Organometallic Chemistry: Structural Isomerization Reactions in Confined Environments

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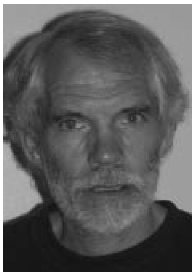
Keywords: Isomerization / Solid-state reactions / Surfaces / Organometallic chemistry / Rhenium

Reactions in the solution phase have dominated the development of chemistry. In recent years, however, the area of solid-state organic chemistry has undergone a renaissance, although the related area of organometallic chemistry is still in its infancy. Indeed, only a limited number of systematic studies on the reactions of organometallic compounds in a confined environment (on a surface, in a zeolite pore, in the bulk phase) have been reported. Herein we summarize some recent results on a specific reaction type in a confined environment, namely the isomerization reaction.

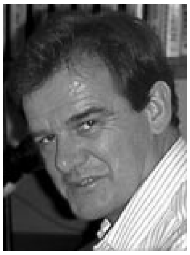
Introduction

The synthesis and characterization of ferrocene is regarded as the event that brought to life the area of organometallic chemistry.[1−3] This event, which took place in 1951, has led to the synthesis of many tens of thousands of organometallic complexes.[4,5] By the late 1980's many of the principles governing the synthesis and reactivity patterns in the discipline of organometallic chemistry had been established and the exotic complexes that had constantly been prepared were found to fit classical bonding patterns and theories.[6]

Much of this early chemistry was studied in solution, brought about by the ready availability of techniques such as IR and NMR spectroscopy. Studies in confined environments such as the solid state were more limited. While X-ray diffractometers were available, use of this technique was time consuming and studies were predominantly undertaken to determine the atom connectivity in complexes. The emphasis was certainly not on the study of reactions *in* the solid state. Developments in the last two decades in diffractometer design (such as the charge coupled device) have resulted in the determination of crystal structures now be-



Neil Coville obtained his BSc (Hons) and MSc degrees at the University of the Witwatersrand ("Wits") before proceeding to McGill University, Montreal where he obtained his PhD (1973) under the supervision of Ian Butler. After postdoctoral work at Harvard University with (the late) John Osborn he returned to Wits in 1976 where he has remained. He is currently the Director of the Molecular Sciences Institute and holds the Chair of Inorganic Chemistry in the School of Chemistry. His current research interests include Fischer−Tropsch chemistry, synthetic routes to carbon (and other) nanotubes, hard material synthesis and organometallic chemistry in the solid state.



Demi Levendis obtained his BSc (Hons) and MSc degrees at the University of the Witwatersrand. After obtaining his Honours degree he worked at the CSIR in Pretoria for three years, and returned to Wits to complete his PhD (1985). Thereafter he spent two years as a postdoctoral researcher with Philip Coppens at SUNY, Buffalo, New York and the Synchrotron (NLS) at Brookhaven National Laboratories. He went back to Wits to take up a full-time lecturing position. After a one year sabbatical with Ivan Bernal at the University of Houston, Texas, USA, he was promoted to Associate Professor, and in due course became team leader of the Jan Boeyens Structural Chemistry Laboratory and of the Structural and Computational Chemistry programme in the Molecular Sciences Institute of the School of Chemistry.

MICROREVIEWS: This feature introduces the readers to the author's research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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ing viewed as a routine analytical procedure in organometallic chemistry. Coupled to this has been the development of commercially available thermal equipment (examples include differential thermal analysis, differential scanning calorimetry, thermal gravimetric analysis, temperature programmed reduction) and surface equipment (atomic force microscopy, scanning tunneling microscopy). These and other related techniques have permitted studies of the composition/reactivity of *molecular* solids that was not available 20 years ago.

Classical inorganic complexes have been studied in the solid state for many years. Further, as pointed out by Braga and co-workers,[7] solid-state organic chemistry also has a long and rich history. The same, however, cannot be said for the area of organometallic chemistry.[8,9] The time thus seems appropriate for the development of the field of organometallic chemistry in confined environments,[10] with particular emphasis on reactions in the solid state.

There are a number of possibilities that need to be considered when describing a "confined" environment and these are listed below.

Supported Molecules

Much work has been carried out on supporting reagents on both inorganic and organic supports, for example on polymers,[11] dendrimers[12] and surfaces.[13] The study of the *chemical* interaction of molecules/ions with a surface has led to the development of SOMC (Surface Organometallic Chemistry), and the information that has been obtained has important implications for the generation of heterogeneous catalysts from organometallic precursors.[14−16] The methodology has also been exploited for the synthesis of organometallic complexes that can subsequently be extracted from surfaces.[17]

Matrix Isolated Complexes

This area of chemistry[18] constitutes another example of solid-state chemistry. In these studies, reactant molecules are generally isolated from each other by a matrix at low temperatures. Reactions are brought about typically by photolytic means and the surrounding matrix acts to modify the reactions of the deposited molecules. The information obtained has been used in the identification of reaction intermediates and pathways.

Molecules Encapsulated in Zeolites and Mesoporous Solids

The variable cavities, all of the same dimension, found in various zeolites and larger pore materials (e.g. MCM-41) provides a means of studying isolated, confined molecules.[19] The cavities range from 3−4 Å to 40−60 Å in width and thus reactions of small to very large molecules are possible.

Crystalline/Amorphous Materials

A molecule in the solid state is considered confined in a cavity generated by the other molecules surrounding it. The molecule is held rigidly in place. This type of solid contains two "types" of molecules: those in the bulk and those at the surface or situated at defects. When solids are heated they can undergo intra-atom/ligand rearrangements as well as inter-molecule rearrangements (e.g. phase changes). Interactions in the solid state *between molecules*, such as H-bonding and dipole-dipole interactions, can have similar energies to those found in covalent/ionic bonds. Braga and others have shown how interactions in organometallic molecular solids lead to the generation of 3-D networks,[7] and thus links directly to the area of supramolecular chemistry.[20]

Much of the focus of this Microreview will be on reactions in the solid state as opposed to reactions on a solid support. It will focus on isomerization reactions entailing physical (not chemical) interactions with the surrounding molecules. Others have highlighted the advantages/disadvantages in performing studies on organic materials in confined environments (e.g. the solid state). These include: solvent free synthesis, the use of enantioselective cavities, and modified reactivity patterns.[21,22] The same factors will apply to the study of organometallic chemistry in confined environments. Furthermore, the study of reversible gas adsorption by organometallic complexes in the solid state could expand the area of sensor studies,[23] while the polymerization of functional groups associated with ligands attached to metals could lead to the generation of new types of polymers.[24]

Isomerization Reactions of [(CpMe)Re(CO)$_2$Br$_2$] — The Breakthrough

As with many entries into new areas of chemistry, serendipity played a crucial role for us. For many years we had been fascinated by the steric control displayed by cyclopentadienyl ligands in reactions.[25] This led us to consider methods of quantifying the size of substituted cyclopentadienyl ligands and to correlate steric measures (cone angle, solid angle) with physical parameters associated with the molecules under investigation. As part of our study we prepared a series of [(CpR)Re(CO)$_2$Br$_2$] complexes and wished to determine the impact of the R group on the *cis*/*trans* isomer ratio of the complexes.[26] In attempting to purify *trans*-[(CpMe)Re(CO)$_2$Br$_2$] by vacuum sublimation we noticed that the material that sublimed onto the cold probe was the *cis* isomer. We soon found that the isomerization reaction did not take place in the gas phase but occurred when the solid sample was simply heated in a flask at a temperature lower than the melting point of either of the isomers. Also surprising was the observation that in solution the isomerization reaction went in the *opposite direction* to that observed in the solid state i.e. the *cis* isomer converted into the *trans* isomer. It was clear that we had discovered a phase-dependent isomerization reaction (Figure 1). This suggested that the environment surrounding the molecule that was to rearrange (or more precisely, the cavity in which the molecule was situated) played a key role in the reaction.

