

Stereochemical Nonrigidity and Geometrical Isomerism in Six-Coordinate Trigonal Prismatic Complexes: The Case of Asymmetric Molybdenum and Tungsten Tris(dithiolenes)

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The isomerization of nine asymmetric tris(dithiolenes) of tungsten and molybdenum, of the general formula $(R_1R_2C_2S_2)_3M$ is studied with NMR methods. In the complexes investigated, $R_1 = H$, $R_2 = p\text{-CH}_3\text{OPh}$, $p\text{-CH}_3\text{-Ph}$, or Ph , and $M = \text{W}$ or Mo , or $R_1 = H$, $R_2 = p\text{-ClPh}$ or $p\text{-BrPh}$, and $M = \text{W}$, or $R_1 = \text{Ph}$, $R_2 = p\text{-CH}_3\text{OPh}$, and $M = \text{W}$, as shown in formula **I**. The complexes are proved to be trigonal prismatic in solution and stereochemically nonrigid at room temperature. An equilibrium favoring the *trans* isomer (formula **III**) is established, with the concentration of this isomer being three times that of the *cis* due to entropy reasons. The kinetics and mechanism of the isomerization is investigated and a scheme is proposed involving the rotation of only one ligand around an axis lying on the dithiolenic ring, passing from the metal to the center of the carbon–carbon bond. This mechanism satisfies energy criteria and is allowed by symmetry selection rules, as theoretical EHMO calculations indicate.

Introduction

Six coordination is dominated by the octahedral geometry and by stereochemical rigidity.¹ Exceptions to the octahedral geometry are the tris(dithiolenes) complexes of molybdenum, tungsten and rhenium and their diselenolene analogues, which in the solid state are known² to be trigonal prismatic. Here we present evidence that this geometry is retained in solution and that it is stereochemically nonrigid.

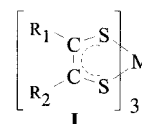
Theoretical studies on six coordination³ indicate that in the trigonal prism the metal to ligand bonds are stronger than in the octahedron or the distorted octahedron. However, octahedral geometry is favored because it minimizes interligand repulsions, by maximizing their distance.

The known prismatic complexes are tris-bidentate. It has been suggested⁴ that $(\text{Ph}_2\text{C}_2\text{S}_2)_2(\text{CO})_2\text{W}$ may also have this geometry. Cases of trigonal prismatic complexes with monodentate ligands are⁵ $[\text{Li}(\text{tmed})_2][\text{ZrMe}_6]$ (*tmed* = *N,N,N',N'* tetramethylenediamine) and possibly⁶ WMe_6 .

In a classic paper by Muetterties,⁷ it was suggested that the trigonal prismatic geometry might be a very unstable structure, as the balance between bond energies and repulsion between substituents is expected to be delicate. Crystal structures of trigonal prismatic complexes give no information on that, so a solution study is necessary.

There have been numerous reports on the dynamics of isomerization in octahedral complexes, and several mechanisms have been proposed.⁸ The studies were mainly performed by NMR or optical spectroscopy methods and were all conducted at temperatures higher than ambient.

The complexes studied in this paper are asymmetric prismatic dithiolenes of the general formula **I**. The metal *M* and the substituents R_1 and R_2 are given in Table 1.



Because of the trigonal prismatic geometry an equilibrium is established between geometrical isomers of this formula (*vide infra*), which can be studied at room and lower temperatures.

Experimental Section

The complexes were prepared as described previously.⁹ NMR spectra were recorded with a Varian Unity Plus 300 spectrometer, operating at 299.940 MHz for protons and 12.43 MHz for ¹⁸³W. Approximately 10 mg samples of the complexes were dissolved in 0.7 mL deuterated chloroform or hexadeuterated acetone and placed in 5

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Table 1. Complexes Studied, Where M, R₁, and R₂ Refer to Formula I

complex	R ₁	R ₂	M
1	<i>p</i> -CH ₃ OPh	H	W
2	<i>p</i> -CH ₃ Ph	H	W
3	Ph	H	W
4	<i>p</i> -ClPh	H	W
5	<i>p</i> -BrPh	H	W
6	<i>p</i> -CH ₃ OPh	H	Mo
7	<i>p</i> -CH ₃ Ph	H	Mo
8	Ph	H	Mo
9	<i>p</i> -CH ₃ OPh	Ph	W

mm NMR tubes. For test experiments at very low temperatures (below -85 °C) a mixture of hexadeuterated acetone and dibromodichloromethane was used as solvent. ¹H NMR spectra were recorded with 90° pulses followed by 2 s acquisition and 3 s relaxation delay.

