"Catalytic C-H bond activation with ruthenium complexes,

and their reactivities toward terminal alkynes"

A Thesis submitted to

The Department of Applied Biology and Chemical Technology

for the degree of Master of Philosophy

at

The Hong Kong Polytechnic University

By

Donald, Chi-Chuen MAK

September, 2000

Declaration

I hereby declare that this thesis summarized my own work carried out since my registration for the Degree of Master of Philosophy in September, 1997; and that has not been previously included in a thesis, dissertation or report submitted to this or any other institution for a degree, diploma or other qualification.

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Donald, Chi-Chuen Mak

September, 2000

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for her love, support, forbearance, patience and concern while I was engaged in this research project.

Finally, I would like to acknowledge the Research Degree Committee of The Hong Kong Polytechnic University for the awarding of a studentship.

Abstract of thesis entitled "Catalytic C-H bond activation with ruthenium complexes and their reactivities toward terminal alkynes"

submitted by Donald, Chi-Chuen Mak

for the degree of Master of Philosophy

at the Hong Kong Polytechnic University

in September, 2000.

Abstract

The Tp (Tp = hydridotris(pyazoleyl)borate) supported ruthenium hydride complexes, $TpRuH(PPh_3)_2$ (**2**) and $TpRuH(CH_3CN)(PPh_3)$ (**4**), have been examined for their activity in C-H bond activation. These complexes activate C-H bonds of common organic solvents like THF, dioxane, diethylether, benzene, toluene, chlorobenzene under 15 bars of hydrogen pressure at 130°C. The C-H activation reactions are evidenced by the catalytic H/D exchange between H_2 and the deuterated solvent substrates. The crucial steps of, for example, H/D exchange between H_2 and benzene-d_6 are σ-metathesis between η^2-C_6D_6 and Ru-H to give the η^2-HD phenyl complex intermediate, and that between η^2-H_2 and Ru-C_6D_5 to form the η^2-C_6D_5H ligand and Ru-H.

THF, diethylether and toluene show regio-selectivities in the H/D exchange reactions. For THF, α C-H bond activation predominates while β C-H bond activation is more important in diethylether. Only the aromatic C-H bonds are activated in the case of toluene.

Complex **4** also activates C-H bond in the reaction of H/D exchange among D_2O, H_2 and organic solvents under similar conditions to yield HD, D_2, HDO, H_2O and the deuterated solvents, but **2** is not active in similar reactions. We believe that **4** can effect this H/D exchange reaction because it is able to generate the metal deuteride, 4-

d_1, via its reaction with D_2O.

The second part of this work concerns the chemistry of ruthenium vinylidene complexes and their reactions. The solvento σ-alkyneyl complex TpRu(C≡C-Ph)(PPh$_3$)(CH$_3$CN) (12) was readily obtained via reaction of TpRu(=C=CHPh)(PPh$_3$)(Cl) (7) with Et$_3$N. Elimination of HCl from 7 was assisted by the formation of the salt Et$_3$NHCl.

The vinylidene complex [TpRu(=C=CHPh)(dppe)](BF$_4$) (11) was synthesized by acidification of TpRu(dppe)H (3) with one equivalent of HBF$_4$·H$_2$O, followed by the addition of excess phenyl acetylene. ^{1}H and ^{31}P{^{1}H} NMR spectroscopy fail to detect any ruthenium intermediate species in the course o'' the conversion of 3 to 11. However, not all reactions of 1-alkyne with the metal complexes yield the vinylidene complexes, addition of methyl propiolate to TpRu(PPh$_3$)(Cl)(CH$_3$CN) (1) yields the carbonyl complex TpRu(PPh$_3$)(Cl)(CO) (13).

The activities of the cationic ruthenium complexes [(Tp)Ru(PPh$_3$)$_2$(CH$_3$CN)]BF$_4$ (8), [(Tpm)Ru(PPh$_3$)$_2$(CH$_3$CN)](BF$_4$)$_2$ (9), and [(Triphos)Ru(CH$_3$CN)](CF$_3$SO$_3$)$_2$ (10) (Tpm = hydrotrispyrazolylmethane; and triphos = MeC(CH$_2$PPh$_2$)$_3$) toward dimerization of alkynes were also studied. They showed catalytic activity toward dimerization of alkynes in the presence of base, NEt$_3$. However, they only catalyzed dimerization of phenylacetaylene with low yield in the absence of base. A mechanistic

interpretation of the dimerization of alkynes, in the absence of base, via a cationic vinylidene intermediate, is proposed.

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List of Schemes

List of Abbreviation

E	Electron
δ	Chemical shift (NMR)
η	Descriptor for hapticity
ν	Frequency
L	Generalized ligand, in particular a 2e ligand
L_nM	Generalized metal fragment with n ligands
Tp	Hydrotris(1-pyrazolyl)borate
Tpm	Hydrotris(1-pyrazolyl)methane
Triphos	$MeC(CH_3PPh_2)$
Triars	$MeC(CH_3AsPPh_2)$
Cp	Cyclopentadienyl
Cp*	Pentamethylcyclopentadienyl
Me_3tacn	1,4,7-trimethyl-1,4,7-triazacyclononane
PCy_3	Tricyclohexylphosphine
PPh_3	Triphenylphosphine
PMe_3	Trimethylphosphine
BPh_4	Tetraphenylborate
HBcat	Catecholborate
Me	Methyl
Et	Ethyl
OEt	Ethoxy
Ph	Phenyl
t-Bu	t-butyl
n-Bt	n-butyl
py	Pyridine
pz	Pyrazolyl
Et_3N	Triethylamine

PNP	$CH_3CH_2CH_2N(CH_2CH_2PPh_2)_2$
dppm	$Ph_2PCH_2PPh_2$
dppe	$Ph_2PCH_2CH_2CH_2PPh_2$
dppp	$Ph_2PCH_2CH_2PPh_2$
dmpe	$Me_2PCH_2CH_2PMe_2$
PP_3	$P(CH_2CH_2PPh_2)_3$
Dmp	2,9-dimethyl-1,10-phenanthroline
FAB-MS	Fast atom bombardment mass spectroscopy
NMR	Nuclear magnetic resonance spectroscopy

TpRu(PPh₃)(CH₃CN)Cl (**1**)
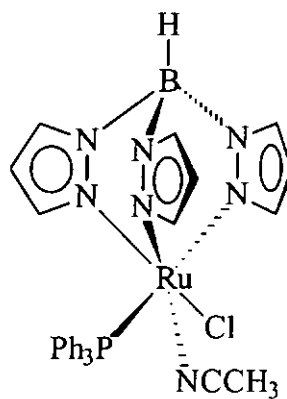
TpRu(PPh₃)₂H (**2**)

TpRu(dppe)H (**3**)

TpRu(PPh₃)(CH₃CN)H (4)

TpRu(PPh₃)(H₂)H (5)

TpRu(PPh₃)₂Cl (6)

TpRu(PPh₃)(Cl)(=C=CHPh) (**7**)

[TpRu(PPh₃)₂(CH₃CN)](BF₄) (**8**)

[TpmRu(PPh₃)₂(CH₃CN)](BF₄)₂ (**9**)

[(triphos)Ru(CH₃CN)₃](CF₃SO₃)₂ **(10)**

$$[(triphos)Ru(CH_3CN)_3](CF_3SO_3)_2 \; (\mathbf{10})$$

[TpRu(dppe)(=C=CHPh)](BF₄) **(11)**

$$[TpRu(dppe)(=C=CHPh)](BF_4) \; (\mathbf{11})$$

TpRu(PPh₃)(CH₃CN)(C≡C-Ph) **(12)**

$$TpRu(PPh_3)(CH_3CN)(C\equiv C\text{-}Ph) \; (\mathbf{12})$$
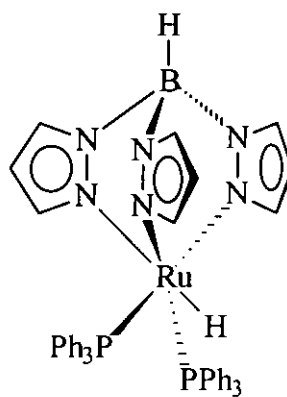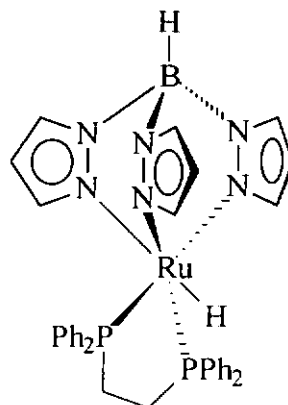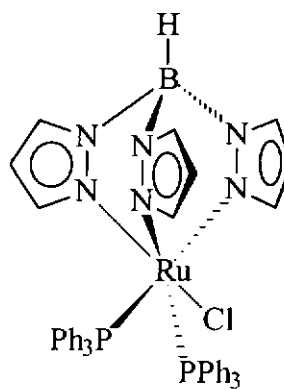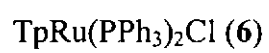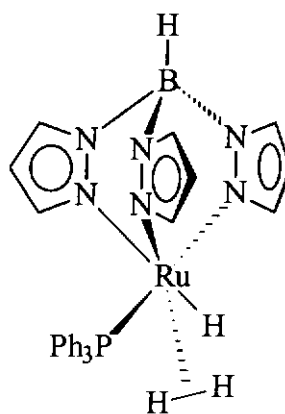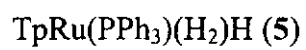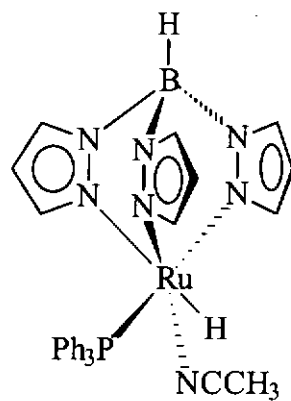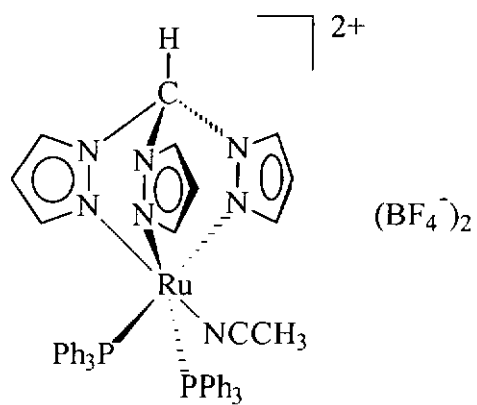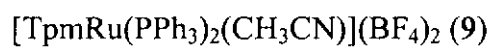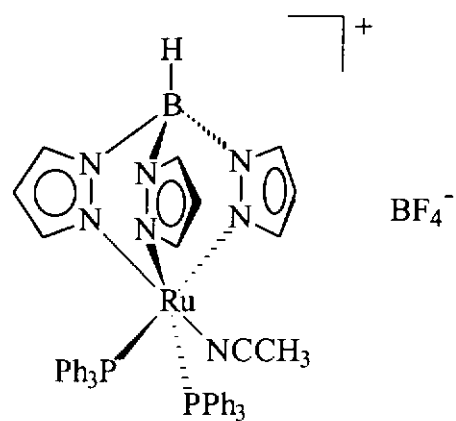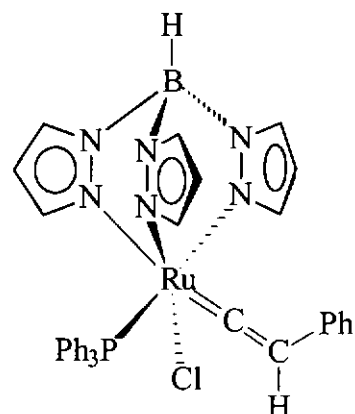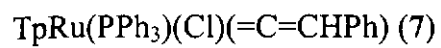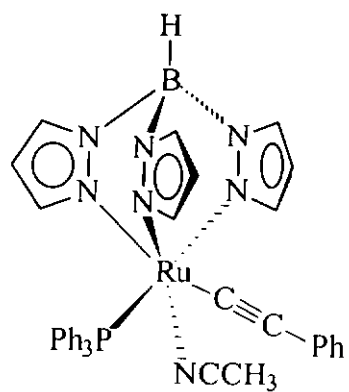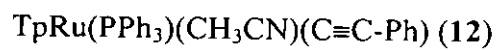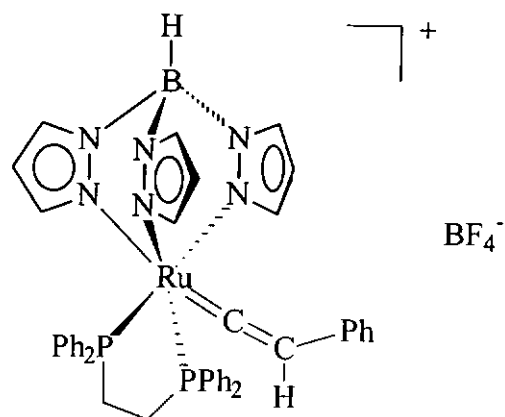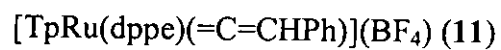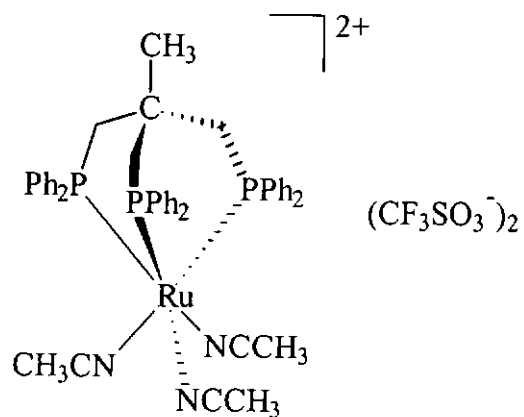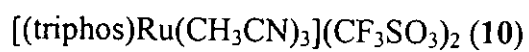
TpRu(PPh₃)(Cl)CO (**13**)
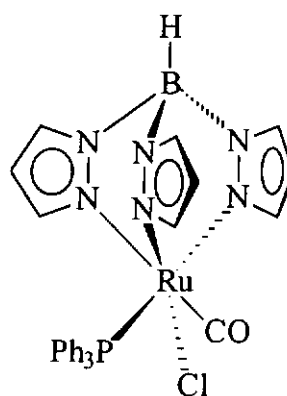
Chapter 1

Introduction

There is an increasing interest in the activation of molecules via the formation of "σ-complexes". Traditional ligands in coordination chemistry, such as amines and phosphines, bond to metal centers through their lone pair electrons. However, recent developments in coordination chemistry have demonstrated that certain σ bonds can coordinate to transition metals in an η^2-fashion without bond cleavage by forming three-center two-electron bonds, giving rise to the so called σ complexes.

The first σ complex [$Cp_2Ti(H_2BH_2)$] was found in the 1960's. However, the simplest ligand that forms a σ complex with transition metals is the dihydrogen molecule. The first dihydrogen complex [$W(\eta^2$-$H_2)(CO)_3(Pcy_3)_2$], discovered by Kubas[1] and coworkers in 1984, is a good model for studying the reactions between a metal center and a η^2-H_2 ligands. The electrons in the σ-bond of H_2 are donated into the vacant d-orbital of the metal, and the filled dπ-orbital of the latter can back-donate electron density into the σ*-orbital of H_2.

The first interaction, σ of H_2 to dσ of metal, weakens but does not break the H-H bonds, the overall bonding can be considered as a three-center two-electron

interaction. The H-H bond still remains intact, but further destabilization comes from the second interaction, $d\pi$ of metal to σ^* of H_2. The bond order of the H-H bond will be significantly lowered by the back donation of electron density from the $d\pi$ of the metal to the σ^* of the H_2. A very important consideration is the electronic and steric influences of ancillary ligands in stabilizing H_2 coordination versus dihydride formation. Increasing the basicity of the metal center in H_2 complexes would be expected to lead to H-H bond cleavage because of higher metal $d_\pi \rightarrow \sigma^*$ donation. Calculations show that mixtures of σ-donor and strong π-acceptor co-ligands favor η^2-H_2 since acceptors, particularly when trans to H_2, interact with the d orbital which populates σ^* of H_2.[2-4] Complexes with all acceptors, e.g., $Mo(CO)_5(H_2)$, are thermally unstable to H_2 loss, possibly because the extent of metal $d_\pi \rightarrow \sigma^*$ H_2 backbonding is too small.
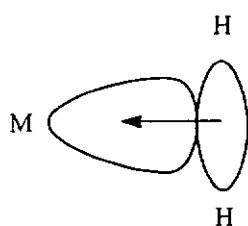
The electrons in the σ-bond of H_2 are donated into the vacant d-orbital of the metal
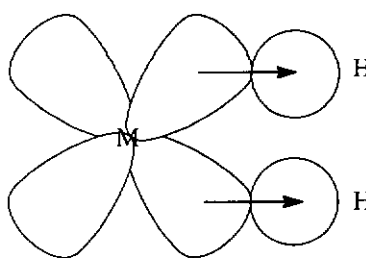
The electrons in the filled d-orbital of the metal are back-donated into the σ^*-orbital of H_2.