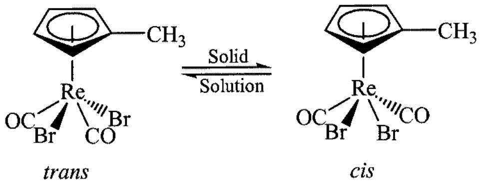

Figure 1. *cis* and *trans* isomers of [(CpMe)Re(CO)$_2$Br$_2$]

A procedure was developed to monitor the above solid-state reaction. This entailed placing small amounts of reactant in a degassed capillary or NMR tube and immersing the tube in an oil bath pre-set at the required temperature. At the end of a pre-determined time the material was removed from the oil bath and was ready for analysis (powder XRD, NMR or IR spectroscopy). The reaction was also monitored by optical microscopy using a specially designed temperature-controlled cell that allowed study under nitrogen.

Before proceeding with our follow up studies, it is worth digressing to indicate studies that had been undertaken by others prior to our finding, as well as some related current studies of pertinence to this Microreview.

Isomerization Reactions in the Solid State

Inorganic Molecules

Reactions of covalent molecules in the solid state have been studied for over 100 years and continue to be studied. Excellent reviews are available that have summarized the early work and thus these early studies will not be discussed in any detail here.[27,28]

Three types of isomerization reactions have been studied: racemization, *cis*/*trans* isomerization and linkage isomerization.

The *cis*/*trans* isomerization of simple four-coordinate compounds such as [Pd(NH$_3$)$_2$X$_2$] (X = Cl, Br, I) continues to provide information on the isomerization reaction mechanism. In this specific case the reaction proceeds from the *cis* to the *trans* isomer in a process that entails the "breaking of Pd−X and Pd−N bonds".[29] Numerous six-coordinate Cr and Co compounds have also been studied.[30] It appears that the presence of water assists the *cis*/*trans* isomerization reaction of Co complexes, with dehydration playing a key role. Extensive studies, including single crystal studies, on the NO$_2$-ONO interconversion in complexes of the type [Co(NH$_3$)$_5$NO$_2$]$^{2+}$ have generated data on the role of pressure, light and cavity size on the reaction.[31] These studies provide a reference point for the study of organometallic complexes viz. typical reaction energies and reaction pathways.

Organic Molecules

Scientific investigations of solid-state organic chemistry dates back to (at least) the early 1800's but Schmidt and coworkers have been credited with the field's revival after their extensive investigations that led to the formulation of the topochemical principle.[32] One of the classic reactions that they described was the photodimerization of *ortho*-ethoxy-*trans*-cinnamic acid, a reaction that depends on which crystal polymorph is irradiated. It is cited in many reviews and textbooks, but a recent detailed analysis of three forms of *ortho*-ethoxycinnamic acid[33] has shown that factors other than the topochemical principles enunciated by Schmidt may apply. These other important factors that influence the course of solid-state reactions include the presence of solvates, planar defects, phase-transitions,[33] disorder and even crystal morphology.[34]

To date, several hundred high-yield solid-state syntheses involving numerous organic reaction types have been reported.[21] Two incentives driving the rapid development are the advantages of "solvent-free syntheses"[14] and the possibility of achieving novel or stereoselective products as a consequence of reactions in a constrained crystalline environment.

One of the predominant reaction types occurring in organic crystals is photo-dimerization/photo-polymerization, but since the 1980's many accompanying (and unique) isomerization reaction types have been reported.[35−37] These include thermal or photochemical interconversion between geometrical isomers, conformers and *E*/*Z* configurations. The interconversion between conformational isomers can occur with relatively low energy barriers in the solid, an occurrence that is sometimes referred to as conformational polymorphism.[38] However, the more space and energy demanding *E*/*Z* isomerization reactions do not generally obey the topochemical principle, and often proceed unidirectionally, either from the *Z* to *E* or from the *E* to *Z* configuration.[39] Mechanisms of solid-state isomerizations have been the subject of intense deliberation in recent years,[39−41] particularly since the application of new techniques such as scanning near field optical microscopy (SNOM) and atomic force microscopy (AFM), which have suggested, for example "phase-rebuilding" mechanisms.[39]

Organometallic Molecules

Three types of reactions can be envisaged for organometallic complexes: (i) isomerization of a ligand, (ii) isomerization at the metal, and (iii) isomerization in the crystal (phase change).

Isomerization of a Ligand

One of the earliest investigations of an isomerization/racemization reaction of an organometallic complex was the report by Ohashi and Sasada on the X-ray induced racemization reaction shown in Figure 2a [base = (*S*)-α-methylbenzylamine].[42] Of significance was the observation that the reaction occurred without crystal decay and this permitted a study of the mechanism of the reaction in a single crystal. Many publications, in which both the organic group and the base have been varied, have emanated from studies by Ohashi and co-workers since this report (Figure 2b). In these later papers they have shown:

a) racemization can be induced by exposure to a xenon lamp.[43,44]

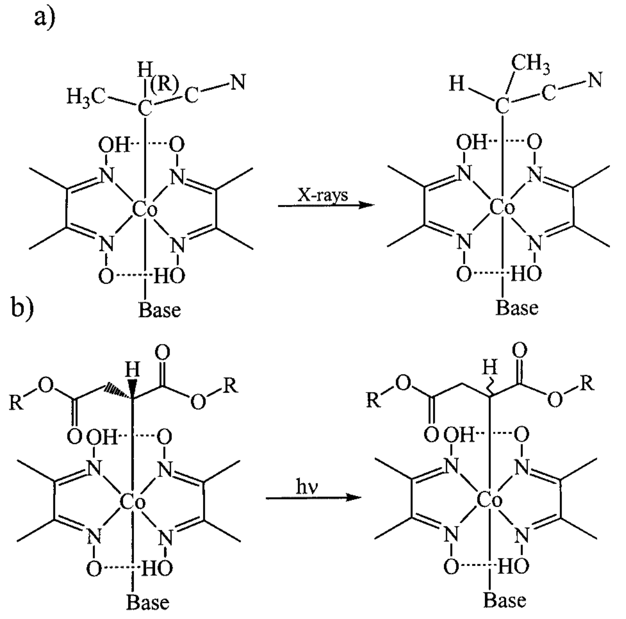

Figure 2. Cobaloxime racemization reactions: (a) X-ray induced [Base = (*S*)-α-methylbenzylamine, pyridine, PMe_2Ph etc.]; (b) light induced (bases as above, R = CH_3, C_2H_5, $CH{=}CH_2$)