¹H{¹⁸³W} HMQC spectra were recorded with a 10 mm, low γ, normal detection broadband probe. The standard HMQC pulse sequence¹⁰ was used, with GARP-1¹¹ modulated ¹⁸³W broadband decoupling during acquisition. A BIRD sequence¹² preceded the HMQC pulses in order to invert the vectors of the spins of the protons attached to ¹⁸³W. A delay of 900 ms followed, during which the spins of the protons not attached to ¹⁸³W were effectively reduced to zero. The 900 ms delay was determined in separate experiments. The HMQC sequence followed immediately afterwards, with the delays optimized for a ¹H-¹⁸³W coupling of 10.5 Hz. Four transients per FID were recorded for a spectral window of 300 Hz in ¹H and 400 Hz in ¹⁸³W. A relaxation delay of 3 s was allowed between each FID. In total 40 FIDs were recorded in States-TPPI¹³ mode. The overall measurement time was approximately 20 min. The final spectrum was of 512 × 512 size, and was presented in the phase-sensitive mode. The ¹⁸³W chemical shifts are referenced to Na₂WO₄, using the Ξ value of 4 166 355.3 Hz, determined in an independent experiment with basic aqueous 1 M Na₂WO₄.

2D EXSY spectra were recorded with the NOESY sequence supplied with the Varian VNMR software, with mixing times ranging from 0.5 to 2 s. Spectra were recorded in the States-TPPI mode with four transients per FID and a total of 32 complex FIDs. The spectrum width was 200 Hz in both dimensions, with 256 points collected for every FID. The final spectrum size was 512 × 512.

The exchange rates were calculated from the volumes of the diagonal and cross-peaks in the 2D spectra, the populations of the species as determined from 1D spectra, and the mixing time using the D2DNMR¹⁴ program. Peak volumes were measured with the ll2d peak picking and analysis subroutines of the VNMR version 5.1A software, supplied by Varian. An average of three measurements were recorded for each complex in every temperature tried.

Spectra at intermediate temperatures were simulated with the DULNMR (dynamic uncoupled line shapes in NMR) program. DULNMR calculates line shapes of exchanging systems without scalar coupling. It produces the same results as the classic coupled Bloch equations but uses the approach that experimental line shape is always the sum of individual transitions.¹⁵ The rate constants at intermediate

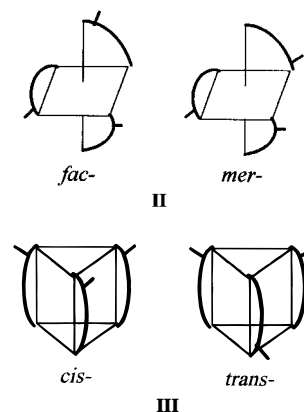
temperatures were estimated from the Arrhenius plots, using the rate constants at lower temperatures.

Extended Hückel MO calculations were performed and Walsh diagrams calculated with the CACAO¹⁶ set of programs. The standard parameters were used for the elements participating in the composition of the complexes. The geometry was that described in published crystal structures,² with the MS₆ core being a perfect prism, each M-S bond length being equal to 2.33 Å and each S-C distance being 1.7 Å. The S-W-S and W-S-C angles were assumed to be 82 and 108°, respectively. The carbons were supposed to be sp². The phenyl ring was rotated by 90° relative to the plane of the dithiolenic ring. Ten intermediate steps for the rotation were calculated, with the diatomic distances being optimized for every step.

Symmetry analysis of the normal modes of vibration was performed with the MOPAC set of programs. The numerical values of the translational vectors were disregarded; only the general direction of the vibration was taken into account.

