Inorg. Chem. **1994**, *33*, 4566−4572

Conformational Flexibility in C_2X_4-Bridged Bimetallic Complexes

Jimmy R. Rogers, Chad K. Johnson, and Dennis S. Marynick*

Department of Chemistry, University of Texas at Arlington, Arlington, Texas 76019-0065

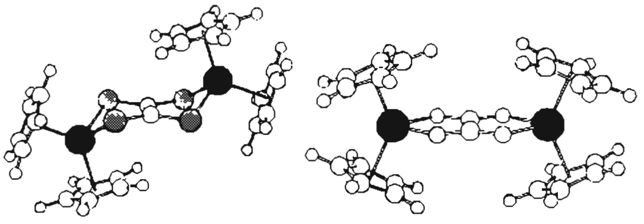
Received September 8, 1993[⊗]

The full two-dimensional potential energy surface for the chair-to-chair rearrangement of $(Cp_2Ti)_2(\mu\text{-}C_2S_4)$ is presented. This complex, in which one metal lies above the plane of the ethylenetetrathiolate bridge while the other lies below the plane in a chairlike conformation, undergoes an intramolecular rearrangement that is facile on the NMR time scale. The transition state for this process possesses a boat-shaped conformation, and the calculated activation energy agrees closely with those found in other related systems. The transition state results from maximizing of carbon−sulfur π antibonding interactions in the boat form. In addition, the electronic effects which dictate the shapes in two analogous systems, $(Cp_2Ti)_2(\mu\text{-}C_2O_4)$ and $(Cp_2Ti)_2(\mu\text{-}C_2(NH)_4)$, are addressed.

Introduction

Complexes which contain C_2X_4 (X = O, S) as a bridging ligand are potentially important for several reasons. These complexes are generally synthesized using carbon disulfide and carbon dioxide as starting materials and thus represent examples of carbon−carbon bond formation. Much effort has centered around the use of transition-metal complexes in the formation of C−C bonds, and this is exemplified by the metal-promoted dimerization of CS_2 to give C_2S_4. C_2X_4-bridged bimetallic complexes also have the potential for electrical conductivity.[1] They are analogous to tetrathiofulvalenes, which are known to be conducting in the solid state,[2,3] and the possible use of C_2S_4 to bridge transition metals in two- and three-dimensional polymeric networks can lead to conducting polymeric systems.[4] Compounds bridged by C_2X_4 are also interesting from a more fundamental electronic/molecular structure perspective, in that different metal oxidation states in seemingly isoelectronic systems correlate to specific structural differences. Yet in spite of the interest engendered by the electronic properties of bimetallic complexes bridged by C_2X_4, only one major theoretical study of a discrete molecular system has appeared.[5]

Reports of two complexes containing C_2S_4 as a bridging ligand appeared in 1982. Broadhurst and co-workers[6] described the synthesis of the tetrairon complex $Fe_4(CO)_{12}(\mu\text{-}C_2S_4)$, while Dahl and co-workers[7] reported the Ni complex $[(C_5Me_5)Ni]_2(\mu\text{-}C_2S_4)$. Since that time, similar complexes have been developed, including complexes with such transition metals as Ti,[5] Rh,[8] Ir,[8] and Pt.[9] Apparently, analogous complexes containing Co and Fe have also been synthesized,[10] but unfortunately the details of this work have never been published. However, a summary of the important geometrical parameters for the Fe, Ni, and Co complexes has recently appeared.[5b] A review article describing the coordination chemistry of thiooxalates also recently appeared.[11]



1 2

Figure 1. 1, $(Cp_2Ti)_2(\mu\text{-}C_2S_4)$; 2, $(Cp_2Ti)_2(\mu\text{-}C_2O_4)$.

A comparison of several C_2X_4 species[5−10,12−16] suggests that C_2S_4 is more capable of delocalizing electrons from the metal than are related bridges. This is especially evident when the two electronically analogous complexes $(Cp_2Ti)_2(\mu\text{-}C_2S_4)$ (**1**) and $(Cp_2Ti)_2(\mu\text{-}C_2O_4)$ (**2**) shown in Figure 1, are compared. The tetrathiolate-bridged complex is a chairlike structure with the Ti atoms out of the C_2S_4 plane by 46°, while the oxalate-bridged structure is a nearly planar boatlike structure with the Ti atoms out of the C_2O_4 plane by only 11° (see Figure 2 for depiction of the "fold angle"). Compound **1** is diamagnetic while compound **2** is paramagnetic. The C−C bond distance for C_2S_4 in **1** is 1.41 Å, while the same bond in the C_2O_4 complex is

---

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1994.

(1) Reynolds, J. R.; Karasz, F. E.; Lillya, C. P.; Chien, J. C. W. *J. Chem. Soc., Chem. Commun.* **1985**, 268−269.

(2) Wudl, F. *Acc. Chem. Res.* **1984**, *17*, 227−232.

(3) Bousseau, M.; Valade, L.; Legros, J. P.; Cassoux, P.; Garbauskas, M.; Interrante, L. V. *J. Am. Chem. Soc.* **1986**, *108*, 1908−1916.

(4) Alvarez, S.; Vicente, R.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 6253−6277.

(5) (a) Harris, H. A.; Rae, A. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1987**, *109*, 4739−4741. (b) Harris, H. A.; Kanis, D. R.; Dahl, L. F. *J. Am Chem. Soc.* **1991**, *113*, 8602−8611.

(6) Broadhurst, P. V.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1982**, 140−141.

(7) Maj, J. J.; Rae, A. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1982**, *104*, 4278-4280.

(8) (a) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *Inorg. Chem.* **1984**, *23*, 4125−4127. (b) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1647−1649. (c) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M.; Zanello, P. *J. Am. Chem. Soc.* **1987**, *109*, 185−198.