Dihydrogen complexes have several distinctive properties that are important in some important steps of catalytic cycles and in the development of new catalytic

systems. For example, hydrogenation of alkenes[5] and alkynes,[6] hydrogenation of ketones, dehydrogenation of alcohols,[7] dimerization of alkynes,[8] and H/D isotopic exchange between H_2 and organic solvents.[9] Depending upon the catalyst system, two types of H-H cleavage have been proposed(eq 1.1):

$$\text{homolytic cleavage:} \quad M \ + \ H_2 \ \longrightarrow \ [\ M \overset{H}{\underset{H}{\diagup\!\mid}} \quad \text{or} \quad M-H-H\ ] \ \longrightarrow \ M\overset{\diagup H}{\underset{\diagdown H}{}}$$
("oxidative addition")

$$\text{heterolytic cleavage:} \quad M-L \ + \ H_2 \ \longrightarrow \ \overset{M---L}{\underset{H---H}{\mid \quad \mid}} \ \longrightarrow \ M-H \ + \ HL$$
(L = basic ligand)

$$(1.1)$$
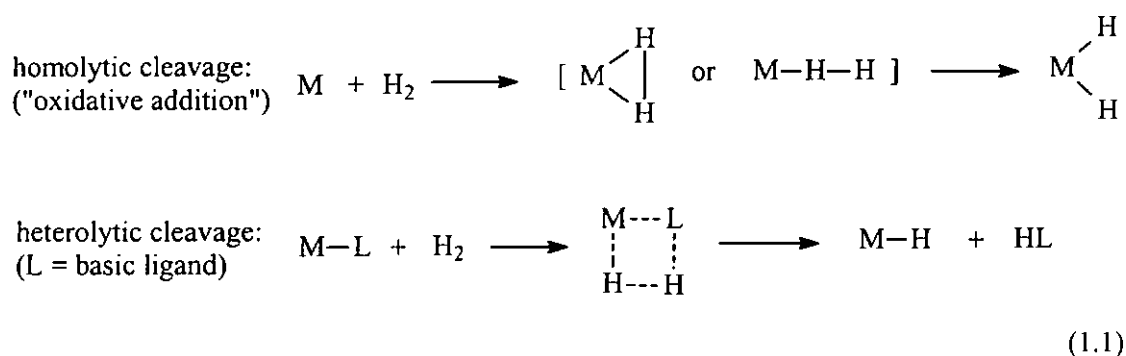
The initial species (e.g., side-on (η^2) vs. end-on bonded H_2) formed upon approach of H_2 to the metal has been speculated upon for many years and was generally regarded to be only a transient one. Now that $\eta^2\text{-}H_2$ complexes are indeed known to be stable.

Large numbers of dihydrogen complexes are known, and numerous studies have been carried out on their syntheses, as well as on their spectroscopic and structural characterizations. It gives impetus to understanding the interaction of σ-coordinating ligands with transition metals. As a result of this challenge, the study of the activation of molecules via the formation of "σ-complexes" has become an important area of

3

research. Nowadays a variety of well-characterized complexes that contain σ-coordinated ligands such as η^2-H$_2$,[10-17], η^2-HSiR$_3$ and η^2-HSnR$_3$ are known.[18-20]

Our research group has reported some examples of H-H bond activation involving η^2 coordination of the H-H bond. A series of Tp Ruthenium η^2-H$_2$ complexes, [TpRu(L)(L')(H$_2$)]$^+$ (where (L)(L') = (PPh$_3$)$_2$,[21] (CH$_3$CN)(PPh$_3$),[21] dppe,[22] (CO)(PPh$_3$)[22]) have been synthesized and characterized. These complexes have been found to be capable of hydrogenating olefins catalytically under hydrogen pressure. Dissociation of PPh$_3$ from the complex generates a vacant site for olefin complexation, a five member ring species can be proposed as the transition structures for the conversion of [TpRu(L)(olefin)(H$_2$)]$^+$ to [TpRu(L)(alkyl)H]$^+$ (eq. 1.2). A final hydrogenolysis step gives a Tp ruthenium complex intermediate containing an η^2-H$_2$ ligand, and finally the hydrogenated product.

(1.2)
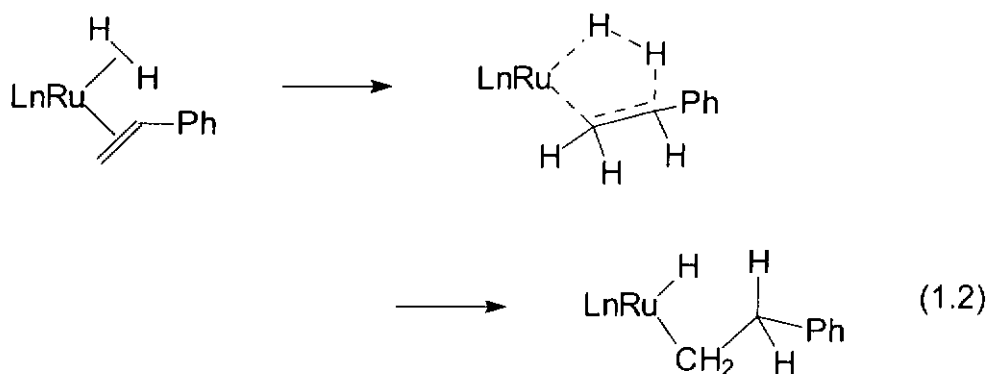
The chemistry of σ-bonded silane ligands has also been intensively investigated. In the light of the similarity of the bonding modes of ligands in η^2-dihydrogen (η^2-H_2) complexes and η^2-silane (η^2-$HSiR_3$) complexes, it is interesting to synthesize and to study the chemical properties of Tp ruthenium complexes containing an η^2-silane ligand. Our group has later found that ruthenium hydrido solvento complex [TpRuH(CH$_3$CN)(PPh$_3$)] reacted with silanes HSiR$_3$ [R$_3$ = Et$_3$, (OEt)$_3$, PH$_3$, HEt$_2$, HPh$_2$ and H$_2$Ph] to yield the silane complex [TpRu(PPh$_3$)"H$_2$SiR$_3$"] which, instead of equilibrating between the η^2-silane and η^2-H_2 tautomeric forms, interchanged H atoms rapidly, ie. [TpRu(PPh$_3$)(η^2-H*SiR$_3$)H] ↔ [TpRu(PPh$_3$)(η^2-HSiR$_3$)H*].[23] The reaction mentioned above suggested that the H-Si bonds of the silane ligands are activated. The silane complex is analogous to the dihydrogen hydride complex [TpRuH(H$_2$)(PPh$_3$)] that we have recently reported.[24] Since C-H is isolobal to H-H and Si-H, therefore, we are interested in studying the activation of C-H bond by TpRuH(CH$_3$CN)(PPh$_3$).

The activation of normally inert C-H bonds, either intra- or intermolecularly, by homogeneous transition-metal systems has been an area of intense research effort.[25-30] The uses of naturally abundant alkane are usually limited to solvents and fuels. Alkanes would be more versatile and valuable if their C-H bonds could be functionalized and converted to other functional groups. However, inertness of the C-H bond is the main barrier. Fortunately, this activation can be facilitated by

organometallic complexes. Toward this goal, much effort was put into the transition

metal mediated C-H bond activation combined with functionalizing the activated

substrate.[31, 32] For example, regioselective C-H bond activation in acrylates,[33]

catalytic ortho C-H bond activation in pyridines [34] and aromatic ketones have

attracted much interest in recent years.[35, 36]

C-H bond activation can be divided into two main categories - intermolecular and

intramolecular(eq. 1.3). [37, 38]

$$M \ + \ R{-}H \longrightarrow M\langle {}^{H}_{R}$$

Intermolecular C-H bond activation

$$M\ \overset{\frown}{}\ R{-}H \longrightarrow \ M\langle {}^{H}_{R} \qquad (1.3)$$

Intramolecular C-H bond activation
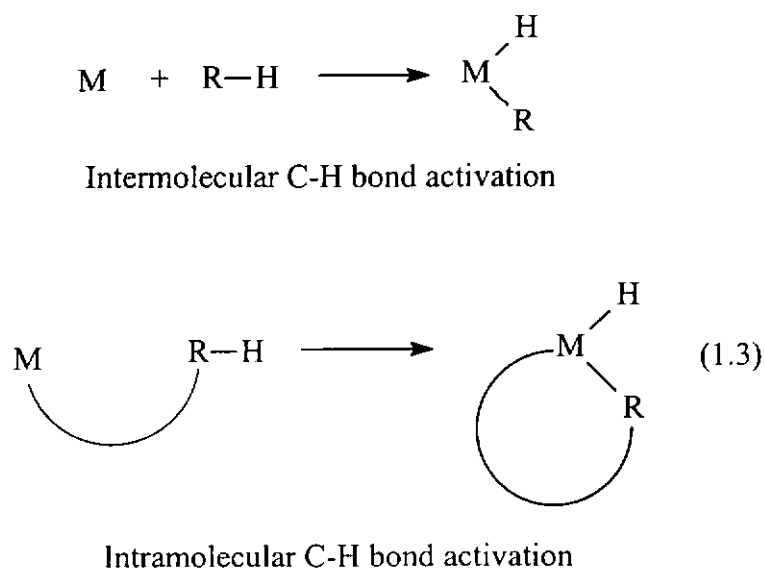
Several examples of intermolecular C-H bond activation [39-41] and

intramolecular activation [42] have been well characterized and their reactions have also

been studied. Sometimes, both inter- and intramolecular C-H bond activation may

exist simultaneously. For example, $Cp^*RhMe_2PCH_2C_6H_5$ can catalytically activate

the C-H bonds of the benzene ring of the coordinated phosphine in competition with

its activation of the C-H bonds of the aromatic solvent (eq 1.4). [42]

(1.4)
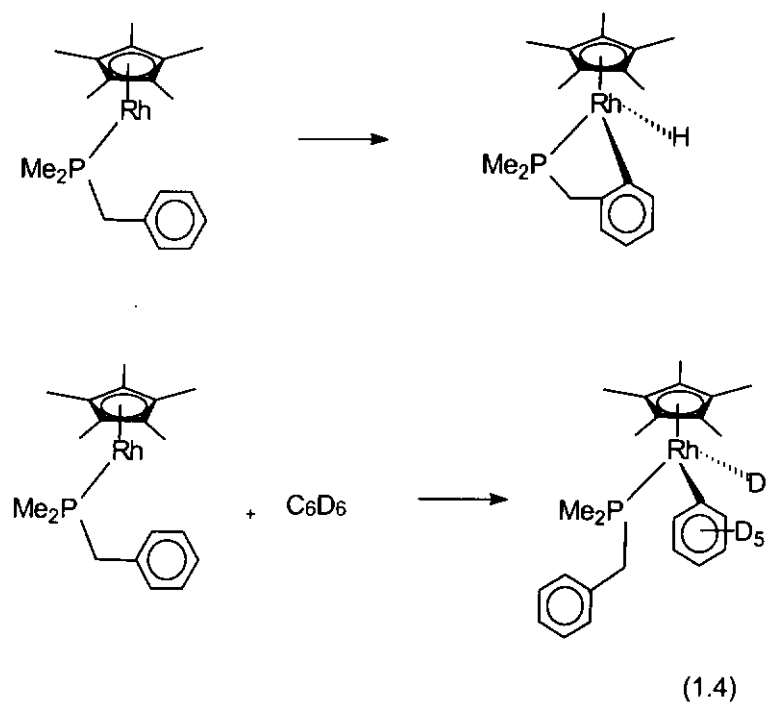
Besides, Marks' group [43-45] has reported exclusive intermolecular activation of

methane by the complex $(C_5Me_5)_2Th(CH_2CMe_2CH_2)$, although they found competitive

intramolecular activation in operation in $(C_5Me_5)_2Th(CH_2CMe_3)_2$. Bergman [26] has

reported both intra- and intermolecular C-H activation upon irradiation of

$(C_5Me_5)Ir(PPh_3)H_2$ in benzene.[43-45]

It is now generally recognized that there are two fundamentally different

mechanisms for cleaving carbon-hydrogen bonds with transition-metal complexes.

The first one is oxidative addition of C-H bond to an electron-rich, coordinatively unsaturated metal center.[36, 46] Many studies indicate that the major step in C-H bond activation is the insertion of metal center into C-H bond via oxidative addition.[26, 44, 45, 47-55] For example, $(\eta^6\text{-arene})Ru(H)_2(SiMe_3)_2$ complexes activate both aromatic and aliphatic C-H bonds and catalyze H/D exchange in alkysilanes upon thermolysis in benzene-d_6. A mechanism based on oxidative-addition/reductive-elimination steps which utilize a Ru(II)-Ru(IV) cycle was proposed by Berry [56] to account for the C-H bond activation and H/D exchange reactions. Other similar reaction mechanisms have been proposed by Bennett [57] and Werner. [58]

The second mechanism is "heterolytic" cleavage by a coordinatively unsaturated, electron-deficient and hence highly electrophilic metal center. This type of process typically utilizes d^0 (or d^0f^n) metals and is usually pictured as involving a highly charged, four-center transition state (eq. 1.5).[36, 46, 59]

$$L_nM-R \ + \ R'-H \ \longrightarrow \ \begin{bmatrix} \overset{\delta-}{R'}-\overset{\delta+}{H} \\ | \quad | \\ \underset{\delta+}{L_nM}-\underset{\delta-}{R} \end{bmatrix}^{\ddagger} \ \longrightarrow \ L_nM-R' \ + \ R-H$$

(1.5)
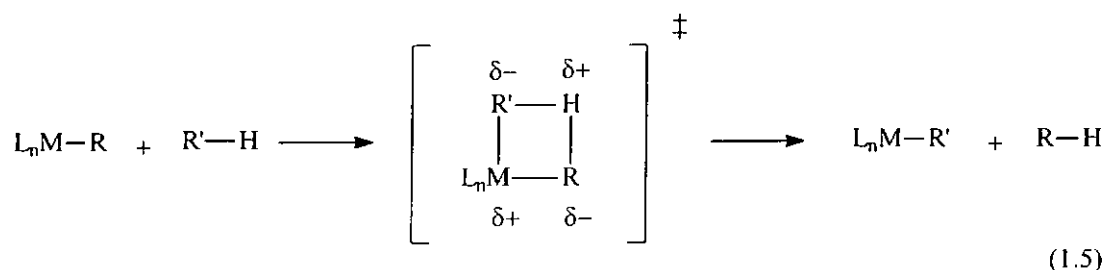
It is generally called "σ-bond metathesis" mechanism. Many theoretical studies of orbital reorganization in σ-bond metathesis have been published. [60-66] For example, Watson[67] has reported that lutetium methyl and hydride complexes $Lu(\eta^5$-$(C_5Me_5)_2)R$ (R = CH_3, H) react readily with various sp^2 and sp^3 C-H bonds. She has also reported the first well-characterized example of a reaction of methane with a homogeneous organometallic complex. A σ-bond metathesis mechanism was proposed to explain the activation of the methane C-H bond.

C-H activations involving counterion or ligand C-H bonds have been observed in systems other than alkanes and these reactions are also believed to proceed by σ-bond metathesis mechanisms that are accessible by initial interaction / coordination of the C-H bond with / to the electrophilic metal centers.[59, 68-72]

My studies concern d^6 Ru complexes that activate C-H bond of organic substrates via σ-bond metathesis as the crucial step. Hartwig [73] has previously reported evidence of σ-bond metathesis with a low-valence, late transition metal complex. Other examples of σ-bond metathesis [54, 74, 75] involving a low-valent, late transition metal alkyl complexes have also been presented.[76] H/D exchange has been employed for monitoring the C-H bond activation of substrates, and the appearance of H_2 and HD in the gas phase has been taken as an indication of catalytic activity.

Ruthenium complexes are not only able to activate sp^3 C-H bond [77] [67] and sp^2 C-H bond, [67, 78] but also to activate an sp C-H bond. [79, 80] [81] For example, activation of the C-H bond of terminal alkyne. Transition metal-mediated dimerization of terminal alkynes is of considerable current interest because it can lead to a wide variety of organic enyne and oligoacetylene products that are useful precursors for synthesizing organic conducting polymers and other carbon-rich allotropes.[8, 59, 82] It is an effective method of forming enynes, but its application to organic synthesis has been limited due to low selectivity for the dimeric products. Recent advances in transition metal-mediated selective dimerization has fueled a resurgence of interest in the catalytic dimerization of terminal alkynes.

Chae and Liu [79, 80] dimerized terminal alkynes using ruthenium hydride complexes $C_5Me_5Ru(L)H_3$ (L = PPh$_3$, PCy$_3$, PMe$_3$). The complexes catalyzed the dimerization of terminal alkynes RC≡CH (R = Ph, t-Bu, SiMe$_3$, CH$_3$Ph, C$_4$H$_9$) to yield cis- and trans-1,4-disubstituted enynes RCH=CHC≡CR and 1,3-disubstituted enynes CH$_2$=C(R)C≡CR.[80]

Kirchner[81] and co-workers have employed the complexes TpRu(PPh$_3$)$_2$Cl and TpRu(PPh$_3$)(py)Cl to catalyze the dimerization of terminal alkynes HC≡CR, where R = Ph, SiMe$_3$, n-Bu, and t-Bu, to give 1,4- and 2,4- disubstituted butenynes. Both the conversion and the selectivity were strongly dependent on the alkyne substituent. The

catalytic precursors were the neutral vinylidene complex $TpRu(PPh_3)(Cl)(=C=CHR)$ and the hydride complex $TpRu(PPh_3)_2H$.

Bianchini *et. al* [8] have studied regio- and stereoselective dimerization of terminal alkynes with an Ru(II)enynyl complex. They have shown that the Ru(II) η^2-H_2 complex $[(PP_3)RuH(H_2)]BPh_4$ or the η^1-dinitrogen derivative $[(PP_3)RuH(N_2)]BPh_4$ $[PP_3 = P(CH_2CH_2PPh_2)_3]$ can be used as a catalyst precursor for the dimerization of $HC\equiv CSiMe_3$ to 1,4-bis(trimethylsilyl)-but-3-en-1-yne(eq. 1.6).

(1.6)
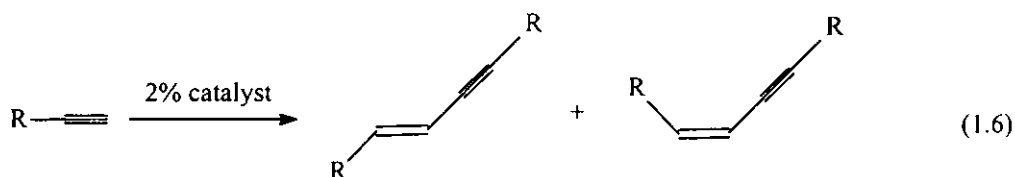
In all aforementioned examples, formation of vinylidene is proposed as the crucial step for the dimerization of alkynes. It is generally agreed that in the initial step the alkyne molecule coordinates in a η^2 mode to the metal center. From this π-intermediate, the system can eventually convert into vinylidene(1,2-hydrogen shift) derivatives(eq 1.7).