Results and Discussion

1. Solution Structure of the Complexes. The possible structures for the complexes 1-8 are shown in formulas II and III.



The possible optical isomers of the octahedral geometry are not taken into account as the substituents used here are not optically active. There are no optical isomers for the trigonal prism geometry because both isomers (*cis* and *trans*) possess reflection planes.

The ¹H NMR spectrum of an equilibrium mixture of the complexes should therefore show four peaks for the dithiolenic hydrogen, if the molecule is octahedral or distorted octahedral (one for the *fac*- and three for the *mer* isomer), but only three peaks (one for the *cis* and two for the *trans*), if the trigonal prismatic geometry is retained in solution. Moreover, two peaks should be observed in the ¹⁸³W spectra in both cases, as there are two distinct environments for the tungsten nucleus.

Figure 1a shows the room temperature ¹H NMR spectrum of complex 1, in the dithiolenic hydrogen region. The satellite peaks (*J* = 10.5 Hz) are due to the natural content (14.6%) of ¹⁸³W in the complex. It is these peaks that allow the acquisition of the ¹⁸³W-¹H HMQC spectrum shown in Figure 1b. The spectrum was recorded with a normal, low γ probe, as described in the Experimental Section. The possibility of folded peaks for ¹⁸³W was ruled out in two ways: First, the ¹⁸³W spectral window was moved and/or reduced in size by approximately 100 Hz, and this did not result in a shift of the position of the peak. Second, a ¹⁸³W-decoupled proton spectrum was recorded with continuous wave irradiation of the ¹⁸³W line determined in the 2D spectrum. An indicative result is shown in Figure

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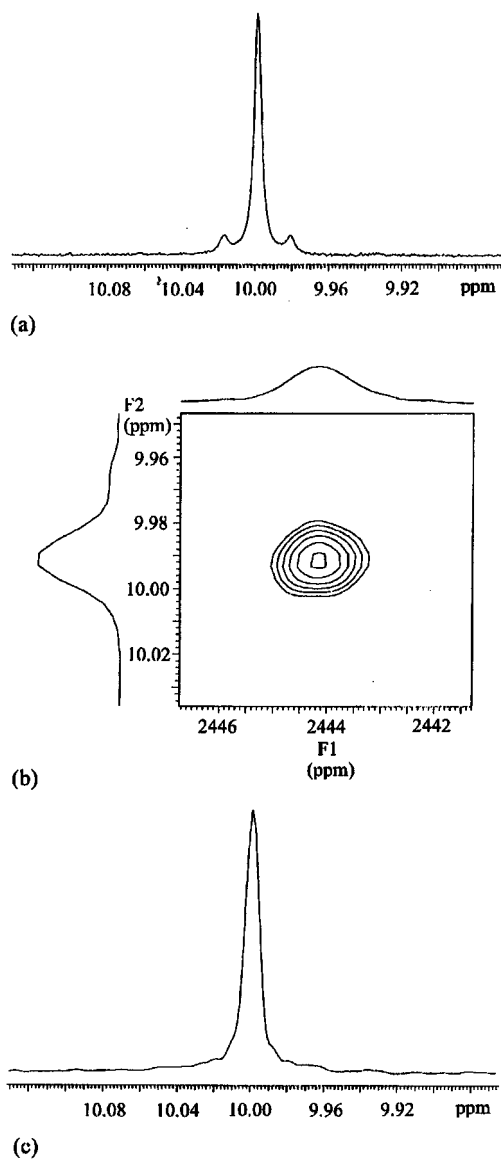


Figure 1. ^1H NMR (a), ^1H - ^{183}W HMQC (b), and CW ^{183}W decoupled spectra of complex **1** in deuterated chloroform at 25 °C at the dithiolenic proton region. The frequency of the ^{183}W decoupling in part c is that determined in part b.

1c, for complex **1**. The disappearance of the ^{183}W satellites confirms the position of the peak. Thus in contrast to our prediction, only one peak is observed for both proton and tungsten. This could be attributed to either limited resolution of the 300 MHz instrument or to a fast exchange between possible sites, leading to magnetic equivalence of the proton and tungsten nuclei. The first case is rather improbable as similar studies for octahedral complexes had been performed previously on 60 and 90 MHz instruments.

