Analysis of Stereochemical Nonrigidity in Five-Coordinate Cyclopentadienylmetal Complexes by the Structure Correlation Method

Jeremy M. Smith and Neil J. Coville*

Centre for Applied Chemistry and Chemical Technology, Chemistry Department, University of the Witwatersrand, Private Bag 3, PO Wits 2050, Johannesburg, South Africa

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The intramolecular *cis/trans* isomerization mechanism of solid-state *pseudo*-five-coordinate complexes of the type $CpML_4$ was examined by the structure correlation technique, and the data revealed that the mechanism most likely proceeds via a combined Berry−turnstile mechanism.

Introduction

The mechanism of stereochemical nonrigidity of five-coordinate σ-bonded complexes, such as ML_5[1] (M = transition metal, L = σ donor ligand), has been comprehensively studied. In addition to other evidence,[2] studies using the structure correlation methodology[3] indicate that the dominant mechanism of fluxionality in solution is the Berry pseudorotation.[4] The mechanism for this process is shown in Scheme 1.

A ubiquitous series of complexes of the type ML_5 are the $CpML_4$ (Cp = substituted and unsubstituted cyclopentadiene) complexes. Since the discovery of the *cis* and *trans* isomers of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(P(NMe_2)_3)I]$ (Figure 1),[5] *cis/trans* isomerization of the *pseudo*-five-coordinate complexes $[(\eta^5\text{-}C_5H_5)M(CO)_2(L)(R)]$ has been extensively studied.[6,7] All experimental evidence accumulated indicates that the isomerization follows an intramolecular pathway.[6] It has been proposed that the mechanism involves a series of Berry-type pseudorotations[4,8] similar to that of the ML_5 complexes shown in Scheme 1. However, in this instance the ground-state structure of $CpML_4$ complexes is generally square pyramidal and the pseudorotation proceeds via a trigonal bipyramidal intermediate[6] as shown in Scheme 2. However, only a limited amount of indirect evidence in support of this proposal has been found.[7,9]

Our interest in the isomerization mechanism for complexes of the type $[(\eta^5\text{-}C_5H_5)M(CO)_2(L)(R)]$ has been fueled by the discovery of solid-state *cis/trans* (*lat/diag*) isomerization reactions in our laboratories.[10] In particular, the observation of the solid-state *trans* → *cis* reaction of $[(\eta^5\text{-}C_5H_4Me)Re(CO)_2Br_2]$ at *ca.* 110 °C suggests that a facile pathway must be available for the interconversion process. In this publication, we present a structure correlation study of five-coordinate cyclopentadienyl complexes in order to ascertain whether the mechanism of the intramolecular isomerization can be established by this procedure. An important difference, when compared to the analysis of other ML_5 complexes, is the presence of the η^5-bonded cyclopentadienyl ligand. This ligand introduces both different steric and electronic constraints to the problem.

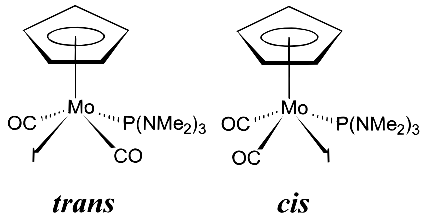
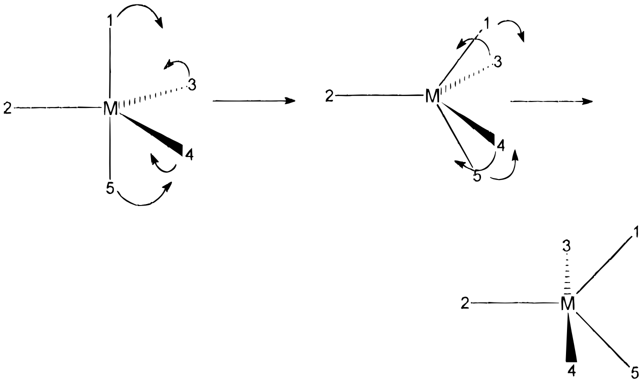


Figure 1. *Cis* and *trans* isomers of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2\text{-}(P(NMe_2)_3)I]$.