(1.7)
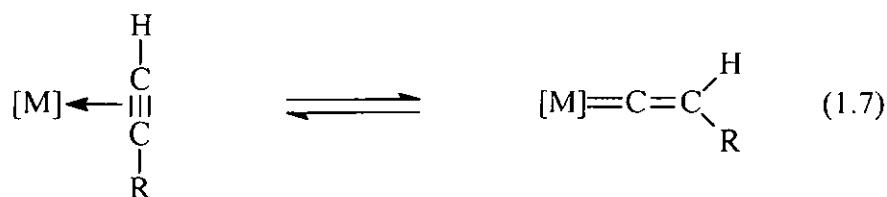
Such isomerizaiton plays a key role in catalytic C-C coupling reaction: coupling of metal-alkynyl and alkyne carbons to form a metal-bound butenynyl group is considered to proceed via prior isomerization of the 1- alkyne into the vinylidene from. Bianchini[8] and co-workers and Wakatsuki[82] have shown that such C-C coupling indeed takes place in Ru(II)-catalyzed dimerization of 1-alkyens to Z-1,4-disubstituted enynes and Z-1,4-disubstituted butatrienes, respectively (eq. 1.8).

(1.8)
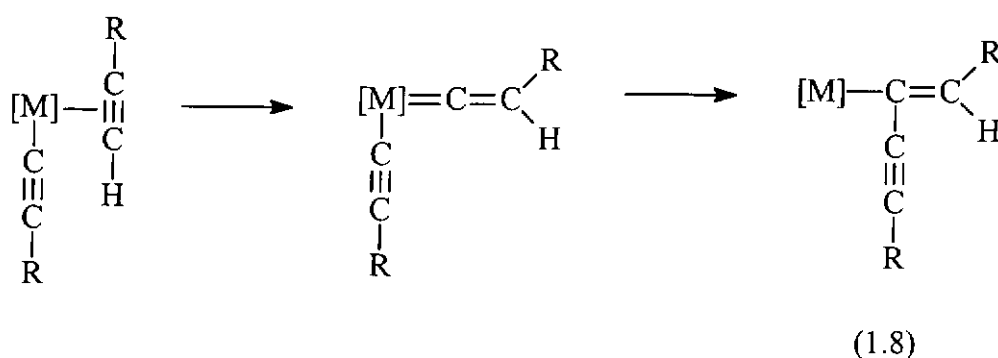
Open sites in metal coordination spheres have long been recognized as essential features of reactive complexes. There has been a concentrated effort to synthesize and isolate complexes that are either coordinatively unsaturated and stabilized by bulky ligands[83] or possess potentially liable ligands such as solvent molecules.[84] In our studies of the transition-metal mediated dimerization of terminal alkynes, all of the catalysts found effective, $[(Tp)Ru(PPh_3)_2(CH_3CN)]BF_4$, $[(Tpm)Ru(PPh_3)_2(CH_3CN)](BF_4)_2$, and $[(Triphos)Ru(CH_3CN)_3](CF_3SO_3)_2$, are supported by a bulky tridentate facial ligand such as Tp, Tpm, or Triphos and carry a labile CH_3CN ligand to provide an open site in metal coordination spheres. These

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facial ligands have found wide applications in co-ordination chemistry, and their complexes with most metals or metaloids in the periodic table have been prepared.[85]

The applications complexes carrying nitrogen donor ligands in homogeneous catalysis have received increasing attention in recent years. Despite the relative novelty of nitrogen-donor ligands containing complexes as homogeneous catalysts compared to the phosphorus ligands, considerable works have been published. For example, the ruthenium complex $[Ru(dmp)_2(CH_3CN)_2]^{2+}$ (dmp = 2,9-dimethly-1,10-phenanthroline) is capable of activating dioxygen and hydrogen peroxide for the oxygenation of hydrocarbons including methane.[86]

Poly(pyrazolyl)borate $(R_nB(pz)_{4-n}^-)$ is a good example of a nitrogen donor facial ligand and a large number of ligands have been prepared[87-92], where R = H, alkyl, or aryl groups and pz = pyrazole or substituted pyrazoles. Poly(pyrazolyl)borate in its bidentate form $(R_2Bpz_2^-)$has been compared to β-diketonates.
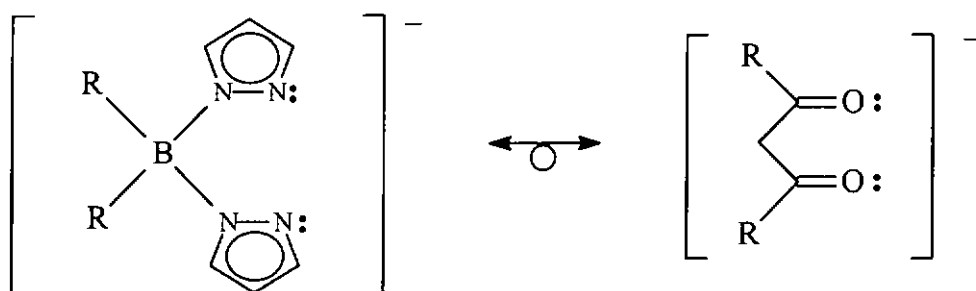
Its tridentate form (RBpz$_3^-$) can be compared to the cyclopentadienyl ligand Cp/Cp*.

RBpz$_3^-$ =
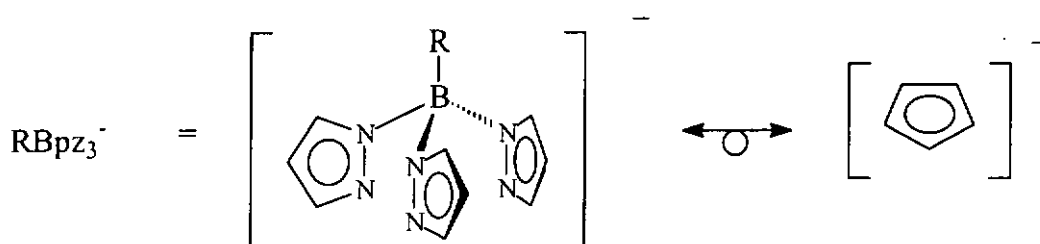
By varying the type of pyrazole, the electronic and steric properties of the poly(pyrazolyl)borates can be fine-tuned so as to change the electronic properties of the metal center. For example, the cone angle of unsubstituted hydrotris(pyrazolyl) borate is 184°, whereas the 3-substituted tert-butylpyrazole analogue has a cone angle of 244°.[93-95] An electron rich poly(pyrazolyl)borate such as hydrotris(3,5-dimethylpyrazolyl)borate can be obtained by substituting the hydrogen atoms with an electron donating alkyl groups. Similarly, replacing the hydrogen atoms with electron

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withdrawing substituent, such as the trifluoromethyl group, results in the less electron

donating hydrotris(3,5-bis(trifluoromethyl)pyrazolyl)borate ligand.[94]

Hydrotrispyrazolylmethane (Tpm) has a structure similar to that of

Hydrotrispyrazolylborate (Tp). They differ in that Tpm is a neutral ligand while Tp

carries a uni-negative charge.

Tpm   =
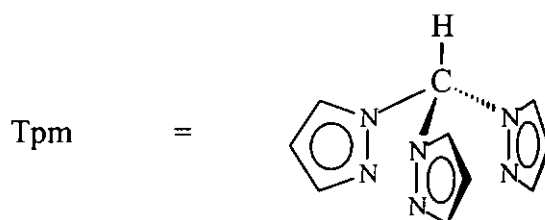
Venanizi[96] and co-workers' interest in solvento transition-metal complexes

containing facially coordinating tripod ligand [tripod = $(MeC(CH_3EPh_2)_3)$, E = P

(triphos) or As (triars)] stems from preliminary studies in which it was found that

$[Rh(MeCN)_3(triphos)](CF_3SO_3)_3$ catalyzed a number of reactions. They have extended

this chemistry to include analogous complexes of ruthenium since coordinately

unsaturated $RuHCl(PPh_3)_3$ and $RuCl_2(PPh_3)_3$ are known to be active catalysts.

Triphos   =

$$
\begin{array}{c}
CH_3 \\
| \\
-C- \\
\diagup \quad | \quad \diagdown \\
PPh_2 \quad | \quad PPh_2 \\
PPh_2
\end{array}
$$
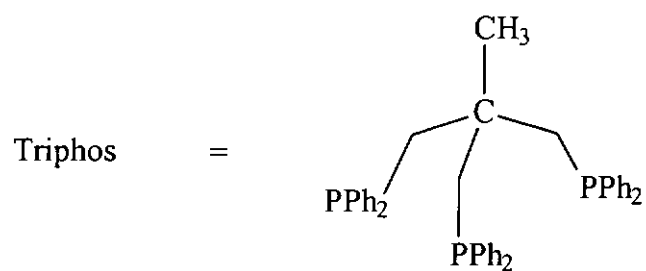
Some solvent-stabilized complexes have also been shown to activate C-H bonds.[48] Such novel reactivity has prompted us to study the catalytic activity of ruthenium complexes toward C-H bond activation.

Chapter 2

C-H Bond Activation by Ruthenium Hydride Complexes

2.1 Introduction

There is currently a great interest in transition metal mediated C-H bond activation.[29, 97, 98] Functionalization of the activated substrates has also been a topic of increasing interest in recent years.[31, 32] Many transition-metal complexes that are capable of activating the C-H bonds in hydrocarbon have been discovered.[43-45, 47-50, 52-55, 67, 70, 99, 100] The focus of many recent studies has moved toward the application of these findings to catalytic processes. Several systems that generate functionalized products based on catalytic carbon-heteroatom or carbon-carbon bond-formation processes have been described. [78, 101-107] The evidence for C-H activation by these compounds include H/D exchange, alkane dehydrogenation, and direct observation of the unstable oxidative addition adduct. Some metal fragment can activate C-H bonds by forming σ-complexes, in which the C-H bond acts as a two-electron donor. Coordination of the C-H bond to the metal center gives rise to a three center-two electron bond, in analogy to the σ/π bonding formalism for η^2-H_2 bonding to a transition metal.

Our research group has reported several examples of H-H bond, and Si-H bond activation involving η^2-coordination of the H-H bond and Si-H bond to some of Tp

supported ruthenium complexes, respectively. We anticipate that these complexes might activate C-H bonds of alkanes in an analogous manner. In this part of the research work, the catalytic activities of Tp supported ruthenium complexes toward C-H bond activation of some common organic solvents have been studied, such activation is evidenced by H/D exchange between H_2 and the deuterated solvents or among D_2O, H_2, and the non-deuterated solvents.

2.2 Experimental

2.2.1   Materials

Ruthenium trichloride, $RuCl_3.xH_2O$ was obtained from Aldrich and Johnson Matthey. Pyrazole, triphenylphosphine, and sodium tetrafluoroborate were purchased from Aldrich. Unless otherwise stated, all manipulations were carried out under a dry dinitrogen atmosphere, using standard Schlenk-tube techniques. All the solvents were distilled and degassed under dry nitrogen atmosphere with appropriate drying agents: (solvent   /drying   agent   )   methanol/Mg-I_2,   ethanol/Mg-I_2,   acetonitrile/CaH$_2$, dichloromethane/CaH$_2$. Tetrahydrofuran, diethyl ether, toluene and hexane were distilled from sodium-benzophenone ketyl. THF-d_8 and CD_2Cl_2 were dried on P_2O_5 and vacuum transferred to a flask capped with a rubber septum.

2.2.2 Instrumentation

NMR spectra were taken on a Bruker DPX 400 spectrometer. ^{1}H NMR spectra were measured at 400.13 MHz, chemical shifts were reported relative to residual protons of the deuterated solvents. ^{31}P{^{1}H} NMR spectra were recorded on the Bruker DPX 400 spectrometer at 161.70 MHz. ^{31}P chemical shifts were externally referenced to 85% H_3PO_4 in D_2O (δ 0.0 ppm). ^{13}C{^{1}H} NMR spectra were measured at 100.63 MHz, chemical shifts of these spectra were referenced to the solvent peaks of the deuterated solvent. Fast Atom Bombardment Mass spectrometry was carried out with a Finnigan MAT 95S mass spectrometer using 3-nitrobnezyl alcohol as matrix. The gases in the headspace of the Wilmad pressure NMR tube and the substrates in it were analyzed with GC-MS. The substrates were analyzed at 50 eV on a HP mass spectrometer, Model No. 5972A, coupled with gas chromatograph. The column used was a 1.5 m, 1/8" column; the flow rate was adjusted to 1mL/min and column temperature was set at 150°C.

2.2.3 Syntheses

The complexes TpRu(PPh$_3$)(CH$_3$CN)Cl (1),[24] TpRu(PPh$_3$)$_2$H (2), [21] and TpRu(dppe)H (3) [22] were synthesized according to reported methods. The complex TpRu(PPh$_3$)(CH$_3$CN)H (4) was synthesized according to published literature. [24]

2.2.4 C-H Activation with TpRu(PPh$_3$)(CH$_3$CN)H (4)

2.2.4.1 H/D exchange between H$_2$ and the deuterated solvents

A Wilmad pressure-valved NMR tube loaded with TpRu(CH$_3$CN)(PPh$_3$)H (**4**) (~20mg) was evacuated and then filled with nitrogen gas for 3 cycles. THF-d_8 (0.3 mL) was added to the tube under N$_2$, and the tube was then sealed. ^{1}H NMR and ^{31}P{^{1}H} NMR spectra were taken at room temperature. The NMR tube was then pressurized with 15 bars of H$_2$ and heated at 130°C for 13 h. After cooling to room temperature, ^{1}H NMR and ^{31}P{^{1}H} NMR spectra were again taken. The H/D exchange between H$_2$ and other deuterated solvents (dioxane-d_8, diethyl ether-d_{10}, benzene-d_6, chlorobenzene-d_5 and toluene-d_8) were studied in a similar manner.

2.2.4.2 H/D exchange among H$_2$, D$_2$O and organic solvents

A Wilmad pressure-valved NMR tube loaded with **4** (~20mg) was evacuated and then filled with nitrogen gas for 3 cycles. Dried, degassed THF (0.3 mL) and 20 μL of D$_2$O were added to the tube under N$_2$, and the tube was then sealed. ^{1}H NMR and ^{31}P{^{1}H} NMR spectra were taken at room temperature. The NMR tube was then pressurized with 15 bars of H$_2$ and was heated at 130° C for 13 h. After cooling the sample to room temperature, ^{1}H NMR and ^{31}P{^{1}H} NMR spectra were again taken. The H/D exchange among H$_2$, D$_2$O, and other organic solvents (dioxane, diethyl ether, benzene, chlorobenzene and toluene) were studied in a similar manner.

2.2.5   C-H Activation Study with TpRu(PPh$_3$)$_2$H (**2**)

2.2.5.1 H/D exchange between H$_2$ and the deuterated solvents

The procedures are the same as that in 2.2.4.1 except that **2** is used as catalyst instead of **4**.

2.2.5.2 H/D exchange among H_2 , D_2O and common organic solvents

The procedures are the same as that in 2.2.4.2 except that **2** is used as catalyst instead of **4**.

2.2.6 C-H Activation Study with TpRu(dppe)H (3)

2.2.6.1 H/D exchange between H_2 and the deuterated solvents

The procedures are the same as that in 2.2.4.1 except that **3** is used as catalyst instead of **4**.

2.2.6.2 H/D exchange among H_2, D_2O and common organic solvents

The procedures are the same as that in 2.2.4.2 except that **3** is used as catalyst instead of **4**.

2.2.7   Study of H/D exchange between D_2O and **4**.

A 5mm NMR tube loaded with **4** (~20mg) was evacuated and then filled with nitrogen gas for 3 cycles. THF-d_8 (0.35mL) was added to the tube. The ^{1}H NMR and ^{31}P{^{1}H} NMR spectra were taken. Excess D_2O (4μL) was then added into the NMR tube, the ^{1}H NMR, ^{2}H NMR and ^{31}P{^{1}H} NMR spectra were again taken. All the processes were performed at room temperature.

A 5mm NMR tube loaded with **4** (~20mg) was evacuated and then filled with nitrogen gas for 3 cycles. THF-d_8 (0.35mL) was added to the tube. The ^{1}H NMR and ^{31}P{^{1}H} NMR spectra were taken. The solution was heat at 70°C for 13h. After cooling to room temperature, ^{1}H NMR and ^{31}P{^{1}H} NMR spectra were again taken.

2.2.8. C-H activation with TpRu(dppe)H (3)

The experiment followed the procedures of 2.2.4.1 except that the complex, TpRu(dppe)H (**3**), was used instead of **4**.

2.2.9 Control Experiments

2.2.9.1 Control experiment for detecting the H/D exchange between H_2 and deuterated solvents in the absence of **4**.

The experiments follow the procedures of 2.2.4.1 except that no complex was added. After the reaction, the resulting solutions were analyzed by ^{1}H NMR.

2.3 Result and discussion

2.3.1 Activation of carbon-hydrogen bonds of aromatic and heteroatom solvents by TpRuH(CH₃CN)(PPh₃) (4)

The use of naturally abundant alkanes has been limited to solvents or fuel. Development of C-H bond activation by transition metal catalyst is necessary in order to discover fundamentally new routes for converting hydrocarbons to more valuable products, such as alcohols, ketones, acids, and peroxides. It also could help reducing petroleum pollution and other environmental problems. [31] Many works devoted to isotope exchange reaction have appeared. [108, 109]

C-H bond activation in the present work was probed by H/D exchange between H_2 and the deuterated solvents. The H/D exchange study was conducted in a 5-mm Wilmad pressure-valved NMR tube; a solution containing a catalytic amount (ca. 20mg) of **4** in the deuterated solvent was heated at 130°C for 13h under 15 bars of H_2. In the course of study, activation of the C-H bonds of the solvent was evidenced by H/D exchange between H_2 and the deuterated solvents, giving HD and D_2 gases on the one hand and partially protiated solvent on the other (eq. 2.1). The presence and the distribution of the HD, D_2, and the production of partially protiated solvents were detected by NMR and MS. (Table 2.1 and 2.2)

$$H_2 + \text{Solvent-}d_x \longrightarrow D_2 + HD + \text{Solvent-}D_{x\text{-}y}H_y \quad (2.1)$$
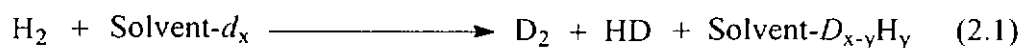
Table 2.1. Mass distribution of gases in the headspace of the NMR tube after the 4-catalyzed H/D exchange reaction between H_2 and the deuterated solvents.[a]

Run	Solvent	Percentage of			
		H_2	HD	D_2	Gas f_D [b]
1	C_6D_6	20.1	58.3	21.6	0.51
2	C_6D_5Cl	21.2	62.4	16.4	0.48
3	Toluene-d_8	15.7	65.6	18.7	0.52
4	THF-d_8	22.4	59.2	18.4	0.48
5	Dioxane-d_8	16.5	61.0	22.5	0.53
6	Ether-d_{10}	18.3	60.1	21.6	0.52

[a] Reaction conditions: 0.032mmol of $TpRuH(CH_3CN)(PPh_3)$ (4) in 0.3mL of deuterated solvent under 15 atm of H_2; reaction temperature 130°C; reaction time 13h.

