

Ligand Dissociation: Planar or Pyramidal Intermediates?

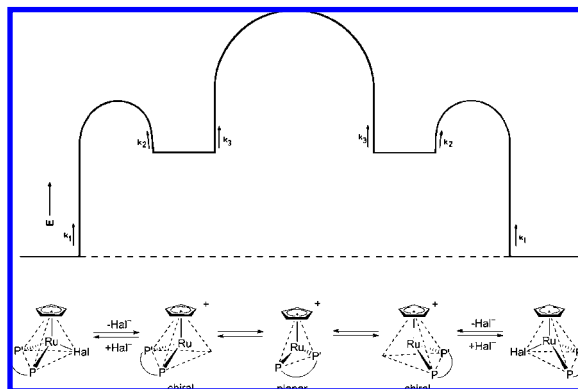
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CON SPECTUS

In organometallic chemistry, ligand dissociation is a key intermediate step in many useful processes. The dissociation of halide from an 18-electron half-sandwich complex (that is, with a single cyclopentadienyl ligand) of the type $[\text{CpRu}(\text{P}-\text{P}')\text{Hal}]$ leaves an unsaturated 16-electron intermediate $[\text{CpRu}(\text{P}-\text{P}')^+]$, which is then ready for subsequent addition reactions. Does the intermediate maintain its structure with a vacant site in place of the dissociated ligand, or does it rearrange, either concurrent with its formation or subsequently? In other words, are the 16-electron species planar or pyramidal? The outcome is relevant for chiral-at-metal compounds $[\text{CpML}^1\text{L}^2\text{L}^3]$ because an intermediate $[\text{CpML}^1\text{L}^2]$ retains its chirality with respect to the metal atom as long as it is pyramidal, whereas it loses its chiral information if it becomes planar. In this Account, we address experimental results and theoretical calculations that help illuminate the energetics of structural rearrangements after halide dissociation.



The rate-determining step in the halide exchange and racemization reactions of (R_{Ru}) - and (S_{Ru}) - $[\text{CpRu}(\text{P}-\text{P}')\text{Cl}]$ is the cleavage of the Ru–Cl bond to give pyramidal intermediates (R_{Ru}) - and (S_{Ru}) - $[\text{CpRu}(\text{P}-\text{P}')^+]$, which have kept the original metal configurations. These unsaturated intermediates can react with added ligands, such as Br^- or I^- (k_2 paths). The substitution products form with retention of the metal configuration. However, the pyramidal intermediates (R_{Ru}) - and (S_{Ru}) - $[\text{CpRu}(\text{P}-\text{P}')^+]$ can also invert to their mirror images (k_3 paths). For (R_{Ru}) - and (S_{Ru}) - $[\text{CpRu}(\text{P}-\text{P}')^+]$, the barrier of the pyramidal inversion (k_3) is much higher than that of the halide addition (k_2).

The competition ratio k_3/k_2 determines how much racemization occurs in a ligand exchange reaction. The competition ratio k_3/k_2 can be determined from the ratio of the (R_{Ru}) - and (S_{Ru}) -products, which is constant throughout the course of the reaction. For compounds like $[\text{CpRu}(\text{P}-\text{P}')\text{Hal}]$, k_3/k_2 is much smaller than 1, resulting in an energy profile that resembles a basilica.

These results, established with chiral-at-metal compounds, are supported by calculations that show that 16-electron half-sandwich intermediates with σ -donating ligands, such as $[\text{CpM}(\text{NH}_3)_2]$, adopt planar structures, whereas strongly π -bonding ligands, as in $[\text{CpM}(\text{CO})_2]$, lead to pyramidal intermediates. The computed activation energies for the pyramidal inversion are on the order of 10 kcal/mol, with the planar species being transition states.

The ligand dissociation behavior of 18-electron transition metal complexes is compared with nucleophile dissociation in main group compounds with octet configurations; here we include new computational results. Without exception, unsaturated main group intermediates, such as the carbenium ions formed in $\text{S}_{\text{N}}1$ reactions, are planar.

Our results and analysis help put transition metal chemistry on a firmer mechanistic foundation, and chiral-at-metal compounds are invaluable to this end.

Introduction

For organometallic compounds of the transition elements, ligand dissociation is a ubiquitous reaction. In the cleavage of the M–L bond, the ligand L takes the electron pair of the coordinative bond. In the resulting intermediate, the metal atom falls short by two electrons compared with the starting material. Given that the metal atom had a closed 18-electron valence shell, then it has 16 electrons in the unsaturated intermediate. Ligand dissociations mostly are the first steps in substitution reactions and in the formation of catalytically active species. In this Account, the ligand dissociation from pseudo-tetrahedral three-legged half-sandwich complexes of the type $[\text{CpML}^1\text{L}^2\text{L}^3]$, having 18 valence electrons, will be compared with the dissociation of nucleophiles from tetrahedral main group compounds, having an electron octet. Three-legged half-sandwich complexes actually are octahedral compounds, because the Cp ligand occupies three *cis*-coordination positions and the angles L–M–L are close to 90° . However, the metal is surrounded by four different ligands. Thus, there is only the isomerism of the tetrahedron with four different substituents, image and mirror image (Scheme 1).

Dissociation Reactions in Main Group Compounds

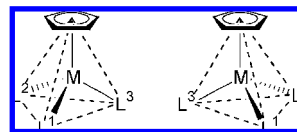
In main group chemistry, a typical example of a “ligand” dissociation is the $\text{S}_{\text{N}}1$ mechanism. In the 1930s, the classical $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ mechanisms of nucleophilic substitution at the saturated carbon atom were established by Hughes and Ingold. Then, the two most important methods of investigation were kinetic measurements and stereochemical studies. The pillar kinetics showed whether a reaction followed first-order or second-order kinetics, whereas the pillar stereochemistry revealed the stereochemical course of a reaction: retention or inversion of configuration and racemization or epimerization.

In the $\text{S}_{\text{N}}1$ mechanism, the heterolytic cleavage of *tert*-alkyl halides to give an alkyl cation and a halide anion follows Scheme 2, proposed by Winstein et al. to account for the kinetics and stereochemistry of solvolysis reactions.^{1–3}

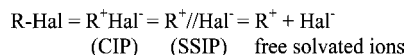
In the first step, which is rate-determining, cleavage of the C–Hal bond produces a contact ion pair (CIP). Subsequently, separation of the ions results in a solvent-separated ion pair (SSIP). In a final step, the free solvated ions are formed. All species can lead to products.