To examine the second possibility we cooled the sample below ambient temperature and recorded the spectra again. Figure 2a shows the ^1H NMR spectrum of the same sample at -40 °C, and Figure 2b the $^1\text{H}\{^{183}\text{W}\}$ HMQC at the same temperature. There are now three distinct, well-resolved, narrow peaks in the proton spectrum with an integral ratio of about 1:2:1. For tungsten, two peaks are observed in the HMQC spectrum. The pattern in the proton spectrum is not a triplet; the distance between the middle and the peak on the left is 10.5 Hz, but the distance between the middle and the peak on the right is 11.5 Hz. The ^{183}W satellite peaks are still present in the proton spectra. The two high field peaks of the proton

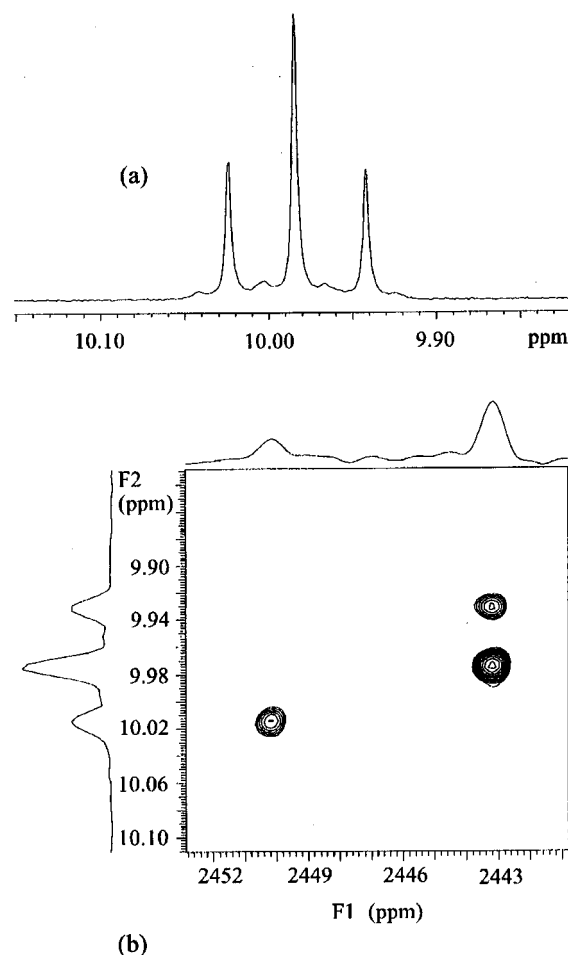


Figure 2. ^1H NMR (a) and the ^1H - ^{183}W HMQC (b) spectra of complex **1** in deuterated chloroform at -40 °C at the dithiolenic proton region.

spectrum correspond to one kind of tungsten, and the third proton peak corresponds to the other tungsten.

These results indicate that the complex is trigonal prismatic in solution and stereochemically nonrigid at room temperature. The two high field proton peaks and the high field tungsten peak are assigned to the *trans* isomer, while the low field ones are assigned to the *cis*. Similar spectra are observed for the rest of the tungsten complexes, **2**–**5**. The spectra remain the same down to -90 °C in acetone, and -120 °C in a mixture of acetone and dibromodifluoromethane.

At this point it must be noted that the octahedral (antiprismatic) *fac*- and the prismatic *cis*-conformers differ from each other only by a rotation of the opposite triangles by 60° , and this is not distinguished by our NMR techniques. The possibility therefore of the coexistence of *fac*-octahedral and *trans*-prismatic isomers¹⁷ cannot be ruled out *a priori*. We believe, however, that it is highly unlikely since the hydrogens and the phenyls do not affect appreciably the bonding scheme of the complexes. The geometry is mainly determined by the six sulfurs and carbons. If the trigonal prismatic geometry is favored for the *trans* isomers, it should also be favored for the *cis*.

