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Solid-State Reaction Study of the Trans-to-cis Isomerization of (η^5-C_5H_4Me)Re(CO)[P(OPh)$_3$]Br$_2$: A New Mechanism for the Isomerization Reaction

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Abstract: Single-crystal X-ray structures have been determined at intermediate stages in the single-crystal to single-crystal trans-to-cis thermal isomerization of (η^5-C_5H_4Me)Re(CO)[P(OPh)$_3$]Br$_2$ at 150 °C. Unit cell parameters and site occupancy factors linked to the induced disorder were monitored and found to follow first-order kinetics in the initial (fast component) stage of the reaction. A rate constant of 30×10^{-6} s^{-1} (0.11 h^{-1}) was obtained to first-order approximation for the reaction. The irreversibility of the isomerization from single crystals of the cis form was also confirmed. Fourier and difference Fourier maps suggest a novel 2-fold rotation mechanism for the trans-to-cis isomerization reaction. This mechanism entails a unidirectional anticlockwise movement of the CO ligand and only one Br atom.

Introduction

The influence of intermolecular forces on the course of a chemical reaction is well recognized. For example, the role of a solvent in influencing the rate or the direction of a chemical reaction in the homogeneous liquid phase has been well studied.[1] Chemical reactions in the solid state provide an extreme case for evaluating the effect of intermolecular forces on a reaction and their influence on a reaction mechanism.[2] In this instance the medium surrounding a molecule (i.e., other identical molecules) provides a rigid, encapsulating environment, the reaction cavity,[3] that can influence the reaction direction. Thus, reactions in the solid state will occur in such a way as to require minimum energy and reactant motion to produce new products. This is a restatement of the topochemical principle (Schmidt and Cohen in ref 4), and the outcome of the principle is that the kinetic rather than the thermodynamic reaction product may be produced.[5] This could of course lead to selective reactions[4,6] since the range of intermediates or transition-state structures available in a confined environment will be limited.

In most instances the onset of a chemical reaction in the solid state leads to movement (rotation, translation) of the whole or part of a molecule with consequent breakdown of the original 3-D order within the original material. This limits the amount of information that can be gleaned and that will permit evaluation of the reaction mechanism within the solid state. There are, however, a limited number of examples of both inorganic[5,7] and organic[4,8] compounds that have been reported in the literature in which solid-state reactions occur without loss of 3-D order, i.e., are single-crystal to single-crystal reactions. This type of reaction permits a study of the reactant to product transformation by techniques used in X-ray and neutron crystallography. Specific examples of inorganic complexes that have shown this capability include the X-ray or photoinduced racemization of cobaloximes,[3,4,9] the thermal dimerization of cyclopentadienyl(*o*-dithiobenzene)cobalt,[10] and the X-ray-, thermal-, and pressure-induced ONO to NO$_2$ linkage isomerization reaction of a series of cobalt complexes.[11]

Recently we have reported on a range of model organometallic complexes of the type (C_5H_4R)ML$_a$X$_b$ (R = Me, Et, ^{i}Pr, ^{t}Bu etc.; M = Re, W, Mo; L = CO, PR$_3$, P(OR)$_3$; X = Br, I) that undergo trans−cis (diag−lat) isomerization in the solid state.[12−14] During the course of these studies we noted that crystals of one member of this series, namely, (η^5-C_5H_4Me)Re(CO)[P(OPh)$_3$]Br$_2$,[14b,15] underwent isomerization in the solid

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Table 1. Crystal Data in $P2_1/c$ for Isomerization of *trans*-(η^5-C_5H_4Me)Re(CO)[P(OPh)$_3$]Br_2 at 150 ± 3 °C[a]

	1 (0 h)	**2** (5.5 h)	**3** (16.5 h)	**4** (50 h)	**5**(100 h)	**6** (150 h)
a/Å	15.8276(7)	15.879(1)	15.9146(9)	15.9260(7)	15.9327(7)	15.923(1)
b/Å	11.1175(5)	11.038(1)	10.9593(6)	10.9451(5)	10.9365(4)	10.9201(8)
c/Å	14.1583(6)	14.198(1)	14.2244(8)	14.2315(6)	14.2369(6)	14.229(1)
β/deg	93.660(1)	94.098(2)	94.403(1)	94.429(1)	94.450(1)	94.463(2)
V/Å^3	2486.2(2)	2482.3(4)	2473.6(2)	2473.3(2)	2473.2(2)	2466.6(3)
$R1$ (all data)	0.0385	0.0644	0.0531	0.0482	0.0460	0.0972
w$R2$ (all data)	0.0962	0.1991	0.1513	0.1255	0.1321	0.0831
sof[b] (CO−Br)	0.0149	0.3656	0.6385	0.7370	0.7740	0.7967

[a] Crystal size 0.40 × 0.28 × 0.14 mm^3. [b] Site occupancy factor.

