Theoretical Evidence of Persistent Chirality in D_3 Homoleptic Hexacoordinate Complexes with Monodentate Ligands**

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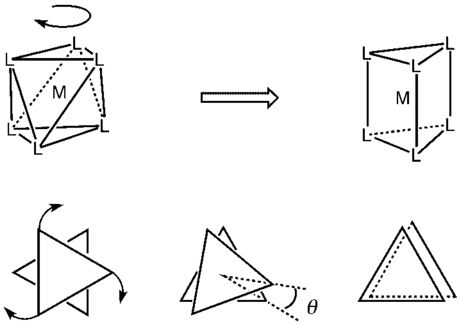
Abstract: A theoretical study of the enantiomer interconversion pathway relevant to racemization reactions of hexacoordinate transition-metal complexes is presented based on density functional calculations. The potential-energy surface for the trigonal twist pathway of the $[Zr(SH)_6]^{2-}$ model compound has been explored. The optimum structure reproduces, to a very good approximation, the experimental geometry of the analogous compound in which the thiolato groups have C_6H_4-4-OMe substituents instead of H atoms. A barrier of about 19 kcal mol^{-1} is estimated for the racemization of $[Zr(SH)_6]^{2-}$ and exploratory calculations for $[Zr(SC_6H_4\text{-}4\text{-}OMe)_6]^{2-}$ indicate that a larger barrier should be expected. For the chiral homoleptic organometallic complexes $[ZrMe_6]^{2-}$ and $[RhMe_6]^{3-}$ no significant racemization barrier is expected.

Keywords: Bailar twist · chirality · coordination chemistry · density functional calculations

Introduction

Chirality of transition-metal complexes is of much current interest because of their potential applications as catalysts for asymmetric synthesis.[1] The main option usually considered for inducing chirality in octahedral complexes is the use of two or three bidentate ligands.[2] We have recently called to attention the possibility of employing *homoleptic* hexacoordinate complexes with monodentate ligands[3] whose chirality is associated to a D_3 symmetry point group. This chiral point group appears in hexacoordinate complexes with structures anywhere in between an exact octahedron and a perfect trigonal prism. The distortive path that links these two extremes is the well-known Bailar twist shown in scheme 1, whereby the octahedron corresponds to $\theta = 60°$ and the trigonal prism to $\theta = 0°$. Furthermore, based on a quantitative analysis of the degree of chirality along this D_3 route carried out with the help of continuous chirality measures (CCM),[4] it was determined that the most chiral D_3 complex is characterized by a twist angle $\theta = 23°$. Since a variety of D_3 hexacoordinate homoleptic complexes have already been synthesized and structurally characterized, two key questions that follow are: Why have the two enantiomers neither been separately characterized nor have their optical rotatory dispersion (ORD) or circular dichroism (CD) spectra been recorded? Could these complexes be useful in chiral catalysis? We believe that the main reason for the lack of chiral-oriented research on these complexes has been the preconception that only bi- and tridentate, but not monodentate,



Scheme 1.

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ligands can give rise to stable enantiomers that do not racemize in solution at room temperature. In this report we provide evidence to the contrary: Homoleptic hexacoordinate metal complexes may be stable enough at room temperature to allow separation of enantiomers and to act as chiral catalysts. We do so by a theoretical investigation of the energy barrier for the trigonal twist associated mainly with the enantiomerization of the model molecular anion $[Zr(SH)_6]^{2-}$, motivated by the identification in our previous work[3] of the most chiral homoleptic complex in the crystal state, $[Zr(SC_6H_4\text{-}4\text{-}OMe)_6]^{2-}$ (Figure 1), a d^0 thiolato complex[5] that crystallizes in the enantiomorphic *R*32 group with a ZrS_6 core that has a twist angle of 30°. Calculations are also reported for this complex as well as for some MMe_6 molecules with prismatic or twisted prismatic structures.