(9) (a) Cetinkaya, B.; Hitchcock, P. B.; Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Chem. Commun.* **1975**, 683−684. (b) Cetinkaya, B.; Hitchcock, P. B.; Lappert, M. F.; Pye, P. L.; Shaw, D. B. *J. J. Chem. Soc., Dalton Trans.* **1979**, 434−440.

(10) Englert, M. H.; Maj, J. J.; Rae, A. D.; Jordan, K. T.; Harris, H. A.; Dahl, L. F. *Abstracts of Papers*, 187th National Meeting of the American Chemical Society, St. Louis, MO, April 1984; American Chemical Society: Washington, DC, 1984; INOR 280.

(11) Dietzsch, W.; Strauch, P.; Hoyer, E. *Coord. Chem. Rev.* **1992**, *121*, 43−130.

(12) (a) Bottomley, F.; Lin, I. J. B.; White, P. S. *J. Organomet. Chem.* **1981**, *212*, 341−349. (b) Francesconi, L. C.; Corbin, D. R.; Clauss, A. W.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.* **1981**, *20*, 2059−2069.

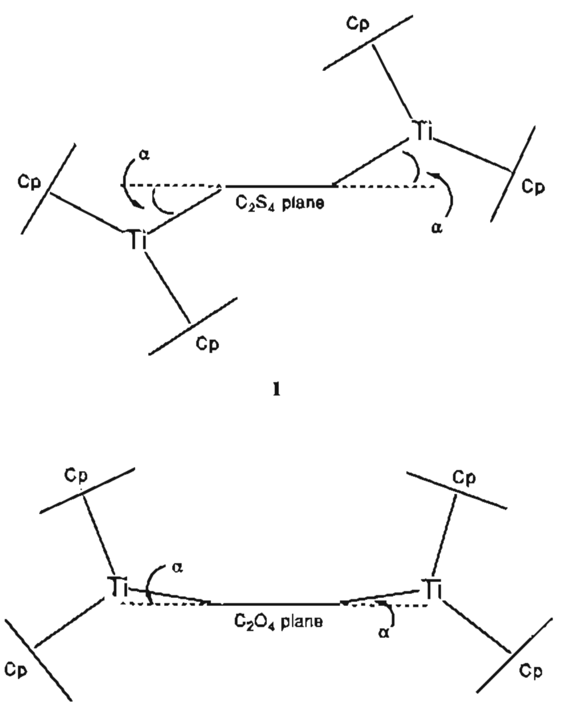
(13) Pasquali, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1981**, *20*, 349−355.

(14) Vicente, R.; Ribas, J.; Alvarez, S.; Segui, A.; Solans, X.; Verdaguer, M. *Inorg. Chem.* **1987**, *26*, 4004−4009.

(15) Hollander, F. J.; Coucouvanis, D. *Inorg. Chem.* **1974**, *13*, 2381−2386.

(16) (a) Coucouvanis, D.; Baenziger, N. C.; Johnson, S. M. *J. Am. Chem. Soc.* **1973**, *95*, 3875−3886. (b) Hollander, F. J.; Leitheiser, M.; Coucouvanis, D. *Inorg. Chem.* **1977**, *16*, 1615−1619.

0020-1669/94/1333-4566$04.50/0



1

2

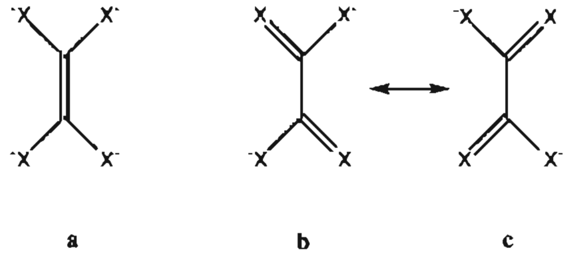
Figure 2. "Chairlike" conformation of compound **1**, $(Cp_2Ti)_2(\mu\text{-}C_2S_4)$, with Ti atoms trans to each other, vs "boatlike" conformation of **2**, $(Cp_2Ti)_2(\mu\text{-}C_2O_4)$, with Ti atoms cis to each other. α represents the "fold angle".

Table 1. Comparison of Compound **1**, $(Cp_2Ti)_2(\mu\text{-}C_2S_4)$, and Compound **2**, $(Cp_2Ti)(\mu\text{-}C_2O_4)$[a]

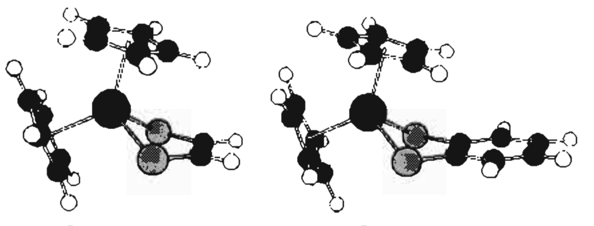
1	**2**
α = 46°	α = 11°
chair	boat
diamagnetic	paramagnetic
C−C = 1.41 Å	C−C = 1.52 Å
C−S = 1.74 Å	C−O = 1.26 Å
Ti(IV)	Ti(III)
$C_2S_4^{4-}$	$C_2O_4^{2-}$
ethylenetetrathiolate	oxalate

[a] References 5 and 11.