state without cracking or other serious crystal deterioration. Herein we show that the trans-to-cis isomerization of (η^5-C_5H_4-Me)Re(CO)[P(OPh)$_3$]Br_2 does proceed with retention of crystallinity and we describe our detailed studies of this material in which the reaction was monitored as a function of time by X-ray crystallography. The study permits an evaluation of the mechanism for the trans−cis isomerization reaction, and our results suggest that the reaction occurs by a mechanism quite different from that proposed for the equivalent solution-state reactions.[16]

Experimental Section

A cell for thermally reacting single crystals in an inert environment for X-ray diffraction studies was designed and built. Samples were reacted in a stream of heated nitrogen gas within an enclosed glass cell. The glass cell was placed under a polarizing microscope, equipped with a CCD camera, for observing crystals during reaction. A standard PID (proportional integral derivative) controller with matching thermocouple was used for controlling temperature and reaction time. The cell was calibrated against known melting points of organic compounds, namely, acetanilide (115 °C), phenacetin (135 °C), and benzanilide (163 °C), as used for calibrating a microscope melting point apparatus. Samples of these compounds were glued to glass fibers in a manner similar to mounting crystals for X-ray analysis. The samples were then heated to their melting points inside the cell and the position of the thermocouple was adjusted to obtain a temperature measurement within ±3 °C of their respective melting points.

A single crystal of *trans*-(η^5-C_5H_4Me)Re(CO)[P(OPh)$_3$]Br_2 with dimensions 0.40 × 0.28 × 0.14 mm^3 was selected and mounted in the standard way. A hemisphere of intensity data was collected at room temperature with redundancy on a Bruker SMART 1K CCD (charged-coupled device) area detector diffractometer with graphite-monochromated Mo Kα radiation (50 kV, 30 mA). The collection method involved 0.3° scans in ω. The crystal was then removed from the goniometer head and reacted in the heating cell and under the microscope. Subsequent X-ray data sets were collected between heating stages.

All reactions were performed at 150 ± 3 °C with a 10 min ramp to and decline from this temperature. Full hemispheres of data were collected for total reaction times of 0, 5.5, 16.5, 50, 100, and 150 h.

The possibility of reversible cis-to-trans isomerization, starting from a single crystal of *cis*-(η^5-C_5H_4Me)Re(CO)[P(OPh)$_3$]Br_2, was also investigated. A full hemisphere of data was collected on a crystal of the cis isomer with dimensions 0.45 × 0.40 × 0.33 mm^3. The crystal was then heated at 150 ± 3 °C for 30 h and intensity data were again collected in the same manner.

Data reduction was carried out with the software SAINT V5.01[17] with reflection spot size estimates kept consistent throughout the reaction experiment. Absorption corrections were made with the program SADABS.[18] Crystal structures were solved by standard Patterson procedures and refined by least-squares methods based on F^2 with SHELXS-97 and SHELXL-97.[19] Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement. Hydrogen atoms were geometrically fixed and allowed to ride on the respective atoms. The general-purpose crystallographic tool PLATON[20] was used for structure analysis and presentation.

Results and Discussion

The red-colored crystal of *trans*-(η^5-C_5H_4Me)Re(CO)[P(OPh)$_3$]-Br_2 was observed to darken inhomogeneously during the reaction at 150 °C. Randomly distributed spots appeared to nucleate on the surface of the crystal. This process continued with no apparent formation of well-defined product domains. The importance of statistically distributed product molecules within the disordered crystal in a single-crystal to single-crystal transformation has been reported previously.[21] After 5 h at 150 °C, the crystal appeared totally dark with no observed fracturing or disintegration.

The structures (**1**−**6** in Table 1) were all solved in the monoclinic space group $P2_1/c$ with disorder in the carbonyl ligand and one bromine ligand. Structures for the pure trans and cis isomers have been solved previously[15] and are shown in Figure 1, panels a and b, respectively. The disordered structure of reacted *trans*-(η^5-C_5H_4Me)Re(CO)[P(OPh)$_3$]Br_2 is shown in Figure 2 with the ordered Br ligand eclipsed by the methyl substituent on the Cp ring. Comparison of bond angles around the square-pyramidal geometry with those of the pure isomers is consistent with the structure corresponding to a superposition of the trans and cis isomers as shown in Table 3.