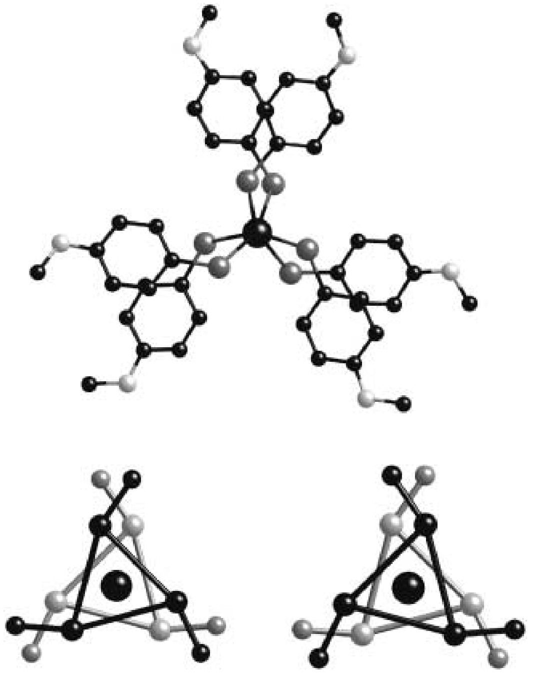
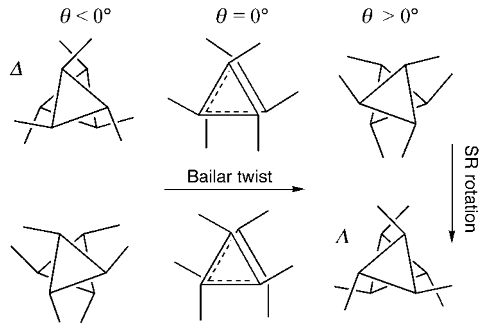
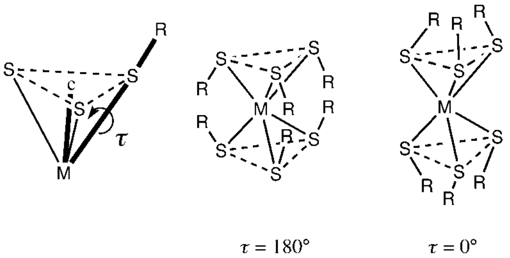


Figure 1. Projections along the trigonal axis of the $[Zr(SC_6H_4\text{-}4\text{-}OMe)_6]^{2-}$ ion (above) and of its inner core showing the trigonal faces and only the *ipso* carbon atom of the organic group (below) as found in the experimental structure (left, Δ isomer) and in its enantiomeric form (right, Λ isomer).



Scheme 2.



Scheme 3.

Two parameters are used to describe the structure of the thiolato complex. The first one is the twist angle between two parallel faces of the coordination polyhedron (θ in Scheme 1). Since in this case clockwise and anticlockwise rotations are not equivalent due to the orientation of the thiolato substituents, we adopt the convention that negative twist angles correspond to an anticlockwise, and positive ones to a clockwise rotation (Scheme 2). The second parameter describes the orientation of the thiolato substituent and is defined by the R-S-M-*c* torsion angle (τ), whereby *c* is the centroid of the corresponding trigonal face, as illustrated in Scheme 3. The experimental values for the structure of the $[Zr(SC_6H_4\text{-}4\text{-}OMe)_6]^{2-}$ ion are $\theta = -30.5°$ and $\tau = 240°$ (shown in projection along the trigonal axis in Scheme 2, and labeled Δ). Hence, the rearrangement of this molecule leading from the Δ to the Λ enantiomer requires two geometrical changes, which may occur in synchronous or asynchronous ways: 1) the Bailar twist of the ZrS_6 core that generates its mirror image (from left to right in Scheme 2), and 2) the rotation of the S–R bonds around the Zr–S axes for the six sulfur atoms (from top to bottom in Scheme 2). An alternative to S–R rotation that will be considered in the discussion of the results is the inversion at the S atoms passing through a linear Zr-S-R transition state. We note here that we have labeled the two enantiomers according to the handedness of the ZrS_6 core, but since the R_6 group is also chiral, at some points along the enantiomerization path the corresponding labels cannot be assigned, a problem of *latent handedness* that has been discussed by one of us recently.[6] This happens, for instance for the geometries with $\theta = 0°$ in Scheme 2.