[b] Fraction of D in the hydrogen gas. (determined by MS)

Using trial 1 as an example for the calculation of Gas

$$f_D = [58.3 \text{ X } 1 + 21.6 \text{ X2 }] / 100 \text{ X } 2$$

Gas $f_D = 0.51$

Table 2.2. Mass distribution in the solutions after the **4**-catalyzed H/D exchange reaction between H_2 and deuterated aromatic solvents.[a]

Run	Solvent	Percentage of solvent-H_x						
		H_5	H_4	H_3	H_2	H_1	H_0	f_H[b]
1	C_6D_6		0.1	1.6	5.2	25.2	67.9	0.07
2	C_6D_5Cl			2.6	12.8	33.4	51.2	0.13
3	Toluene-d_8			0.4	12.6	12.4	74.6	0.08
4	THF-d_8			1.0	15.6	25.9	57.5	0.08
5	Dioxane-d_8			2.3	6.5	18.2	73.0	0.05
6	Ether-d_{10}			3.5	15.2	38.9	42.4	0.08

[a] Reaction conditions: 0.032mmol of $TpRuH(CH_3CN)(PPh_3)$ (**4**) in 0.3mL of deuterated solvent under 15 bars of H_2; reaction temperature 130°C; reaction time 13h.

b Fraction of hydrogen atom in the solvents. (determined by MS)

Using trial 1 as an example for the calculation of f_H

f_H = [0.1 X 4+1.6 X 3+5.2 X 2+25.2 X 1] / 100 X 6

f_H = 0.07

For example, after heating a benzene-d_6 solution of 4 at 130°C under 15 atm of H_2 for 13 h, the proton signal of free H_2 at δ 4.77 ppm diminished, while a new 1:1:1 triplet attributable to HD gas emerged at δ 4.43 ppm ($^1J_{HD}$ = 42.6Hz). In the upfield region, it was observed that the doublet due to Ru-H of 4 at δ -12.80 ppm ($^2J_{HP}$ = 29.2Hz) decreased in intensity, and a multiplet (δ -9.47 to δ -9.54 ppm), which is attributable to TpRu(PPh₃)(H₂)H (5), was observed[24]. The intensity of the signal due to coordinated CH_3CN at δ 0.61 decreased with concomitant appearance of the free CH_3CN signal at δ 1.14 ppm. It was also observed that the intensity of the residual peak of C_6D_6 at δ 7.16 ppm greatly increased. In the $^{31}P\{^1H\}$ MNR spectrum, the singlet at δ 78.3 ppm, which is due to 4, diminished, on the other hand, a new singlet at δ 74.4 ppm, which is due to η^2-dihydrogen & hydride species 5 was detected[24]. H_2 reacts with other deuterated solvents in an analogous manner.

Analogous to 4, the bis-phosphine complex TpRu(PPh₃)₂H (2) also catalyzes C-H bond activation of common solvents in a similar manner. The PPh₃ and CH_3CN dissociate under thermal conditions (130°C) from 2 and 4, respectively, to provide the coordinatively unsaturated active species TpRuH(PPh₃) (I). The organic substrate (C_6D_6) coordinates to the metal in a η^2-bonding mode giving II. η^2-coordination of arene to metal center is not uncommon, Parshall has suggested that arene may precoordinate to the metal in an η^2 fashion prior to activation, [25] a formulation that was postulated as early as 1965 by Chatt (eq. 2.2)

(i)   M   (ii)   H
                                               M

(2.2)
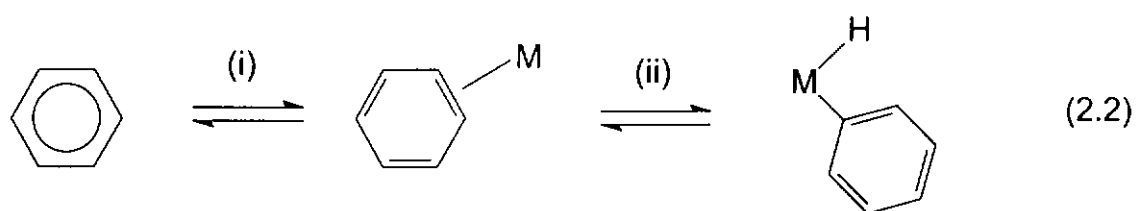
Besides, Jones and coworkers have previously reported evidence for the formation of an η^2-benzene complex along the reaction pathway for activation of benzene by $[(C_5Me_5)Rh(PMe_3)]$.[110] The ability of aromatic hydrocarbons to coordinate in a η^2-mode prior to C-H activation has been demonstrated. Further examination of the reactions between metal and fused, polycyclic aromatics has revealed origin of the tendency to form η^2-complexes with arene. [111] In the present work, we believed that benzene was first coordinated to the metal in an η^2-fashion but the η^2-coordinated intermediate does not undergo oxidative addition to form the phenyl hydride intermediate because such process increases the coordination number and leads to the formation of a 7-coordinated intermediate (Scheme. 2.1). To date, genuine 7-coordinated Tp ruthenium complex is still unknown.

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where S = PPh₃, **2**

S = CH₃CN, **4**

☐ = Vacant Site

Tp⁻ =
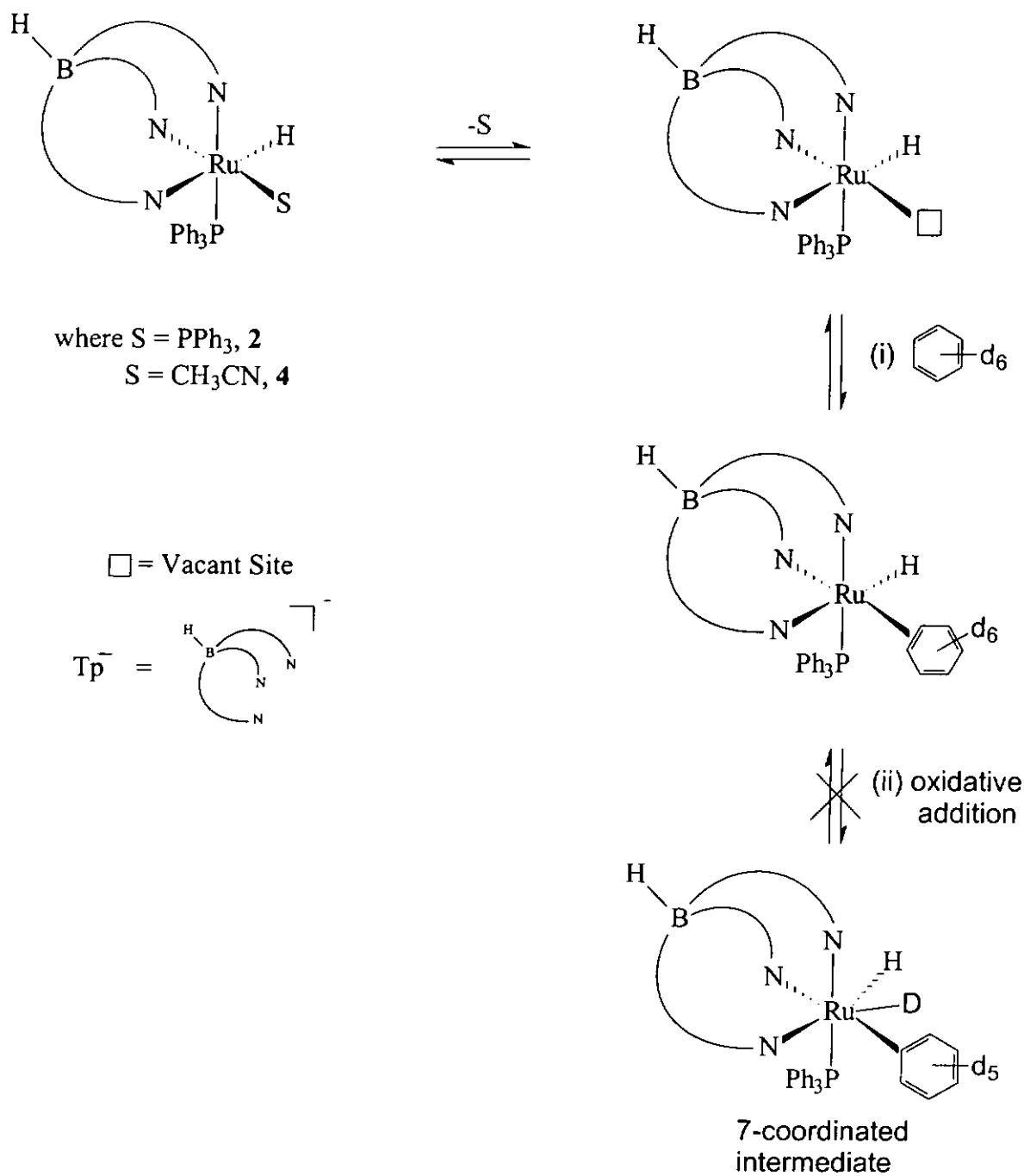
Scheme 2.1. Precoodination of aromatic substrate to metal center

Besides Rh(I) and Ir(I), generally, for Ru(II), d^6 system, C-H bonds are usually cleaved via an oxidative addition to the metal. Much research have indicated that the major step for C-H bond activation is the insertion of metal center into C-H bond. [26, 44, 45, 47-55, 67] For example, the (η^6-arene)Ru(H)$_2$(SiMe$_3$)$_2$ (arene = C$_6$Me$_6$, p-cymene, C$_6$H$_6$) complex activates both aromatic and aliphatic C-H bonds and catalyzes H/D exchange between deuterated solvent and hydride ligand in benzene-d_6. A mechanism based on reductive-elimination/oxidative-addition steps which utilizes a Ru(IV)-Ru(II) cycle has been proposed by Berry[56] to account for the C-H bond activation. On the other hand, C-H bond can be activated via σ-bond metathesis, which is a well-recognized reaction in the field of early transition metal, lanthanide and actinide chemistry. [98, 112] Recent experimental [73, 113-118] and theoretical [119, 120] findings, however, suggest that these reactions could also occur with middle and late transition-metal systems.

Complexes 2 and 4 are Tp containing ruthenium complexes, and the steric bulk of the Tp ligand which has a cone angle of 180° [76], disfavors higher coordination number of the metal center. Furthermore, the Tp ruthenium fragment is strongly hybridized biased to bind preferentially three additional ligands for an octahedral six-coordinate structure[121]. Therefore, processes involving an increase of coordination number, viz, oxidative addition and associative nucleophilic substitutions at metal center, are less likely for the Tp supported complexes. There is no report of genuine seven-coordinate ruthenium Tp compounds yet.[121] Thus, polyhydride complexes of high hydrogen

content favor dihydrogen rather than dihydride coordination in order to maintain octahedral geometry as in $Ru(HB(pz)_3)(\eta^2-H_2)_2H$[122, 123] and $Ru(HB(pz)_3)(PCy_3)(\eta^2-H_2)H$.[124] We found that Tp supported ruthenium complexes always support 6-coordinated dihydrogen complexes, rather than the 7-coordinated dihydrides. From previous experience of our research group and those of the others, protonation reactions of the complexes $TpRu(PPh_3)_2H$ and $TpRu(CH_3CN)(PPh_3)H$ with $HBF_4 \cdot Et_2O$ yield the corresponding dihydrogen complexes $[TpRu(H_2)(PPh_3)_2]BF_4$ and $[TpRu(H_2)(CH_3CN)(PPh_3)]BF_4$, respectively. [21] The dihydrogen complexes $[TpRu(H_2)(dppe)]BF_4$ and $[TpRu(H_2)(CO)(PPh_3)]BF_4$ were also prepared with a similar strategy by our research group.

Hartwig[73] has shown evidence for σ–bond metathesis with a low-valent, late transition metal, addition of catecholborate(HBcat) to the low-valent CpRu(PPh₃)₂Me complex which leads to the corresponding ruthenium hydride and methylcatecholborane (scheme 2.2). Kinetic experiments conclusively showed that oxidative addition of the B-H bond did not occur.
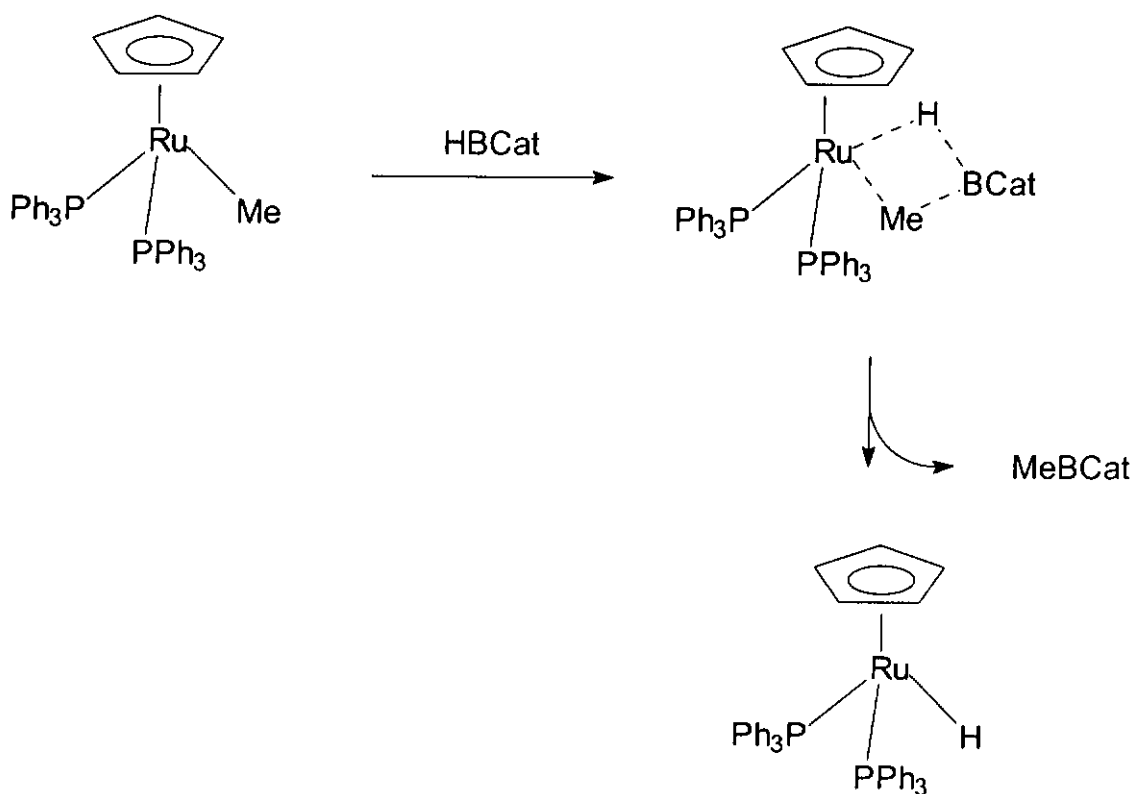
Scheme 2.2. σ-bond metathesis between ruthenium hydride and methylcatecholborane proposed by Hartwig.

Other researchers have shown examples of σ-bond metathesis involving low-valent, late transition metal alkyl complexes too. [54, 59, 67, 74, 75] Therefore, we propose that the H/D exchange reaction with **2** and **4** proceed via a σ-bond metathesis intermediate rather than the oxidative addition/reductive elimination sequence. More solid support for the preponderance of C-H bond activation over σ-metathesis will await results of theoretical calculations.