Scheme 1. Berry Pseudorotation Mechanism for ML_5 Complexes



Results and Discussion

Previous studies of ML_5 complexes[1] have found that an examination of certain bonding angles (e.g. θ_{CP3} in Figure 2) as a function of the *trans*-basal dihedral angle

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* To whom correspondence should be addressed.

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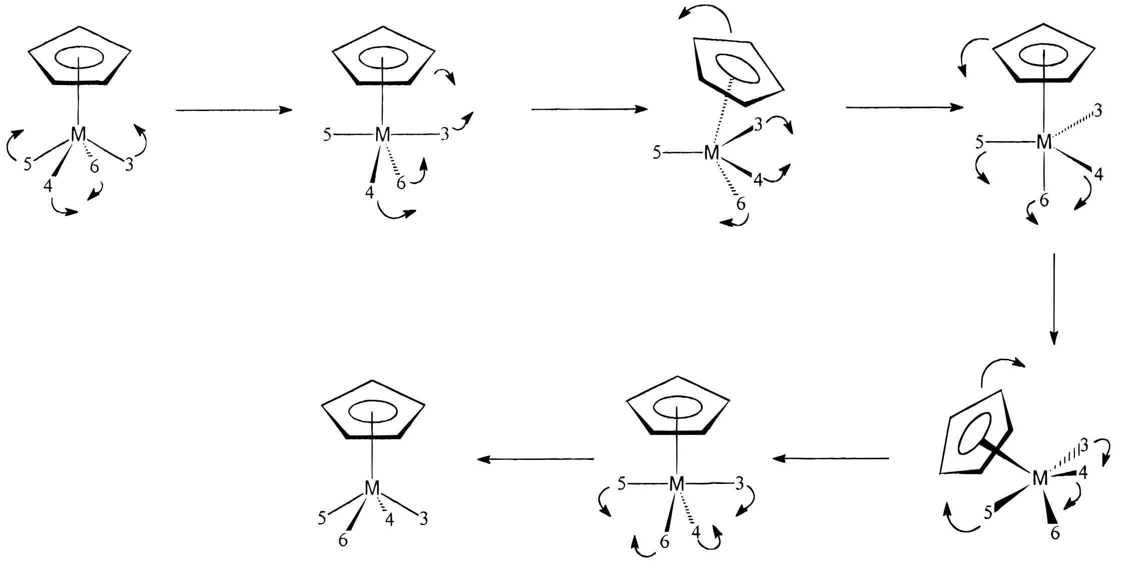
Scheme 2. Berry Pseudorotation Mechanism for $CpML_4$ Complexes



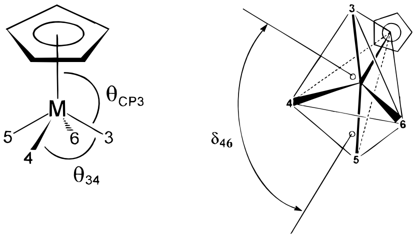


Figure 2. Atom and angle labeling scheme used in this publication.

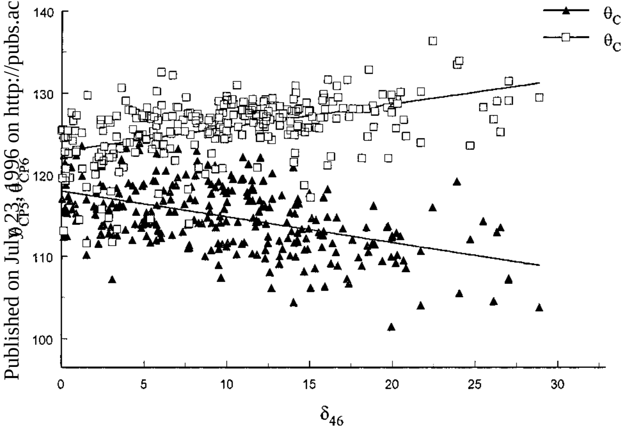


Figure 3. Plot of the angles from the cyclopentadienyl ring, θ_{CP3} and θ_{CP4}, as a function of the *trans* basal dihedral angle, δ_{46}.