Hexamethyl complexes of early transition metals also present a variety of twist angles (see reference [3] for more references and data). That d^0 to d^2 complexes with σ-donor ligands must be trigonal prismatic was first proposed based on qualitative MO analysis[7] and later on through ab initio calculations.[8] The report of the crystal structure of the $[Zr(CH_3)_6]^{2-}$ ion[9] and of the electron diffraction structure of $[W(CH_3)_6]$[10] prompted new theoretical studies on hexamethyl complexes of the early transition metals, and it seems now clear that a nearly trigonal prismatic (in some cases distorted to C_{3v}) structure is preferred for complexes with d^0 to d^2 electron configurations.[11] Although twisted geometries, intermediate between octahedral and trigonal prismatic, have been predicted computationally for the d^0 $[Mo(SH)_6]$ complex,[11d] no attention has been paid so far to the chirality and the racemization processes for this family of compounds. Since $[ZrMe_6]^{2-}$ is isoelectronic with $[Zr(SC_6H_4\text{-}4\text{-}OMe)_6]^{2-}$, we have also carried out calculations on the hexamethyl derivative, as well as on other hexamethyl complexes, $[NbMe_6]^-$, $[WMe_6]$, and $[RhMe_6]^{3-}$, for the sake of comparison.

Computational Methods

Density functional calculations were carried out with the B3LYP method and the LANL2DZ double-ζ basis set with pseudopotentials for the inner orbitals by using the Gaussian 98 program.[12] For most of our calculations the thiolato groups were replaced by SH$^-$, thus $[Zr(SH)_6]^{2-}$ was used as a model complex. To keep the model as simple as possible we limited our study to the two essential parameters θ and τ, keeping the Zr–S and S–H bond lengths and the Zr-S-H angles constant at 2.574 and 1.25 Å and 110°, respectively. The same relative orientation for all six S–H bonds was assumed, and the two S-S-S basal planes were kept coplanar in all the geometries studied. These geometrical features were those found experimentally for $[Zr(SC_6H_4\text{-}4\text{-}OMe)_6]^{2-}$ and were chosen to provide a qualitative estimate of the energy changes for the full structure. Calculations were performed for the range $-60° \leq \theta \leq 60°$ (at 5° intervals) and $0° \leq \tau \leq 180°$ (at 10° intervals). To further test our model results, we carried out single point calculations on the full anionic complex, $[Zr(SC_6H_4\text{-}4\text{-}OMe)_6]^{2-}$, with four relevant structures of the coordination sphere. The orientation of the six C_6H_4-4-OMe groups was optimized at each rotation angle by molecular mechanics calculations, freezing the position of the S atoms and replacing Zr by a dummy atom. The energy profile through the Bailar twist was calculated also for some selected $[MMe_6]$ complexes. Since in this case clockwise and anticlockwise rotations are equivalent we only explored the range $0° \leq \theta \leq 60°$ at 10° intervals.

Results

Energy and chirality surfaces: The energy of our model compound $[Zr(SH)_6]^{2-}$, calculated as a function of the two parameters, θ and τ, is presented as a contour plot in Figure 2 and the corresponding values for some singular points are summarized in Table 1. We note that points related by inversion through **X** or **Y** correspond to enantiomeric structures, whereas points separated by a 120° interval along the θ axis represent identical structures. Two of the energy minima found (**A** and **A′** in Figure 2) correspond to the two enantiomeric forms. It is remarkable that this simplified model, in which the C_6H_4-4-OMe groups have been substituted by hydrogen atoms, is able to reproduce to an excellent approximation both the twist and torsion angles of the experimental structure (−30.5 and 240°, respectively).

Three different pathways connecting the minima can be found in the potential-energy surface:

1) The least motion path connecting points **A** and **A′** goes through a transition state **L** (or **L′**) with a barrier of about 19 kcal mol^{-1}.

Table 1. Position, relative energies [kcal mol^{-1}] and continuous chirality measures (CCM) of some relevant points of the potential-energy surface of $[Zr(SH)_6]^{2-}$ (Figure 1), together with the experimental values for $[Zr(SC_6H_4\text{-}4\text{-}OMe)_6]^{2-}$.

Point	Nature	θ	τ	CCM	Energy
A	minimum	−32	225	1.68	0
B	minimum	18	319	2.92	9.9
L	transition state	−35	180	3.57	18.7
M	transition state	30	211	1.48	16.3
N	transition state	60	280	3.88	19.3
P	transition state	0	360	0.00	18.2
X	maximum	0	180	0.00	22.5
Y	maximum	60	180	0.00	19.4
Z	maximum	10	260	1.85	43.3
	experimental	−30.5	240	2.16	–

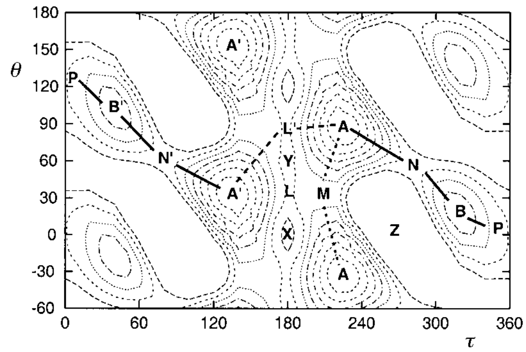


Figure 2. Potential-energy surface calculated for $[Zr(SH)_6]^{2-}$ as a function of the Bailar twist angle (θ) and the orientation of the SH bonds (τ). Points labeled **A**, **A′**, **B**, and **B′** correspond to energy minima and the isoenergy curves are plotted at 3 kcal mol^{-1} intervals.