1.52 Å. Furthermore, the C−S bond distance in **1** is 1.74 Å, characteristic of a shortened C−S single bond, while the C−O bond length in **2** is 1.26 Å, which is slightly longer than a C═O double bond. These differences are summarized in Table 1, and they suggest that, to a first approximation, C_2S_4 in compound **1** can be described as the ethylenetetrathiolate *tetraanion*, illustrated by structure **a**, while C_2O_4 in compound **2** is best described as the well-known oxalate *dianion*, for which the two resonance structures are illustrated in **b** and **c**. In fact, the only prior theoretical study of **1** describes this system as having a nonintegral oxidation state, intermediate between Ti(III) and Ti(IV). This description provides a nice rationalization of the somewhat elongated C−C double bond distance found for **1**, although we shall see that other explanations are possible.



a **b** **c**



Ti(η^5-$C_5H_5)_2S_2C_2H_2$
ΔE‡ = 14.8 kcal/mol

Ti(η^5-$C_5H_5)_2S_2C_6H_4$
ΔE‡ = 14.0 kcal/mol

Figure 3. Two monotitanium dithiolate complexes and the activation barriers for their fluxional behavior.[16]

It is clear that even though the two Ti complexes are nominally isoelectronic, they are actually quite dissimilar, both structurally and electronically. When the bridging ligand is $C_2S_4^{4-}$, the oxidation state of the metal can be considered to be approaching Ti(IV), with a d^0 electronic state, accounting for the diamagnetic character of **1**. On the other hand, when the bridging ligand is $C_2O_4^{2-}$, the metal centers adopt an oxidation state of Ti(III), with a d^1 electronic configuration, resulting in the paramagnetic character exhibited by **2**. Thus, the C_2S_4 moiety appears to be more capable of delocalizing electron density from metals than its oxygen counterpart.

In addition to the interaction between the charge on the bridging ligand and the oxidation state of the metal, there is evidence that these complexes undergo fluxional behavior. This is illustrated by a number of monotitanium complexes with bidentate dithiolate ligands which are quite similar to the dinuclear species described above. Many such monotitanium dithiolate complexes are known.[17−23] The first important feature is that the titanium atom is out of the S_2C_2 plane and forms a fold angle comparable to that described above for the dititanium complexes (see Figure 3). In fact, the monotitanium systems exhibit fold angles in the range 43−46°, which closely corresponds to the 46° fold angle in compound **1**. This fold angle is attributed by Lauher and Hoffmann[24] to the interaction of a Ti(IV) acceptor orbital with a π-type donor orbital on the dithiolate ligand. These complexes are also fluxional on the NMR time scale. The activation barriers for this conformational process, based upon temperature dependent NMR studies, are in the range 12−15 kcal/mol.

Recently, a theoretical study of $(Cp_2Ti)_2(\mu\text{-}C_2S_4)$ and $(Cp_2Ti)_2(\mu\text{-}C_2O_4)$ by Harris et al. appeared.[5b] That work employed the Fenske−Hall molecular orbital method to examine the electronic differences between $(Cp_2Ti)_2(\mu\text{-}C_2S_4)$ (**1**) and $(Cp_2Ti)_2(\mu\text{-}C_2O_4)$ (**2**), and it presents a rationale for the structural differences of compounds **1** and **2**, as well as a rationale for the difference in titanium oxidation states of the two compounds. The explanation given for these differences centers around the existence of a low-lying π-acceptor orbital in the $C_2S_4^{2-}$ moiety which accepts a single electron from each Ti atom, resulting in a $C_2S_4^{4-}$ bridging ligand and two Ti(IV) centers. The chairlike geometry which **1** exhibits is then due to inductive stabilization

---

(17) Köpf, H. *Angew. Chem., Int. Ed. Engl* **1971**, *10*, 134−135.
(18) Kutoglu, A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 2891−2897.
(19) McCleverty, J. A. *Prog. Inorg. Chem.* **1968**, *10*, 200−211.
(20) King, R. B.; Eggers, C. A. *Inorg. Chem.* **1968**, *7*, 340−345.
(21) Villa, A. C.; Manfredotti, A. G.; Guastini, C. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 909−914.
(22) Bolinger, C. M.; Rauchfuss, T. B. *Inorg. Chem.* **1982**, *21*, 3947−3954.
(23) Kutoglu, A. Z. *Anorg. Allg. Chem.* **1972**, *390*, 195−209.
(24) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729−1742.

of the ethylenetetrathiolate π system. In contrast, the corresponding π-acceptor orbital in $C_2O_4^{2-}$ was shown to be energetically inaccessible, resulting in **2** being planar with two paramagnetic Ti(III) centers.

While Harris and co-workers provide a very useful qualitative description of frontier orbital effects on the conformations of **1** and **2**, their work relies on the Fenske–Hall methodology, which is unable to produce meaningful total energies. Indeed, the Harris work bases its conclusions on an analysis of the total overlap populations of idealized geometries. Thus, there is a clear need for further theoretical study of these systems which employs computational methodology appropriate for conformational analyses and extensive geometry optimization. In this paper, we present a theoretical study of ethylenetetrathiolate complexes and analogous compounds with an emphasis on the structural aspects of these complexes. This work represents the first theoretical examination of these systems involving extensive geometry optimizations within a nonempirical framework. We present here the full two-dimensional potential energy surface for the chair–to-chair interconversion of $(Cp_2Ti)_2(\mu\text{-}C_2S_4)$, and we isolate and characterize the transition state for this intramolecular process.

In order to compare the effects of different ligands, oxidation states, and metals in bimetallic complexes bridged by C_2X_4 ligands, we examined three complexes, $(Cp_2Ti)_2(\mu\text{-}C_2S_4)$, $(Cp_2Ti)_2(\mu\text{-}C_2O_4)$, and $(Cp_2Ti)_2[\mu\text{-}C_2(NR)_4]$. Our study of these systems encompasses several objectives. Our first goal is to determine the potential energy surface for the chair-to-chair interconversion of compound **1**, which is a fluxional process similar to that described above for the monotitanium dithiolate complexes. Having calculated the potential energy surface and located the transition state, we then want to identify the important orbitals which dictate the conformational preferences of the ground and transition states and to estimate the activation barrier for the chair-to-chair interconversion. Finally, we want to confirm the fundamental conclusions of Harris et al.[5] concerning the electronic and structural differences of bimetallic complexes bridged by oxalate and tetrathiolate using a higher level of theory.