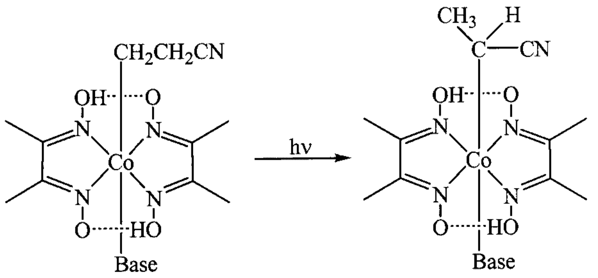

Figure 3. Cobaloxime isomerization reaction (e.g. B = 3-Mepyridine) (ref.[46])

b) isomerization reactions, for example of β-cyanoethyl to α-cyanoethyl ligands, with production of a scalemic chiral complex from a pro-chiral complex (Figure 3).[45,46]

c) asymmetric synthesis in a "cavity" i.e. generation of a preferred isomer from a racemic mixture.[47]

d) the detailed mechanism of the reaction by neutron diffraction studies entailing deuterium labelling experiments.[48−50]

By varying the R group and the base (situated below the cobaloxime ring) the ability of the R group to racemise or isomerise has been correlated with the concept of a reaction cavity.[51,52] In particular, the studies have shown that the reaction does not correlate with the density of the crystal (i.e. the packing of the whole molecule) but rather with the packing of the reactive group. The reaction cavity was defined as "*the space limited by a concave surface of spheres of the surrounding atoms around the reactive group in the crystal*".[51,52] Cavity volumes have been calculated and it has been observed that, in general, the larger the cavity volume the greater the reaction rate. For example, in a number of the complexes studied there are two crystallographically different molecules in the unit cell (i.e. two molecules per asymmetric unit). Comparison of volume data for the two independent molecules, A and B (Table 1), contained in the same crystal, reveals that inversion of the ligand only occurs when the cavity size exceeds a certain dimension and that selective reaction occurs, typically for the "B" molecules.[52] This relationship between reaction cavity size and reaction rate also holds for structures that contain only one molecule in the asymmetric unit (Table 1).

However, the *shape* of the cavity can also play a role. This is shown, for example, by studies on (cobaloxime)-Co[(*R*)-1,2-bis(ethoxycarbonyl)ethyl] (*S*)-1-phenylethylamine L complexes (Table 1).[43] Thus, the complex with L = pyridine racemizes on exposure to light, while the complex with L = PPh_2Me, with an equivalent cavity volume, does not. A detailed comparison of the shapes of the cavities revealed that movement of the ligand atoms in the cavity for L = PPh_2Me is not possible if an intact single crystal is to be maintained.

Isomerization at the Metal

Isomerization of six-coordinate complexes *in the ligand sphere* are also known. The first "organometallic-type" complexes to show *cis*/*trans* isomerization in the solid state

Table 1. Cavity volumes for cobaloxime complexes[a]

R	Base	*V* (Å^3) A	B	Molecule racemised	Ref
(*R*)-1-cyanoethyl[b]	4-cyanopyridine	7.97	10.37	B only	[[51]]
PPh_2Me	17.08	18.01	A and B	[[51]]	
3-methylpyridine	10.24	14.29	B > A	[[51]]	
piperidine	7.0	14.2	B	[[47]]	
(*R*)-1,2-bis(ethoxycarbonyl)ethyl[c]	(*S*)-1-phenylethylamine	68.8	–	none	[[43]]
pyridine	76.5	–	yes	[[43]]	
propylamine	58.9	–	none	[[43]]	
PPh_2Me	75.8	–	none[d]	[[43]]	
(*R*)-1,2-bis(methoxycarbonyl)ethyl	PPh_2Me	47.4	55.0	B only	[[44]]

[a] Structures are given in Figure 2. [b] Two independent molecules were found per asymmetric unit (A and B). Each has a different cavity size and the reaction only occurs in the larger cavity (ref.[51]). [c] Structures given in Figure 2b. [d] Reaction expected, but shape of the cavity did not allow for reaction.

were reported by Nelson and co-workers.[53,54] In this study a series of Ru complexes underwent *trans* to *cis* rearrangements, as shown in Figure 4, and the solution data suggested the movement of the bulky phosphane group in the isomerization reaction (ttt to ccc and ccc to cct, Figure 4a). In the solid state the reaction could occur via the interchange of only two small groups. We have recently measured the activation energy of the isomerization reaction (ttt to cct) in the solid state for a range of these complexes and find that the values fall in the range 70 ± 20 $kJ\cdot mol^{-1}$, values that are consistent with a simple ligand-rotation process.[55]

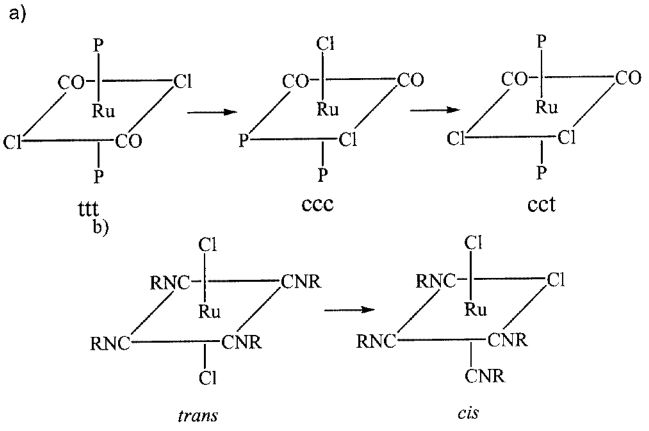

Figure 4. Solid-state isomerization reactions: (a) $[Ru(CO)_2P_2Cl_2]$ (P = phosphane) and (b) $[RuCl_2(RNC)_4]$

In a related study some Ru isocyanide complexes (Figure 4b) were also shown to undergo *trans* to *cis* isomerization in the solid state.[56]

Another type of isomerization reaction that occurs in the solid state is the η^1-acetylene to vinylidene rearrangement reaction (Figure 5).[57] This reaction involves the migration of an H-atom from the metal to the ligand. Numerous examples of this reaction type have been reported.[9]

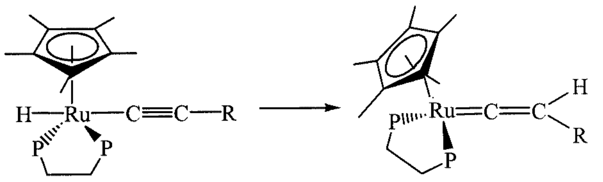

Figure 5. An η^1-alkynyl to vinylidene conversion of $[(C_5Me_5)RuH(diphos)(\eta^1\text{-}CCR)]$ in the solid state

Isomerization in the Crystal

It appears that this is a little explored area in the field of solid-state organometallic chemistry. The relationship between phase transitions and chemical reactions has been the subject of continued debate.[38] One well-known example is that of ferrocene, which can exist in three distinct configurations, [staggered (D_{5d}), eclipsed (D_{5h}) and D_5] in the crystalline form, and can transform between these configurations as the crystals undergo phase transitions between different stable polymorphs.[38] In more recent work, Braga et al. reported on the fascinating solid-solid phase transition and solid-state reaction of bis(formyl)ferrocene.[58]

Isomerization of $CpML_4$ Complexes in the Solid State

The discovery of the solid-state isomerization reaction of $[(CpMe)Re(CO)_2Br_2]$ posed many interesting questions — how general is the reaction?, what are the factors that determine the direction of the reaction?, what is the mechanism of the reaction? These and other questions have provided the basis for our ongoing investigation into this area of organometallic chemistry.