2) A second path connects two equivalent geometries **A** at a fixed value of $\tau = 225°$ by a trigonal twist of 120°, passing through transition state **M**, with a slightly smaller energy barrier (16 kcal mol^{-1}).

3) A long path with energy barriers of about 18 kcal mol^{-1}, which connects the two enantiomers **A** and **A′** through points **N**, **B**, **P**, **B′**, and **N′**. Of these, **N**, **N′**, and **P** are transition states, whereas **B** and **B′** are relative minima, 10 kcal mol^{-1} above the global minimum.

Single-point calculations were also carried out for the full anionic complex $[Zr(SC_6H_4\text{-}4\text{-}OMe)_6]^{2-}$. The estimated energy barrier for the **AMA** process is 24.6 kcal mol^{-1}, of the same order of magnitude but significantly higher than for the simplified model (16.3 kcal mol^{-1}, given by the energy difference between points **A** and **M**). The geometries corresponding to a pseudooctahedral trigonal antiprism ($\theta = 60°$) and to a trigonal prism ($\theta = 0°$), which are along the **AM** pathway, are calculated to be 5.1 and 8.0 kcal mol^{-1} above that of **A**, in excellent agreement with the topology of the corresponding pathway in the potential-energy surface of the simplified model. Calculations were also performed for the rotation of only one thiolato group in $[Zr(SC_6H_4\text{-}4\text{-}OMe)_6]^{2-}$, while keeping the rest of the molecule fixed and a high energy barrier (19.4 kcal mol^{-1}) was found.

It is of fundamental interest to understand how the chirality of a dissymmetric molecule changes along an enantiomerization path, since, contrary to intuition, the interconversion of right- and left-handed enantiomers of a molecule need not go through an achiral transition state,[13] and the present case provides us with the opportunity to enhance our understanding of such all-chiral pathways. For that reason we plot in Figure 3 the continuous chirality measure (CCM) of $[Zr(SH)_6]^{2-}$ as a function of θ and τ. The corresponding values at special points are given in Table 1. Among the three pathways described in the potential-energy surface, the **AMA** pathway is associated to an automerization process (i.e., it does not involve enantiomerization), which does, however, pass through a chiral transition state (Figure 3, point **M**). As for the enantiomerization routes, the **AL′A′** path has a chiral transition state **L′**, but the **APA′** pathway goes through the achiral transition state **P** (Figure 3), which corresponds to two aligned trigonal prisms, namely of H_6 and ZrS_6.

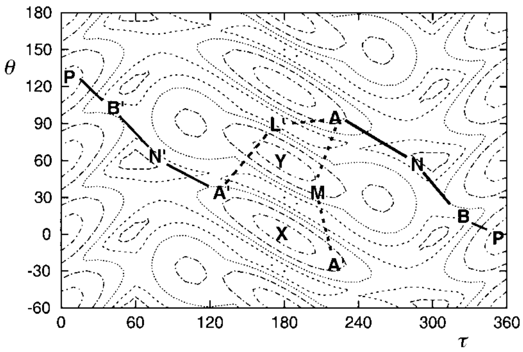


Figure 3. Continuous chirality measure of $[Zr(SH)_6]^{2-}$ as a function of the Bailar twist angle (θ) and the orientation of the SH bonds (τ). Labeling of specific points as in Figure 2.

Since the homoleptic hexamethyl complexes of some transition metals appear as trigonal metaprisms[14] (see twist angles in Table 2), it is worth comparing their energy profiles along the Bailar path with our results for the zirconium thiolato complex. The calculated twist angles, the experimental data, and the calculated energies for the trigonal prismatic ($\theta = 0°$) and octahedral ($\theta = 60°$) geometries are presented in Table 2.