Molybdenum complexes show similar proton spectra, but the acquisition of a ^{95}Mo spectrum is difficult, since this is a spin $5/2$ nucleus with a large quadrupole moment, requiring a symmetric (tetrahedral or octahedral) environment for detection; the indirect technique is applied only on spin $1/2$ nuclei. Moreover, the spectra reported¹⁸ show very broad lines (a line

(17) As suggested by one of the reviewers.

width of 2000 Hz is not unusual) which are not informative about the fine structure around the nucleus.

In complex **9** there is no dithiolenic ring proton, and thus the asymmetry is lower; there is difference only after the seventh atom away from the metal. Consequently the splitting is much smaller, approximately 4 Hz. Also, as there is no proton–tungsten coupling, no tungsten spectrum can be recorded.

With the ^{13}C spectra the pattern is similar: the peaks split in three as with protons.

2. The *cis*–*trans* Equilibrium. The previous results indicate that at ambient temperature there is an equilibrium. The two forms are rapidly interchanging. The equilibrium constant for the *cis*–*trans* equilibrium can be calculated from the integrals of the proton spectra. The ratio of the integrals of the two high field peaks divided by the integral of the low field peak yields the equilibrium constant.

A graph of $\ln K$ vs $1/T$ for complex **1** shows that the slope, corresponding to $-\Delta H/R$, is positive in the case of acetone and negative in the case of chloroform. In both cases, the values of the enthalpy are very small, and taking into account that the method has an inherent error of about 0.5 kcal/mol, we may conclude that, within experimental error, there is a zero enthalpy difference between the two isomers. The situation is the same for all the other complexes, with temperature independent equilibrium constants of ca. 2.8–2.9. This is also seen in the UV–vis and the IR spectra of the complexes, where there is no indication of two species. This is not surprising, as in both forms there are exactly the same bonds between the same atoms and the same orbitals. Should there have been a significant difference, this would have been evident in the IR spectrum, as the IR transitions are much faster than the NMR ones; two peaks would have been observed for each vibration, one for the *cis* and the other for the *trans* isomer.

The two isomers differ in entropy, the *trans* isomer is more “irregular”, less symmetric (symmetry point group: C_s) than the *cis* (symmetry point group: C_{3v}). If there are N different ways of arranging a number of molecules in an ensemble, all equally probable, then the molar entropy is equal¹⁹ to $R \ln N$. Taking into account that there are two ways to arrange the ligand to form the *cis* isomer and six to form the *trans*, we end up with an entropy difference of $\Delta S = R \ln 3$. Incorporating the well-known free energy relation, we conclude that K should be equal to 3.

This equilibrium constant does not depend on temperature; in an equilibrium mixture there should always be three times more *trans* molecules than *cis*. The experimental results bear this out.

3. The Mechanism of the Isomerization. Figure 3 shows the 2D-EXSY spectrum of complex **1** in the dithiolenic proton region, recorded at -40°C with a mixing time of 2 s. It can be seen that all protons exchange with each other; the *cis* isomer is being converted to the *trans* and the *trans* isomers are being converted to *cis* and to each other. The rate constants for one of the complexes (complex **1**) calculated from the 2D spectra are given in Table 2. Each entry in this table is an average of three measurements. The protons of the *cis* isomer are labeled as protons 1 (site 1), the two equivalent protons of the *trans* isomer are labeled as protons 2 (site 2) and the lone proton of

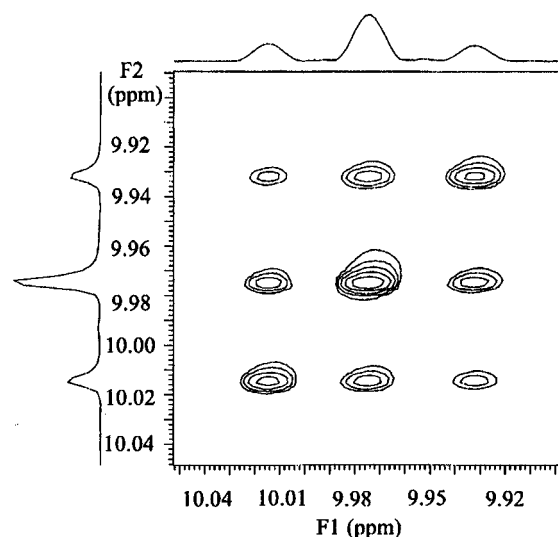


Figure 3. 2D-EXSY spectrum of complex **1** at -40°C in the dithiolenic proton region, with a mixing time of two seconds.