The kinetics of solvolyses of tertiary alkyl halides in protic polar solvents is unimolecular. The stereochemistry typically shows 20–35% inversion of configuration.^{4,5} The free energy barrier of the rate-determining step of the hydrolysis of *tert*-

SCHEME 1. Enantiomers of Three-Legged Half-Sandwich Complexes $[\text{CpML}^1\text{L}^2\text{L}^3]$



SCHEME 2. Steps Involved in the $\text{S}_{\text{N}}1$ Dissociation of a *tert*-Alkyl Halide



butyl chloride in water was determined experimentally to be 19.5 kcal/mol at ambient temperature.^{1–3} Energy profiles such as that in Figure 1 have been suggested for this solvolysis reaction, in which solvent-separated ion pairs are not included as extra species.^{2,6}

Calculations of the hydrolysis of Me_3CCl in water consistently gave barriers in the range of 20–23 kcal, close to the experimental value.^{6–8} However, the depth of the potential well, in which the contact ion pair $\text{Me}_3\text{C}^+\text{Cl}^-$ resides with respect to the rate-determining transition state and the free ions, remains a question of debate.

A calculation of the hypothetical heterolysis of Me_3SiCl in water was carried out recently,⁸ hypothetical because there is no heterolysis of $\text{R}_3\text{Si-Hal}$ bonds in solution. R_3SiHal compounds react with nucleophiles in associative mechanisms involving pentacoordinate intermediates.⁹ The computed barrier for the dissociation of the Si–Cl bond in Me_3SiCl was 40.8 kcal and thus prohibitively higher than the 22.3 kcal of the calculated barrier of the corresponding C–Cl bond.⁸

The $\text{S}_{\text{N}}1$ dissociation of Me_3CCl is a well-established mechanism. Related compounds of main group elements, such as $[\text{Me}_3\text{BCl}]^-$ and $[\text{Me}_3\text{BNMe}_3]$, should behave similarly when the coordinative bonds are broken. On dissociation of Cl^- and NMe_3 , the planar molecule Me_3B , which is the neutral analog of the carbenium ion Me_3C^+ , will planarize. There is no reason for an unsaturated six-electron main group species to remain pyramidal. Thus, an octet-configured main group compound with four substituents has no choice; dissociation of a nucleophile will leave an intermediate that definitely will become planar. How about transition metal compounds with 18 valence electrons, such as $[\text{CpML}^1\text{L}^2\text{L}^3]$? Will the 16-elec-

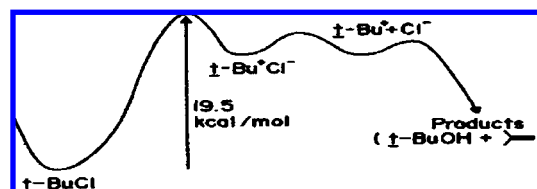
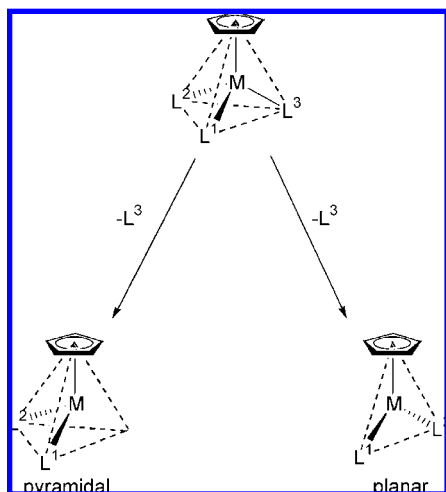


FIGURE 1. Reaction profile for the hydrolysis of Me_3CCl in water.

SCHEME 3. Dissociation of L^3 from the Three-Legged Half-Sandwich Complex $[\text{CpML}^1\text{L}^2\text{L}^3]$: Is the Resulting Intermediate $[\text{CpML}^1\text{L}^2]$ Pyramidal or Planar?



SCHEME 4. (R_{Mn}) - $[\text{CpMn}(\text{NO})(\text{PPh}_3)\text{COOMe}]$ and (R_{Mn}) - $[\text{CpMn}(\text{NO})(\text{PPh}_3)\text{C}(\text{O})\text{Ph}]$



tron intermediate $[\text{CpML}^1\text{L}^2]$ after dissociation of L^3 rearrange or keep its structure with an empty coordination site (Scheme 3)? The answer will be yes and no, depending on the ligands L^1 and L^2 .

Hall Church Energy Profile: The System $[\text{CpMn}(\text{NO})(\text{PPh}_3)\text{X}]$ with Fast Pyramidal Inversion

The chiral-at-metal half-sandwich compounds $[\text{CpMn}(\text{NO})(\text{PPh}_3)\text{COOR}']$ ($R' = \text{CH}_3, \text{L-C}_{10}\text{H}_{19}$)^{10–13} and $[\text{CpMn}(\text{NO})(\text{PPh}_3)\text{C}(\text{O})\text{R}']$ ($R' = \text{CH}_3, \text{C}_6\text{H}_5,$ and $p\text{-C}_6\text{H}_4\text{R}'$)^{14–18} (Scheme 4) are configurationally stable in the solid state.