The site occupancy factor (sof) linked to the CO−Br disorder was used to measure the extent of reaction α, where $\alpha = 0$ corresponds to the pure trans isomer (reactant) and $\alpha = 1$ corresponds to the pure cis isomer (product). The relationship between α and the sof was validated by solving the structures of the pure isomers with the CO−Br disorder included. For the trans isomer (**1**), a sof of 0.0149 was obtained while the cis isomer (**7**) gave 0.983 for the same parameter. These values are favorably close to the range boundaries of α. Results of the attempted reaction on a crystal of the cis isomer are shown in Table 2. There appears to be no appreciable change between **7** and **8**, thus confirming the irreversible nature of the trans-to-

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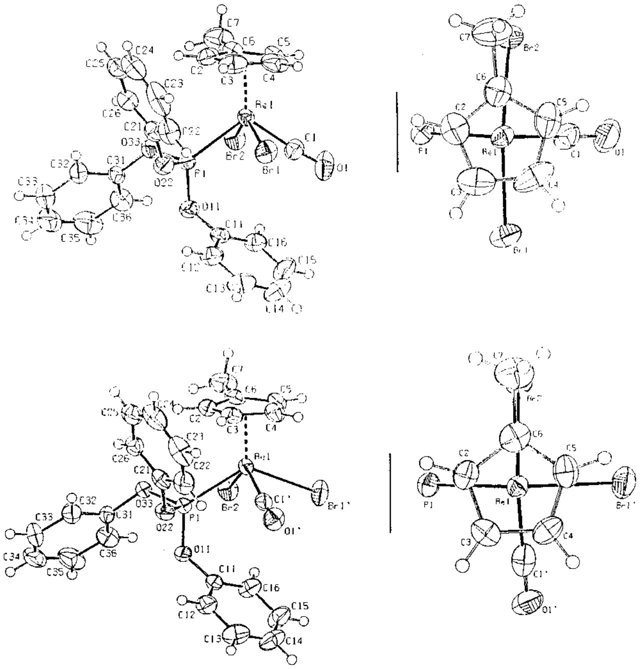

Figure 1. ORTEP diagrams of (a, top panel) *trans*-(η^5-C_5H_4Me)Re(CO)-[P(OPh)$_3$]Br_2 and (b, bottom panel) *cis*-(η^5-C_5H_4Me)Re(CO)[P(OPh)$_3$]Br_2 (50% probability thermal ellipsoids are shown).

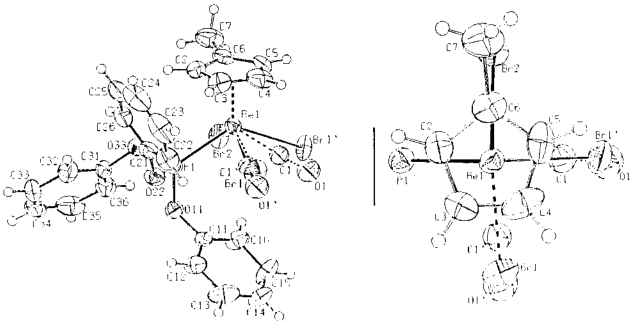

Figure 2. ORTEP diagram of reacted *trans*-(η^5-C_5H_4Me)Re(CO)[P(OPh)$_3$]-Br_2 (50% probability thermal ellipsoids are shown).

Table 2. Crystal Data in $P2_1/c$ for Attempted Reaction on *cis*-(η^5-C_5H_4Me)Re(CO)[P(OPh)$_3$]Br_2 at 150 ± 3 °C[a]

	7 (0 h)	**8** (30 h)
a/Å	15.9366(15)	15.9345(15)
b/Å	10.8774(10)	10.8729(10)
c/Å	14.2459(13)	14.2493(13)
β/deg	94.526(2)	94.547(2)
V/Å^3	2461.8(4)	2461.0(4)
*R*1 (all data)	0.0555	0.0543
w*R*2 (all data)	0.0663	0.0645
sof[b] (CO−Br)	0.983(2)	0.984(2)

[a] Crystal size 0.45 × 0.40 × 0.33 mm^3. [b] Site occupancy factor.

Table 3. Selected Bond Lengths and Angles for *trans*-, *cis*-, and Reacted (η^5- C_5H_4Me)Re(CO)[P(OPh)$_3$]Br_2

	6 (150 h at 150 °C)	**1** trans isomer	**7** cis isomer
Bond Lengths (in angstroms)			
Re1−Br2	2.5980(9)	2.5919(6)	2.5992(6)
Re1−P1	2.342(2)	2.379(1)	2.333(1)
C7···Br2 (nonbonded)	3.408(9)	3.296(7)	3.440(6)
Bond Angles ((in degrees)			
Br1−Re1−Br2	136.1(1)	138.77(2)	
Br1′∠Re1−Br2	79.31(3)		79.52(2)
O1−Re1−Br2	76.4(5)	76.17(8)	
O1′∠Re1−Br2	128.9(2)		128.80(8)
P1−Re1−O1	115.7(5)	110.78(9)	
P1−Re−O1′	80.2(2)		81.03(9)
P1−Re1−Br1	84.5(1)	81.53(3)	
P1−Re1−Br1′	126.96(6)		127.78(4)
Torsion Angles (in degrees)			
C7−Cp[a]−Re1−Br2	2.0(4)	9.4(2)	0.9(2)

[a] Cyclopentadienyl ring centroid.