Table 2. Rate Constants^a for the Isomerization of Complex **1** at Various Temperatures and in Two Solvents

	k_{12}^b	$k_{13}^{b,c}$	k_{23}^b	k_{21}^b	$k_{31}^{b,c}$	k_{32}^b
Chloroform						
-30^d	2.714	0.657	1.280	1.433	0.714	2.626
-35	1.354	0.532	0.643	0.720	0.575	1.305
-40	0.604	0.274	0.365	0.325	0.296	0.736
-45	0.372	0.156	0.189	0.196	0.165	0.380
-50	0.165	0.0727	0.0977	0.0851	0.0756	0.197
E_a^e	14.8	12.1	13.7	14.9	12.4	13.78
Acetone						
-35	1.664	0.501	0.974	1.001	0.592	1.913
-37.5	1.342	0.452	0.726	0.764	0.531	1.498
-40	0.901	0.278	0.467	0.514	0.325	0.956
-42.5	0.738	0.236	0.359	0.358	0.271	0.851
-45	0.491	0.154	0.265	0.277	0.178	0.542
E_a^e	13.1	13.0	14.2	14.3	13.3	13.3

^a Calculated with the D2DNMR program.¹³ ^b In s^{-1} . ^c A large error is expected for these rate constants due to large error in the measurement of the peak volume (see text). ^d All temperatures in $^\circ\text{C}$. ^e In kcal/mol, ± 1 kcal/mol.

the *trans* isomer is labeled as proton 3 (site 3). The overall populations of the three kinds of protons are 1:2:1, for sites 1, 2, and 3 (*vide supra*). The rate constant for the conversion of proton 1 to proton 2 is labeled, accordingly, k_{12} . The five other rate constants are labeled similarly.

The activation energies were determined from Arrhenius plots for each rate constant separately. The values of the activation energies for the six rate constants are within experimental error the same: 13.6 ± 1 kcal/mol. All transformations for the same complex require the same activation and within experimental error the activation energies of the various complexes are also the same. The difference between solvents is also insignificant.

The scatter in the values of the rate constants originates from fluctuations of the temperature (0.1 – 0.2°C), from overlaps due to small separation of the peaks (ca. 0.05 ppm), and to propagation and magnification of the error in calculating the inverse matrix. Moreover, the errors for the rate constants k_{13} and k_{31} are expected to be large, because the peaks that correspond to them are the lowest peaks in the spectrum and the measurement of their volume is difficult. Nevertheless, errors are not unusual for kinetic measurements.

The Arrhenius plots can be used to calculate the rate constants at temperatures where the application of the 2D method is not

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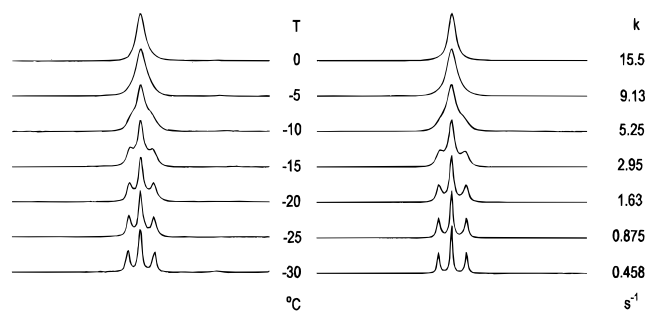


Figure 4. Experimental (left) and computer-simulated (right) spectra of complex **6** in chloroform at various temperatures between the slow and fast exchange limit. The values of the rate constants used were extrapolated from the Arrhenius plots of rate constants at lower temperatures.

possible, e.g. between the slow and fast exchange limit. A comparison of the experimental and calculated line shapes is shown in Figure 4 for complex **6**. This molybdenum complex does not have satellites to the main peaks, and the line shape analysis method is more readily applied. As can be seen the experimental and theoretical line shapes are in agreement.