In conclusion, σ-bond metathesis between the C-D bond of the solvents and Ru-H via a "four-center" intermediate is believed to be the crucial step for the H/D exchange. Typical σ-bond metathesis is shown as eq. 2.3.

$$L_nM-R \ + \ R'-H \ \longrightarrow \ \left[\begin{array}{cc} \overset{\delta-}{R'}\!\!-\!\!\overset{\delta+}{H} \\ | \qquad | \\ \underset{\delta+}{L_nM}\!\!-\!\!\underset{\delta-}{R} \end{array} \right]^{\ddagger} \ \longrightarrow \ L_nM-R' \ + \ R-H$$

$$(2.3)$$
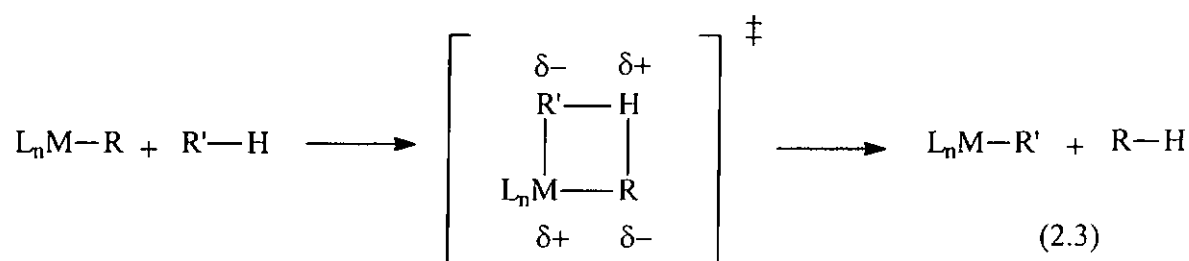
Scheme 2.3 shows a proposed mechanism for the H/D exchange between H_2 and deuterated solvent, using benzene-d_6 as an example. According to Scheme 2.3, σ-bond metathesis between Ru-H and C-D proceeds via the intermediacy of a 4-centered transient species **III** to afford the η^2-HD aryl intermediate **IV**. Facile exchange between η^2-HD and free H_2 gives free HD and the η^2-H_2 intermediate **V**. Finally, a second σ-

metathesis process between η^2-H_2 and the Ru-aryl group, and subsequent dissociation of the protiated benzene regenerates the unsaturated metal hydride which starts the cycle again. Eq. 2.4 shows the net equation for the H/D exchange between H_2 and deuterated solvents.

$$H_2 \ + \ \text{d-Solvent} \quad \xrightarrow[130^\circ C, \ 13hrs]{\textbf{2 or 4}} \quad D_2 \ + \ HD \ + \ \text{partially protiated d-solvent} \qquad (2.4)$$

[Ru]—H
|
L

where   [Ru] = TpRu(PPh₃)
L = CH₃CN, **4**
L = PPh₃, **2**
□ = vacant site

L ↿⇂ -L

[Ru]—H
|
□   **I**

C₆D₆

C₆D₅H

C₆D₆

[Ru]—H
⬡ d₆
II

σ-bond
metathesis

[Ru]---H
⬡---D
d₅
III

[Ru]—H
⬡ d₅

[Ru]—H / D
⬡ d₅
IV

[Ru]---H
⬡----H
d₅

H₂

HD

σ-bond
metathesis

[Ru]—H / H
⬡ d₅
V
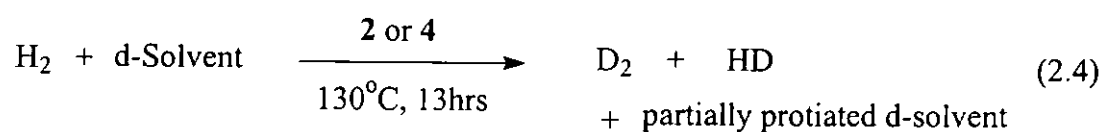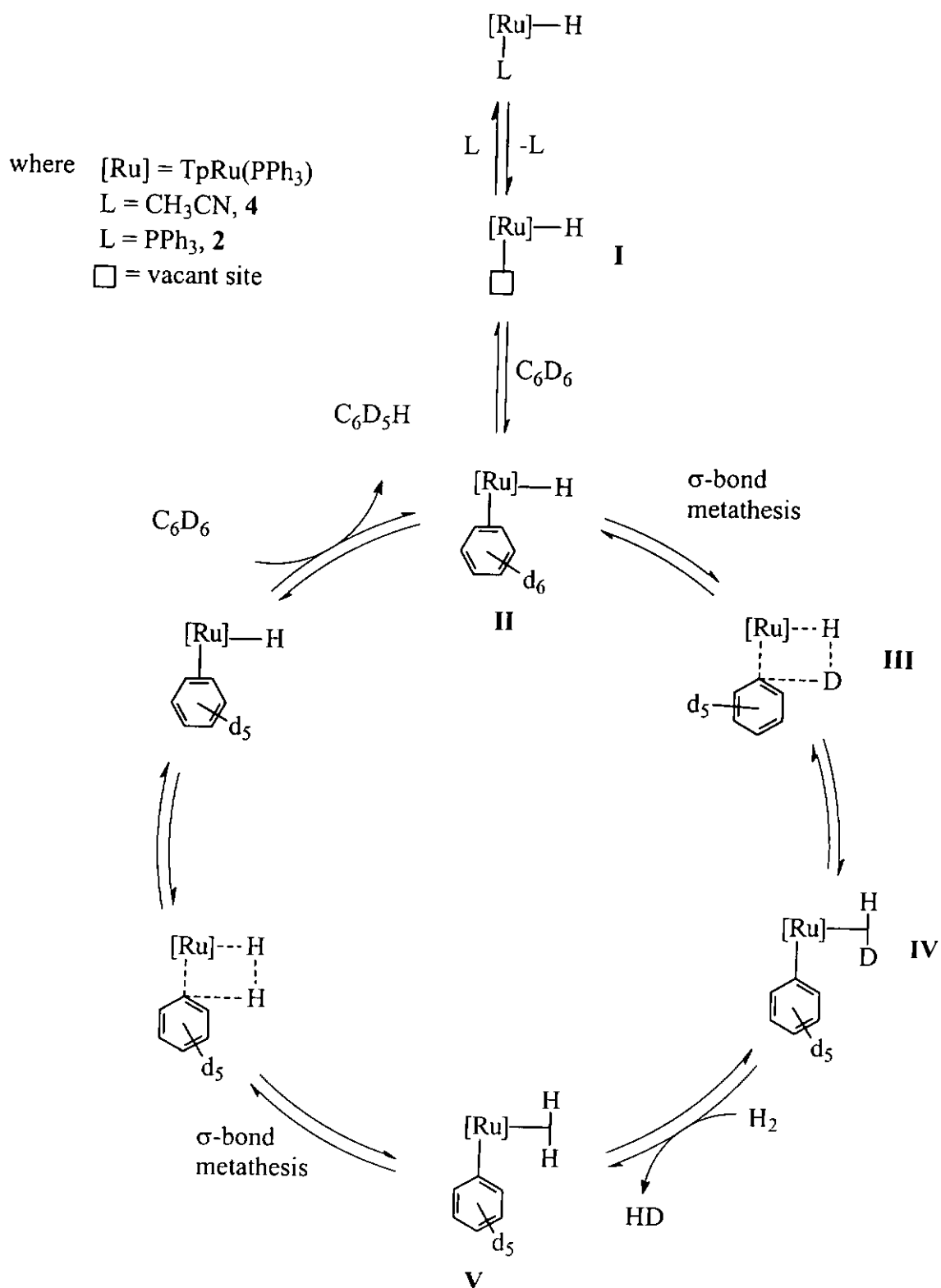
Scheme 2.3. Proposed mechanism for the H/D exchange between H₂ and benzene-d_6.

Other than aromatic solvents, heteroatom solvents such as deuterated THF, dioxane and

diethylether also undergo H/D exchange with H_2, the solvents coordinate to the metal via

the oxygen atom before activation of the C-H bond. Scheme 2.4 shows the coordination

of each of the organic solvents onto the metal center.
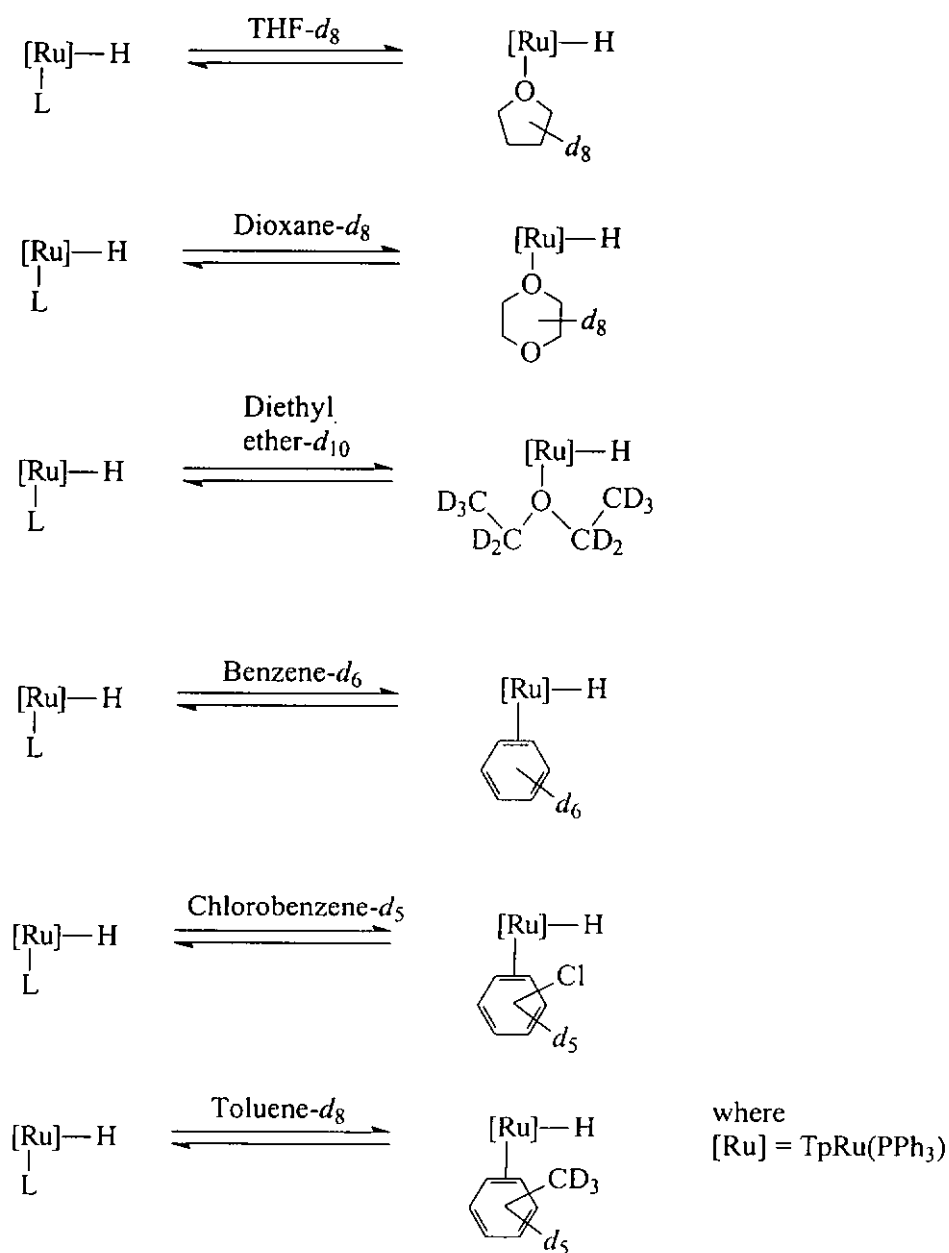
Scheme 2.4. Coordination of different solvents to the metal

Lenges and co-workers[125-127] showed that the key to increase reactivity of $[(C_5Me_5)Co(C_2H_3R)_2]$ as a catalyst for H/D exchange between C_6D_6 and R of the complex $C_5Me_5Co(CH_2=CHR)_2$ (R = H, SiMe$_3$) in aromatic solvents is the bulky trimethylvinylsilane which is lost in the first step to generate the reactive 16-electron fragment $[C_5Me_5Co(C_2H_3R)_2]$ capable of C-H bond activations.

The complex TpRu(dppe)H, (3) was used in place of 2 or 4, and it was found that the former was not effective in catalyzing H/D exchange between H$_2$ and deuterated solvents, probably due to its inability to provide a vacant site for the precoordination of the substrate. This experiment lends support to the proposed mechanism in which the first step of the catalytic cycle is thermo ligand dissociation to generate the active species **I**.

In each of the H/D exchange reactions, it was found that after heating a solution of **4** in the deuterated solvent at 130° C and under 15 bars of H$_2$ for 13 h, the hydride signal of **4** diminished, with concomitant formation of a multiplet at about δ -9.8 ppm in the ^{1}HNMR spectrum. The appearance of the new peak is due to the formation of the trihydride species **5** [24] (eq. 2.5). This highly fluxional trihydride complex was synthesized and isolated by our research group.[24]

(2.5)
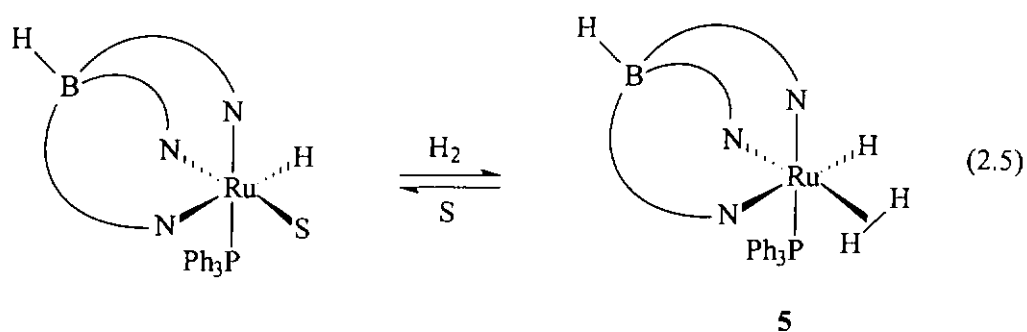
where S = PPh$_3$, **2**
S = CH$_3$CN, **4**

Tp$^-$ =
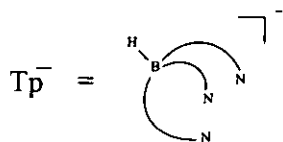
The multiplicity of hydride signal at δ -9.8 ppm is due to the presence of the various

isotopomers of TpRuH$_3$(PPh$_3$) (**5**), TpRuH$_2$D(PPh$_3$) (**5**-d_1), and TpRuHD$_2$(PPh$_3$) (**5**-d_2).

The HD coupling constant ($^2J_{HD}$) of 7.8-8.0 Hz can be discerned. Scheme 2.5 shows the

pathway leading to the generation of **5**-d_1,and **5**-d_2 from **5** and HD.
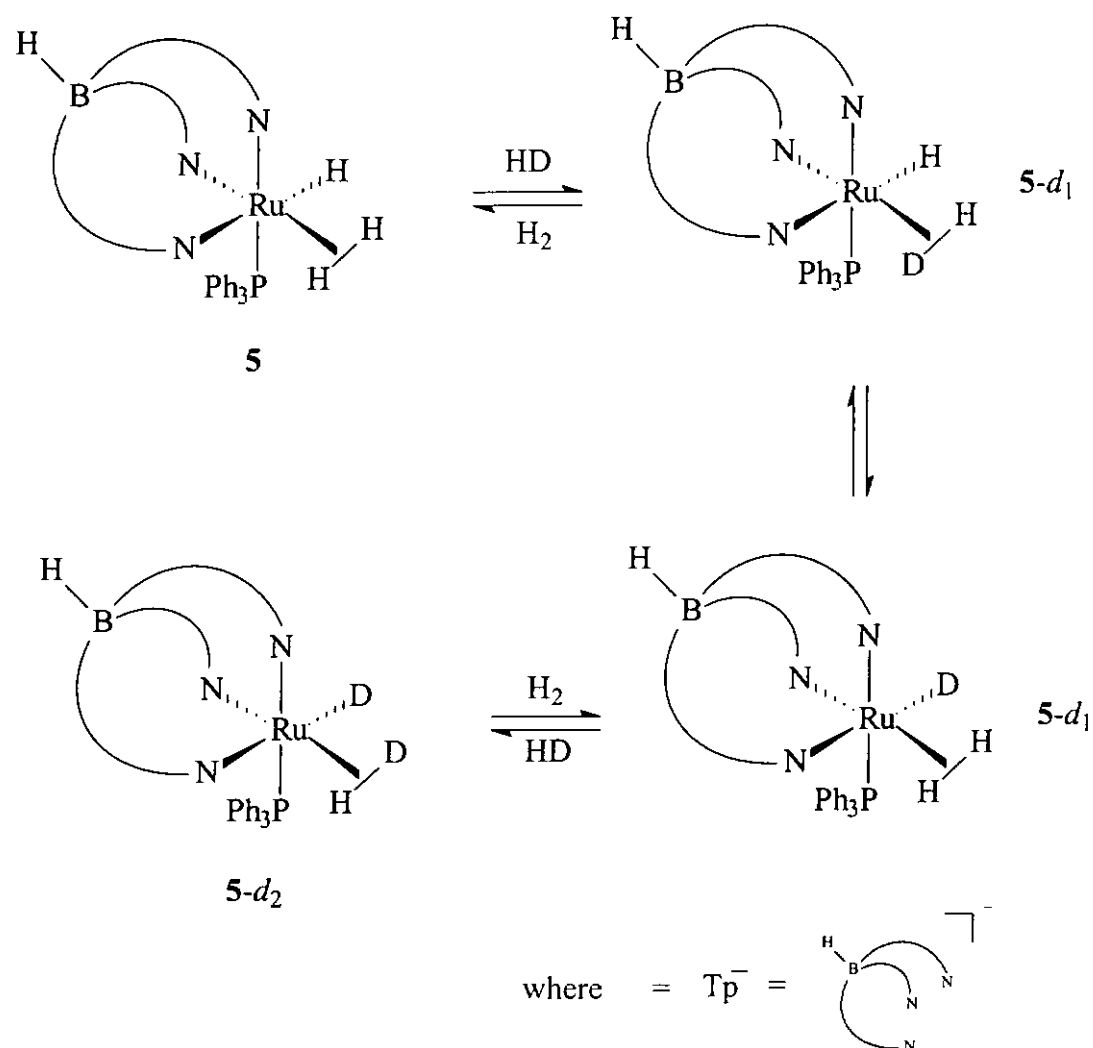
Scheme 2.5. Reaction pathway for the formation of 5-d_1 and 5-d_2 from 5 and HD

For the H/D exchange reaction between H_2 and toluene-d_8, it is found that only the aromatic C-D bonds are activated. ^1H NMR spectroscopy shows that the intensity of residual aromatic proton peaks are enhanced while that of the residual methyl proton remained unchanged. In the case of THF-d_8, α-C-D bond activation predominates, as

evidenced by the drastic enhancement of the α-H signal at $\delta 3.7$ ppm in the ^{1}H NMR spectrum. On the other hand, the peak of the residual β-H at $\delta 1.85$ppm remained basically unchanged in intensity.

The regio-selectivity of the H/D exchange of THF-d_8 with H_2 may be due to the following reasons: 1. Coordination of oxygen atom of THF-d_8 to ruthenium metal is considered to be the origin of high α selectivity. It brings the α-D of THF-d_8 into the right position for σ-bond metathesis. Matusbara,[128] Kim[129], Dixneuf,[130] and Oi,[131] have shown similar α selectivity for C-H bond activation. On the other hand, the β-D's bent away from the hydride ligand, therefore σ-bond metathesis between the Ru-H and the β-C-D bond is unlikely to happen. 2. Higher acidity for the α-D due to the electronic effect of the oxygen which may also contribute to the α selectivity.

