanocene fragment and depopulating the HOMO of the ligand. This would make no difference for the resulting orbital energies at the EHT level.) In the nonfolded case, the correlation diagram (see Scheme 7) shows an energetically unfavorable four-electron interaction between the b_1-symmetric HOMOs of the titanocene fragment and the chelate ligand. The LUMO of the metal fragment cannot interact with the ligand HOMO because it is symmetric concerning the nodal plane of the π orbitals.

Breaking the C_{2v} symmetry by folding provides the possibility for a stabilizing interaction of the ligand HOMO with the titanocene LUMO (see Scheme 8). Consequently, the energy of the MO 23a′, the HOMO of the folded complex, decreases for increasing folding angle. This corresponds to the previously described driving force for the folding.[17] But, in addition to this, we identify a competing effect, the destabilization of the MO 22a′. This orbital clearly belongs to the set of orbitals representing the Cp→Ti donor interaction. Obviously, the folding of the chelate ligand interferes with the Ti−Cp bonding and makes it less effective in the folded structure. Interferences of this type have been called mutual ligand influence. We realize that the destabilization of the MO 22a′ is just an example of such a mutual ligand influence.

Scheme 8



Only if this Cp−Ti bonding orbital 22a′ is included into the consideration can we account for the different folding angles resulting for the chelate ligands with sulfur and oxygen donor atoms. (The frontier orbital picture for the S and O complexes should favor the folding in both cases.) By examining the Walsh diagrams (Figure 5), we realize with increasing folding angle a stronger decrease of the energy of the MO 23a′ in the sulfur case compared to the oxygen one, whereas the energy of the MO 22a′ increases comparably in both cases. Thus, with sulfur donor atoms in the chelate ring, the destabilization is strongly overcompensated by the additional S→Ti donor interaction, whereas the corresponding O→Ti interaction does not compensate the loss in the Cp−Ti interaction. Therefore, no folding results for the oxygen-containing compounds at the EHT level of theory.

This finding is in agreement with the HSAB principle,[25] according to which the softer sulfur atom should be the better donor in these complexes. So, what seems to be a qualitative difference at this level of theory (0° vs 40° folding) is in fact the result of a tradeoff between two contrarily acting driving forces, which differ only slightly in magnitude. On the basis of this MO analysis one might consider to tune the donor ability of the Cp ligands, for instance by suitable substituents, and, thus, influence the folding of the chelate ring possibly to such an extent that the situation for oxygen- and sulfur-containing ligands might be reversed.

Conclusions

DFT optimizations of the mono- and binuclear titanocene complexes with dithiolene-like ligands have proved that the characteristic chelate ring folding has a truly intramolecular origin. The folding is consistent with the formal bonding situation assuming Ti(IV)

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(25) Pearson, R. G. *Chemical Hardness*; J. Wiley: New York, 1997.

centers and a dianionic ligand for the mononuclear case and a tetraanionic ligand for the binuclear one. Basically, the tendency to fold is independent of the type of donor atoms, sulfur or oxygen. However, the gradual differences (stronger folding for sulfur, weak folding for oxygen donors) can be traced back to a mutual ligand influence, namely, the competing donor abilities of the folded chelate ligand and the coordinating Cp rings.

No folding can be expected for the alternative formal bonding situation with Ti(II) centers and a neutral ligand in the mononuclear systems or, correspondingly, Ti(III) centers and a dianionic ligand in the binuclear ones. For the mononuclear complexes, the alternative bonding situation is associated with a nonfolded minimum structure, which is relatively high in energy and, therefore, not likely to be observed experimentally. For the binuclear complexes, the alternative bonding situation has relevance and is favored in the case of oxygen donor atoms, both in the experiment and in the calculations. This is consistent with the result that the stabilizing effect of the folding is weaker for ligands with oxygen donors compared to the stronger donating sulfur.

We conclude from this study that the existence of titanocene derivatives with folded oxygen-containing dithiolene-analogue ligands is not out of the question, as they are found as stable minima in the optimizations. Even more likely to exist is the binuclear nonfolded paramagnetic titanocene complex with the tetrathiooxalato bridging ligand, as the energy difference to its folded diamagnetic counterpart is rather small. Possibly, appropriate synthetic routes could trap the complex systems in these alternative bonding situations with strongly different structural and electronic properties.

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