(δ_{46} in Figure 2) provides a reliable method of mapping the intramolecular reaction coordinate from the trigonal-bipyramidal to square-pyramidal structure. As the dihedral angle δ_{46} opens from 0° in a square-pyramidal complex to 53.1° in a perfectly trigonal-bipyramidal structure, there should be concomitant opening and closing of the θ_{CP6} (or θ_{CP4}) and θ_{CP5} (or θ_{CP3}) angles, respectively.[1]

A plot of the equivalent angles from the cyclopentadienyl ring, θ_{CP5} (or θ_{CP3}) and θ_{CP6} (or θ_{CP4}), as a function of δ_{46} (Figure 3) reveals a facile reaction coordinate connecting the square-pyramidal and trigonal-bipyramidal structures. The plot implies that an isomerization mechanism via a Berry pathway requires a trigonal-bipyramidal structure having the cyclopentadienyl ligand in an *equatorial* position. Note that one further Berry pseudorotation is required to reach a trigonal bipyramidal structure where the cyclopentadienyl ligand occupies an *axial* position, as in the proposed mechanism (see Scheme 2).

Table 1. Idealized Bond Angles (deg) for the Square-Pyramidal (SP) and Trigonal-Bipyramidal (TBP) Structures of $CpML_4$ Complexes

struct	θ_{CP3}	θ_{CP4}	θ_{CP5}	θ_{CP6}	θ_{34}	θ_{35}	θ_{36}	θ_{45}	θ_{46}	θ_{56}
SP	120	120	120	120	75.6	120	75.6	75.6	120	75.6
TBP	108	130	108	130	78.5	144	78.5	78.5	100	78.5

From the graphs, an idealized square-pyramid structure with θ_{CPL} angles of about 120° and *trans* basal angles also of about 120° are predicted. This is in contrast to the usual *trans* basal angle of about 140–174° found for the PL_5 and ML_5[1] structures. This is due to the fact that one of the reference points is not occupied by a single atom but rather by a plane of atoms, the cyclopentadienyl ring, which itself may also have substituents. Thus the size of the *trans* basal angle is sterically limited. In addition, the trigonal-bipyramidal structure is also predicted not to have LML angles of 90 and 120° due to the bulkiness of the cyclopentadienyl ring. The angles of the idealized structures predicted from these graphs are listed in Table 1.

Another point of note is that there is some variability in the geometry of the "ideal" square-pyramidal structure. This is highlighted by an examination of five structures (Table 2) which have a near-perfect square-pyramidal geometry. The structures of $[(\eta^5\text{-}C_5H_4\text{-}COMe)V(CO)_4]$,[11] *trans*-$[(\eta^5\text{-}C_5Me_5)Cr(CO)_2(P(OMe)_3)_2]^+[BF_4]^-$,[12] $[(\eta^5\text{-}C_5H_4{}^iPr)WCl_4]$,[13] $[(\eta^5\text{-}C_5Me_5)TaCl_2Me_2]$,[14] and $[PhMe_3N][(\eta^5\text{-}C_5Me_5)MoI_4]$[15] all have their θ_{CPL} angles within 2°. However, the variation in these angles

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Table 2. Selected Angles (deg) and Distances (Å) for Square-Pyramidal $CpML_4$ Complexes