Table 2. Optimized twist angles [°] and relative energies [kcal mol^{-1}] of the trigonal prismatic ($\theta = 0°$) and octahedral ($\theta = 60°$) structures of some hexamethyl transition metal complexes.

	θ_{opt}	E ($\theta = 0°$)	E ($\theta = 60°$)	CCM$_{calcd}$	θ_{exptl}	CCM$_{exptl}$	space group	ref.
$[ZrMe_6]^{2-}$	20.2	0.7	2.3	2.05	11.2	0.63	*Aba*2	[9]
$[NbMe_6]^-$	0	0.0	71.0	0.00	3.0	0.03	$P2_12_12_1$	[15]
$[WMe_6]$	0	0.0	105.6	0.00	1.4	0.01	$Pbc2_1$	[15]
$[RhMe_6]^{3-}$	44.6	1.9	0.3	0.56	44.0	0.70	$R\bar{3}c$	[16]

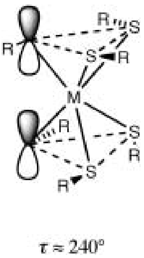
Discussion

It is important to realize that the **ALA′** pathway crosses the $\tau = 180°$ line, which implies steric repulsion between the thiolato substituents (see Scheme 3), a repulsion that is expected to increase significantly when the hydrogen atoms of our model are replaced by the bulky phenyl groups in the experimental compound. Hence this enantiomerization path can be ruled out as a possible mechanism for the racemization reaction of the real compound. Since the **AMA** pathway corresponds to an automerization process, we are left with the **APA′** path as the most likely one for the enantiomerization of $[Zr(SR)_6]^{2-}$ with R ≠ H. This pathway requires a 180° twist around the trigonal axis, combined with a 280° rotation of the S–R groups around the Zr–S bonds through the outer part of the octahedron (i.e., passing through $\tau = 0°$, point **P** in Figure 3), and its associated energy barrier (19.3 kcal mol^{-1}) corresponds to the relative energy of point **N**. This large value implies that the racemization of $[Zr(SC_6H_4\text{-}4\text{-}OMe)_6]^{2-}$ must be quite slow at room temperature. For comparison we note that, for example, the barrier for the racemization of tris(dithiocarbamato)ruthenium complexes was found to be about 10 kcal mol^{-1}.[17]

The results of single-point calculations for $[Zr(SC_6H_4\text{-}4\text{-}OMe)_6]^{2-}$ show how well the simpler model represents the behavior of the full molecule, even at the semiquantitative level. A molecular model, however, tells us that the three thiolato groups at one trigonal face cannot simultaneously adopt the $\tau = 0°$ orientation owing to severe steric congestion (independent of the twist angle). An alternative mechanism could imply asynchronous rotations of the thiolato groups, that is, one at a time. However, rotation of only one thiolato group, while keeping the rest fixed still requires a relatively high energy (19.4 kcal mol^{-1}) according to our calculations. Although this barrier could be somewhat lowered if the two S-S-S basal planes would be allowed to tilt from co-planarity, no substantial decrease of the barrier is expected in this situation. The alternative mechanism that involves linearization of the Zr-S-H backbones is calculated to have a barrier of 145.6 kcal mol^{-1} (24.3 kcal mol^{-1} per SH group), so we do not expect such a mechanism to give a lower barrier than thiolato rotation. We therefore conclude that even for a nonconcerted inversion of the six thiolato groups, the enantiomerization barrier of $[Zr(SC_6H_4\text{-}4\text{-}OMe)_6]^{2-}$ should be always higher than that of the simpler model $[Zr(SH)_6]^{2-}$, and no racemization reactions should be expected to occur at room temperature.

As the results of our calculations have shown that a chiral trigonal metaprism is the most stable geometry for $[Zr(SH)_6]^{2-}$ and that there is a substantial barrier for the racemization reaction, we need to look for the reasons behind this conclusion. In contrast to the d^0 complexes with σ-donor ligands, such as CH_3, which prefer the trigonal prismatic geometry,[11] the Zr complexes with π-donor ligands studied here prefer a metaprism. The reason for the twist can be found by analyzing the S⋯S overlap populations. Although the effect of π-bonding contributions[11d] cannot be totally ruled out, the leading term seems to be the repulsion between the lone pairs of the S atoms on opposite trigonal faces at the ideal trigonal prism ($\theta = 0°$). The orientation of the substituents found in both $[Zr(SC_6H_4\text{-}4\text{-}OMe)_6]^{2-}$ (experimentally) and in $[Zr(SH)_6]^{2-}$ (computationally) is nearly coplanar to the trigonal faces, hence the π-type lone pairs would strongly overlap in a trigonal prismatic ZrS_6 core, as shown in Scheme 4, resulting in net electron pair repulsions. A trigonal twist significantly reduces those interactions and stabilizes the molecule. Since the orientation of the thiolato groups can be significantly modulated by steric or π-stacking interactions between the substituents, we anticipate that some variability in the rotation angle will be found, depending on the nature of those substituents.