On the contrary, it is observed that preferential H/D exchange occurs at the β-position in diethylether-d_{10}. ^{1}H NMR spectroscopy shows intensity enhancement of the peak at $\delta 1.0$ppm, which is due to the residual β-H on deuterated diethylether. On the other hand, the intensity of the peak at $\delta 3.30$ppm, which is due to the residual α-H, remains more or less the same. The preponderance of β-C-D activation over α-C-D activation of diethylether is probably due to the flexibility of its $-CD_2$-CD_3 chain. The β-CD is able to approach the metal center more readily than the α-CD.

C-H bond activation of the solvents is further evidenced by the H/D exchange among D_2O, H_2 and the solvents (Eq. 2.6). Therefore, after heating a solution of 4 in the undeuterated solvent, in the presence of excess (4µL) of D_2O, in 5mm Wilmak pressure NMR tube under 15 bars of H_2 at 130°C for 13 h, HDO, H_2O, HD, and D_2 gases were produced, and the solvent became partially deuterated solvents. Tables 2.3 and 2.4 show the mass distribution of gases in the headspace of the NMR tube after the 4-catalyzed H/D exchange reaction among H_2, D_2O and the organic solvents (non-deuterated) and the mass distribution in the solvents after the 4-catalyzed H/D exchange reactions among H_2, D_2O and organic solvents (non-deuterated), respectively.

$$D_2O + \text{Solvent} + H_2 \xrightarrow[\text{130°C, 20 hours}]{\text{TpRuH(CH}_3\text{CN)(PPh}_3\text{)}} \text{HDO} + \text{Solvent-}Dx + \text{HD} + H_2O + D_2 \qquad (2.6)$$
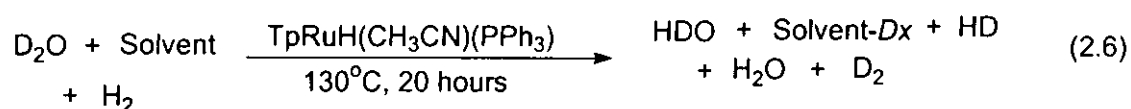
Table 2.3. Mass distribution of gases in the headspace of the NMR tube after the 4-catalyzed H/D exchange reaction among H_2, D_2O and organic solvents (non-deuterated).[a]

Run	Solvent	Percentage of			
		H_2	HD	D_2	Gas f_D [b]
1	C_6H_6	19.0	64.4	16.6	0.49
2	C_6H_5Cl	16.9	63.1	20.0	0.52
3	Toluene	14.6	63.0	22.4	0.54
4	THF	32.4	59.0	8.6	0.38
5	Dioxane	17.9	63.0	19.1	0.51
6	Ether	28.1	56.5	15.4	0.44

[a] Reaction conditions: 0.032mmol of $TpRu(CH_3CN)(PPh_3)H$ (4) in 0.3mL of deuterated solvent under 15 atm of H_2; excess (4μL) D_2O; reaction temperature 130°C; reaction time 13h.

[b] Fraction of D in the hydrogen gas (determined by MS).

Using trial 1 as an example for the calculation of Gas f_D

Gas f_D = [64.4 X 1+16.6 X 2] / 100 X 2

Gas f_D = 0.49

Table 2.4. Mass distribution in the solvents after the **4**-catalyzed H/D exchange reactions among H_2, D_2O and organic solvents (non-deuterated).[a]

Run	Solvent	Percentage of solvent-D_x						
		D_5	D_4	D_3	D_2	D_1	D_0	f_D[b]
1	C_6H_6			0.2	2.7	21.0	76.1	0.05
2	C_6H_5Cl		0.3	2.3	13.6	42.6	41.2	0.16
3	Toluene			0.7	5.8	27.6	65.9	0.08
4	THF		0.1	1.1	7.5	29.9	61.4	0.06
5	Dioxane				1.0	10.8	88.2	0.02
6	Ether	0.4	1.2	3.0	6.5	17.5	71.4	0.05

[a] Reaction conditions: 0.032mmol of $TpRuH(CH_3CN)(PPh_3)$ (**4**) in 0.3mL of organic solvent (non-deuterated) under 15 atm of H_2; excess (4μL) D_2O; reaction temperature 130°C; reaction time 13h.

[b] Fraction of D atom in the solvents (determined by MS).

Using trial 1 as an example for the calculation of f_D

$$f_D = [0.2 \times 3 + 2.7 \times 2 + 21 \times 1] / 100 \times 6$$

$$f_D = 0.05$$

In the present case of H/D exchange reaction, D_2O acts as the only source of deuterium. In order to study how the deuterium source gets into the catalytic cycle, an independent experiment was performed. A 5mm NMR tube loaded with 4 (~20mg) was evacuated and then filled with nitrogen gas for 3 cycles. THF-d_8 (0.35mL) was added to the tube. The ^1H NMR and $^{31}P\{^1H\}$ NMR spectra were taken at room temperature. Excess D_2O (4μL) was then added into the NMR tube at room temperature, the ^1H NMR and $^{31}P\{^1H\}$ NMR spectra were again taken at room temperature. It was found that there was H/D exchange between D_2O and 4, yielding HDO and deuterated complex, 4-d_1 at room temperature. As seen in the spectroscopic evidence, in the upfield region, it was observed that the doublet due to Ru-H of 4 at δ -12.80 ppm ($^2J_{HP}$ = 29.2Hz) decreased in intensity (about one tenth of the original one) immediately after addition of D_2O while all the other peaks remained constant. The proposed mechanism of the H/D exchange between 4 and D_2O is shown in scheme 2.6. On the other hand, in the absence of D_2O, heating a THF-d_8 solution of 4 does not result in H/D exchange, therefore confirming that D_2O acts as the only source for the formation of 4-d_1.

S = CH₃CN

4

4-d₁
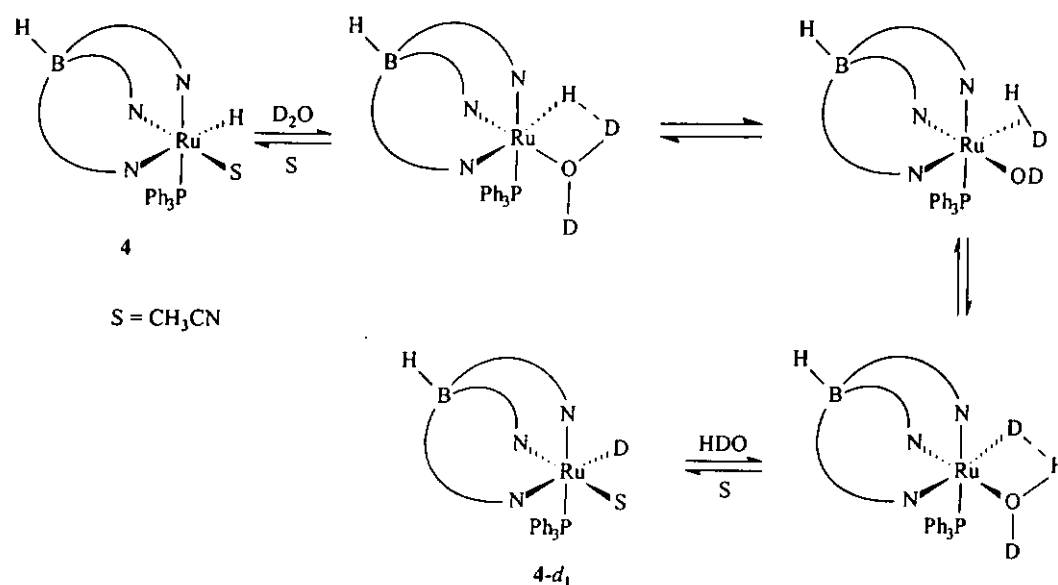
Scheme 2.6. Proposed mechanism of the H/D exchange between **4** and D_2O.

Displacement of CH_3CN in **4** by D_2O, followed by σ-bond metathesis between D_2O and Ru-H, yields the η^2-HD-hydroxyl intermediate. Milet and co-workers [132] have studied similar σ-bond metathesis between hydroxyl ligand and η^2-H_2 and revealed that any ligand having a lone pair, like the hydroxo or an alkoxo ligand, would be a good candidate for undergoing a σ-bond metathesis process. The reverse process, i.e. the σ-bond metathesis reaction of water with a metal hydride, should also be feasible. [132] Scheme 2.7 shows a proposed mechanism for the H/D exchange among D_2O, H_2 and benzene.
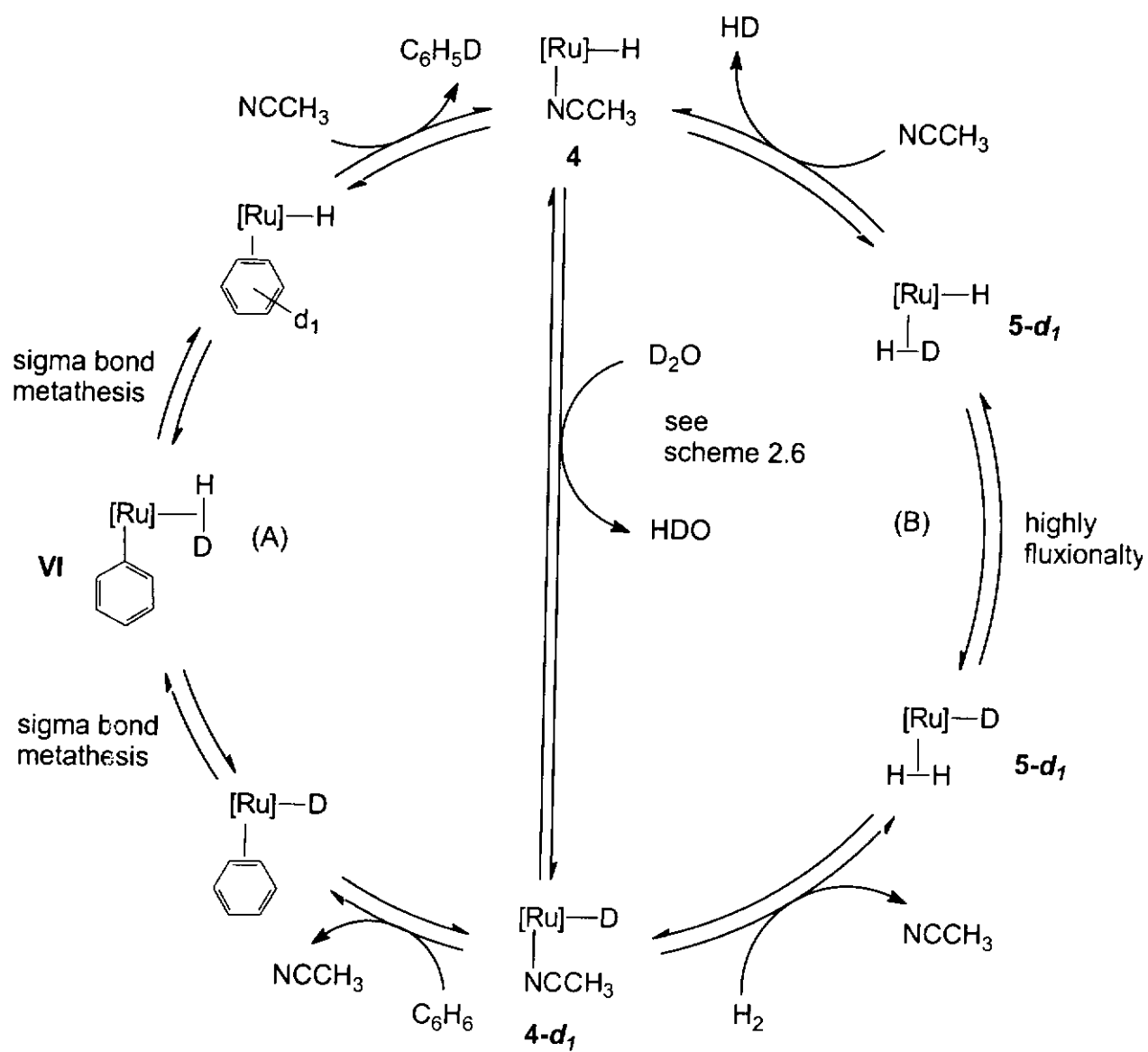
Scheme 2.7. Proposed mechanism for the H/D exchange among D_2O, H_2 and benzene.

After the formation of $4\text{-}d_1$, benzene coordinated onto the metal by displacing the coordinated CH_3CN. The intermediates undergo σ-bond metathesis to cleave the C-H bond of benzene, via a four-centered transient species, to afford the η^2-HD-phenyl intermediate **VI** and another σ-bond metathesis between η^2-HD and Ru-C_6H_5 afford $TpRuH(\eta^2\text{-}C_6H_5D)(PPh_3)$. Finally, the incoming CH_3CN displaces the η^2-C_6H_5D to complete the catalytic cycle. Therefore, by following cycle A, **4** catalyzes the H/D exchange between C_6H_6 and D_2O to afford C_6D_5H and HDO

On the other hand, **4** also catalyzes the H/D exchange between D_2O and H_2 via the sequence of cycle B. Therefore, H_2 displaces $NCCH_3$ in $4\text{-}d_1$, yielding deuterated trihydride species $5\text{-}d_1$, and due to its high fluxionality. H/D exchange readily occurs between the η^2-H_2 and deuterated ligand. Finally, the incoming CH_3CN displaces the η^2-HD, yielding **4** again to complete the catalytic cycle.

Chlorobenzene undergoes H/D exchange more readily than benzene and toluene, as reflected by the higher f_H and f_D values in tables 2.2 and 2.4 respectively. This is in accord with increased acidity of the aryl hydrogens in the presence of an electron-withdrawing substituents on the benzene ring. Acidic aryl hydrogen is more capable of generating the aryl η^2-dihydrogen complex intermediate, since after all, formation of η^2-

H_2 can be considered as a result of the protonation of Ru-H by an aryl hydrogen of the η^2-coordinated aromatic substrate.

Chapter 3

Synthesis and Characterization of Ruthenium Vinylidene Complexes and their Role in the Dimerization of Alkynes

3.1 Introduction

Transition metal-catalyzed dimerization of terminal alkynes is an effective method of forming enynes, but its synthetic application in organic synthesis has been limited due to low selectivity in the dimeric products. Recent advances in transition metal-mediated selective dimerization reactions have fueled a resurgence of interest in the catalytic dimerization of terminal alkynes.[8, 82, 133-145] The chemistry of transition-metal vinylidene complexes has also attracted much attention in recent years, due to their occurrence as key intermediates in stoichiometric and catalytic transformations of organic molecules.[82, 146-149] Kirchner and co-workers [150] have shown that the neutral vinylidene complex TpRu(PPh₃)(Cl)(=C=CHPh) (6) is capable of initiating the catalytic dimerization of terminal acetylenes to give enynes. This reaction proceeds via the coordinatively unsaturated alkynyl complex TpRu(PPh₃)(C≡CPh) (VII), which is formed as an intermediate by 1,3-elimination of HCl as shown in scheme 3.1. [150, 151] There are plenty of literature discussions on the generation of alkynyl species, aided by an external base or by elimination of small molecule, as the initiating step of the catalytic cycle.(eq. 3.1 and 3.2.)[8, 79, 82, 135, 138, 150]

PPh$_3$

[Ru]

Cl   PPh$_3$

6

$\xrightarrow{-PPh_3}$

[Ru]—PPh$_3$

Cl

where [Ru] = TpRu(II)

7

PPh$_3$

[Ru]=C

Cl   C   Ph

H

-HCl

Ph—≡—Ph

PPh$_3$

[Ru]

C≡C

Ph

VII

≡—Ph

≡—Ph

PPh$_3$ Ph

[Ru]   C≡C

C

Ph

PPh$_3$

[Ru]

C≡C

Ph—≡

Ph
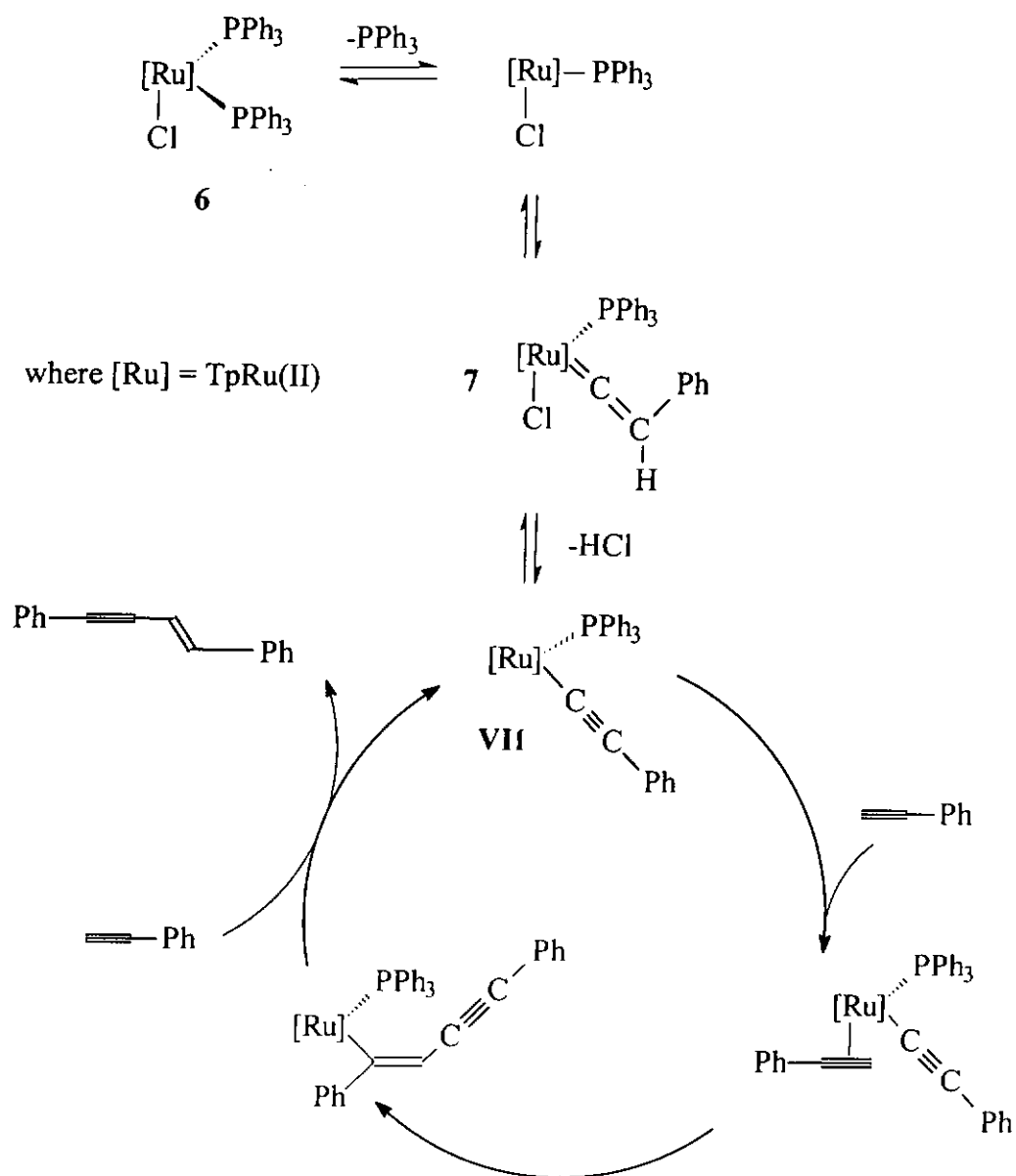
Scheme 3.1. Mechanism for the catalytic dimerization of
terminal acetylenes to give enynes proposed by Kirchner et. al.