struct	θ_{CP3}	θ_{CP4}	θ_{CP5}	θ_{CP6}	δ_{46}	χ_2	χ_3	d_{M-CP}	d_{M3}	d_{M4}	d_{M5}	d_{M6}	ref
$[(\eta^5\text{-}C_5H_4COMe)V(CO)_4]$	118.8	118.5	119.4	120.2	0.27	0.53	30.31	1.920	1.955	1.949	1.935	1.933	11
$[(\eta^5\text{-}C_5Me_5)Cr(CO)_2(P(OMe)_3)_2]^+[BF_4]^-$	117.4	117.4	118.4	119.4	10.13	0.13	21.84	1.856	1.848	2.287	1.853	2.292	12
$[(\eta^5\text{-}C_5H_4{}^iPr)WCl_4]$	110.2	111.2	110.5	111.6	1.52	9.70	40.17	1.994	2.234	2.347	2.339	2.339	13
$[(\eta^5\text{-}C_5Me_5)TaCl_2Me_2]$	113.2	113.2	115.1	115.1	0.00	8.84	38.72	2.075	2.364	2.364	2.387	2.387	14
$[PhMe_3N][(\eta^5\text{-}C_5Me_5)MoI_4]$	112.4	112.1	112.8	113.1	0.14	19.84	38.72	2.021	2.817	2.784	2.802	2.814	15

among the structures is apparent. It is to be noted that there is some degree of "softness" in the geometries of these complexes, which depends on the metal and its electronic structure,[16] the σ- and π-bonding characteristics of the L ligands,[16] and the steric requirements of the cyclopentadienyl ligand. Also worthy of note is the comparatively large δ_{46} angle of *trans*-$[(\eta^5\text{-}C_5Me_5)Cr(CO)_2(P(OMe)_3)_2]^+[BF_4]^-$ (see below).

The results of the correlation of Figure 3 only give information on the first step of the proposed mechanism.[6,8] It requires two more Berry rotations to reach a trigonal-bipyramidal intermediate where the cyclopentadienyl ligand occupies an axial position, and a further two to lead to isomerization of the ligand set (see Scheme 2). It is to be appreciated that this isomerization mechanism requires movement of a bulky cyclopentadienyl group in addition to the other four ligands, an issue not addressed by Faller.[6] We have attempted to map this isomerization pathway by a plot of the absolute differences in bond angles between the observed structure and square-pyramidal structure ($\Sigma|\theta_i - \theta_{i,SP}|$) against the absolute differences in bond angles between the observed structure and trigonal-bipyramidal structure with the cyclopentadienyl ligand in an axial position ($\Sigma|\theta_i - \theta_{i,TBP}|$), but this was not successful.

One possibility is that isomerization may occur via a turnstile rotation[17] from a *pseudo*-trigonal-bipyramidal intermediate. To differentiate between a purely Berry and a combination Berry–turnstile mechanism, the angles of deviation of the local 2- (χ_2) and 3-fold (χ_3) axes of rotation from collinearity with the vectors from the midpoints of their respective planes to the metal as a function of δ_{46} were examined.[18] In this study, the χ_2 angle is defined as the angle between the perpendicular bisector of the CP-3 (or CP-5) vector which passes through the metal and the line from the midpoint of the CP-3 (or CP-5) vector to the metal. The angle χ_3 is defined as the angle between the normal to the plane through atoms 4,5,6 (or 3,4,6) and the vector from the metal to the midpoint of this plane (Figure 4).

The general trend from the plots χ_2 and χ_3 as a function of δ_{46} is that, as the structure distorts from the square-pyramidal toward the trigonal bipyramidal structure, χ_3 tends toward 0° and that χ_2 remains fairly constant and close to 0° (Figure 5). A similar trend is observed from the data for the other two χ angles (see Figure 4). Although the data are not conclusive (χ_3 does not reach 0°), it is suggestive of three of the ligands orienting around a local 3-fold axis of rotation in anticipation of a turnstile rotation.