Calculations

The molecular orbital method partial retention of diatomic differential overlap (PRDDO)[25] was used to optimize the geometries and examine the energetics and wave functions of all the systems examined in this paper. PRDDO is an approximate molecular orbital method which simulates Hartree–Fock calculations with the same basis set (a minimal Slater-type-orbital basis set) in a fraction of the time. It has been shown to be an appropriate method to use in large transition metal systems, since it combines speed with a reasonable level of accuracy. The computational efficiency of PRDDO is illustrated by the fact that a single-point energy calculation of $(Cp_2Ti)_2(\mu\text{-}C_2S_4)$, utilizing 202 basis functions, required only 420 s on a Convex C220 computer, 164 s on an IBM RS 6000-370, and 91 s on a Cray Y-MP computer. Because of its speed and accuracy, PRDDO is particularly well-suited for geometry optimizations and determination of potential energy surfaces for large transition metal systems and has been used in this fashion quite successfully for a number of systems,[26] especially systems containing titanium.[27]

Calculations involving $(Cp_2Ti)_2(\mu\text{-}C_2S_4)$ (**1**) began by optimizing the ground state structure with the following constraints: all C–H bond distances were fixed at 1.07 Å, the Cp rings were constrained to planarity, as was the C_2S_4 ligand, and since the molecule is known experimentally to have C_{2h} symmetry, the ground state was constrained to that symmetry. **1** was optimized by utilizing two different basis sets, including the standard PRDDO basis set, which is a minimal basis set consisting of 202 functions for this molecule, and a basis set which augmented the sulfur atoms with d-type polarization functions, resulting in 222 basis functions. Furthermore, we optimized **1** within both the restricted Hartree–Fock (RHF) formalism, which treated the complex as a closed shell system, and the unrestricted Hartree–Fock (UHF) formalism, which treated the system as an open shell system containing two unpaired electrons, one on each titanium. Although cyclopentadienyl rings are known to exhibit nearly free rotation when they are ligated to transition metals in an η^5 fashion, we fixed the orientation of the Cp rings in order to avoid the complexity of breaking symmetry. In order to determine the least-energy orientation of the Cp rings, the four Cp rings were individually rotated to allow the C–H bond in the σ_h plane to be either pointing toward the bridging ligand ("endo") or pointing away from the bridging ligand ("exo"). The Cp orientation which was most stable resulted in each Ti center having one Cp in an endo orientation and one Cp in an exo orientation, such that the Cp ring closer to the bridging ligand possessed the exo orientation and the overall molecule possessed C_{2h} symmetry. The other Cp orientations resulted in conformations which were higher by 1–7 kcal/mol than the ground state conformation. When both Cp rings on a metal center were allowed to rotate in a coupled fashion, the energy barrier was calculated to be only 1 kcal/mol. This relative orientation of Cp rings was assumed to hold for compounds **2** and **3** as well.

In order to perform initial explorations of the potential energy surface for the chair-to-chair interconversion of compound **1**, a series of conformations were optimized, including a planar structure, a half-chair structure, and a boat structure. In contrast to the geometry optimization of the C_{2h} ground state described above, these structures were constrained to C_s symmetry. In the planar structure, both titanium atoms were fixed in the C_2S_4 plane, whereas in the half-chair structure one Ti was fixed in the C_2S_4 plane while the other Ti was allowed freedom to move within the plane of symmetry. In the boat structure, the Ti atoms were placed cis to each other relative to the C_2S_4 ligand and the resulting fold angles formed by the Ti atoms with the C_2S_4 plane were assumed to be equal. An examination of the chair, half-chair, and boat structures revealed that the only geometrical parameters significantly affecting energy were the two angles formed by the Ti atoms with the $S_2C_2S_2$ plane (i. e., the "fold angles"). For example, the C–C distances optimized to 1.344, 1.337, and 1.336 Å for the chair, half-chair, and boat, respectively, with a standard deviation of only 0.004 Å. In fact, the standard deviations for all important bond lengths and bond angles were less than 0.007 Å and 0.4°, except for the S–Ti distance, where the standard deviation was less than 0.02 Å. These facts suggest that a very reasonable potential energy surface for the chair-to-chair interconversion of **1** could be developed by determining the total energy of compound **1** as a function of the two fold angles. Therefore a standard geometry was derived by averaging all bond lengths and bond angles from the optimized chair, half-chair, and boat structures. PRDDO was then used to explore the full two-dimensional potential energy surface by varying the two fold angles from +60 to −60° in increments of 5° each. This required 625 energy determinations, but since the surface is symmetrical with respect to the diagonal line from the lower left to the upper right, it was only necessary to calculate 325 points. The orientation of the Cp rings was fixed as described above, with the result that the two minima on the surface represent two different structures whose difference in energy is less than 1 kcal/mol. In determining the potential energy surface, we used RHF closed-shell calculations and the basis set containing sulfur d orbitals. The calculated potential energy surface with total energy plotted as a function of the two fold angles will be presented below.

---

[25] (a) Marynick, D. S.; Lipscomb, W. N. *Proc. Natl. Acad. Sci. U. S. A.* **1982**, *79*, 1341–1345. (b) Halgren, T. A.; Lipscomb, W. N. *J. Chem. Phys.* **1973**, *58*, 1569–1591.

[26] (a) Rogers, J. R.; Kwon, O.; Marynick, D. S. *Organometallics* **1991**, *10*, 2816–2823. (b) Lawless, M. S.; Marynick, D. S. *J. Am. Chem. Soc.* **1991**, *113*, 7513–7521. (c) Lawless, M. S.; Marynick, D. S. *Organometallics* **1991**, *10*, 543-545. (d) Marynick, D. S.; Axe, F. U.; Kirkpatrick, C. M.; Throckmorton, L. *Chem. Phys. Lett.* **1983**, *99*, 406–410.