In solution, however, they are configurationally labile. They change the metal configuration in first-order reactions approaching the racemization equilibrium. In nonpolar solvents, the half-lives are in the range of minutes to hours at ambient temperatures.^{10,11,14–16} The concentration and solvent dependence of the racemization has been investigated including Hammett correlations and the addition of triphenylphosphine.^{11,13–16} These studies as well as exchange reactions with deuterated triphenylphosphine¹³ and substitution reactions with other phosphines, which occurred with partial retention of configuration,^{14,17,18} are in accord with Scheme 5. Reviews summarizing these mechanistic studies are available.^{19–23}

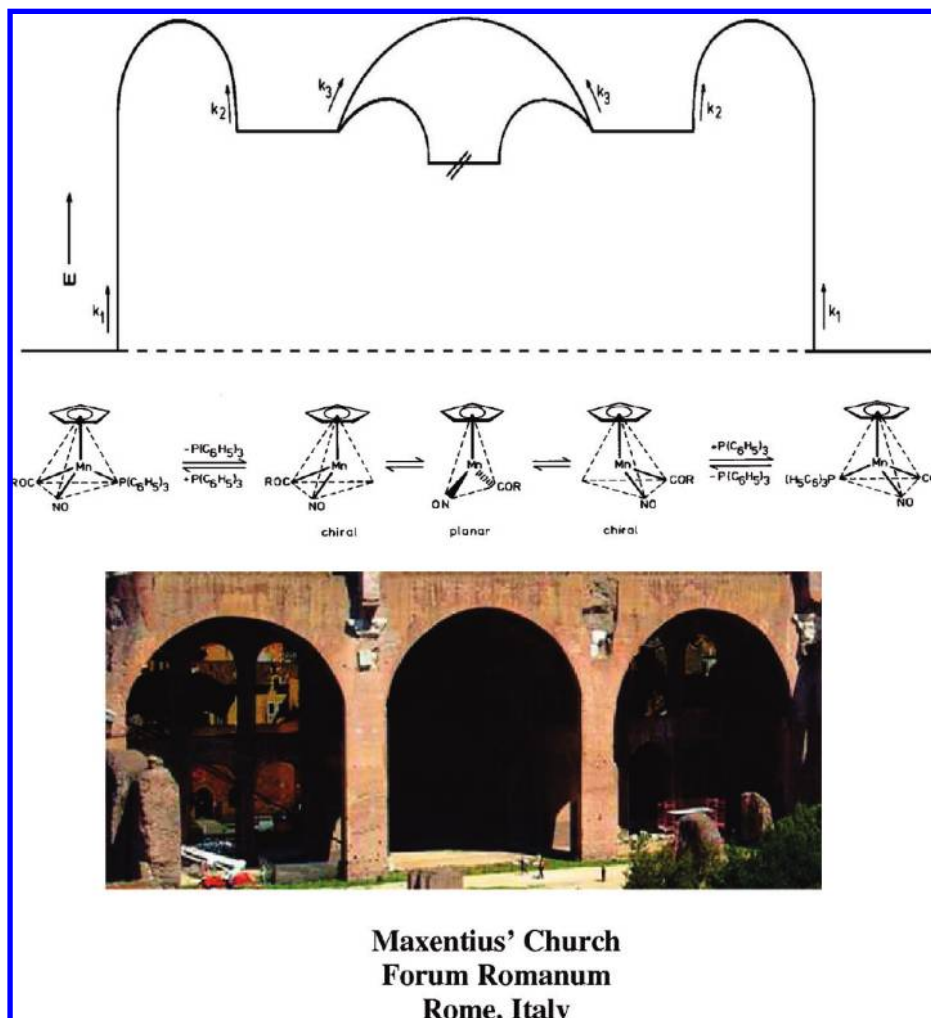
Omitting the crossed out part, the energy profile of Scheme 5 resembles the cross-section of a hall church in which the central nave and the side naves have the same height. Such hall churches were dominantly built in the late Gothic period (15th century) in Europe. Scheme 5 shows Maxentius' church on the Forum Romanum in Rome, Italy.

The rate-determining step in the racemization of (R_{Mn}) - $[\text{CpMn}(\text{NO})(\text{PPh}_3)\text{C}(\text{O})\text{R}]$ in Scheme 5 is the cleavage of the manganese–triphenylphosphine bond giving free triphenylphosphine and a pyramidal intermediate (R_{Mn}) - $[\text{CpMn}(\text{NO})\text{C}(\text{O})\text{R}]$ with an empty coordination site. Activation energies are on the order of 105–125 kJ/mol.^{11,15,16} Activation entropies are strongly positive in agreement with the dissociation of a neutral complex into two neutral parts. The unsaturated intermediate (R_{Mn}) - $[\text{CpMn}(\text{NO})\text{C}(\text{O})\text{R}]$ is high in energy and cannot be detected by spectroscopy. It can react with the dissociated or with added triphenylphosphine, with deuterated triphenylphosphine, or with other added ligands. All these reactions occur with retention of the metal configuration. However, the pyramidal intermediate (R_{Mn}) - $[\text{CpMn}(\text{NO})\text{C}(\text{O})\text{R}]$ can also invert to its mirror image (S_{Mn}) - $[\text{CpMn}(\text{NO})\text{C}(\text{O})\text{R}]$ from which the opposite configurational side is accessible. The barriers to the right (k_3) and to the left (k_2) from the pyramidal intermediate (R_{Mn}) - $[\text{CpMn}(\text{NO})\text{C}(\text{O})\text{R}]$ are assumed to have about the same height. Due to the air sensitivity and the instability (formation of paramagnetic impurities), detailed investigations of the competition ratio k_3/k_2 have not been possible in the CpMn system.

A crucial point is the middle part of Scheme 5. The assumption of the pyramidal intermediates (R_{Mn}) - and (S_{Mn}) - $[\text{CpMn}(\text{NO})\text{C}(\text{O})\text{R}]$ is unavoidable, because partial retention of configuration in substitution reactions could not be explained with a planar intermediate, $[\text{CpMn}(\text{NO})\text{C}(\text{O})\text{R}]$. However, the stereochemical results do not rule out the additional formation of a planar intermediate. Therefore, the question remains whether the planar species $[\text{CpMn}(\text{NO})\text{C}(\text{O})\text{R}]$ is an intermediate or a transition state in the interconversion of the pyramids (R_{Mn}) - and (S_{Mn}) - $[\text{CpMn}(\text{NO})\text{C}(\text{O})\text{R}]$.