50

$$HC\equiv CR'$$
$$+$$
$$B \qquad\qquad\qquad BH^+$$

$$[M] \xrightarrow{\hspace{4cm}} [M]-C\equiv CR' \qquad (3.1)$$
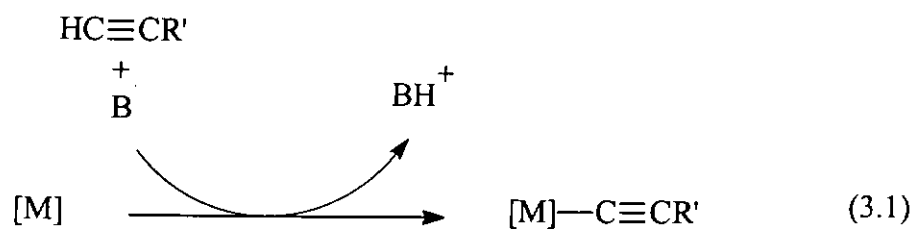
with the addition of external base

$$HC\equiv CR' \qquad\qquad H-R$$

$$[M]-R \xrightarrow{\hspace{4cm}} [M]-C\equiv CR' \qquad (3.2)$$
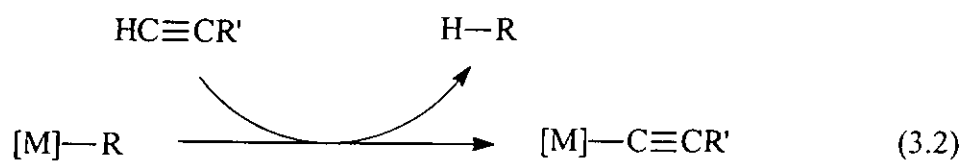
by elimination of small molecule

where   R = H or Alkyl
R' = H or Alkyl
M = Ru, Zr, or Ac
B = Base

This part of the research program concentrates on the syntheses and the reactivity studies of some ruthenium vinylidene and alkynyl complexes. We have also investigated the mechanism of dimerization of alkynes with solvento ruthenium complexes in the presence or absence of a base. Valuable mechanistic informations concerning the catalytic cycle were provided by independent studies of reactions between the catalyst and phenylacetylene, in the absence and presence of base, to yield vinylidene and alkynyl complexes, respectively. These reactions are aimed at mimicking the initial steps of the proposed catalytic cycles. In the presence of base, alkynyl complex is formed as the active species while vinylidene complex is formed in the absence of base.

3.2 Experimental

3.2.1 Materials

Ruthenium trichloride, ($RuCl_3.xH_2O$) pyrazole, triphenylphosphine, sodium tetrafluoroborate, and potassium tetrafluoroborate were purchased from Aldrich. Unless otherwise stated, all manipulations were carried out under a dry dinitrogen atmosphere, using standard Schlenk-tube techniques. All the solvents were distilled and degassed under a dry nitrogen atmosphere with appropriate drying agents: (solvent /drying agent) methanol/Mg-I_2, ethanol/Mg-I_2, acetonitrile/CaH_2, dichloromethane/CaH_2. Tetrahydrofuran, diethyl ether, toluene and hexane were distilled from sodium-benzophenone ketyl. THF-d_8 and CD_2Cl_2 were dried over P_2O_5.

The complexes $TpRu(PPh_3)(Cl)(CH_3CN)$ (1) [24], $TpRu(dppe)(H)$ (3) [22], $TpRu(PPh_3)(H_2)H$ (5) [24], $TpRu(PPh_3)_2Cl$ (6) [152], $TpRu(=C=CHPh)(PPh_3)(Cl)$ (7)[158], $[(Tp)Ru(PPh_3)_2CH_3CN](BF_4)$ (8) [21], $[(Tpm)Ru(PPh_3)_2CH_3CN](BF_4)_2$ (9), $[(triphos)Ru(MeCN)_3](CF_3SO_3)_2$ (10), were prepared according to literature methods.

3.2.2 Instrumentation

NMR spectra were taken on a Bruker DPX 400 spectrometer. ^{1}H NMR spectra were measured at 400.13 MHz, chemical shifts were reported relative to residual protons of the deuterated solvents. ^{31}P{^{1}H} NMR spectra were recorded on the Bruker DPX 400 spectrometer at 161.70 MHz, chemical shifts were externally referenced to 85% H_3PO_4 in D_2O (δ 0.00ppm). ^{13}C{^{1}H} NMR spectra were measured at 100.63 MHz, chemical shifts of these spectra were referenced to solvent peaks of the deuterated solvent.

3.2.3 Syntheses and reactions

3.2.3.1 Synthesis of the Vinylidene Complex, [TpRu(=C=CHPh)(dppe)](BF$_4$) (11).

To a suspension of TpRu(dppe)H (3) (0.20 g, 0.19 mmol) in dichloromethane (20 mL), one equiv. of HBF$_4$ was added, and the mixture was stirred at room temperature for half an hour. An excess of phenylacteylene (PhC≡CH) was added and the resulting mixture was stirred at room temperature until it turned red. The purple red precipitate was filtered off, washed with diethyl ether (20mL) and dried under vacuum. Yield: 0.18g (74%). Anal. Calcd for C$_{43}$H$_{40}$BN$_6$P$_2$Ru: C, 63.39; H, 4.91; N, 10.32. Found: C, 63.48; H, 4.83; N, 10.31. ^{1}H NMR (400 MHz, CDCl$_3$, 25°C): δ 3.47-3.48 (m, 4H CH_2CH_2), δ 3.87 (d, 1H, β-H), δ 5.35 (d, 1H), δ 5.69 (d, 1H), H^4 on the pyrazoles, δ 6.25 (d, 2H), H^3 on the pyrazoles, δ 6.50 (d, 2H), H^5 on the pyrazole, δ 6.69-7.45 (m, 20H, PPh$_2$), δ 7.60 (d, 1H) δ 7.87 (d, 2H), H^3 on the pyrazoles, all the nine hydrogen atoms on the pyrazoles have coupling constants of about 2 Hz. ^{31}P{^{1}H}(161.9 MHz, CDCl$_3$, 25°C) : δ 54.8(s).

3.2.3.2 Synthesis of the Alkynyl Complex, TpRu(C≡C-Ph)(PPh₃)(CH₃CN) (12).

A sample of TpRu(=C=CHPh)(PPh₃)Cl (7) (0.60g, 0.50 mmol) was dissolved in tetrahydrofuran (5 mL) containing 1 mL of Et₃N (excess), acetonitrile (0.5mL) was introduced and the reaction mixture was stirred at room temperature for half an hour. At the end of the reaction, the solution was filtered and the solvent was removed under vacuum. The residue was washed with diethylether several times and then dried under vacuum. Yield: 0.58g (90%). Anal. Calcd for $C_{37}H_{33}BN_6PRu$: C, 69.38; H, 5.16; N, 13.13. Found: C, 69.72; H, 5.26; N, 13.88. ^1H NMR (400 MHz, CDCl₃, 25°C): δ 2.02 (s, 3H, CH_3CN), δ 5.78(t, 1H, H^4 on the pyrazoles), δ 5.89 (t, 1H, H^4 on the pyrazoles), δ 6.12(d, 1H, H^4 on the pyrazoles), δ 6.84 (d, 2H, H^5 on the pyrazoles), δ 7.13 (d, 1H, H^5 on the pyrazoles, δ 7.29-7.40 (m, 15H of PPh₃), δ 7.64 (d, 2H, H^3 on the pyrazoles), δ 8.05 (d, 1H, H^3 on the pyrazoles), all the nine hydrogen atoms on the pyrazoles have coupling constants of about 2 Hz. $^{31}P\{^1H\}$ (161.9MHz, CDCl3, 25°C) : δ 59.9 (s).

3.2.3.3 Reaction of TpRu(PPh₃)(Cl)(CH₃CN) (1)with methyl propiolate

A solution of the solvento complex 1 in THF (5mL) was treated with excess methyl propiolate (300µL) and the mixture was stirred at room temperature for 36 h. After removal of the solvent, the residue was dissolved in dichloromethane (0.5mL) and the reddish-purple product precipitated upon addition of diethyl ether (20mL). The resultant mixture was filtered and the solid was dried under vacuum to yield a well know complex TpRu(Cl)(PPh₃)(CO) (13). Yield : 0.25g (90%).^1H NMR (400MHz, CDCl₃,

25C): δ 5.73 (t, 1H, H^4 of pyrazole), δ 5.87 (t, 1H, H^4 of pyrazole), δ 6.17 (t, 1H, H^4 of

pyrazole), δ 6.29 (d, 1H, H^5 on the pyrazole), δ 6.88 (d, 1H, H^5 on the pyrazole), δ 7.53

(d, 1H, H^5 on the pyrazole), δ 7.20-7.40 (m, 15H of PPh$_3$), δ 7.59 (d, 1H), δ 7.64 (d, 1H),

δ7.96 (d, 1H), H^3 on the pyrazole. All the nine hydrogen atoms on the pyrazoles have

coupling constants of about 2 Hz.

3.2.3.4 General procedure for catalytic dimerization of alkynes

Cationic ruthenium catalyst (0.01 mmol) was dissolved in 5 mL of THF in a

25mL thick-walled Schlenk tube equipped with a Telfon stopcock, excess alkyne (2

mmol) was added to the solution, and the reaction mixture was heated at 90°C for 48 h in

a closed system under N$_2$. After the reaction mixture was cooled to room temperature, a

small sample was drawn and analyzed by ^{1}H NMR spectroscopy.

3.3 Results and Discussion

In order to study the mechanism of dimerization of alkynes, some hydridotris(pyrazolyl)borato ruthenium complexes were synthesized as model complexes of the intermediates in the reaction. The vinylidene complex [TpRu(=C=CHPh)(dppe)](BF$_4$) (11) was synthesized by acidification of TpRu(dppe)H (3) with one equivalent of HBF$_4$·H$_2$O, followed by the addition of excess phenyl acetylene as shown in scheme 3.2. Bruce,[151] Bianchini,[147] and Kirchner[150] have published similar preparation routes for vinylidene complexes. For example, the Ru(II) complex mer,trans-(PNP)RuCl$_2$(PPh$_3$) [PNP = CH$_3$CH$_2$CH$_2$N(CH$_2$CH$_2$PPh$_2$)$_2$] reacts with either phenylacetylene or p-tolylacetylene to give fac,cis-(PNP)RuCl$_2${C=CHCR)}(R = Ph, p-tolyl) in refluxing THF.[139] A terminal alkyne ligand displaces a neutral ligand, typically a phosphine, however, in our case, a dihydrogen ligand is replaced by a phenylacetylene, followed by rearrangement of the π-alkyne to give vinylidene complexes. We believe that the formation of 11 from 3 proceeds via a dihydrogen intermediate [TpRu(η^2-H$_2$)(dppe)]$^+$ rather than a corresponding dihydride intermediate [TpRu(H)$_2$(dppe)]$^+$. Dihydrogen complexes such as [TpRu(η^2-H$_2$)(dppm)](BF$_4$) and [TpRu(η^2-H$_2$)(dppp)](BF$_4$) had been synthesized and reported by our research group. They were prepared by addition of 1 equiv. of HBF$_4$·H$_2$O to the corresponding hydride precursors TpRuH(dppm) and TpRuH(dppp), respectively. Unfortunately, in the protonation reaction of 3, the expected dihydrogen complex intermediate [TpRu(η^2-H$_2$)(dppe)](BF$_4$) was not detected or isolated, probably due to the high temperature of the reaction. The formation of vinylidene complex 11, arising from

the well documented (η^2-alkyne)Ru → (η^1-vinylidene)Ru tautomerization (Scheme 3.2), which often constitutes the first step of terminal alkyne activation by transition-metal complex.

3

where   Tp⁻ =

11
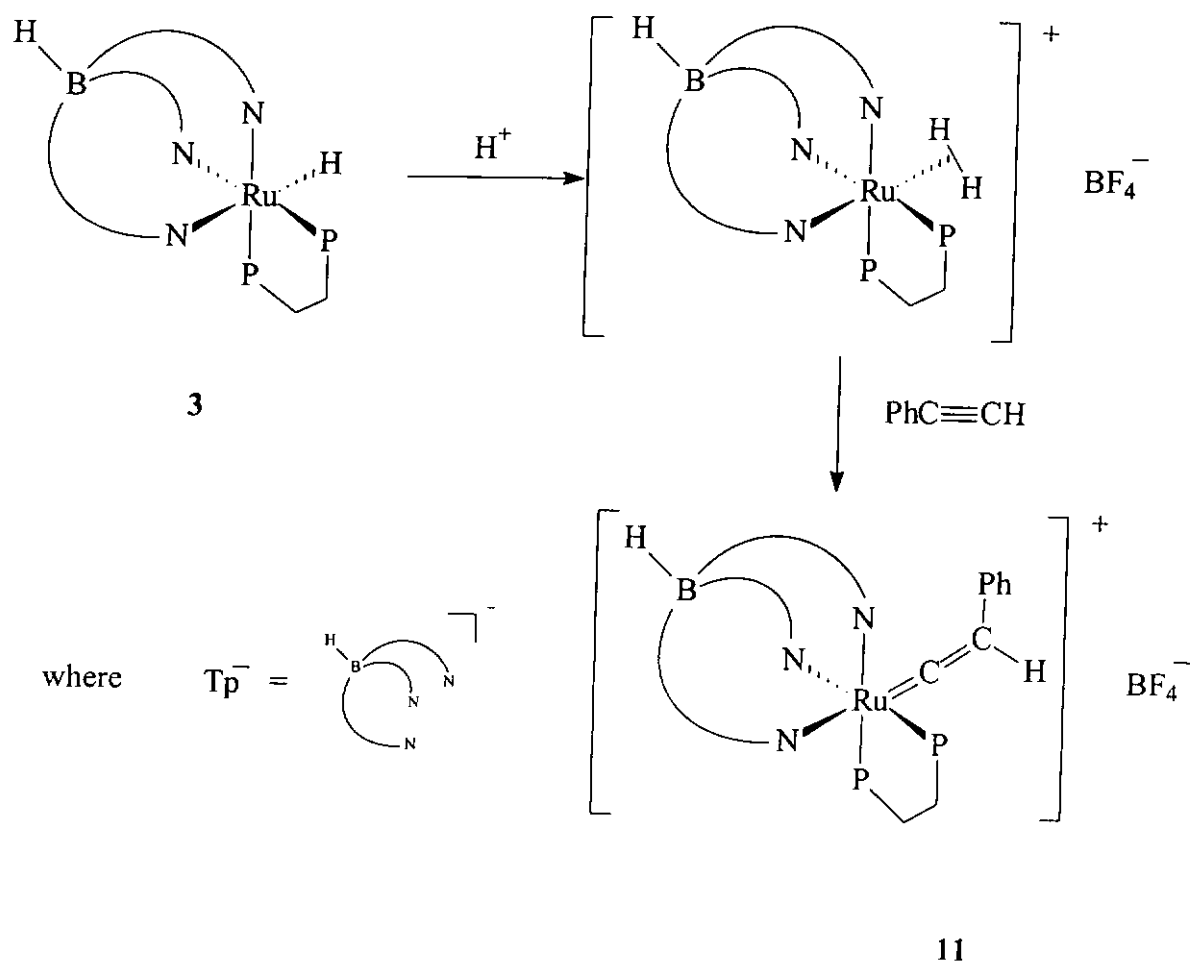
Scheme 3.2. Formation of vinylidene complex 11

Numerous examples of the conversion of coordinated terminal alkynes to vinylidene ligands have been described in the literature. [146, 153] Some representative examples are shown in equations 3.3[154], 3.4[155] and 3.5[156, 157]

$$[Ru] = [(Me_3tacn)Ru(PMe_3)]^+$$

(3.3)