[27] Lawless, M. S.; Marynick, D. S. *Inorg. Chem.* **1991**, *30*, 3547–3551. This study focused on the Cp_2TiS_5 ring system, and the results showed a qualitative agreement between PRDDO and large basis set ab initio calculations.

Table 2. Comparison of Experimental and Calculated Geometries for the Ground State of Compound **1**, $(Cp_2Ti)_2(\mu\text{-}C_2S_4)$ (in Degrees and Angstroms)

	exp[a]	closed shell[b]	closed shell[b] with d orbitals on S	open shell[c,d]
basic functions		202[d]	222[e]	202
α	46	45	47	2
C−C	1.41	1.35	1.43	1.51
C−S	1.74	1.74	1.66	1.66
Ti−S	2.41	2.32	2.29	2.50
Ti−Cp[f]	2.07	2.13	2.13	2.09
S−Ti−S	82	86	86	80
S−C−S	119	117	119	118
Ti−S−C	96	95	95	109
S−C−C	120	121	121	121

[a] Reference 5a, supplementary material. [b] The complex was treated as closed shell by using RHF calculations. [c] The complex was treated as open shell with two unpaired electrons by using UHF calculations. [d] This structure was determined using the standard PRDDO minimal basis set. [e] This structure was determined using the standard PRDDO minimal basis set augmented by additional d-type polarization functions on the sulfur atoms. [f] Ti−Cp denotes the mean distance from the titanium atom to the centroid of the cyclopentadienyl ring.

Table 3. Comparison of Ti(III) and Ti(IV) Complexes

	sum of d orbital occupancies	Valency of Ti	Mulliken charge on Ti
$(Cp_2Ti)_2(\mu\text{-}C_2S_4)$[a]	2.053	6.297	0.499
$(Cp_2Ti)_2(\mu\text{-}C_2S_4)$[b]	2.042	6.282	0.596
$(Cp_2Ti)_2(\mu\text{-}C_2S_4)$[c]	2.155	6.143	0.485
$(Cp_2Ti)_2(\mu\text{-}C_2O_4)$[d]	2.097	5.756	1.021
$TiCp_2S_5$	2.069	6.422	0.370
$TiCp_2Cl_2$	1.954	6.130	0.925

[a] Closed-shell (RHF) calculation of compound **1** with minimal basis set. [b] Closed-shell (RHF) calculation of compound **1** with d orbitals on sulfur atoms. [c] Open−shell (UHF) calculation of compound **1**. [d] Open−shell (UHF) calculation of compound **2**.

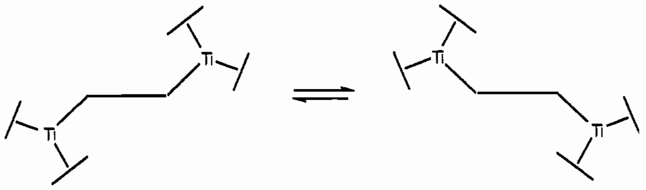


Figure 4. Chair-to-chair rearrangement in **1**, $(Cp_2Ti)_2(\mu\text{-}C_2S_4)$.

The ground states of compounds **2**−**4** were optimized analogously to **1** above, except that they were constrained to C_s symmetry rather than C_{2h}. All C−H distances were fixed at 1.07 Å, and the Cp rings and C_2X_4 ligands were constrained to be planar. The fold angles were optimized simultaneously for both the boat- and chairlike structures. All three structures were optimized at the RHF and UHF levels within PRDDO.

Results and Discussion

$(Cp_2Ti)_2(\mu\text{-}C_2S_4)$. (a) Ground State. When the geometry of compound **1** was optimized using closed-shell RHF calculations, the calculated conformation was, in most respects, comparable to the experimentally known structure. At the minimal basis set level, each titanium atom optimized to a location 45° out of the C_2S_4 plane, practically identical to the experimentally known 46° fold angle[5] and virtually the same as the analogous angle in a number of monotitanium species.[17−23] The optimized C−S bond distance also duplicated the experimentally measured distance of 1.74 Å. Furthermore, in agreement with experiment, the calculated C−C distance of 1.35 Å is characteristic of a C−C double bond, though our calculated value is 0.06 Å shorter than the crystallographically determined distance of 1.41 Å. In order to assess the importance of sulfur d orbitals, we repeated the ground state optimization of **1** with d orbitals added to the sulfurs. A comparison of the optimized ground state with and without sulfur d orbitals is given in Table 2. Adding sulfur d orbitals lengthens and thus improves the C−C distance (relative to the experimentally known structure) but shortens the C−S distance by 0.08 Å.

Since compound **1** is known to be diamagnetic, our geometry optimizations on this system initially assumed a closed-shell RHF wave function. However, in order to explore the changes in geometry that would result if compound **1** were paramagnetic, we also optimized the geometry of **1** with two unpaired electrons at the UHF level. As Table 2 indicates, the UHF PRDDO optimization procedure results in a structure which exhibits a longer C−C bond (1.51 Å) and a shorter C−S bond (1.66 Å), with both titanium atoms occupying the same plane as the $\mu\text{-}C_2S_4$ bridging ligand. Thus, when $(Cp_2Ti)_2(\mu\text{-}C_2S_4)$ is treated as an open-shell system, the molecular conformation changes dramatically, with the bridging ligand approximating a $C_2S_4^{2-}$ dianion (with a single C−C bond and partially double C−S bonds) and with the resulting change in the oxidation state of the metal to Ti(III). This is quite different from the experimentally known structure and diamagnetic character of **1** and is reminiscent of compound **2**, $(Cp_2Ti)_2(\mu\text{-}C_2O_4)$, which, as was described above, is characterized by a dianion bridging ligand and Ti(III) oxidation states.