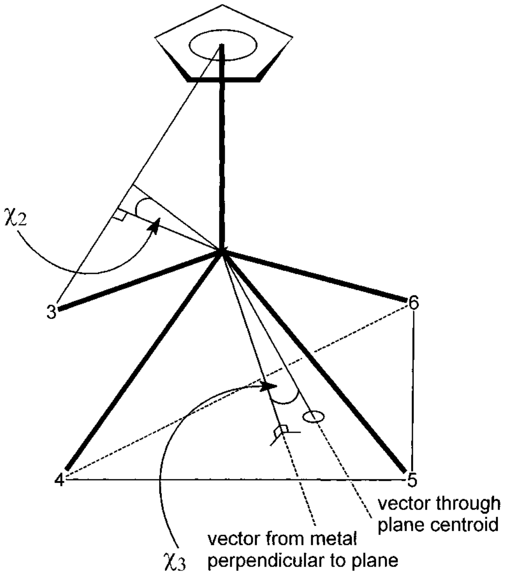

Figure 4. Definition of the angles of distortion from the local 2- and 3-fold axes of rotation, χ_2 and χ_3. Note that two other such angles, χ_2' and χ_3', exist.

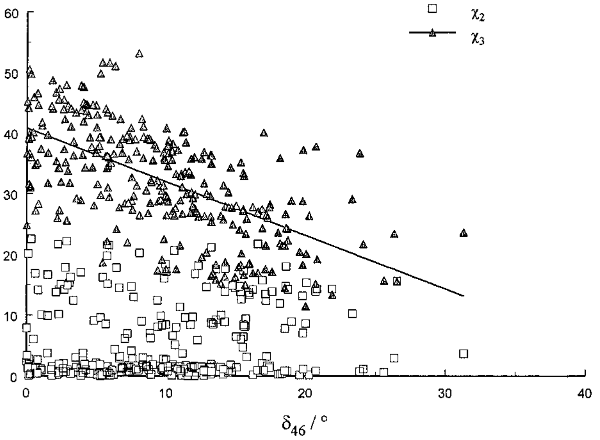

Figure 5. Plot of the angles of distortion from the local 2- and 3-fold axes of rotation, χ_2 and χ_3, as a function of the *trans* basal dihedral angle, δ_{46}.

By a combination of the above results, the mechanism of isomerization could involve a combined Berry–turnstile mechanism, where bending about the M–L bonds will occur toward a distorted trigonal-bipyramidal structure followed by a 60° rotation about the local 3-fold axis to complete the isomerization (Scheme 3). This pathway is considerably shorter than the alternative[4,8] of a series of six Berry rotations. In addition, only three of the L groups undergo substantial movement, and the cyclopentadienyl ring does not need to move at all. The purely Berry pathway requires movement of all the ligands, including the cyclopentadienyl ring. Although it has been suggested that the trigonal-bipyramidal geometry lies in a minimum of higher energy than the square-pyramidal structure for $CpML_4$ complexes,[8] no study into the relative energy barriers to a purely Berry rotation between these two structures has been made. It is to be noted, however, that a trigonal-bipyramidal

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Scheme 3. Combined Berry−Turnstile Isomerization Mechanism for $CpML_4$ Complexes

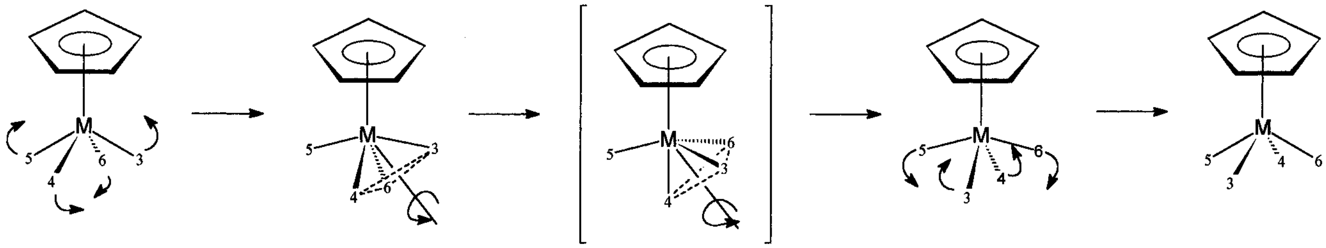

Table 3. Selected Angles (deg) and Bond Lengths (Å) for Complexes with δ_{46} Close to 0°