Calculations and UV Photolysis

There are only a few theoretical studies, dealing with the geometry of coordinatively unsaturated 16-electron species of the type $[\text{CpML}_2]$.^{24,25} Extended Hückel methodology as well as density functional theory have been used. Whereas for fragments with strongly π -accepting ligands, such as $[\text{CpMn}(\text{CO})_2]$ and $[\text{CpFe}(\text{CO})_2]^+$, pyramidal structures with inversion barriers of about 10 kcal/mol were calculated, fragments with σ -donor ligands, such as $[\text{CpMn}(\text{PH}_3)_2]$ and $[\text{CpFe}(\text{PH}_3)_2]^+$,

SCHEME 5. Hall Church Energy Diagram for the Racemization of the Compounds $[\text{CpMn}(\text{NO})(\text{PPh}_3)\text{C}(\text{OR})]$ and Example of a Hall Church

were predicted to adopt planar geometries. In the DFT geometry optimization of $[\text{CpFe}(\text{CO})_2]^+$ the $\text{OC}-\text{Fe}-\text{CO}$ angle in the pyramidal species was 94.14° , while in the planar transition state it was 103.02° . B3LYP energy optimization showed that $[\text{CpRu}(\text{NH}_3)_2]^+$ was planar with an angle $\text{N}-\text{Ru}-\text{N}$ of 91° , whereas $[\text{CpRu}(\text{PH}_3)_2]^+$ was pyramidal with an angle $\text{P}-\text{Ru}-\text{P}$ of 96° .²⁶ Thus, ref 25 assigned planar configuration to the 16-electron fragment $[\text{CpFe}(\text{PH}_3)_2]^+$, whereas according to ref 26, its homologue $[\text{CpRu}(\text{PH}_3)_2]^+$ should have pyramidal configuration.

In the photolysis of $[\text{CpMn}(\text{CO})_3]$, the 16-electron species $[\text{CpMn}(\text{CO})_2]$ is formed.^{27–30} A combination of UV/vis monitoring and time-resolved IR spectroscopy allowed the nature and reactivity of the primary photoproduct $[\text{CpMn}(\text{CO})_2]$ to be probed.³¹ In cyclohexane solution, the primary photoproduct $[\text{CpMn}(\text{CO})_2]$ does not exist as an unsaturated intermediate with an empty coordination site, but rather as a $[\text{CpMn}(\text{CO})_2(\text{solvent})]$ complex, in which the solvent cyclohexane is a weakly bound “token” ligand.³¹ Therefore, the bond angle

$\text{OC}-\text{Mn}-\text{CO}$ 91.4° , obtained from the relative intensities of the two CO bands in the IR, is not the angle of the intermediate $[\text{CpMn}(\text{CO})_2]$, but that of $[\text{CpMn}(\text{CO})_2(\text{solvent})]$.^{30,31} The rate constants for reactions of $[\text{CpMn}(\text{CO})_2(\text{solvent})]$ are greater in *n*-heptane than in cyclohexane, indicating that *n*-heptane coordinates more weakly than cyclohexane.³¹ The rate of the reaction of $[\text{CpMn}(\text{CO})_2(\text{solvent})]$ with PPh_3 , leading to $[\text{CpMn}(\text{CO})_2\text{PPh}_3]$, is slower than that with CO or N_2 .³¹ Temperature-dependence studies showed that the reaction of $[\text{CpMn}(\text{CO})_2(\text{solvent})]$ with PPh_3 has a significant activation barrier, which must be attributed to the dissociation of the ligand solvent from the fragment $[\text{CpMn}(\text{CO})_2]$.³¹

Basilica-type Energy Profile: The System $[\text{CpRu}(\text{Prophos})\text{Hal}]$ with Slow Pyramidal Inversion

In Cp^*Ru chemistry ($\text{Cp}^* = \text{C}_5\text{Me}_5$), 16-electron complexes have been prepared. In contrast, the number of characterized 16-electron CpRu complexes, such as $[\text{CpRu}(\text{TMEDA})\text{X}]$,³² is rather lim-

ited. Complexes $[\text{Cp}^*\text{Ru}(\text{P}-\text{P})\text{X}]$ have been isolated; complexes $[\text{CpRu}(\text{P}-\text{P})\text{X}]$, however, are unknown. Planarity was assigned to species such as $[\text{CpRu}(\text{P}-\text{P})]^+$ on the basis of spectroscopy.³³ Investigation of this problem with the help of chirality, reviewed here, allowed additional and unequivocal information not accessible with other methods. The 16-electron species $[\text{CpRu}(\text{P}-\text{P})]^+$ are pyramidal, the planar species being transition states.³⁴ The system $[\text{CpRu}(\text{P}-\text{P})\text{Hal}]$ was not studied with the chiral-at-metal enantiomers $(R_{\text{Ru}})/(S_{\text{Ru}})$ but with the diastereomers $(R_{\text{Ru}},R_{\text{C}})$ - and $(S_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{Hal}]$ (ligand $\text{P}-\text{P}' = (R)\text{-Prophos}$, $\text{Hal} = \text{Cl}$, Br , I) in which the diastereomers $(R_{\text{Ru}},R_{\text{C}})$ and $(S_{\text{Ru}},R_{\text{C}})$ give rise to different signals in the NMR.³⁴ With diastereomers, the energy profile becomes unsymmetrical, right and left halves being different (Scheme 6).

The energy profile of Scheme 6 resembles the cross-section of a basilica in which the central part is much higher than the side parts. Basilica-type architecture has been used in profane and ecclesiastical buildings since the late Roman times as shown in Scheme 6 with Konstantin's arch on the Forum Romanum in Rome, Italy.

The main difference between Scheme 5 and Scheme 6 is the competition ratio k_3/k_2 of the intermediates $[\text{CpRu}(\text{P}-\text{P})]^+$ for pyramidal inversion versus the back reaction with halide or other nucleophiles. For the Mn compounds in Scheme 5, the competition ratio k_3/k_2 is about 1. That means that substitution reactions with added nucleophiles inevitably are accompanied by extensive racemization. For the Ru compounds in Scheme 6, however, the competition ratio k_3/k_2 is much smaller than 1, because k_3 is much smaller than k_2 , implying a significant retardation of the pyramidal inversion. As a consequence the back reaction of the unsaturated intermediates with halides or other nucleophiles, which proceeds with retention of the metal configuration, is fast compared with pyramidal inversion, involving a change of the metal configuration.³⁴

Halide Exchange in $[\text{CpRu}(\text{Prophos})\text{Cl}]$

The kinetics of the Cl/I exchange in $(R_{\text{Ru}},R_{\text{C}})$ - and $(S_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{Cl}]$ (Scheme 7) was measured with an excess of $[\text{Bu}_4\text{N}]\text{I}$ in the solvent mixture $\text{CDCl}_3/\text{CH}_3\text{OH}$ 9:1 at 27 °C.³⁴