The most immediate conclusion from an analysis of the ground state structure of **1** is that the valence bond arguments presented in the Introduction are reasonable in portraying this complex as consisting of two Ti(IV) metals bridged by the ethylenetetrathiolate anion. While it has been argued[5] that the C−C bond length of 1.41 Å is evidence for a nonintegral oxidation state of the metal (i.e., that Ti has an oxidation state in **1** intermediate between +3 and +4), it is difficult to rationalize the large fold angle if a significant contribution from a Ti(III) state is present, since that state should be planar. Additionally, our population analyses are entirely consistent with a Ti(IV) species. In fact, when compared to the case of Cp_2TiS_5, an obvious Ti(IV) species, the sum of d orbital occupancies and net atomic charges of **1** are all very similar (see Table 3). As described below, the lengthening of the C−C double bond can be ascribed to partial delocalization of a sulfur lone-pair orbital into the C−C π^* system.

(b) Potential Energy Surface. The presence of only one ^1H NMR peak for compound **1** indicates that all cyclopentadienyl hydrogens in this complex are equivalent on the NMR time scale. This condition is not satisfied by ring rotation, because there are two symmetry-distinct cyclopentadienyl rings bound to each metal center. (The lowest energy ground state structure consists of the Cp ring closest to the bridge being exo and the ring furthest from the bridge being endo, although, as stated earlier, when the cyclopentadienyl ring rotations are coupled in **1**, the barrier to rotation is only 1 kcal/mol.) Therefore the presence of only one NMR peak is consistent with a chair-to-chair rearrangement (see Figure 4) which must have a sufficiently low barrier to be facile on the NMR time scale.

The calculated potential energy surface for the chair-to-chair interconversion of $(Cp_2Ti)_2(\mu\text{-}C_2S_4)$ as a function of the two fold angles is presented in Figure 5. The vertical axis represents the fold angle on one side of the molecule, while the horizontal axis represents the complementary fold angle. As is evident from the surface, the least energy pathway for this fluxional process involves changing one fold angle at a time such that the interconversion of the complex proceeds as follows: chair

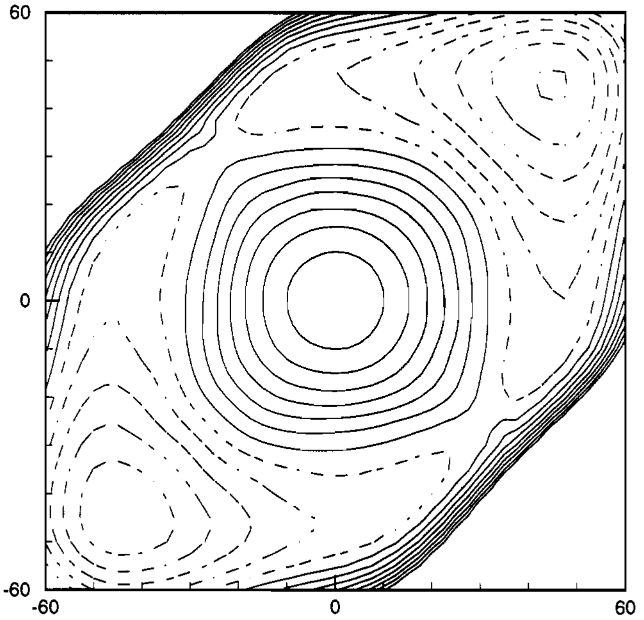


Figure 5. Potential energy surface for the chair-to-chair interconversion of **1**, $(Cp_2Ti)_2(\mu\text{-}C_2S_4)$. The vertical axis represents the fold angle on one side of the molecule; the horizontal axis represents the complementary fold angle (solid contour values 0.004, 0.008, 0.012, 0.016, 0.020, 0.024, 0.028, 0.032 au; dashed contour values 0.00, −0.004, −0.008, −0.012, −0.016, −0.020 au).

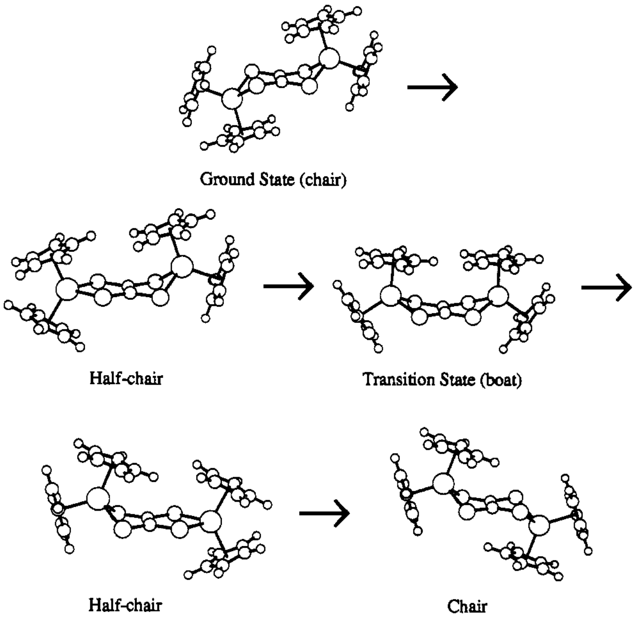


Figure 6. Least energy pathway for the chair-to-chair interconversion of **1**, $(Cp_2Ti)_2(\mu\text{-}C_2S_4)$.

→ half-chair → boat → half-chair → chair (see Figure 6). The transition state is calculated to be a boatlike structure with fold angles of 28° and an activation energy of 14 kcal/mol. This activation energy was determined by an independent optimization of the transition state, including the same geometrical parameters optimized for the ground state. The final optimized geometry was found to be quite similar to the geometry of the transition state estimated from the potential energy surface.[28] The magnitude of our calculated barrier is very reasonable, given the experimentally known activation barriers of 11.5−14.8 kcal/mol for the corresponding fluxional inversion process in monotitanium dithiolate complexes.[17−23] Furthermore, the conformation in which both metal centers are located in the same plane as the C_2S_4 bridge is found to be a local maximum, approximately 27 kcal/mol higher in energy than the ground state structure.