struct	θ_{CP3}	θ_{CP4}	θ_{CP5}	θ_{CP6}	δ_{46}	χ_2	χ_3	d_{M-CP}	d_{M3}	d_{M4}	d_{M5}	d_{M6}	ref
$[(\eta^5\text{-}C_5H_4Me)Cr(CO)_3]_2$	116.5	124.0	115.3	124.7	0.31	0.28	49.73	1.841	3.247	1.863	1.833	1.859	21
$[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_3T_a$	120.3	124.4	116.4	125.4	0.78	0.41	46.56	1.991	2.938	2.008	1.978	1.968	22
$[(\eta^5\text{-}C_5H_4COMe)V(CO)_4]$	119.4	118.6	118.6	120.2	0.27	1.19	30.96	1.920	1.935	1.949	1.955	1.933	11
$[(\eta^5\text{-}C_5H_5)Mn(CO)_2\{(\eta^5\text{-}C_5H_5)Mn(CO)_2SbCl_2\}]$	112.3	122.5	112.5	125.4	0.36	22.51	39.33	1.787	2.642	1.754	2.598	1.796	23
$[PhMe_3N][(\eta^5\text{-}C_5Me_5)MoI_4]$	112.8	112.1	112.4	113.1	0.14	20.09	39.07	2.021	2.802	2.784	2.817	2.814	15

geometry is known for at least two $CpML_4$ complexes.[9,19] This does not necessarily contradict our predicted mechanism, as a 30° rotation about the 3-fold axis would result in a trigonal-bipyramidal structure where the cyclopentadienyl ligand occupies a near-axial position (see Scheme 3). However, the trigonal-bipyramidal geometry of $[(C_5Me_5)WMe_4][PF_6]$[8] is not presently accounted for by electronic arguments.[16]

Analysis of Data Scattering. With at least one exception,[20] previous structure correlation studies of ML_5 complexes have been notable for the minimal scattering of data points. However, in this study, considerable scattering of data points in Figures 3 and 5 is observed. Here we attempt to analyze the reasons for the scatter.

Table 3 lists some complexes for which the basal dihedral angle, δ_{46}, is close to 0°. In principle, these complexes should have geometries with minimal distortion from square pyramidal.[1] However, these complexes are not all of the same geometry, as shown by the variation in the θ angles tabulated. Two of the complexes, $[(\eta^5\text{-}C_5H_4COMe)V(CO)_4]$[12] and $[PhMe_3N][(\eta^5\text{-}C_5Me_5)MoI_4]$,[15] are close to square-pyramidal geometry. However, the other complexes $[(\eta^5\text{-}C_5H_4Me)Cr(CO)_3]_2$,[21] $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_3Ta$,[22] and $[(\eta^5\text{-}C_5H_5)Mn(CO)_2\{(\eta^5\text{-}C_5H_5)Mn(CO)_2SbCl_2\}]$[23] show an appreciable distortion along the Berry pathway. The reason for the very small δ_{46} angle is that at least one of the metal−ligand bonds is significantly longer than the others, which results in a "distorted" dihedral angle measurement. This problem cannot be solved using the present CSD software. In addition, two of the complexes show "nonuniform" distortion (i.e. θ_{CP4} vs θ_{CP6}) along the Berry pathway. This once again highlights the "softness" in the structure of these complexes.[16]

Implications for Solid-State Isomerization. We have found that the complex $[(\eta^5\text{-}C_5H_4Me)Re(CO)_2Br_2]$ undergoes solid-state isomerization from the *trans* (*diag*) to the *cis* (*lat*) isomer in the solid state but not in the reverse direction.[10] Using the crystal structure data of these isomers,[24] we have plotted the relevant data on the graph of the absolute differences in bond angles[1] between the observed structure and theoretical square-pyramidal and trigonal-bipyramidal structures using the structural data in Table 1 (Figure 6, highlighted). This plot maps the transition from the square-pyramidal geometry to the trigonal-bipyramidal structure with the cyclopentadienyl ligand in an equatorial position. The *trans* isomer lies toward the trigonal bipyramidal end of the plot, and it thus appears that, in the solid state, the *trans* isomer is "primed" for isomerization. The *cis* complex lies toward the square-pyramidal side and would therefore need to undergo substantial bending motion before being able to isomerize. While appreciating that ligand σ- and π-characteristics will influence the *direction* of the distortion away from square pyramidal,[16] intermolecular forces can be the determining factor as to the *extent* of the distortion and as to whether isomerization will indeed occur.[24]