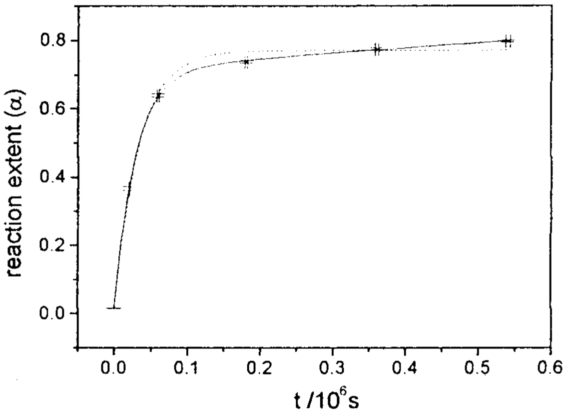

Figure 3. Isomerization kinetics for a single crystal of *trans*-(η^5-C_5H_4-Me)Re(CO)[P(OPh)$_3$]Br_2 at 150 ± 3 °C. (—) Double-exponential fit according to eq 1; (---) first-order exponential fit.

cis isomerization on single crystals of this complex and the precision of the CO−Br sof used for measuring the reaction extent, α.

A plot of α versus time for the reaction on *trans*-(η^5-C_5H_4-Me)Re(CO)[P(OPh)$_3$]Br_2 at 150 °C is shown in Figure 3. The total darkening of the crystal after 5.5 h with a proposed 37% isomer conversion suggests the reaction to be largely surface-initiated. Surface phenomena, which in general depend on crystallographic orientation,[22] appear to be important in determining the initial stage of this solid-state process. Even with the small number of points available, the curve can be seen to be deceleratory and this shape is often associated with diffusion-controlled reactions. There is no indication of any acceleratory process that gives rise to a sigmoid-type curve.[25a]

The approximating relationship used in fitting the data obtained for the reaction extent parameter is given by

$$\alpha = 1 - C\exp(-k_1t) - (1 - C)\exp(-k_2t) \qquad (1)$$

where k_1 and k_2 describe the rates of fast and slow components, respectively.

The values obtained for the reaction are $C = 0.706$, $k_1 = 36 \times 10^{-6}\ s^{-1}$, and $k_2 = 0.7 \times 10^{-6}\ s^{-1}$. Rate parameter k_2 is clearly much less than k_1, although not negligible according to the accuracy of our data. A simple first-order approximation leads to a rate constant of $30 \times 10^{-6}\ s^{-1}$, which corresponds to k_1 in eq 1 above. This is shown as the dashed curve in Figure 3, and it is apparent that the slow component of the reaction

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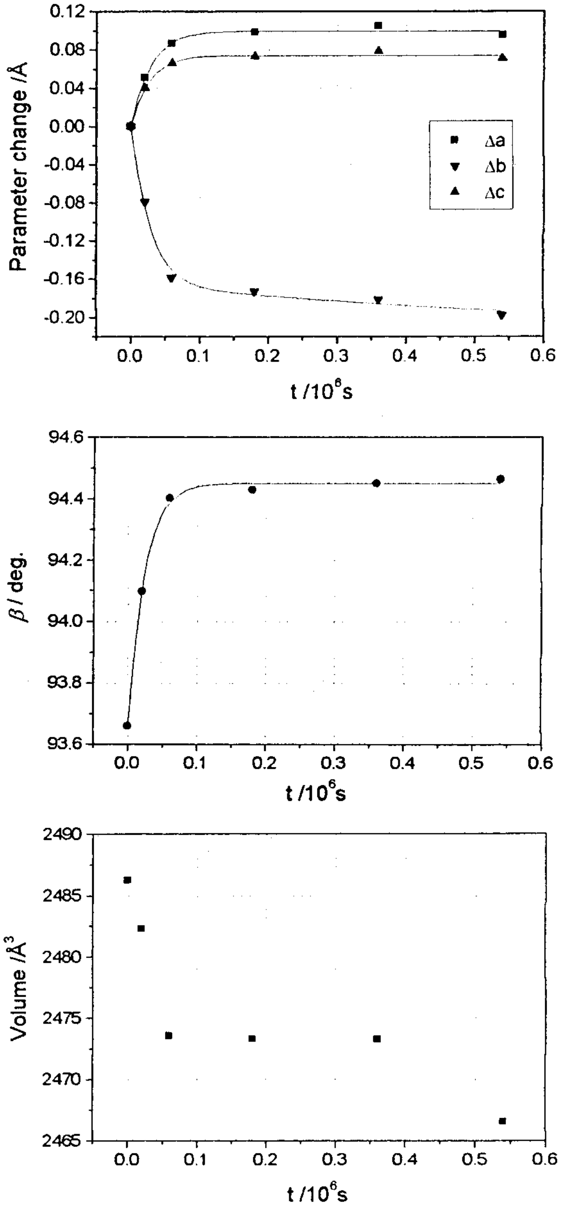