Generality of the Reaction

The first issue addressed was to establish the breadth of the reaction.

Variation of the Substituents on the Cyclopentadienyl Ring

A series of $[(CpR)Re(CO)_2Br_2]$ (R = $SiMe_3$, *t*Bu, Et, C_6H_{11}) complexes was prepared but none of these complexes underwent *trans/cis* isomerization in the solid state.[26] Indeed, melting occurred prior to isomerization and *isomerization was found to occur in the melt.* Interestingly reaction also occurred from the *trans* to the *cis* isomer in the melt. Later studies have shown that for R = *i*Pr, a solid-state reaction does take place (Table 2).[59] Attempts to extend the reaction to disubstituted ring complexes such as $[\{Cp(SiMe_3)_2\}Re(CO)_2Br_2]$ were also made, but again the new complexes did not isomerise in the solid state.[60]

Variation of the L Groups

Substitution of CO in $[(CpR)Re(CO)_2Br_2]$ (R = Me, *t*Bu, $SiMe_3$) by L (L= phosphanes, phosphites and isocyanides) using NMe_3O-induced CO displacement techniques[61] readily gave the $[(CpR)Re(CO)LBr_2]$ complexes in good yield. Typically more than 80% of the product was synthesized as the *trans* isomer (Table 2).[62] These complexes all isomerize completely in the solid state — in every instance from the *trans* to the *cis* isomer. This is the same direction as found for the solution state isomerization reaction.

Variation of the Metal

Extension of the reaction to complexes of the type $[(CpR)M(CO)_2LX]$ (Figure 6; M = Mo, W; R = Me, Et etc.; L = phosphites, phosphanes, isocyanides; X = Br, I) has also been achieved.[63,64] Reaction of $[(CpR)M(CO)_3X]$ with L (in the presence of NMe_3O) gave a mixture of *cis/trans* isomers that could be separated by column chromatography. Reactions performed on either the pure *cis* or *trans* isomers gave the same *cis/trans* isomer equilibrium ratio (typically 65:35) in the solid state. The reaction goes from either direction to yield equilibrium mixtures of the two isomers, but the reaction is accompanied by decomposition (see below).

Interestingly, there have been two other reports of solid-state reactions of similar group 6 metal complexes in the literature. In a short comment Barnett and co-workers reported that $[CpMo(CO)_2\{P(nBu)_3\}I]$ isomerizes from the

Table 2. Thermal solid-state isomerization reactions of $[(CpR)Re(CO)LX_2]$[a]

Complex	M.p. (°C)	Reaction temp. (°C)	Yield (%)
trans-$[(\eta^5\text{-}C_5H_4Me)Re(CO)_2Br_2]$	116−118	105−107	98
cis-$[(\eta^5\text{-}C_5H_4Me)Re(CO)_2Br_2]$	158−160		
trans-$[(\eta^5\text{-}C_5H_4\textit{i}Pr)Re(CO)_2Br_2]$	112−114	97−99	95
cis-$[(\eta^5\text{-}C_5H_4\textit{i}Pr)Re(CO)_2Br_2]$	127−129		
trans-$[(\eta^5\text{-}C_5H_4Me)Re(CO)_2BrI]$	125−127	108−110	85
cis-$[(\eta^5\text{-}C_5H_4Me)Re(CO)_2BrI]$	135−137		
trans-$[(\eta^5\text{-}C_5H_4Me)Re(CO)\{P(OMe)_3\}Br_2]$	114−116	100−105	96
cis-$[(\eta^5\text{-}C_5H_4Me)Re(CO)\{P(OMe)_3\}Br_2]$	116−118		
trans-$[(\eta^5\text{-}C_5H_4Me)Re(CO)\{P(OPh)_3\}Br_2]$	164−166	145−150	80
cis-$[(\eta^5\text{-}C_5H_4Me)Re(CO)\{P(OPh)_3\}Br_2]$	183−185		
trans-$[(\eta^5\text{-}C_5H_4Me)Re(CO)(PPh)_3]Br_2]$	186−188	145−150	72
cis-$[(\eta^5\text{-}C_5H_4Me)Re(CO)(PPh)_3]Br_2]$	200−202		
trans-$[(\eta^5\text{-}C_5H_4Me)Re(CO)(NCC_6H_3Me_2)Br_2]$	154−156	140−145	86
cis-$[(\eta^5\text{-}C_5H_4Me)Re(CO)(NCC_6H_3Me_2)Br_2]$	192−194		
trans-$[(\eta^5\text{-}C_5H_4Me)Re(CO)(NCC_6H_3Me_2)BrI]$	155−157	135−140	85
cis-$[(\eta^5\text{-}C_5H_4Me)Re(CO)(NCC_6H_3Me_2)BrI]$	193−195		
trans-$[(\eta^5\text{-}C_5H_4\textit{t}Bu)Re(CO)(NCC_6H_3Me_2)Br_2]$	142−144	130−135	94
cis-$[(\eta^5\text{-}C_5H_4\textit{t}Bu)Re(CO)(NCC_6H_3Me_2)Br_2]$	194−196		
trans-$[(\eta^5\text{-}C_5H_4\textit{t}Bu)Re(CO)\{P(OMe)_3\}Br_2]$	123−125	103−110	82
cis-$[(\eta^5\text{-}C_5H_4\textit{t}Bu)Re(CO)]\{P(OMe)_3\}Br_2]$	154−156		
trans-$[(\eta^5\text{-}C_5H_4\textit{t}Bu)Re(CO)\{P(O\textit{i}Pr)_3\}Br_2]$	126−128	105−110	70
cis-$[(\eta^5\text{-}C_5H_4\textit{t}Bu)Re(CO)\{P(O\textit{i}Pr)_3\}Br_2]$	170−172		
trans-$[(\eta^5\text{-}C_5H_4\textit{t}Bu)Re(CO)(PPh_3)Br_2]$	172−174	140−145	85
cis-$[(\eta^5\text{-}C_5H_4\textit{t}Bu)Re(CO)(PPh_3)Br_2]$	190−192		
trans-$[(\eta^5\text{-}C_5H_4\textit{t}Bu)Re(CO)\{P(OPh)_3\}Br_2]$	124−126	108−110	85
cis-$[(\eta^5\text{-}C_5H_4\textit{t}Bu)Re(CO)\{P(OPh)_3\}Br_2]$	158−160		
trans-$[(\eta^5\text{-}C_5H_4SiMe_3)Re(CO)(NCC_6H_3Me_2)Br_2]$	144−146	130−135	76
cis-$[(\eta^5\text{-}C_5H_4SiMe_3)Re(CO)(NCC_6H_3Me_2)Br_2]$	179−181		
trans-$[(\eta^5\text{-}C_5H_4SiMe_3)Re(CO)\{P(O\textit{i}Pr)_3\}Br_2]$	106−108	90−95	70
cis-$[(\eta^5\text{-}C_5H_4SiMe_3)Re(CO)\{P(O\textit{i}Pr)_3\}Br_2]$	159−161		
trans-$[(\eta^5\text{-}C_5H_4SiMe_3)Re(CO)(PPh_3)Br_2]$	155−157	130−135	75
cis-$[(\eta^5\text{-}C_5H_4SiMe_3)Re(CO)(PPh_3)Br_2]$	187−189		
trans-$[(\eta^5\text{-}C_5H_4SiMe_3)Re(CO)\{P(OPh)_3\}Br_2]$	124−126	108−110	85
cis-$[(\eta^5\text{-}C_5H_4SiMe_3)Re(CO)\{P(OPh)_3\}Br_2]$	154−156		

[a] Reaction goes from the *trans* to the *cis* isomer.