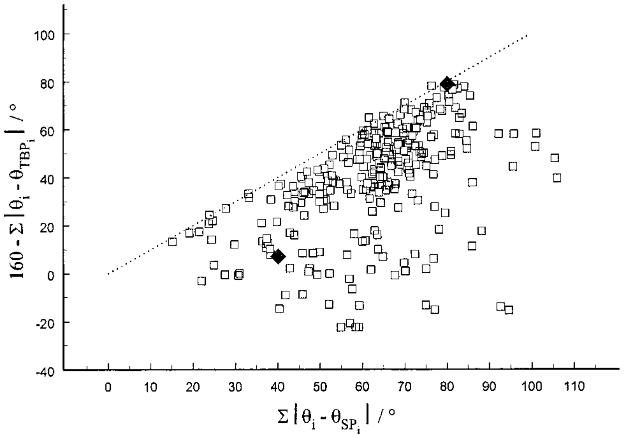

Figure 6. Plot of the absolute differences in bond angles from the idealized square-pyramidal and trigonal-bipyramidal structures in Table 1. The data points for the *cis (lat)* and *trans (diag)* $[(\eta^5\text{-}C_5H_4Me)Re(CO)_2Br_2]$ complexes are highlighted.

In recent work[10] we have found that the complex $[(\eta^5\text{-}C_5H_4Me)Re(CO)(P(OPh)_3)Br_2]$ also undergoes a solid-state isomerization reaction. In this case, a combination Berry−turnstile mechanism would account nicely for

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this observation, as both the cyclopentadienyl and phosphite ligands would require minimal movement for isomerization to occur. Determination of the crystal structure of this and other complexes should add weight to our proposed mechanism.

Experimental Section

All crystallographic data used were retrieved from crystal structures within the Cambridge Structural Database (CSD version 5.9 containing 146 272 structures). The main criterion used in the search was to analyze all structures in which a *pseudo*-five-coordinate metal atom was bonded to a cyclopentadienyl ligand. Only complexes with the metal in a nonchelating-type environment were considered, which had the effect of excluding cluster complexes and those complexes where moieties such as bridging carbonyls were bonded to the metal atom of interest. In addition, the search was restricted to complexes for which atomic coordinates were available, which were error-free, were nonpolymeric, and had an *R*-factor of less than 10% with no reported disorder. Complexes which contained substituted cyclopentadienyl rings were also included in the study. An initial search of five-coordinate cyclopentadienylmetal complexes revealed a total of 356 structures fitting the above criteria. In an initial analysis, many complexes containing allylic ligands were found to distort the geometry around the metal significantly, by dramatically reducing the sizes of LML angles, and thus these structures were excluded from the full analysis. Complexes that had chelating rings involving the cyclopentadienyl ring (not defined as such by the CSD) causing distortion of the geometry around the metal by reducing one of the CpML angles were manually eliminated.

All bond angles and dihedral angles around the metal atom were calculated and retrieved during the search. Angles involving the cyclopentadienyl ligand were measured from a calculated ring centroid. In order to retrieve the angles in accordance with the defined numbering scheme (Figure 2), the search program was used to sort certain key angles. This had the effect of sorting all the angles correctly and gave 271 hits, with a total of 296 data points for every parameter. As it was impossible to verify if the correct or complementary basal dihedral angle, δ_{46}, was retrieved, this angle was normalized by the relationship $\delta_{46} = \arcsin(\sin(\delta_{46}))$. A similar transformation was applied to the angle of distortion from the 3-fold axis of rotation, χ_3.

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