Other members of the $[Zr(SC_6H_4R)_6]^{2-}$ family have been structurally characterized and have twist angles between 15 and 36° (R = *p*-OMe, *o*-Cl, and H).[18] It remains to be



Scheme 4.

explained why the analogous thiolato complex, $[Zr(SC_6H_4\text{-}4\text{-}Me)_6]^{2-}$, reported by the same authors crystallizes in a centrosymmetric space group and, therefore, combines the two enantiomers in the solid state with a significantly smaller rotation angle ($\theta = 9.2°$, $\tau = 126.7°$). We note, however, that the geometry of this compound is still inside the low-energy valley around the minimum **A**, and the structures found for the two compounds are expected to differ by less than 5 kcal mol^{-1} according to Figure 2.

Contrary to the intuitive idea that interconversion of the left- and right-handed enantiomers should proceed through an achiral intermediate, one of the two enantiomerization pathways just discussed has a chiral transition state (Figure 3, point **L**). However, it has been proposed by Pinto and Avnir[6] that most enantiomerization processes may proceed through chiral transition states, because the requirement to have a mirror plane at the transition state is too stringent. The reason for a chiral transition state in this case is that both the ZrS_6 and the H_6 fragments are chiral at the minimum; hence, enantiomerization requires the generation of the mirror image of both groups. Since on going from **A** to **L** the twist angle of the ZrS_6 core does not change, its chirality is retained (even if the degree of chirality changes slightly) and its mirror image is generated after the transition state (from **L** to **A′**). In other words, changes of chirality of the two chiral fragments along the enantiomerization pathway are asynchronous.

The optimized geometries of two hexamethyl complexes, $[ZrMe_6]^{2-}$ and $[RhMe_6]^{3-}$, are also found to be metaprisms, in agreement with their experimental twist angles (Table 2). The first case is in contrast to the behavior of the isoelectronic analogues $[NbMe_6]^-$ and $[MoMe_6]$, which are nearly perfect trigonal prisms. The significant twist found for the Rh^{III} complex ($\theta = 44°$), both experimentally and theoretically, is in contradiction with the idea that d^6 complexes with σ-donor ligands must be perfectly octahedral, but we have not found a simple explanation for this computational result. The estimated barriers for racemization of these two complexes (corresponding to the relative energy at $\theta = 0°$), however, are less than 2 kcal mol^{-1}, and preparation of enantiopure compounds is unlikely according to the present computational results. We note that $[WMe_6]$, $[ZrMe_6]^{2-}$, and $[RhMe_6]^{3-}$ crystallize in non-enantiomorphic space groups with the two enantiomers present in the unit cell, a fact that is consistent with the calculated low racemization energy barrier (Table 2). On the other hand, although $[NbMe_6]^-$ crystallizes in an enantiomorphic space group and is, therefore, enantiopure in the solid state, the small twist angle may be induced by a chiral packing of the counterions, and no chiroptical properties should be expected in solution.

Conclusion

Twisted chiral conformations found in homoleptic hexacoordinate complexes with monodentate ligands may have substantial barriers for racemization as computationally shown here for the $[Zr(SH)_6]^{2-}$ ion. The fact that the simplified model reproduces the geometry of the experimentally reported $[Zr(SC_6H_4\text{-}4\text{-}OMe)_6]^{2-}$ ion very well, together with the molecular orbital analysis of the geometrical preference, indicates that departure from the trigonal prism and a substantial barrier for racemization in thiolato d^0 complexes is electronically and not sterically imposed. It also shows that the racemization process may proceed through a chiral transition state, because the two stereogenic groups, R_6 and ZrS_6 in $[Zr(SR)_6]^{2-}$, evolve asynchronously. Chiral hexamethyl complexes, in contrast, should be expected to present very low racemization energy barriers. We hope that the present theoretical results will encourage active experimental search for as yet unreported manifestations of optical activity in homoleptic transition-metal complexes.

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