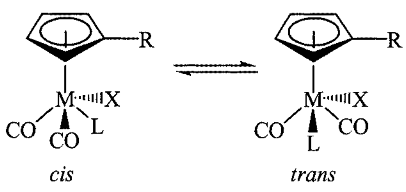

Figure 6. *cis* and *trans* isomers of $[(CpR)M(CO)_2LX]$ (M = Mo, W; L = phosphane, phosphite, isocyanide; X = halide)

cis to the *trans* isomer on standing at room temperature.[65] Also, while our work was in progress, Filippou and coworkers reported on the isomerization reaction (*cis* to *trans*) of $[(C_5R_5)W(CO)_2(PMe_3)GeCl_3]$ (R = H, Me) and $[(C_5Me_5)Mo(CO)_2(PMe_3)GeCl_3]$ in the solid state.[66]

Variation of the Halide

$[(CpMe)Re(CO)_2I_2]$ was synthesized (see below) and, remarkably, this complex isomerized from the *cis* to the *trans* isomer (>90%) — the reverse of the reaction for [(CpMe)Re(CO)$_2$Br$_2$].[67] The isomerization reaction, which takes place in the melt, and possibly the solid state, is more rapid for the iodo complex than for the bromo complex.[26][68] The mixed-halide complex [(CpMe)Re(CO)$_2$IBr] has also been synthesized and isomerizes from the *trans* (dihalide) to the *cis* (dihalide) isomer. More interestingly, reaction of [(CpMe)Re(CO)$_2$IBr] with 2,6-Me$_2$C$_6$H$_3$NC (RNC) yields [(CpMe)Re(CO)(RNC)IBr], a complex with *five different* substituents. This complex also undergoes a *trans* to *cis* isomerization reaction in the solid state (Table 2) and should provide interesting information on subtle features associated with the reaction mechanism (see below).[59]

From the above it can be seen that the reaction type is quite general and no doubt many other "pseudo" five-coordinate complexes will be discovered that will show solid-state isomerization behavior. However, no obvious pattern can be established that indicates which complexes will indeed isomerize and even the direction undertaken in the isomerization reaction. The data do however indicate that: (a) the isomerization can occur in the solid state if the temperatures of the melting point and the isomerization reaction are well separated, but that this in itself is not a sufficient criterion for isomerization to occur, and (b) reaction occurs from the complex with the lower melting point to that with the higher melting point.

Factors that Drive the Reaction

General Considerations

If a unidirectional isomerization reaction occurs in the solid state it suggests that the *kinetic* product is obtained during the precipitation reaction and that the *thermodynamic* product is formed on heating the solid. Either inter- or intramolecular interactions or, combinations of both factors, can drive the reaction to the thermodynamically favored product in the solid state. A more important question that has to be addressed is: does the isomerization reaction drive the change in the overall structure or do changes in the bulk structure drive the isomerization reaction?

Further, the reaction can be viewed as occurring by independent individual reactions in cavities (topotactic reaction[69]) *or* by a concerted process in which a rearrangement within a molecule (or between molecules) drives molecules in close proximity to rearrange.[70] In this latter instance the surface and defects will play an important role in the reaction.

Intramolecular Factors

Here both steric and electronic factors could play a role in determining the favored isomer. Indeed, reactions in solution are normally rationalized using these factors (e.g. *cis* and *trans* effects, cone angles, solid angles etc.). Data need to be evaluated from crystallographic analyses and it can be expected that even small *inter*molecular effects could be difficult to eliminate in the analysis.

Intermolecular Effects

The close proximity of atoms in the solid state can lead to attractive forces that could lead to the preference of one structure (e.g. isomer) over another; these forces could override intramolecular factors. These effects can, in principle, be detected by unit cell volume changes, measurement of bond lengths/angles and phase changes.

Attempts to Determine Factors that Influence the Isomerization Reaction

X-ray structural analyses

Structure determinations were undertaken for both isomers of a series of Re complexes in an attempt to evaluate the factors responsible for the reaction direction.[71−73] Three pairs of *cis*/*trans* isomers were chosen for study. The structures covered the range in which isomerization occurred with {[(CpMe)Re(CO)$_2$Br$_2$]} and without {[(CpMe)Re(CO){P(OPh)$_3$}Br$_2$]} single crystal disintegration, and a *cis*/*trans* pair in which no isomerization was detected {[(Cp*t*Bu)Re(CO)$_2$Br$_2$]}.

Table 3. Structural parameters for *cis* and *trans* isomers of [(CpR)Re(CO)LBr$_2$] complexes [R = *t*Bu, Me; L = CO, P(OPh)$_3$] (taken from refs.[71−73])

Complex	Space group		V (Å^3)[a]		Dir[b]
	cis	trans	cis	trans	
[(CpMe)Re(CO)$_2$Br$_2$]	$P2_1/c$	$P1$	1078	535	t→c
[(Cp*t*Bu)Re(CO)$_2$Br$_2$]	$P2_1/a$	Pbca	1375	2829	nr
[(CpMe)Re(CO){P(OPh)$_3$}Br$_2$]	$P2_1/c$	$P2_1/c$	2468	2481	t→c

[a] Note that in some instances there are half the number of molecules per unit cell. [b] Dir = direction of the isomerization reaction in the solid state.

Key data are shown in Table 3. Analysis of this data reveals that:

a) No correlation between volume changes and the isomerization reaction/direction is apparent.

b) No unusual inter-atomic bond lengths are noted (see refs.[71−73]).

c) A change in space group does not rule out an isomerization reaction.

d) The single crystal to single crystal reaction of [(CpMe)Re(CO){P(OPh)$_3$}Br$_2$] occurs in the same space group but this is not a necessary requirement for a single crystal reaction to occur.

Powder diffraction studies carried out on [(CpMe)Re(CO)$_2$Br$_2$] revealed that the *cis* isomer generated by heating the *trans* isomer is identical to the *cis* isomer prepared independently in the solution reaction. Thus, no polymorphs were produced in the reaction.[72]

Molecular Mechanics Calculations

Attempts were made to determine the preferred isomer of [(CpMe)Re(CO)$_2$Br$_2$] by use of molecular mechanics and semi-empirical methods, both for the isolated molecules and for the crystalline form. The data did not distinguish between the two isomers.[74] The failure of this analysis related to our inability to correctly allow for the evaluation of intermolecular interactions in our calculations. More sophisticated analyses may assist here.

Differential Scanning Calorimetry (DSC) Data

An extensive DSC study of selected Re samples revealed that the position and shape of exotherms, corresponding to the isomerization reaction, were influenced by both heating rates and crystal dimensions.[75] Indeed, at high heating rates (e.g. 20 °C/min) simultaneous melting and isomerization reactions could be detected.