Figure 4. Cell parameter kinetics for the single-crystal isomerization of (η^5-C_5H_4Me)Re(CO)[P(OPh)$_3$]Br$_2$ at 150 ± 3 °C.

has been ignored in this case. The more common expressions used in kinetic studies of solid-state processes[23] were found less suitable for describing this isomerization reaction, but this does not rule out a complex reaction mechanism.[24]

The effect of the isomerization reaction on unit cell parameters is shown in Table 1 and Figure 4. Cell lengths show an exponential variation at the initial stages of reaction, similar to the reaction extent parameter, α (Figure 3). First-order exponential decay functions were used in fitting the data obtained for $\Delta a = a - 15.8276$ Å, $\Delta c = c - 14.1583$ Å, and cell angle β. This corresponds to the limiting case of $k_1 \gg k_2$ in eq 1. Unit cell parameter b is unique, involving a large contraction relative to the smaller expansions along the a and c axes. Equation 1, with the maximum range of unity replaced by the maximum change in b between the cis and trans isomers, was used in fitting the data for Δb. The approximating relationships used are $\Delta a = 0.0995\{1 - \exp[-(36 \times 10^{-6})t]\}$, $\Delta c = 0.0741\{1 - \exp[-(39 \times 10^{-6})t]\}$, $\beta = 0.79\{1 - \exp[-(40 \times 10^{-6})t]\} + 93.66$, and $\Delta b = -0.240 + 0.166 \exp[-(35 \times 10^{-6})t] + 0.0738 \exp[-(0.8 \times 10^{-6})t]$, which are shown as solid curves in Figure 4. The rate of change of the cell parameters a, b, c and β in the fast or transient region of reaction as indicated by the above time constants are comparable with the rate of reaction expressed by k_1 for the reaction extent parameter, α. Changes in unit cell volume are also plotted in Figure 4, showing a general volume contraction throughout the reaction. No further deductions are made due to the possibility of cumulative error in the unit cell volume calculation.

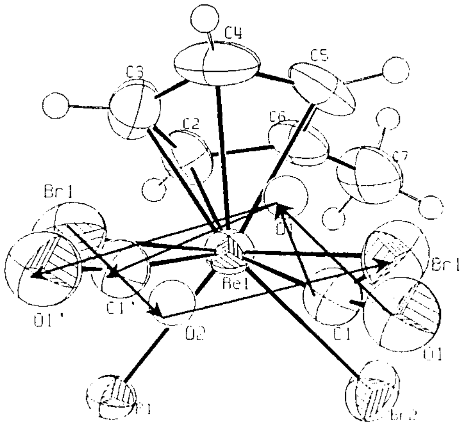

Figure 5. Proposed mechanism for the isomerization of (η^5-C_5H_4Me)Re(CO)[P(OPh)$_3$]Br$_2$ (50% probability thermal ellipsoids are shown).

As already noted, the plots of α and the unit cell parameters suggest two distinct processes. The initial transient or fast component appears to correspond to the nucleation and growth of product material, commencing at the crystal surface and possibly at defects within the crystal. Nucleation of product material in solid-state reactions is consistent with first-order exponential behavior.[25b]

The slow-component region in which α is almost linear with time might be linked to a reaction process that includes annealing, allowing for a faster rate of reaction relative to first-order kinetics. In this respect it is noted that the reaction temperature of 150 °C is appreciably close to a melting point of 164−166 °C for *trans*-(η^5-C_5H_4Me)Re(CO)[P(OPh)$_3$]Br$_2$, previously measured by differential scanning calorimetry.[12] The corresponding cis isomer has a melting point in the range 183−185 °C.[12] We are still unsure as to the interpretation of the slow component of reaction, and the successive heating and cooling procedure used throughout the experiment might also influence this issue in future analysis.

Reaction Mechanism. In evaluating a mechanism for the isomerization reaction, the molecule is viewed as being pseudo-five-coordinate with the cyclopentadienyl ligand occupying one coordinate site at the rhenium. The reaction can then be expected to proceed via a modification of the classical Berry pseudorotation or a combination Berry−turnstile mechanism.[26,27] Indeed the Berry mechanism was the model used by Faller and Anderson[16] to evaluate the solution cis−*t*rans isomerization of a series of *(*η^5-C_5H_5*)MoWL*$_3$*X* complexes. In an *e*arlier paper we attempted to rationalize the solid-state data of a wide range of pseudo-five-coordinate molecules using the structure cor-