Regarding kinetic stability, a mixed solution of two complexes (for example a mixture of complexes **1** and **2** or complexes **1** and **8**) does not change in composition with time in the solvents studied; i.e. the UV-vis and NMR spectra remain the same, even after boiling at reflux. This observation bears directly on the mechanism, since it excludes ligand transfer, e.g. through dissociative release to the solution and recombination.

In the case of octahedral complexes several mechanisms for isomerizations have been proposed,⁷ which can be divided to three main categories: associative, dissociative and intramolecular.

Associative mechanisms generally involve the coordination of a solvent molecule, thus increasing the coordination number of the metal atom, leading to a seven-coordinate transition state. The isomerization rate depends strongly on the solvent. The results summarised in Table 2 together with the results obtained for all the other complexes show that in our case the isomerization rate and the activation energies are rather insensitive to the solvent used, for two quite different, noncoordinating solvents. An associative path seems therefore unlikely.

Dissociative mechanisms involve bond breaking and formation of a five-coordinate intermediate with a dangling ligand or a four-coordinate intermediate, with only two chelate ligands. Usually the free positions are occupied again by solvent molecules, but this is not necessary, and the intermediate may rearrange to form the other isomer after recoordination of the dissociated part. In our case, a dissociative path cannot be totally ruled out, but there are several objections. The NMR data imply that a dissociation, if any, would give only small steady state amounts of four- or five-coordinate species. This is because the strong ¹H-¹⁸³W coupling, indicative of the existence of a bond, persists even at room temperature, the integral ratio of the satellite peaks over the main peak is 14.4%, and there is no evidence for ligand exchange or free or dangling ligands in the spectrum. The lack of mixing between complexes is also an argument against a dissociative mechanism, at least of a complete ligand dissociation one, in the solvents used. The fact that there is no solvent dependence, combined with the fact that the activation energies are low and the rates high, makes it unlikely that the strong metal-to-ligand bonds break. Moreover there is also the penalty for disturbing the delocalized aromatic system of the molecule. In short, the dissociative path is also unlikely.

Intramolecular mechanisms of interconversion in octahedral isomers involve the rotation of ligands around the bonds to the metal. The trigonal twist of the octahedron, i.e. the 120° rotation of three ligands around a C₃ axis through a trigonal prismatic intermediate, has no physical meaning for the prism, as the prism itself cannot be twisted more than 60° around the C₃ axis without bond stretching and breaking.

All the other twisting mechanisms proposed for the isomerization of octahedral complexes involve the rotation of at least two ligands, again through trigonal prismatic intermediates. During these processes the distance between the ligand atoms remains large, and the enhanced interligand repulsion in the intermediate is overcome by increasing the temperature. In our case, however, such a double rotation path is considered improbable for energetic reasons.

The published crystal structures² of the tris(dithiolenes) show that the distance between sulfur atoms of the same and neighbouring rings are approximately the same, i.e. 3.05 Å. Therefore, the trigonal prism formed has three nearly square faces. The rotation of only one ligand around the axis defined by the metal atom and the center of the carbon-carbon bond on the dithiolenic ring, involves an intermediate at $\theta = 90^\circ$ in which sulfur atoms are at long distances from each other as shown in Figure 5. This intermediate is actually a trigonal prism as well, and further rotation by 90° gives the interchanged product. The mechanism reminds us of a common rotary electric switch.

In contrast to the rotation mechanisms proposed for octahedral complexes, the middle stage here is a stage without enhanced repulsions. It is probably this characteristic that makes the tris-dithiolenic complexes stereochemically nonrigid at ambient temperature.

The rate constants are interpreted as the probability that a proton of a certain kind (site) will be transformed into a proton of another kind (site). All dithiolenic rings have equal probability to rotate, independently of whether or not they contain protons of different kinds (sites 1, 2 or 3). If a ring containing a proton 1 rotates, two protons of type 2 and simultaneously one proton of type 3 are generated. The probability therefore for the 1-to-2 transformation is double of that for the 1-to-3 transformation, so $k_{12} = 2k_{13}$. The rotation of a ring containing a proton of type 3 involves the transformation of one proton 3 to proton 1 and indirectly but simultaneously the transformation of two site 2 protons into two site 1 protons. The probabilities per proton for the 3-to-1 and 2-to-1 transformations are equal, $k_{31} = k_{21}$. Finally, the rotation of a ring with a site 2 proton involves the transformations of 2-to-3, and 3-to-2, the second occurring twice as fast as the first, because for every site 3 proton two site 2 protons are created. Therefore, $k_{32} = 2k_{23}$.