Initially it appeared that the DSC technique could be used to screen isomers for their ability to transform in the solid state. However, some recent results obtained from studies on [(CpMe)Mo$(CO)_2$LI] [L = PPh_3, P(O*i*Pr)$_3$] have indicated cases in which isomerization occurs in the solid state but without the presence of an accompanying exotherm being detected by DSC. When the above reactions are monitored by NMR spectroscopy at temperatures below 100 °C, isomerization is noted yet no DSC exotherm is detected in the DSC profile.[63][64] The exotherms noted at temperatures above 100 °C correspond to decomposition reactions. A combination of DSC, powder XRD, solution NMR studies of reactants and optical microscopy studies of the Mo complexes reveals that isomerization commences prior to decomposition of the *cis* isomer to give as yet unidentifiable Mo complexes and $OPPh_3$.[64]

The inability to detect a DSC exotherm corresponding to a chemical reaction has been commented on by Dunitz[76] and reveals the danger of using only one technique to evaluate changes in a reaction.

Optical Microscopy Studies

An optical microscopy study of the Re complexes indicated that both crystal fragmentation and the presence of single crystal to single crystal reactions could be detected by this procedure. Two examples are described. In the first instance the isomerization of *trans*-[(CpMe)Re$(CO)_2Br_2$] was monitored as a function of time, and pictures taken at t = 0.5 h, 1 h, 3 h, 3 h (expanded) are shown in Figure 7. Disintegration of the crystal can be seen on the crystal edges after 1 h and indeed darkening (formation of the *cis* isomer) within the crystal can also be detected. The isomerization occurs with formation of a *new crystalline material*, as seen in Figure 7d, which is an expanded portion of the top left hand corner of Figure 7c.

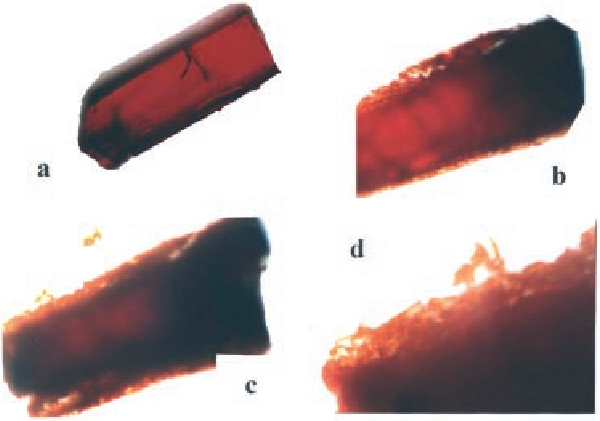

Figure 7. The isomerization of *trans* [(CpMe)Re$(CO)_2Br_2$] as a function of time (a = 0.5 h, b = 1 h, c = 3 h, c = 3 h − at higher magnification)

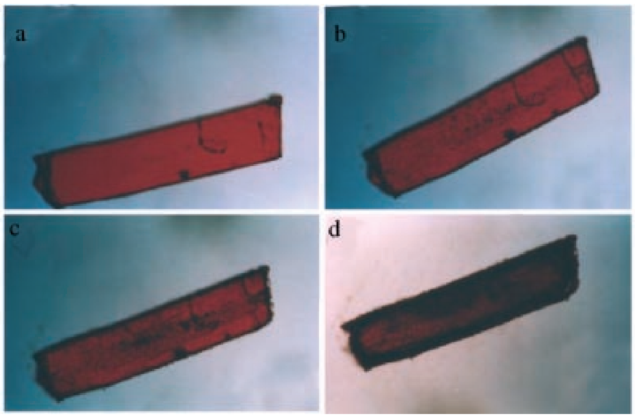

Figure 8. The isomerization of *trans*-[(CpMe)Re(CO)(2,6-$Me_2C_6H_4NC)Br_2$] as a function of time (a = 0 h, b = 2 h, c = 6 h, d = 17 h)

Figure 8 shows the isomerization reaction of *trans*-[(CpMe)Re(CO)(2,6-$Me_2C_6H_4NC)Br_2$] with time (t = 0 h, 2 h, 6 h, 17 h). Darkening (corresponding to formation of the *cis* isomer) can be seen to occur at the surface as well as at cracks on the surface. The surface becomes rough with time but essentially the crystal remains single. No obvious pattern relating to the isomerization can be detected at this magnification. However, studies by Kaupp, using scanning tunneling microscopy (STM) on reactions in organic crystals, have suggested that “phase rebuilding” should be expected in many solid-state reactions, and indeed could be occurring here.[77]

In the case of [(CpMe)Re(CO)$\{P(OPh)_3\}Br_2$] (data not shown) the crystal retained its crystallinity throughout the isomerization reaction as determined by optical microscopy. Interestingly, when the crystal appeared to be completely converted, as detected by a homogeneous dark surface coloring under the optical microscope, only 22% of the *cis* isomer was detected by X-ray crystallography.

All the data is thus consistent with reactions commencing at the surface (or at defects). For all three Re compounds the pictures clearly reveal the heterogeneous nature of the reaction.

Reaction Mechanism

Two extreme mechanisms can be envisaged: (a) all ligands are attached to the metal atom, or (b) some ligands dissociate/re-associate (either as ions, atoms or molecules) in the reaction.

The reaction mechanism for the solution state *cis*-*trans* isomerization reaction of [CpMo(CO)$_2$LX] complexes was studied in the 1970's by Faller,[78,79] Poilblanc[80] and coworkers. Faller proposed a mechanism based on a variation of a Berry pseudorotation model. The lowest energy pathway in the reaction involves a trigonal bipyramidal intermediate with the Cp ring and the L group in axial positions (Figure 9). In this mechanism all groups move extensively, a situation made possible in a solvent.

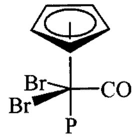

Figure 9. A proposed intermediate/transition state for the *cis*/*trans* isomerization reaction of [CpMo(CO)$_2$LX] (ref.[79])

In an early attempt to evaluate the mechanism of the isomerization reaction in the solid state we carried out a structure correlation analysis of a wide range of ML$_5$ complexes using the Cambridge Structural Database.[81] Our data indicated that a modified Berry−Turnstile mechanism could fit the data (see Figure 10). For example, the isomerization of [(CpMe)Re(CO){P(OPh)$_3$}Br$_2$] could be rationalized with a mechanism that requires the two bulky groups [Cp, P(OPh)$_3$] to act as pivots while the movement of the three small groups undergoes rotation around a threefold axis through the metal. Some motion of the bulky groups (e.g. flexing) to accommodate the isomerization reaction is possible but the key feature entails rotation of the three nonbulky groups in the reaction.