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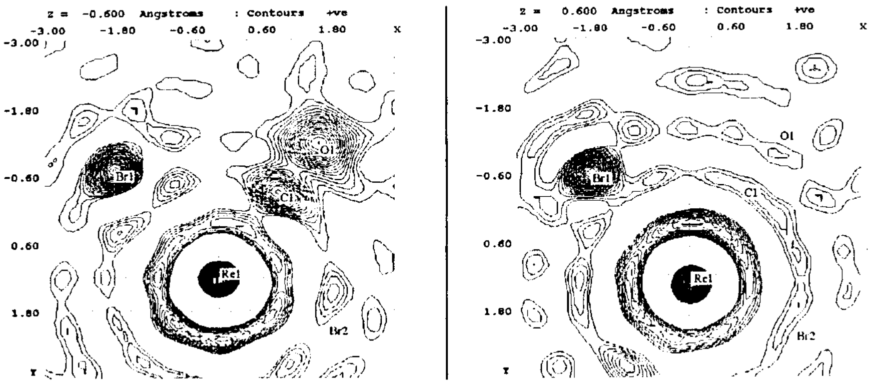
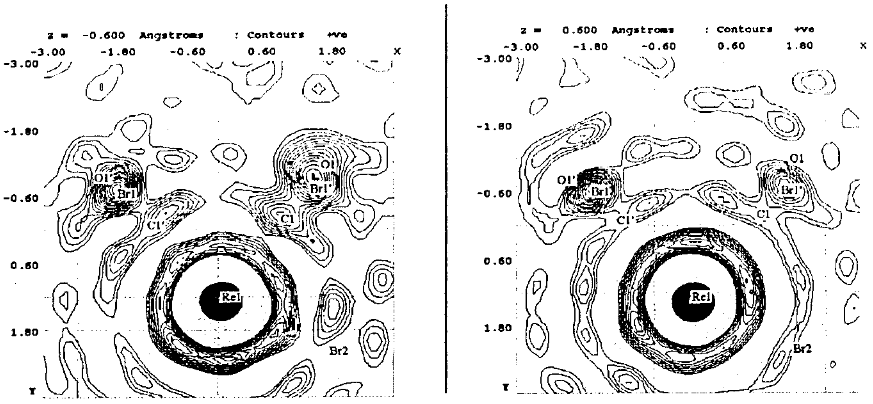
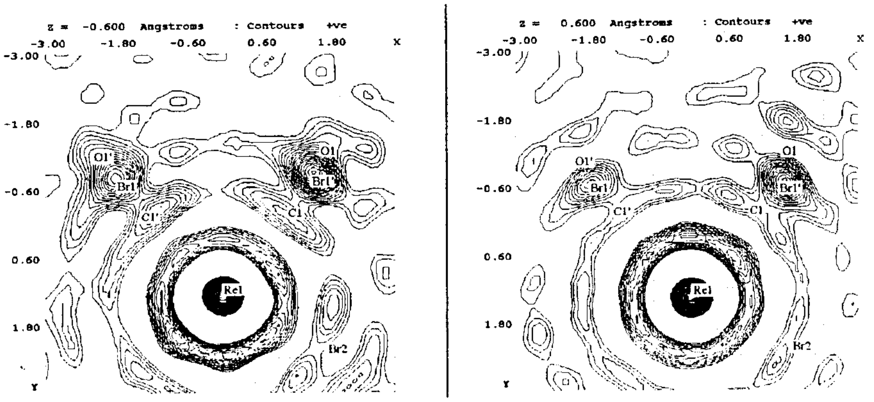


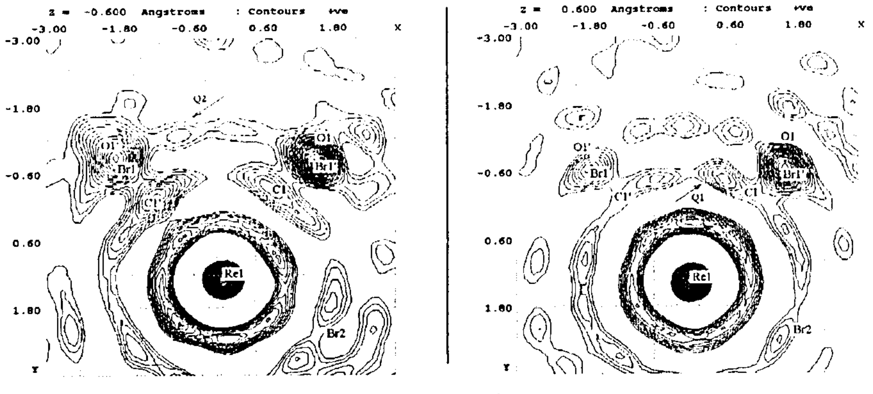
No heating *(1)*



After 5.5hrs at 150°C *(2)*



After 16.5hrs at 150°C *(3)*



After 50hrs at 150°C *(4)*

Figure 6. Fourier maps of reacted (η^5-C_5H_4Me)Re(CO)[P(OPh)$_3$]Br_2, parallel to the Br1−Re1−Br1′ plane. Contours are at intervals of 0.5 e$Å^{-3}$. Left-hand panels are 0.1 Å slices positioned 0.6 Å from the Br1−Re1−Br1′ plane out of the paper (away from the Cp ring); right-hand panels are 0.1 Å slices positioned 0.6 Å from the Br1−Re1−Br1′ plane into the paper (toward the Cp ring).

relation method,[21] and we noted that a variant of the turnstile mechanism gave the best fit to the available X-ray crystallographic data.