(c) Electronic Contributions to Conformational Fluxionality. As pointed out previously, Lauher and Hoffmann[24] attribute the fold angle in monotitanium dithiolate systems to the interaction of a Ti(IV) acceptor orbital with a π-type donor orbital on the dithiolate ligand. This immediately raises a question: Why is the transition state a boatlike structure rather than a planar or half-chair structure? If the dominant stabilizing influence in the potential energy surface is the overlap of metal d orbitals with the ligand π system and if that overlap is greatest when α is large and is least when $\alpha = 0°$, then we would expect the boat to represent a local minimum on the potential energy surface. The fact that the transition state is a boat rather than a half-chair or planar structure suggests that other stabilizing and/or destabilizing effects are occurring, and therefore it is important to examine other electronic factors which may be influential in the chair-to-chair interconversion process.

Let us initially consider how the various bonding interactions change upon going from the chair to the boat. The following comparisons of overlap populations and optimized geometries are useful:

	overlap pop.		optimized dist (Å)	
	Ti−S	C−S	Ti−S	C−S
chair	0.457	0.800	2.294	1.658
boat	0.487	0.786	2.322	1.666

The Ti−S distance increases in the boat, which suggests that a destabilization of this interaction may be important. However, the Ti−S overlap population *increases*, suggesting the opposite trend. The C−S parameters show a consistent trend, with the C−S distance increasing and the overlap population decreasing in the boat. These comparisons are complicated by the fact that the fold angles in the chair and the boat are significantly different. It is more meaningful to compare a chair and a boat with the same fold angles (28°, that of the optimized boat structure):

	overlap pop.		optimized dist (Å)	
	Ti−S	C−S	Ti−S	C−S
chair (28°)	0.489	0.797	2.319	1.659
boat (28°)	0.487	0.786	2.322	1.666

There is little or no change in the Ti−S parameters but a clear trend in the C−S parameters: The C−S bond is lengthened and the overlap population decreases in the transition state. Therefore, we focus our attention on the orbitals which affect C−S bonding.

To understand the origin of the boatlike transition state, it is useful to consider the shapes and energies of the first four occupied molecular orbitals. The evolution of these orbitals from the chair to the boat structure is illustrated in Figure 7. All four orbitals are composed of essentially pure p atomic orbitals on the bridging ligand. The highest occupied molecular orbital (HOMO), orbital **a**, is a weakly antibonding admixture of an a′ nonbonding orbital arising from the sulfur lone pairs and the occupied C−C π orbital (the corresponding bonding interaction lies much lower in energy). All of these orbitals are primarily based on the bridging ligand. Orbitals **b** and **d** are mainly nonbonding in character, while orbital **c** has a small amount of C−C π^* character. It is this orbital which is most likely responsible for the somewhat elongated C−C double bond

---

[28] Geometrical parameters of the optimized transition state include the following: $\alpha_1 = 28°$, $\alpha_2 = 29°$, C−C = 1.41 Å, S−Ti−S = 86°, S−C−S = 117°, S−C−C = 122°. Other important parameters are presented in the text.

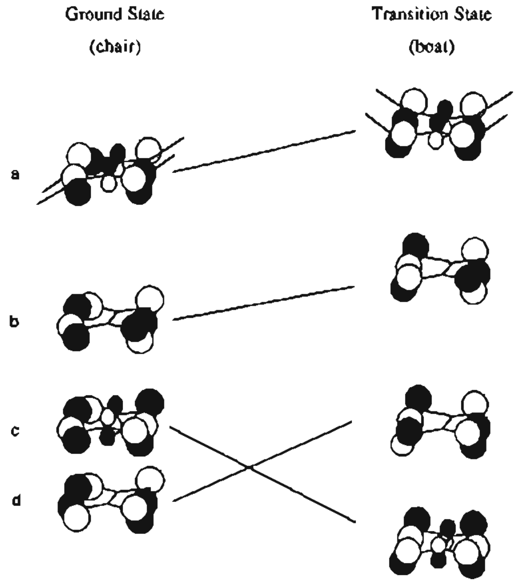


Figure 7. Evolution of the four highest occupied molecular orbitals in the chair-to-chair interconversion of **1**, $(Cp_2Ti)_2(\mu\text{-}C_2S_4)$. Orbital **a** is the HOMO.

Table 4. Comparison of Experimental and Calculated Geometries for the Ground State of Compound **2**, $(Cp_2Ti)_2(\mu-C_2O_4)$ (in Degrees and Angstroms)

	exp[a]	open shell[b]	closed shell[c]
C−C	1.52	1.52	1.35
C−O	1.26	1.26	1.34
Ti−O	2.16	2.02	1.80
Ti−Cp	2.06	2.08	2.13
$Ti-C_{Cp}$	2.35	2.39	2.43
$C_{Cp}-C_{Cp}$	1.39	1.39	1.39
O−Ti−O	75.8	78.3	84.3
Ti−O−C	114.7	116.6	111.0
O−C−C	116.7	114.3	113.5
O−C−O	126.5	131.4	133.1
α	11 (boat)	0.0 (planar)	23.2 (chair)

[a] Reference 11a. [b] The optimized structure from the UHF formalism with one unpaired electron on each Ti atom. [c] The optimized structure from the RHF formalism.

distance in the ground state. The C−C π system has a significant effect on the energy of orbital **a**, the origin of which is clear from Figure 7. Because of the antibonding relationship between the sulfur and carbon p orbitals, this orbital is *destabilized* in the boat. This destabilization is maximized in the transition state and is clearly responsible for the boat structure having the highest energy along the reaction path. A second, less important effect of the C−C π system is the stabilization of orbital **c** in the boat structure via enhanced delocalization into the C−C π^* orbital. The net destabilizing effect of these four orbitals is evidenced by the sum of their eigenvalues, which increase by 0.62 eV upon proceeding from the chair to the boat.