Figure 2 shows the results of the reaction of a sample of $(R_{\text{Ru}},R_{\text{C}})$ -/ $(S_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{Cl}]$ 85:15 with an excess of $[\text{Bu}_4\text{N}]\text{I}$. The concentration of $(R_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{Cl}]$ decreased with time, whereas the concentrations of $(S_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{I}]$ and $(R_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{I}]$ increased. Surprisingly, the concentration of $(S_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{Cl}]$ did not change appreciably, which means that the $(S_{\text{Ru}},R_{\text{C}})$ -diastereomer reacted much more slowly with $[\text{Bu}_4\text{N}]\text{I}$ than the

$(R_{\text{Ru}},R_{\text{C}})$ -diastereomer. The first-order disappearance of $(R_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{Cl}]$ at 27 °C had a half-life of $\tau_{1/2} = 96$ min.

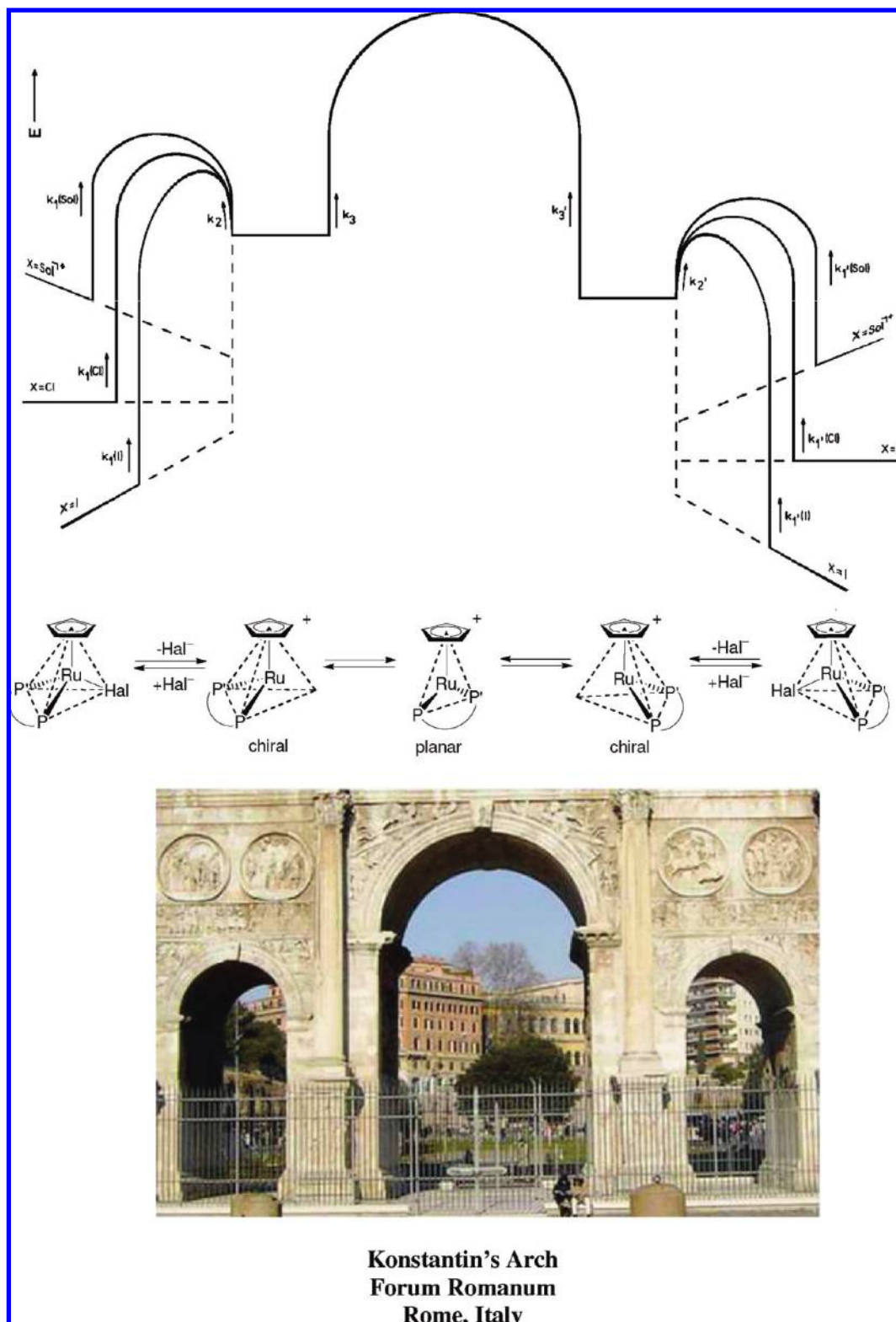
As the concentration of $(S_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{Cl}]$ stayed almost constant, the two substitution products $(S_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{I}]$ and $(R_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{I}]$ must have originated from the disappearing $(R_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{Cl}]$. It mainly transformed to $(S_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{I}]$. $(R_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{Cl}]$ and $(S_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{I}]$ have the same relative configuration, because the change of the configurational symbol is only due to a change in the ligand priority sequence $\text{Cp} > \text{Cl} > \text{PCHMe} > \text{PCH}_2$ versus $\text{I} > \text{Cp} > \text{PCHMe} > \text{PCH}_2$. Thus, the Cl/I exchange in $(R_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{Cl}]$ occurred predominantly with retention of configuration at the metal atom. Definitely, however, a small amount of $(R_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{Cl}]$ was converted into $(R_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{I}]$ with inversion of the metal configuration.

These observations are in accord with the energy profile in Scheme 6. The Cl/I exchange in $(R_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{Cl}]$ starts on the left side with the rate-determining cleavage of the Ru-Cl bond, which requires a high activation energy. An unsaturated intermediate $(R_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})]^+$ with pyramidal geometry is formed, which has kept its metal configuration. This intermediate can react in a fast reaction with iodide to give the substitution product $(S_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{I}]$ with retention of the metal configuration. It can also react with the solvents to give the species $(R_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{solvent}]^+$, which temporarily parks it in a way, discussed in the section UV Photolysis. However, the intermediate $(R_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})]^+$ can also invert its configuration, crossing the middle of Scheme 6, to form its diastereomer $(S_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})]^+$, which subsequently is quenched to $(R_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{I}]$.