An evaluation of the X-ray data generated in this study suggests that only one Br atom in (η^5-C_5H_4Me)Re(CO)[P(OPh)$_3$]Br_2 exchanges with the CO ligand. This can be seen in the ORTEP diagram shown in Figure 2.

To further analyze the disordered region of the structure as a function of time, difference Fourier maps with the bromine and carbonyl ligands selectively omitted from the structure factor calculation were obtained. The additional peaks obtained from the omit map around the square-pyramidal geometry were compared with Re−Br and Re−C bond lengths found in either isomer. Two peaks, Q1 and Q2 in Figure 5, were found with distances to rhenium that are comparable with Re−C and Re−Br bond lengths. The distances obtained were Re1−Q1 = 1.8(1) Å and Re1−Q2 = 2.61(1) Å. To further monitor the progress and obtain additional information about the disordered region incorporating Q1 and Q2, Fourier maps parallel to the plane through Br1, Re1, and Br1′ were calculated with the crystallographic software WINGX.[28]

Distances from Q1 and Q2 to the plane defined by Br1, Re1, and Br1′ were calculated to be 0.57 and 0.60 Å, respectively. Fourier maps with a depth of 0.1 Å were then calculated 0.6 Å to either side of the Br1−Re1−Br1′ plane and are shown in Figure 6.

The left-hand panels in Figure 6 show 0.1 Å slices positioned 0.6 Å from the Br1−Re1−Br1′ plane, away from the Cp ring. Bridging between Br1 and Br1′ is observed as the reaction proceeds and corresponds to the omit map peak Q2. Similarly, 0.1 Å slices positioned 0.6 Å from the Br1−Re1−Br1′ plane toward the Cp ring (Figure 6, right-hand panels) show bridging between C1 and C1′. This appears to correspond to the omit map peak Q1.

A feature of both the Berry pseudorotation and the turnstile mechanisms is that they both require the simultaneous movement of three or more atoms. In principle a more simple process of atom/ligand movement entails a two-atom/ligand movement. Movement of other atoms will thus entail multiple movements within this simple two-atom movement process. In this study, the distances measured from the Re to the two peaks Q1 and Q2 are consistent with the CO ligand corresponding to Q1 and the Br atom to Q2. The CO and Br thus appear to exchange places in a rotational process about an axis through the Re center, with the direction entailing movement of the CO ligand toward the Cp ring as it exchanges with the Br atom. Thus there appears to be a unique pathway for the trans-to-cis isomerization of (η^5-C_5H_4Me)Re(CO)[P(OPh)$_3$]Br_2. It is not clear as to whether the Br and CO need to remain bound to the Re center during reaction. Indeed, it might be expected that the exchange of CO and Br attached to Re would be a high-energy process and that the homolytic cleavage of Br (or less likely CO) would take place more readily in the occupied cavity. Further experiments will be needed to evaluate this issue.

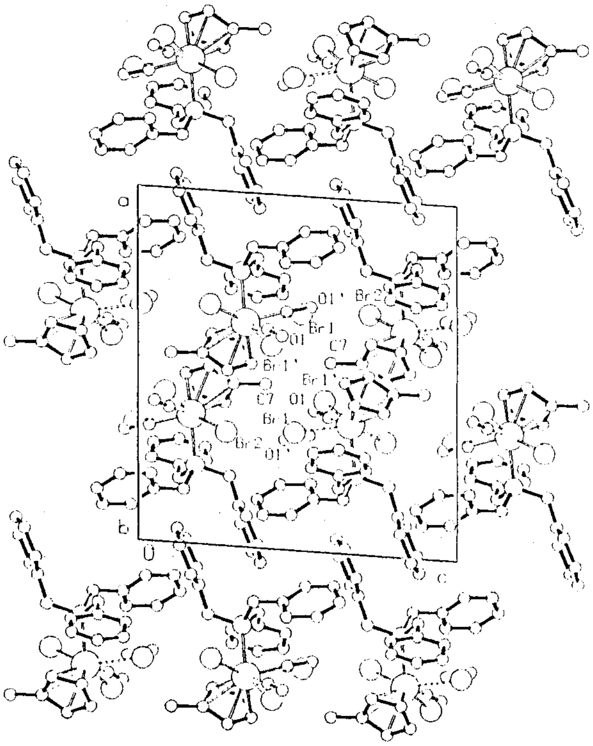


Figure 7. Packing diagram of reacted (η^5-C_5H_4Me)Re(CO)[P(OPh)$_3$]Br_2, view down *b*-axis.