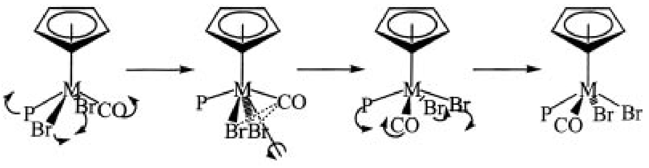

Figure 10. Proposed isomerization reaction for [(CpMe)Re(CO){P(OPh)$_3$}Br$_2$] based on the movement of three ligands. (ref.[81])

A recent study has led to a more detailed understanding of the reaction mechanism.[73] The single crystal to single crystal reaction of [(CpMe)Re(CO){P(OPh)$_3$}Br$_2$] was monitored by X-ray crystallography as a function of time. A consideration of the electron density changes indicated that only *one* of the Br ligands exchanges with the CO ligand. This suggests that the mechanism for the isomerization reaction entails rotation of the CO and one of the Br groups by 180° around an axis through the metal (Figure 11). This unexpected result relates to the size of the "cavity" in which a [(CpMe)Re(CO){P(OPh)$_3$}Br$_2$] molecule is confined. The second Br group is close to the ring Me group and appears to be sterically constrained in the lattice. A plot of the unit cell down the *b* axis suggests that there is a cavity of sufficient size to allow for the two-atom rotation. Notwithstanding this, the optical microscopy study also suggests that the reaction may be initiated from the "cavity surface" by a phase rebuilding process (see above).

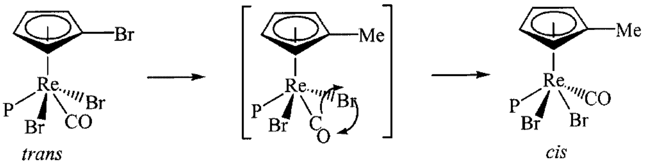

Figure 11. Proposed isomerization reaction for [(CpMe)Re(CO){P(OPh)$_3$}Br$_2$] based on the movement of two ligands

The electron density maps recorded as a function of isomer conversion suggested that the rotation occurs such that the CO (not the Br) ligand approaches the ring. In the rotation process, the other ligands could flex to allow for formation of a larger cavity. Indeed, the issue of a fixed versus flexible cavity *in general* is topical and currently under investigation.[82]

The *trans* to *cis* isomerization reaction of [(CpMe)Re(CO){P(OPh)$_3$}Br$_2$] has been monitored as a function of temperature (115−150 °C) (Figure 12).[83] The kinetic study suggests that the reaction is first order, but that two first order terms are required to give a good fit to the data. The smaller term derived from the rate expression has tentatively been assigned to an annealing process that follows the isomerization reaction.[73] An activation energy of 100 ± 9 kJ·mol^{-1} has been measured for the reaction.[83]

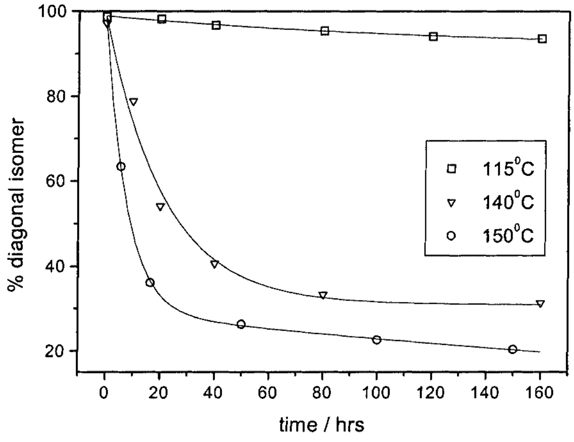

Figure 12. The *trans* to *cis* isomerization reaction of [(CpMe)Re(CO){P(OPh)$_3$}Br$_2$] as a function of temperature (115−150 °C)

These data do not as yet differentiate between the possibility of a process in which the two exchanging atoms (Br, CO) are bonded at all times to Re and one in which the Re−Br bond is cleaved and then reforms. (It is unlikely that CO dissociates during the reaction as the high temperatures required to induce isomerization, typically 110 °C to 145 °C, would result in loss of CO from the crystal).

Experiments to evaluate the possibility of halide-metal bond cleavage occurring during the isomerization reaction were performed. Reaction of *trans*-[(CpMe)Re(CO$_2$)Br$_2$] with NaI (excess) gave *trans*-[(CpMe)Re(CO$_2$)I$_2$] in quantitative yield.[26] Although this suggests a mechanism entailing halide exchange the finding may not have bearing on the isomerization reaction. Studies on [(CpMe)Re$(CO)_2$BrI] are currently underway to evaluate this issue further.

Isomerization of $CpML_4$ Complexes in Matrices

Hill and co-workers have investigated photochemically induced isomerization reactions in frozen matrices for a range of $CpML_4$ complexes.[84−88] The results of the investigations can be summarized as follows:

i) For complexes of the type [CpRe$(CO)_2Br_2$] and [CpM$(CO)_2$LX] (Mo, W), photolysis induces *CO loss* and the intermediates formed at low temperature (e.g. 12 K) either retained (Mo, W) or lost (Re) the geometry of the starting isomer. At higher temperatures (100 K) the Mo and W *cis*/*trans* isomers inter-converted (Figure 13).[84]

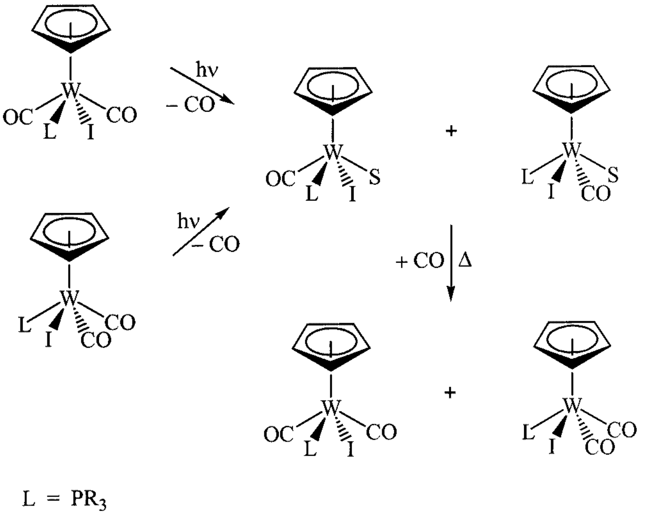

Figure 13. Photolysed low temperature *cis*/*trans* isomerization reaction of [CpW$(CO)_2$LI] (ref.[84])

ii) The isomerization ratio was similar to data observed in solution.

These data again indicate the powerful role played by the reaction cavity in the reaction. In this instance, the cavity acts to limit movement of CO away from the metal, but even under the conditions studied, preferential isomerization is seen to occur.

Isomerization of $CpML_4$ Complexes on Surfaces

Surfaces provide a range of active functional groups with which a molecule can interact. Indeed, chemical reactions between a molecule and a surface (chemisorption) provide a means to synthesize both catalysts and new reagents. To the best of our knowledge this interaction has not been exploited in isomerization reactions. However, the exploitation of the interaction of a molecule with a surface via weak dipole or van der Waals interactions to induce isomerization reactions has been reported (see below).

Hill and co-workers [88] have studied the photolytic isomerization of [(C_5Me_5)Re$(CO)_2Br_2$] on Si (111) surfaces at low temperature. The reaction occurred from the *cis* to the *trans* isomer, the same direction as found in solution. Photolysis of the intermediate produced at low temperature generated a second unsaturated isomer that gave the *cis* isomer on warming. (Figure 14).