In conclusion, since all rotations are equally probable, the relations between the rate constants can be combined and thus we obtain

$$k_{13}:k_{21}:k_{31}:k_{23}:k_{12}:k_{32} = 1:1:1:1:2:2$$

This is the ratio obtained experimentally (Table 2) and assumed for the line shape analysis.

4. Theoretical Considerations. In trying to elucidate the isomerization further, we performed extended Hückel calculations for the above "rotary switch" mechanism. The energy level diagram produced for the rotation of one ligand of complex **3** around the metal to the center of the carbon-carbon bond axis shows no energy level crossing. This means that the process is allowed by symmetry rules and can take place thermally, without photochemical activation. There is clearly a lowering of energy at $\theta = 90^\circ$ due to the increased distances

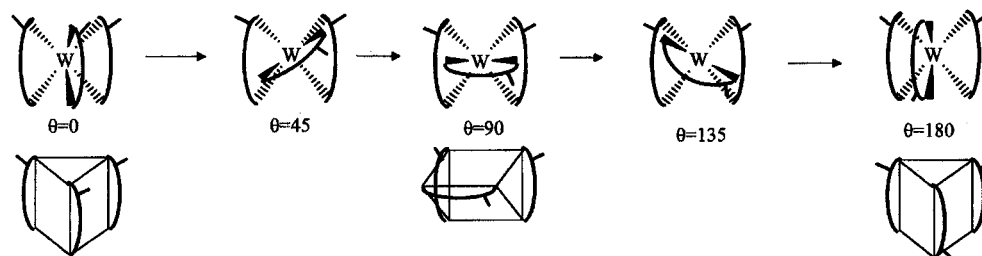


Figure 5. Proposed mechanism for the isomerization. The rotation of one only ligand has no steric hindrance, and the intermediate is also a trigonal prism. The movement reminds us of a rotary electric switch.

between the ligand atoms at the intermediate trigonal prism, comprising a local energy minimum for the process. We were unable, however, to detect the intermediate corresponding to this minimum. The two local maxima appear at 45° and probably result from the interligand repulsions during the rotation. The occupied orbitals contributing to the total energy are of ligand character, with strong in-plane components.³ The overall energy difference, is calculated to be 0.79 eV, corresponding to 18 kcal/mol, in fairly good agreement with the experimentally measured value of the activation energy. Thus, theory supports the “rotary switch” mechanism.

Finally, we performed a symmetry analysis of the normal modes of vibration of the molecule. Out of the 51 normal vibrational modes for the complex with $R_1 = R_2 = H$, the one with symmetry A_1'' represents a movement toward the postulated rotation, which leads to the isomerization.

Conclusions

NMR data prove that the tris(1,2-dithiolenes) studied are trigonal prismatic in solution and stereochemically nonrigid at room temperature. The *trans* isomer is favored for entropy reasons; an equilibrium mixture contains three times more *trans* isomer than *cis*. The isomerization proceeds most probably by

an intramolecular rotation of one ligand around the metal center of the carbon–carbon double bond axis. The energy required for this process is found to be small and agrees with the theoretically calculated activation energy. The process is symmetry allowed, as indicated by EHMO calculations and corresponds to one of the normal vibrational modes of the molecule.

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Supporting Information Available: Figure S-1 showing the low temperature ^1H spectrum of complex **9**, Figure S-2 showing the $\ln K$ vs $1/T$ graph for Complex **1**, Table S-3 showing the activation energies calculated for the rest of the complexes, Figure S-4 showing the Walsh diagram for the ligand rotation, and Figure S-5 showing the vibration which could start the isomerization (4 pages). Ordering information is given on any current masthead page.

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