The crucial point of the Cl/I exchange in $(R_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{Cl}]$ is the choice of the intermediate $(R_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})]^+$ to invert its configuration (k_3 path) or to react to the iodo complex $(S_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{I}]$ with retention of configuration (k_2 path). This choice is treated with the competition ratio k_3/k_2 , which can be determined from the product ratio $(R_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{I}]/(S_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{I}]$, constant throughout the reaction. The competition ratio $k_3/k_2 = 0.08$ for the Cl/I exchange in $(R_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{Cl}]$ shows that the inversion of the intermediate (k_3 path) is slow compared with the reaction of the intermediate with excess iodide (k_2 path), indicating a basilica type energy profile as in Scheme 6.

To measure the Cl/I exchange in the $(S_{\text{Ru}},R_{\text{C}})$ -diastereomer, the major component in the diastereomer equilibrium $(S_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{Cl}] \rightleftharpoons (R_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{Cl}]$, a sample $(S_{\text{Ru}},R_{\text{C}})$ -/ $(R_{\text{Ru}},R_{\text{C}})$ - $[\text{CpRu}(\text{Prophos})\text{Cl}]$ 97:3 was treated with excess

SCHEME 6. Basilica-type Energy Diagram for the Epimerization of the Compounds $[\text{CpRu}(\text{P}-\text{P}')\text{Hal}]$ and Example of a Basilica. Permission to reprint the photograph given by F. Höper



$[\text{Bu}_4\text{N}]$ in $\text{CDCl}_3/\text{CH}_3\text{OH}$ 9:1. The rate constants for the disappearance of $(S_{\text{Ru}}, R_{\text{C}})\text{-}[\text{CpRu}(\text{Prophos})\text{Cl}]$ are about 10 times slower than those for $(R_{\text{Ru}}, R_{\text{C}})\text{-}[\text{CpRu}(\text{Prophos})\text{Cl}]$. The reason is

that $(S_{\text{Ru}}, R_{\text{C}})\text{-}[\text{CpRu}(\text{Prophos})\text{Cl}]$, the right-side species in Scheme 6, is the thermodynamically more stable diastereomer. It dominates the equilibrium $(S_{\text{Ru}}, R_{\text{C}})\text{-}[\text{CpRu}(\text{Prophos})\text{Cl}]/(R_{\text{Ru}}, R_{\text{C}})\text{-}[\text{CpRu}$

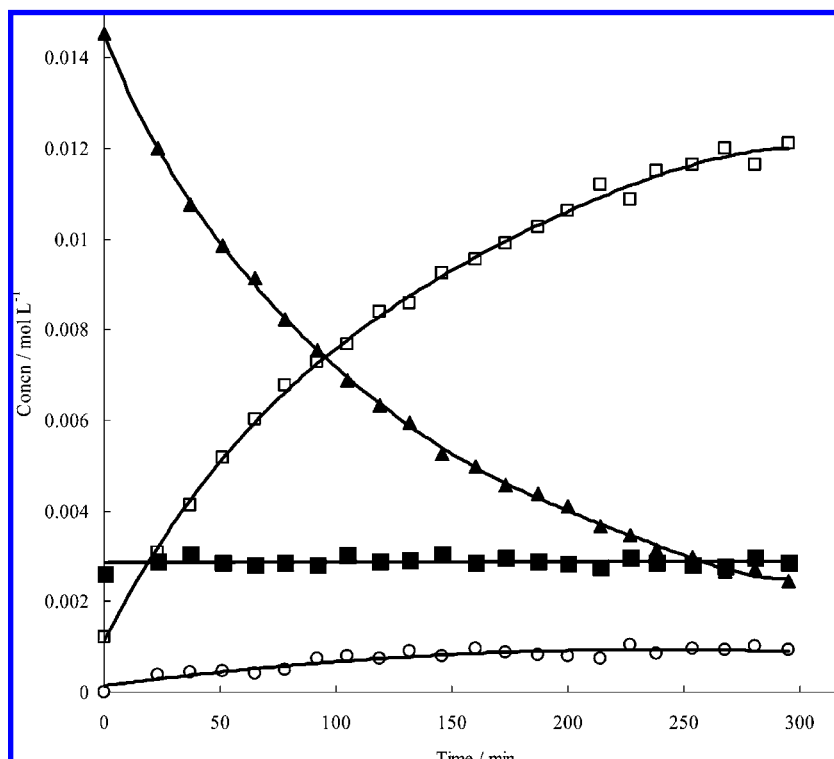
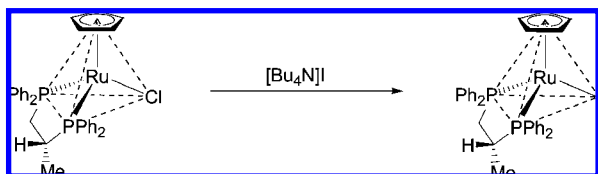


FIGURE 2. Cl/I exchange in (R_{Ru},R_C) -/ (S_{Ru},R_C) -[CpRu(Prophos)Cl] 85:15 ($\blacktriangle/\blacksquare$) with excess $[\text{Bu}_4\text{N}]\text{I}$ in $\text{CDCl}_3/\text{CH}_3\text{OH}$ 9:1 at 27 °C. The products are (S_{Ru},R_C) -[CpRu(Prophos)I] (\square) and (R_{Ru},R_C) -[CpRu(Prophos)I] (\circ).

SCHEME 7. Halide Exchange in (R_{Ru},R_C) -[CpRu(Prophos)Cl] To Give (S_{Ru},R_C) -[CpRu(Prophos)I] with Retention of the Metal Configuration



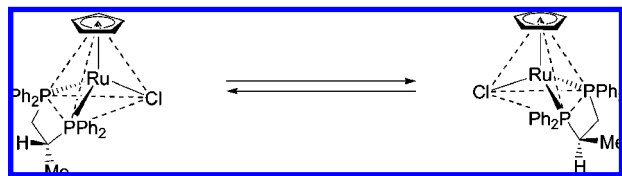
(Prophos)Cl] = 85:15, which means that it is more stable (and less reactive) than (R_{Ru},R_C) -[CpRu(Prophos)Cl]. This is reflected by a higher activation energy for k_1 and k_3 , compared with k_1 and k_3 (Scheme 6).