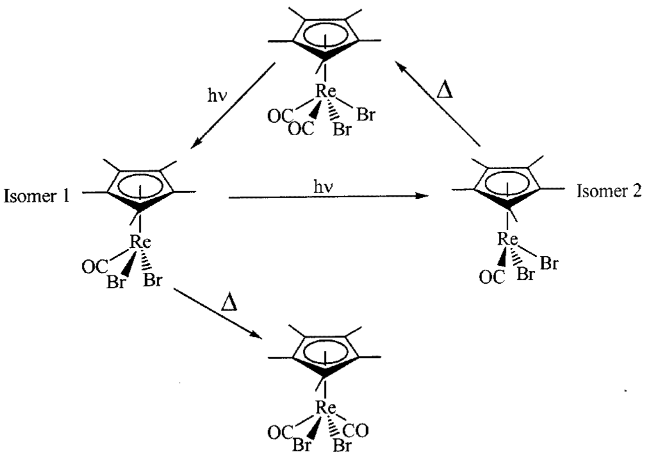

Figure 14. *cis*/*trans* isomerization reactions of [(C_5Me_5)Re$(CO)_2Br_2$] (film) on the surface of Si (111); irradiation of the *cis* isomer (at 77 K) gives isomer 1 which then generates both the *trans* isomer (on warming) and isomer 2; isomer 2 on warming reverts back to the *cis* isomer (ref.[88])

Addition of *cis* or *trans* isomers of [(CpR)Re$(CO)_2X_2$] (R = H, Me; X = Br, I)[68] and [{Cp$(SiMe_3)_2$}Re$(CO)_2Br_2$][60] to silica supports, followed by room temperature photolysis with a 200 W light source, has resulted in isomerization of the isomers to equilibrium isomer mixtures. After reaction the material can be extracted from the support to yield the isomer mixture in good yield (typically >85%). Reactions to evaluate the reaction mechanism were performed:

a) Selective removal of the surface OH groups with Me_2SiCl_2 gave a reaction that correlated with the amount of OH groups retained on the surface.

b) Irradiation of the reactants in the absence of support gave no isomerization reaction.

c) Irradiation of [(CpMe)Re$(CO)_2Br_2$]/NaI (excess) on SiO_2 gave *cis* and *trans*-[(CpMe)Re$(CO)_2I_2$].

d) Irradiation of a 50:50 mixture of *cis*/*trans* [(CpMe)Re$(CO)_2Br_2$]/[(CpMe)Re$(CO)_2I_2$] on SiO_2 gave a mixture of products that included both isomers of [(CpMe)Re$(CO)_2$BrI].

These data are consistent with interaction between the Br ligand and the surface OH groups. However, they do not distinguish between a radical or an ionic mechanism. A possible ionic mechanism involving Br interaction with a silica OH group is shown in Figure 15.[68] The kinetics of the reaction have been monitored and the data can be interpreted in terms of first order kinetics.[89] The isomerization rate on the surface follows the order [CpRe$(CO)_2I_2$] > [CpRe$(CO)_2Br_2$] > [(CpMe)Re$(CO)_2Br_2$], with the activation energy for all of the reactions lying in the range 60−75 kJ·mol^{-1}.

Table 4. Summary of isomerization reaction data in a confined environment[a]

Complex	Crystal/ powder	Melt	Solution	On support
[(CpMe)Re(CO)$_2$Br$_2$]	$t \rightarrow c$	($t \rightarrow c$)[b]	$c \rightarrow t$	$t \rightarrow c$
[(CpEt)Re(CO)$_2$Br$_2$]	na	$t \rightarrow c$[c]	$c \rightarrow t$	$t \rightarrow c$
[(CpMe)Re(CO)$_2$I$_2$]	$c \rightarrow t$[d]	$c \rightarrow$ t	$c \rightarrow t$	$c \rightarrow t$
[(CpMe)Re(CO){P(OPh)$_3$}Br$_2$]	$t \rightarrow c$	na	$t \rightarrow c$	$t \rightarrow c$
[CpW(CO)$_2${P(O*i*Pr)$_3$}I]	$t \rightleftarrows c$[e]	na	$t \rightleftarrows c$[f]	

[a] *t* = *trans*, *c* = *cis*; na = not applicable. [b] Reaction occurs in the solid. However, when the reaction is monitored by DSC at high heating rates, it appears that a reaction can be induced in the melt. [c] An equilibrium is established (ca. 65:35 *cis*/*trans*). [d] It is possible that a reaction in the solid state precedes the reaction in the melt. [e] Reaction proceeds from either isomer to yield a 30:70 *cis*/*trans* ratio of isomers. [f] In benzene (reflux) the equilibrium ratio is 70:30 *cis*/*trans*.

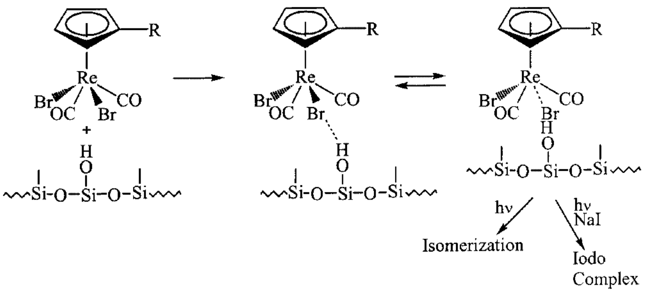

Figure 15. Possible ionic mechanism for the *trans* to *cis* isomerization of [(CpMe)Re(CO)$_2$Br$_2$] on the surface of silica (ref.[67])

Isomerization of CpML$_4$ Complexes on Zeolite/Mesoporous Surfaces

The reaction described above has also been performed on high surface area MCM-41 zeolite whose pores (42 Å) are large enough to accommodate the Re molecules.[89] The data were obtained for [(CpR)Re(CO)$_2$Br$_2$] (R = H, Me; both isomers) In all instances reaction occurred to yield equilibrium mixtures favoring the *cis* isomer. Only pure silica zeolites could be used, as reactions on *acidic* alumina generate [(CpR)Re(CO)$_3$] from the [(CpR)Re(CO)$_2$Br$_2$].[89]

A small-pore zeolite would only function as support by use of the external zeolite surface as the pores are too small to accommodate the reagent molecules.

Conclusions and Future Prospects

This Microreview has concentrated on a limited area of solid-state organometallic chemistry. A summary of some of the results obtained indicates the influence of the reaction environment and the reactant on the direction of a reaction (Table 4). The study has also indicated that the reaction mechanism may be different from that found in solution. Indeed, a host of mechanisms have been proposed/detected for the simple *cis*/*trans* isomerization reaction in different environments.

Clearly much work is still required to put in place the rules that permit the prediction of the reaction direction.

Other reaction types such as ligand replacement, ligand addition and ligand conversion have also been little explored in the solid state, and it is expected that such studies will yield mechanisms different from that observed in solution.

Extension of solid-state synthetic studies in organometallic chemistry to reagent mixing in the solid state to generate solventless chemical procedures has not been systematically explored to date and so the area is open for development.[90] Furthermore, the possibility of performing reactions between solids/liquids, solids/gases and carrying out reactions in the melt are still in their infancy.[9]

The remarkable success currently being achieved in the area of solid-state organic chemistry attests to the importance of the general area of solid-state chemistry. It is hoped that the same may be found true for the area of organometallic chemistry.

Acknowledgments

We would like to acknowledge the many postgraduate students in our group who have contributed to the development of this area of chemistry and in particular to Lin Cheng whose initial observations were so critical to what has since been discovered. We are also thankful to our funding sources for continued support (THRIP, SASTECH, NRF and the University of the Witwatersrand).

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Received April 17, 2002
[I02201]