$(Cp_2Ti)_2(\mu\text{-}C_2O_4)$. Compound **2**, $(Cp_2Ti)_2(\mu\text{-}C_2O_4)$, is analogous to compound **1**, the only difference being the oxalate bridge in place of the ethylenetetrathiolate bridge. Changing the bridging ligand results in a dramatically different structure and electronic state, however, and Table 4 presents a comparison of the experimentally known geometry of **2** with our calculated geometries. $(Cp_2Ti)_2(\mu\text{-}C_2O_4)$ is a paramagnetic molecule, and as Table 4 illustrates, when it is optimized with two unpaired electrons within the UHF formalism, the resulting PRDDO structure is quite similar to the actual conformation. The optimized C−O distance of 1.257 Å is virtually identical to the experimentally known distance of 1.256 Å, and the optimized C−C bond length of 1.517 Å also compares extremely well to the crystallographic value of 1.523 Å. The optimized bond angles compare quite well to the actual conformation, the only exception being the fold angle α, which represents the angle formed by the Ti atom with the C_2O_4 plane. The PRDDO-optimized geometry of **2** places both titanium atoms in the plane of the C_2O_4 bridging ligand with a resulting fold angle of 0°, while the crystallographically determined structure is boatlike with 11° fold angles. We calculate, however, that the energy required to bend both Cp_2Ti fragments out of the plane by 11° is only 1.7 kcal/mol. This suggests that the experimental boat structure may be due to crystal packing effects, since the total energy that we calculate is essentially that of a gas-phase isolated molecule.

Table 5. Comparison of Experimental and Calculated Geometries for the Ground State of Compound **3**, $(Cp_2Ti)_2(\mu-C_2(NR)_4)$ (in Degrees and Angstroms)

	exp[a]	calc	
	R = p−MeC_6H_4	R = H	R = CH_3
C−C	1.50	1.51	1.51
C−N	1.33	1.31	1.32
Ti−N	2.17	2.09	2.07
Ti−Cp	2.10	2.11	2.12
α	11.2 (chair)	0.7 (~planar)	3.5 (chair)

[a] Reference 12.

When $(Cp_2Ti)_2(\mu\text{-}C_2O_4)$ is optimized as a closed shell system utilizing RHF calculations, the C−C bond distance shortens to 1.35 Å, the C−O distance lengthens to 1.34 Å, and the Cp_2Ti fragments bend out of the C_2O_4 plane, resulting in a chairlike structure with fold angles of 23° (see Table 4). This resembles the ground state structure for compound **1**, which consists of Ti(IV) metals in conjunction with a tetraanion bridge.

$(Cp_2Ti)_2(\mu\text{-}C_2(NR)_4)$. Except for the fold angle, which we underestimate, our calculated geometrical parameters for R = H and R = CH_3 agree extremely well with the experimental structure (Table 5). This species is isoelectronic with $(Cp_2Ti)_2(\mu\text{-}C_2O_4)$ and thus has a paramagnetic ground state with Ti(III) centers. It is interesting to note that the experimental conformation of $(Cp_2Ti)_2(\mu\text{-}C_2(NR)_4)$ is a *chair* and not the shallow *boat* seen in $(Cp_2Ti)_2(\mu\text{-}C_2O_4)$. This lends credibility to the argument that the conformations of the Ti(III) species are due not to any intrinsic electronic effects but to other steric factors. As mentioned above, crystal packing forces are the likely explanation for the conformation of $(Cp_2Ti)_2(\mu\text{-}C_2O_4)$. For $(Cp_2Ti)_2(\mu\text{-}C_2(NR)_4)$, it is likely that the nitrogen substituents are responsible for the nonplanar conformation. Some indications of this can be gleaned from our optimized geometries, which yield an essentially planar conformation for R = H but a fold angle of ~3.5° for the bulkier methyl substituent. The experimentally observed system has R = p-MeC_6H_4. The steric bulkiness of this substituent is most likely responsible for the fold angle of ~11°. However, because it is so similar to the isoelectronic $(Cp_2Ti)_2(\mu\text{-}C_2O_4)$ species, we have not done any calculations on the actual experimentally observed system. Finally, we note that the calculated energy difference for R = H between the planar conformation and one in which α is fixed at 11° is only 0.7 kcal/mol, again suggesting that electronic effects do not play a major role in determining the conformations of these Ti(III) species.

Conclusions

$C_2X_4{}^{4-}$ species display a fascinating array of structures and electronic states, even among seemingly closely related systems. The electronic structures of several of these species have been investigated, and the qualitative effects that influence the nature of the electronic ground state, particularly the energetic accessibility of the LUMO of the $C_2X_4^{2-}$ bridging ligand, are now well-understood. With X = O or N, the above-mentioned LUMO lies high in energy, forcing two electrons to remain on Ti, which results in Ti(III) centers. When X = S, the LUMO of the bridging ligand is energetically accessible, resulting in a complex which can be described as two Ti(IV) centers bridged by $C_2S_4^{4-}$.

We have presented the first detailed conformational analysis of intramolecular motion in a bimetallic complex with C_2S_4 as a bridging ligand. The calculation of the full two-dimensional potential energy surface for this species revealed an unusual boat-shaped transition state, with an activation energy in excellent agreement with those found for other related systems. The boatlike geometry of the transition state was traced to an unfavorable C−S π interaction in the HOMO.

Acknowledgment. This work was supported by the Robert A. Welch foundation (Grant Y-743), the UT System Center for High Performance Computing, and Cray Research, Inc.