For the Cl/I exchange in (R_{Ru},R_C) - and (S_{Ru},R_C) -[CpRu(Prophos)Cl], which starts with the cleavage of the Ru–Cl bond, negative values were found for the entropy of activation, whereas for reactions of the Mn compounds, described above, in which the initial step was the cleavage of the M–PPh₃ bond, activation entropies had been positive. Both reaction types are dissociations in which the number of particles increases. However, in the Mn system, a neutral complex breaks up into two neutral fragments leading to a positive entropy of activation. Differently, in the Ru system a neutral complex forms two ions, which are strongly solvated in polar solvents. This increases the order reflected by a negative entropy of activation.

The kinetics of the Cl/Br exchange in (R_{Ru},R_C) - and (S_{Ru},R_C) -[CpRu(Prophos)Cl] was measured with an excess of $[\text{Bu}_4\text{N}]\text{Br}$ under similar conditions as the Cl/I exchange. Within the limits of error, the rate constants for the Cl/Br and the Cl/I exchange were the same. This also held for the temperature dependence of the rate constants. The reason for this is obvious from Scheme 6. For both processes, the Cl/Br and the Cl/I exchange, the rate-determining step is the cleavage of the Ru–Cl bond in (R_{Ru},R_C) -[CpRu(Prophos)Cl] in which the unsaturated intermediate (R_{Ru},R_C) -[CpRu(Prophos)]⁺ is formed. Quenching of the intermediate with excess bromide or excess iodide is a fast reaction, which does not affect the rate-determining step. The competition ratios k_3/k_2 in the Cl/Br exchange reactions were similar to those of the Cl/I systems. As expected, going from $\text{CDCl}_3/\text{CH}_3\text{OH}$ 9:1 to 1:1, and to pure CD_3OD , the rates of the halide exchange reactions increased,³⁴ whereas in chloroform and in C_6D_6 , the Cl/I exchange in (R_{Ru},R_C) - and (S_{Ru},R_C) -[CpRu(Prophos)Cl] was much slower than in methanol-containing solvents.³⁵

Epimerization of [CpRu(Prophos)Cl] and [CpRu(Prophos)I]

(R_{Ru},R_C) - and (S_{Ru},R_C) -[CpRu(Prophos)Cl] have extensively been used as starting materials for reactions occurring with retention of configuration in methanol at room temperature and

SCHEME 8. Epimerization of (R_{Ru},R_C)- and (S_{Ru},R_C)-[CpRu(Prophos)Cl]

also in boiling methanol.³⁶ They were assumed to be configurationally stable in solution. However, our studies showed that (R_{Ru},R_C)- and (S_{Ru},R_C)-[CpRu(Prophos)Cl] did epimerize at the metal center in methanol-containing solvents (Scheme 8).³⁴

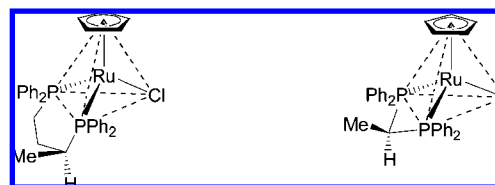
In $CDCl_3/CH_3OH$ 9:1, a sample (R_{Ru},R_C)- and (S_{Ru},R_C)-[CpRu(Prophos)Cl] = 94:6 epimerized at 27 °C to the equilibrium composition (R_{Ru},R_C)- and (S_{Ru},R_C)-[CpRu(Prophos)Cl] = 15:85 with a half-life $\tau_{1/2} = 27$ h for the approach to equilibrium.³⁴

Compared with the rates of the halide exchange reactions, the rates for the forward and backward reactions in the epimerization are about 10 times slower, because in the epimerization reaction the intermediates (R_{Ru},R_C)- and (S_{Ru},R_C)-[CpRu(Prophos)]⁺ have to cross another barrier of appreciable height in the basilica-type energy profile of Scheme 6. The entropy of activation for the epimerization of (R_{Ru},R_C)- and (S_{Ru},R_C)-[CpRu(Prophos)Cl] is negative, as discussed in the context of the Cl/I exchange reactions.

After the cleavage of the Ru–Cl bond in the epimerization of (R_{Ru},R_C)-/(S_{Ru},R_C)-[CpRu(Prophos)Cl] the dissociation products (R_{Ru},R_C)-/(S_{Ru},R_C)-[CpRu(Prophos)]⁺ and Cl[−] are present in very low concentration, which disfavors the back reactions to (R_{Ru},R_C)-/(S_{Ru},R_C)-[CpRu(Prophos)Cl] according to Scheme 6. Performance of the epimerization in the presence of a soluble chloride salt, however, should favor the back reactions and lead to a substantial decrease of the rate of epimerization. This was observed in measurements with excess [Bu₄N]Cl. A 10-fold excess of [Bu₄N]Cl reduced the rate by a factor of about 10.³⁴

The epimerization of (R_{Ru},R_C)- and (S_{Ru},R_C)-[CpRu(Prophos)Cl] in $CDCl_3/CD_3OD$ 1:1 was about 10–20 times faster than in $CDCl_3/CH_3OH$ 9:1, the equilibrium compositions and activation parameters remaining about the same. Thus, at 40 °C, the half-life of the epimerization was down to 4 min.³⁴ On the other hand, in C₆D₆ the epimerization of a diastereomer mixture (R_{Ru},R_C)-/(S_{Ru},R_C)-[CpRu(Prophos)Cl] = 97:3 at 40 °C slowed down dramatically to a half-life of 1080 min.³⁵ The epimerization reaction in C₆D₆ is surprising, because it involves the dissociation of a neutral molecule to give ions.