Table 4. Selected Intermolecular Distances for the Isomerization of *trans*-(η^5-C_5H_4Me)Re(CO)[P(OPh)$_3$]Br_2 at 150 ± 3 °C

interatomic contact	symmetry and translation applied to the second atom[a]	**1** (0 h)/Å	**2** (5.5 h)/Å	**3** (16.5 h)/Å	**6** (150 h)/Å	**7** cis isomer/Å
Br1···O1	(3) 1, 1, 0	4.3602(2)	4.35(2)	4.3940(2)	4.3475(3)	
Br1′···O1′	(3) 1, 1, 0		4.31(5)	4.2593(2)	4.2876(3)	4.2646(4)
Br2···O1	(4) 0, 1, 0	4.6312(1)	4.68(2)	4.6800(2)	4.7389(3)	
Br2···O1′	(4) 0, 1, 0		6.42(4)	6.0731(3)	6.0281(4)	6.0035(5)
Br1···Br1	(3) 1, 1, 0	5.8562(2)	5.908(3)	5.9813(3)	5.9837(3)	
Br1′···Br1′	(3) 1, 1, 0		4.409(6)	4.4047(1)	4.4006(2)	4.3975(2)
Br1···C7	(4) 0, 0, −1	4.2331(1)	4.28(2)	4.2679(2)	4.3183(2)	
Br1′···C7	(2) 1, 0, 0		3.79(2)	3.8405(2)	3.8090(2)	3.8092(3)
O1···C7	(2) 1, 0, 0	3.5874(1)	3.62(3)	3.7168(1)	3.6361(2)	
O1′···C7	(4) 0, 0, −1		4.26(5)	4.4399(2)	4.5213(2)	4.5264(3)
Br1···H2	(4) 0, 0, −1	3.1051(1)	2.990(2)	3.0051(1)	2.9715(2)	
Br1′···H4	(3) 1, 1, 0		2.755(4)	2.8251(1)	2.8106(2)	2.8480(2)
O1···H4	(3) 1, 1, 0	2.5177(1)	2.59(2)	2.6458(1)	2.6440(1)	
O1′···H2	(4) 0, 0, −1		2.78(3)	2.8198(1)	2.8185(1)	2.8469(2)

[a] Symmetry operations applied: (1) x, y, z; (2) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (3) $-x, -y, -z$; (4) $x, \frac{1}{2} - y, \frac{1}{2} + z$; and translations ($x_t, y_t, z_t$) as units along each axis.

What factors drive the reaction? Consideration of the two-atom/ligand exchange process from the perspective of the unit cell is revealing in determining a driving force for the reaction. A packing diagram of the reacted structure is shown in Figure 7, in which channels between adjacent molecules, bounded by Br1, O1, Br2, and C7, are apparent. A reaction cavity is likely to be contained within these channels in a close-packed structure. Selected intermolecular distances involving the isomerizing ligands and the methyl substituent C7 were thus measured and are given in Table 4. Compression along the *b*-axis and expansion along the *a*- and *c*-axes has already been noted. This in turn corresponds to a decrease in certain of the closest intermolecular distances involving Br1, O1, and C7 in proceeding from the trans to cis isomer as shown in Table 4. Br1′ and O1′ correspond to the cis structure according to the results given in Table 3. The contacts given in Table 4 characterizing the trans structure generally tend to increase and hence weaken as

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[28] WINGX: Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837−838.

the reaction proceeds. Contacts corresponding to the cis structure tend to contract, complementary to their trans counterparts, except for the contacts to the methyl substituent C7 and the hydrogens H2 and H4. In particular, all contacts to Br1′ given in Table 4 are shorter compared with their trans counterparts. This is most noticeable for the Br1′···Br1′ contact. The known behavior of the halogens (X = Cl, Br, I) to form short X···X contacts has been reported previously.[29] The shortest intermolecular distances between hydrogens and the isomerizing ligands (Br1, CO) are also given; however, these interactions do not appear to promote the isomerization reaction.

Conclusion

The single-crystal to single-crystal isomerization of *trans*-(η^5-C_5H_4Me)Re(CO)[P(OPh)$_3$]Br_2 provides a unique window into the mechanism of this solid-state reaction. To our surprise, we found that our data suggest a trivial two-atom/ligand exchange (CO and Br) and not a three- or four-ligand turnstile or Berry-rotation pathway. Thus, a two-atom exchange process might require a lower activation energy relative to alternative mechanisms for this reaction.

The study thus provides the first evidence for a two-atom isomerization process of a pseudo-five-coordinate molecule. The implication is that solid-state isomerization reactions entailing square-planar and octahedral[30] geometries might also be likely to proceed in this way, and efforts to extend our studies to these other types of reactions are currently underway.

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Supporting Information Available: Eight tables listing crystal data, refinement parameters, positional coordinates, and equivalent isotropic thermal parameters for all structures. This material is available free of charge via the Internet at http//pubs.acs.org. See any current masthead page for ordering information and Web access instructions.

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