The epimerization kinetics of (R_{Ru},R_C)-/(S_{Ru},R_C)-[CpRu(Prophos)] was measured in $CDCl_3/CH_3OH$ = 9:1 and $CDCl_3/CD_3OD$ = 1:1 using diastereomerically pure (R_{Ru},R_C)-[CpRu-

SCHEME 9. Compounds (R_{Ru},S_C)-[CpRu(Chairphos)Cl] and *cis*-[CpRu(Me-dppm)]

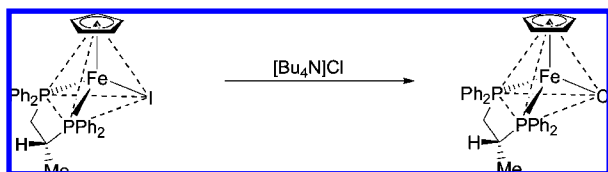
(Prophos)]]. With equilibrium ratios of (R_{Ru},R_C)-/(S_{Ru},R_C)-[CpRu(Prophos)] = 87:13 for both solvent mixtures, the half-lives of the approach to equilibrium at 40 °C were 710 min in $CDCl_3/CH_3OH$ 9:1 and 95 min in $CDCl_3/CD_3OD$ 1:1. Thus, the configurational stability of [CpRu(Prophos)] is higher than that of [CpRu(Prophos)Cl] by a factor of about 10.³⁴

Extensions

In [CpRu(PPh₃)₂Cl], the parent compound of the chelate complexes studied here, the P–Ru–P angle³⁷ is 103.79(3)° similar to the angles in the calculations.²⁵ Usually, in five-membered chelate rings the P–M–P angles are smaller. Thus, the P–Ru–P angle³⁸ in [CpRu(Prophos)Cl] is 82.9°. The puckered Ru-Prophos chelate ring, the λ -conformation of which is dictated by the equatorial orientation of the methyl group, is relatively rigid and cannot increase the P–Ru–P angle appreciably. The chelate ring will resist a widening of the P–Ru–P angle, which in the planar 18-electron complex CpRh(PPh₃)₂ is 98.17°.³⁹ Thus, the small P–Ru–P angle in the five-membered chelate ring strongly favors a pyramidal structure of the 16-electron fragments (R_{Ru},R_C)- and (S_{Ru},R_C)-[CpRu(Prophos)]⁺ and increases the inversion barrier, because in the planar transition state even larger P–Ru–P angles are required. This should be analogous to the inversion of the amine nitrogen, which is slowed dramatically by introducing the nitrogen atom into small rings. Thus, aziridines with their 60° angles greatly resist pyramidal inversion, which needs expanded angles in the planar transition state.⁴⁰

An increase of the P–Ru–P angle in (R_{Ru},S_C)- and (S_{Ru},S_C)-[CpRu(Chairphos)Cl] (Scheme 9) with the ligand Chairphos Ph₂P–CHMe–CH₂–CH₂–PPh₂, having one CH₂ group more than Prophos, leads to a slight decrease of the barrier of the pyramidal inversion.³⁵ In contrast, a decrease of the size of the chelate ring in [CpRu(Me-dppm)] (Scheme 9) with the ligand Me-dppm = 1,1-bis(diphenylphosphanyl)ethane, having one CH₂ group less than Prophos, increased the inversion barrier significantly. This is obvious from the half-life of the isomerization 5100 min at 40 °C in $CDCl_3/CH_3OH$ 9:1, compared with 710 min for (S_{Ru},R_C)- and (R_{Ru},R_C)-[CpRu(Prophos)Cl] under the same conditions.^{34,35} This could result in the develop-

SCHEME 10. Halide Exchange in (S_{Fe},R_C) -[CpFe(Prophos)I] To Give (R_{Fe},R_C) -[CpFe(Prophos)Cl] with Retention of the Metal Configuration



ment of efficient chiral-at-metal Lewis acids of the type (R_{Ru}) - and (S_{Ru}) -[CpRu(P–P)]⁺ for enantioselective catalysis.²³

(R_{Ru},R_C) - and (S_{Ru},R_C) -[CpFe(Prophos)Hal] undergo halide exchange and epimerization. Interestingly, the direction of the halide exchange is different compared with the homologues (R_{Ru},R_C) - and (S_{Ru},R_C) -[CpRu(Prophos)Hal]. In the Ru series, [CpRu(Prophos)Cl] reacted quantitatively with iodide to give [CpRu(Prophos)I], because Ru/Cl is a soft/hard and Ru/I a soft/soft combination. In the Fe series, [CpFe(Prophos)I] reacted with chloride to afford [CpFe(Prophos)Cl] (Scheme 10), because Fe/I is a hard/soft and Fe/Cl a hard/hard combination.³⁵

Unlike organic chemistry, knowledge of detailed mechanisms in transition metal chemistry is scarce. The field is still a diamond in the rough. To harvest this treasure, in particular, chiral-at-metal compounds will be indispensable for studying the stereochemical course of reactions.

This article is dedicated to Prof. Dr. Dr.h.c. Helmut Werner on the occasion of his 75th birthday, in appreciation of his merits for organometallic chemistry.

BIOGRAPHICAL INFORMATION

Henri Brunner was born in Burkhardtsdorf, Germany, in 1935. He studied chemistry at the University of Munich, where he got his Ph.D. with Nobel laureate E. O. Fischer in 1963. Subsequently, he was a postdoctoral fellow with H. D. Kaesz at UCLA. In 1969, he finished his Habilitation at TU Munich. In 1971, he was appointed full professor at the University of Regensburg, where he became Emeritus in 2004. He received the Carl Duisberg Award and the Horst Pracejus Award of the German Chemical Society, an Award of the Fonds of the Chemical Industry, the French-German Gay Lussac-Alexander von Humboldt Award, the Max Planck Award, and the Doctoris honoris causa of TU Munich. His research interests include preparative organometallic chemistry, stereochemistry of chiral-at-metal compounds, enantioselective catalysis, and cancer therapy with platinum compounds.

Takashi Tsuno was born in Tokyo, Japan, in 1964. He got his Ph.D. degrees at the University of Shizuoka under the supervision of M. Sato in 2005 and at the University of Regensburg under the supervision of H. Brunner in 2007. He is Associate Professor at Nihon University. His research interests include synthesis and stereochemistry of chiral-at-metal compounds, photochemical reactions of electron-deficient alkenes with

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FOOTNOTES

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