(3.4)

$$R = Ph, Me, {}^{n}Bu, {}^{t}Bu$$
$$CH_2OH, CH_2OMe$$
$$CO_2Me, CH_2Cl$$

(3.5)
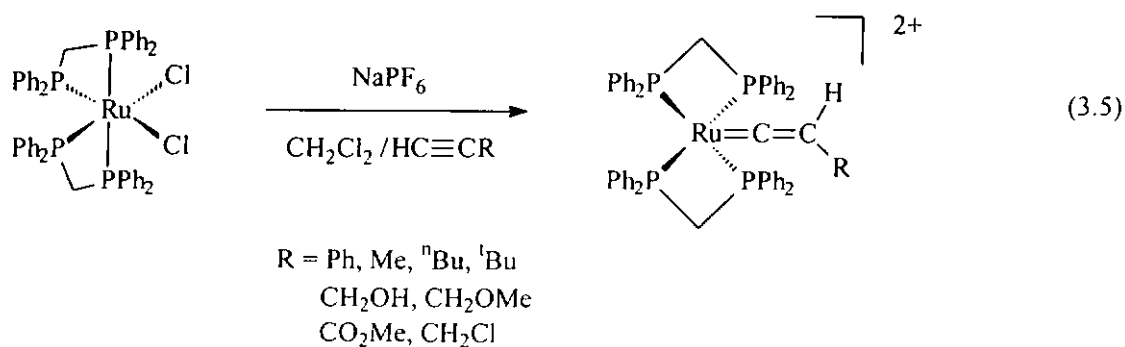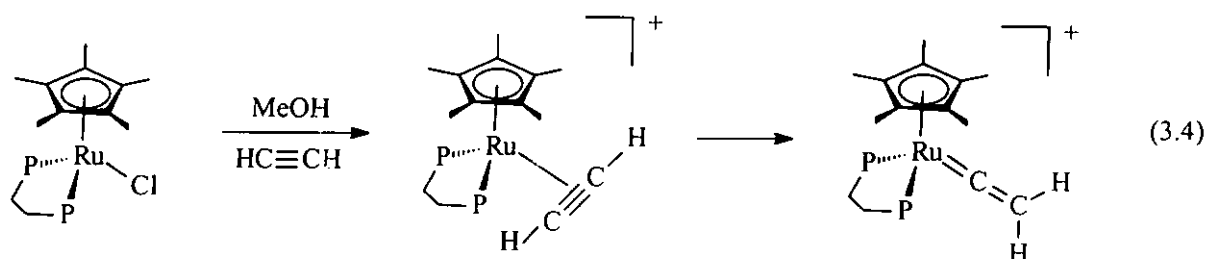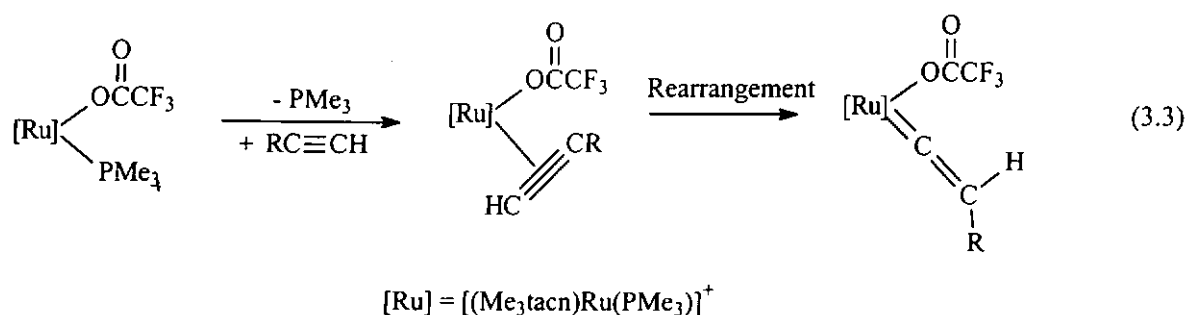
The tautomerization via the π-alkyne adducts is thought to occur by a slippage of the η^2-alkyne ligand leading to σ-η^1 coordination, followed by a subsequent 1,2-

hydrogen migration to yield the vinylidene complex as shown in eq. 3.6.[144, 146, 153, 158, 159]

$$L_nM \longrightarrow \overset{\overset{\displaystyle H}{|}}{\underset{\displaystyle R}{|\!|}} \longrightarrow L_nM \underset{\overset{\displaystyle }{R}}{\overset{\overset{\displaystyle H}{\diagup}}{\diagdown}} \longrightarrow L_nM{=}C{=}C\overset{\displaystyle H}{\underset{\displaystyle R}{}} \qquad (3.6)$$
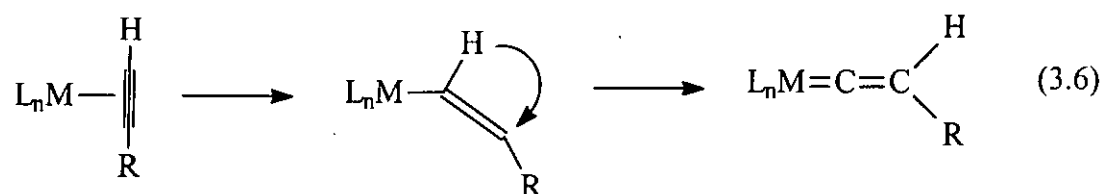
A different mechanism operates when the tautomerization occurs via hydrido-alkynyl complexes, and a concerted 1,3-hydrogen shift has been proposed, as shown in eq. 3.7. [146, 153, 159]

$$L_nM \longrightarrow \overset{\overset{\displaystyle H}{|}}{\underset{\displaystyle R}{|\!|}} \longrightarrow L_nM \underset{\overset{\displaystyle C}{\underset{\overset{\displaystyle }{R}}{\|\!|}}C}{\overset{\overset{\displaystyle H}{\diagup}}{\diagdown}} \longrightarrow L_nM{=}C{=}C\overset{\displaystyle H}{\underset{\displaystyle R}{}} \qquad (3.7)$$
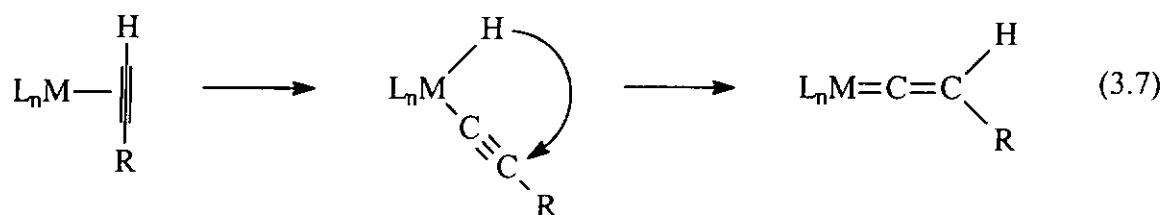
However, this mechanism has been found to be energetically too costly for Ru^{II} (d^6) complexes[144, 159], it has been supported by the fact that all hydrido-alkynyl complexes of ruthenium reported are stable species, which do not rearrange to their vinylidene isomers.[160, 161]

Monitoring the reaction in deuterated solvent by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy does not lead to the detection of any ruthenium intermediate species in the

course of the conversion of **3** to the vinylidene complex **11**. The displacement of the η^2-H_2 molecule by the incoming $PhC\equiv CH$ is too fast on the NMR time scale to render the intermediates to be identified. The magnetic equivalence of the two phosphine atoms of dppe in complex **11** is consistent with a structure in which the vinylidene ligand is located trans to a pyrazole group. The ^1H MNR spectrum of **11** shows the typical vinylidene hydrogen ligand signal at δ 3.87ppm [146]. The ^1H and ^{31}P NMR spectra of **11** are temperature invariant down to -70°C, consistent with a low-energy barrier of rotation of the vinylidene group on the $Ru=C=C$ axis.

It is well-documented that deprotonation of the vinylidene ligand by a base leads

to the formation of a σ-alkyne complex [146]. The solvento σ-alkyne complex **12** was

therefore readily obtained via reaction of **7** with Et_3N (eq.3.8). Elimination of HCl from **7**

was assisted by formation of the salt Et_3NHCl. [150] The neutral vinylidene complex **7** is

capable of initiating the catalytic dimerization of terminal acetylenes to give enynes in

the presence of base. This reaction proceeds via the coordinatively unsaturated alkynyl

complex $RuTp(PPh_3)(C\equiv CPh)$, that is formed as an intermediate by 1,3-elimination of

HCl.[150, 151]

(3.8)

7   **12**

where Tp^- =
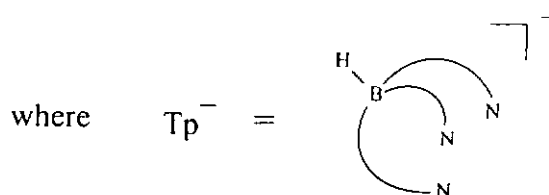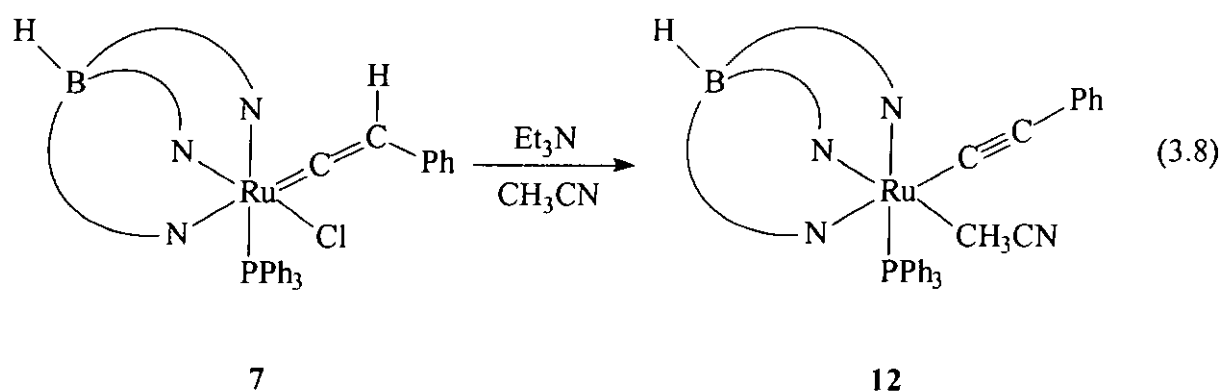
The coordinatively unsaturated species, $TpRu(PPh_3)(C\equiv CPh)$ which is one of the

intermediates in the catalytic dimerization of acetylene (scheme 3.1), is trapped by

formation of the solvento complex $TpRu(C\equiv C-Ph)(PPh_3)(CH_3CN)$ **12**. Bianchini[162]

has used similar tactic to trap the unsaturated alkynyl complex by adding a coordinating

solvent such as H_2O (or D_2O).(eq. 3.9)

(3.9)
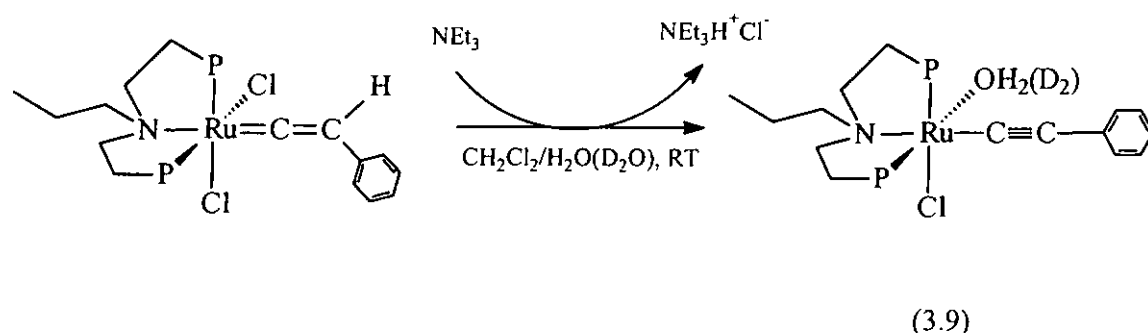
It should be informative to study the reaction of **12** with H_2, because such a

reaction might generate some interesting intermediates. A sample of **12** was dissolved in

THF-d_8. The solution was treated with H_2 gas (10 bars) and then heated to 80°C for 16

hours. ^1H NMR study of the resulting solution showed one at δ -9.97 (d, $^2J_{PH}$ = 17 Hz,

3H), and the $^{31}P\{^1H\}$ NMR spectrum showed a peak at 79.9ppm, which could be

attributed to the complex $TpRu(PPh_3)(H)_2H$ (**5**).[24] Scheme 3.3 shows the sequence of

the reaction of **12** with H_2. The η^2-hydrogen species **VIII** is believed to be generated via

displacement of CH_3CN in **12** by a dihydrogen ligand. A similar reaction has been

studied by our research group. Therefore when $TpRu(PPh_3)(CH_3CN)H$ (**4**) was

pressurized with hydrogen gas, H_2 molecule displaces the coordinated CH_3CN and forms

the dihydrogen complex **5** rather than trihydride complex $TpRu(PPh_3)H_3$ under hydrogen

pressure. [24] The intermediate **VIII** then can undergo metathesis (a) or proceeds via route (b), which involves intramolecular protonation of the σ-alkyl ligand by η^2-H_2, followed by vinylidene → η^2-alkyne tautomerization to form the η^2-alkyne species **IX**. Finally, a H_2 molecule displaces the coordinated alkyne to give trihydride species **5**.

12

H₂

VIII

(a)   (b)

IX

H₂

5
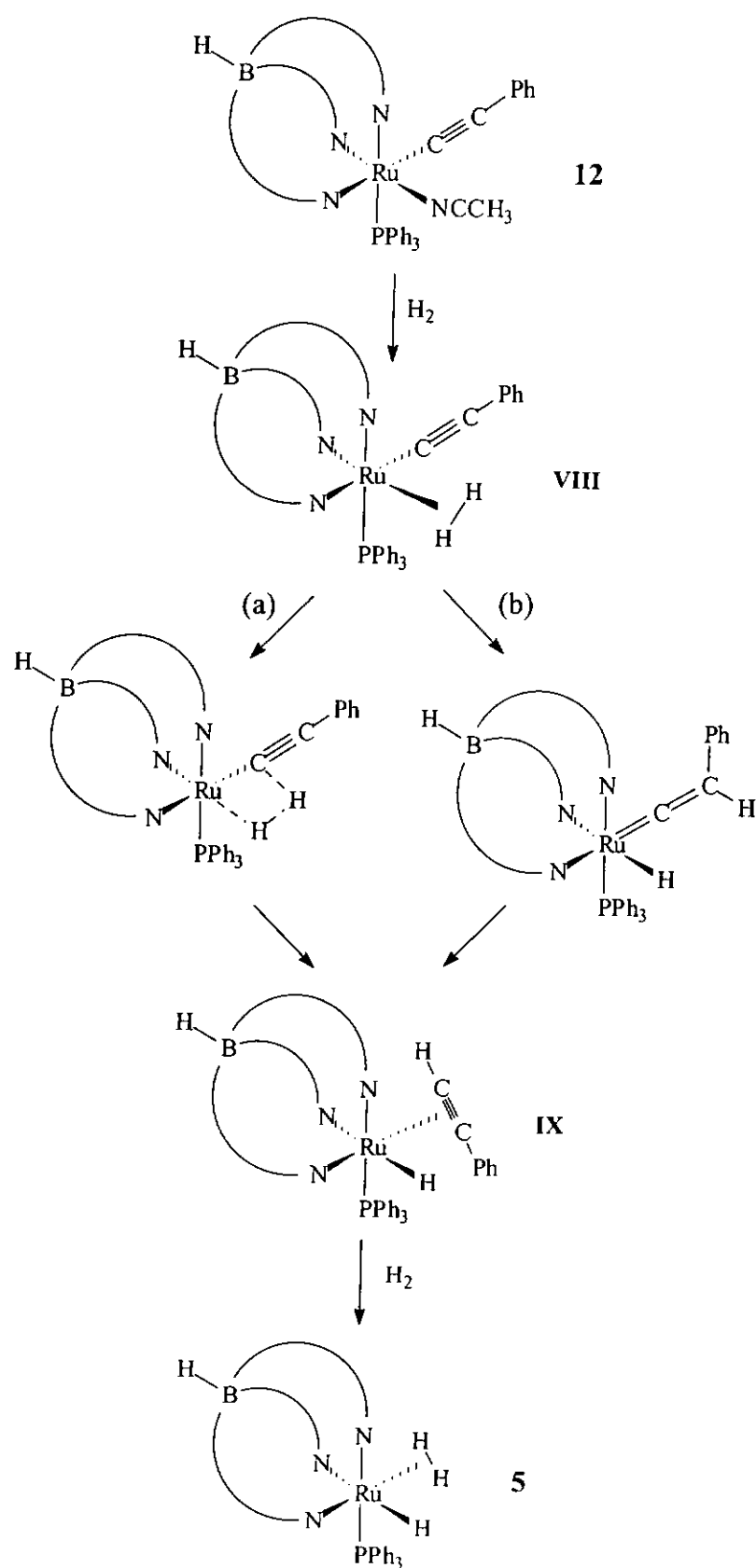
Scheme 3.3. The proposed sequence of the reaction of **12** with H₂

We first expected that methylpropiolate should react with **1** to form vinylidene complex by displacing the CH_3CN and followed by η^2-alkyne $\rightarrow$ vinylidene tautomerization to yield $TpRu(PPh_3)(Cl)(=C=CHCOOCH_3)$ (**X**). However, the complex $TpRu(PPh_3)(Cl)(CO)$ (**13**) was formed instead of the expected vinylidene complex. The $^{13}C\{^1H\}$ NMR spectrum of **13** shows a peak at δ 203.5 ppm, which is due to the carbonyl ligand. A proposed mechanism for the formation of **13** is depicted in scheme 3.4. Thermal dissociation of CH_3CN provides a vacant site for interaction between the ruthenium metal center and methyl propiolate, which rapidly tautomerizes to form the vinylidene intermediate **X**. After the formation of **X**, adventitious water in the solvent comes into play, H_2O molecule displaces the Cl^- ligand to generate the aquo vinylidene complex **XI**. The hydroxycarbene intermediate **XIII** then formed by stepwise H^+/OH^- transfer from the coordinated water molecule via the carbyne intermediate **XII**. In the proposed mechanism, coordinated H_2O molecule acts as an acid, which protonates the adjacent vinylidene ligand to form the metal-carbyne. Subsequent migration of the hydroxo group to the electrophilic α-carbon of **XII** gives the hydroxycarbene complex **XIII**. Elimination of HCl then gives the unsaturated σ-acyl complex **XIV**. Subsequent CO deinsertion of **XIV**, followed by removal of the carbomethoxylmethyl ligand by HCl gives the metal carbonyl product **13**. Bianchini et al. [162] have reported the formation of a carbonyl complex via the reaction of mer, trans-$(PNP)RuCl_2(PPh_3)$ with phenylacetylene and water, and a similar mechanism for the formation of carbonyl complex was proposed, as shown in scheme 3.5. Common in our proposed mechanism and that of Bianchini's work are: 1-alkyne to vinylidene tautomerism, conversion of a vinylidene ligand to hydroxycarbene by intramolecular attack of water, deprotonation of

hydroxycarbene to σ-acyl, deinsertion of CO from the acyl ligand, and hydrocarbon elimination by protonation of the metal-alkyl moiety.
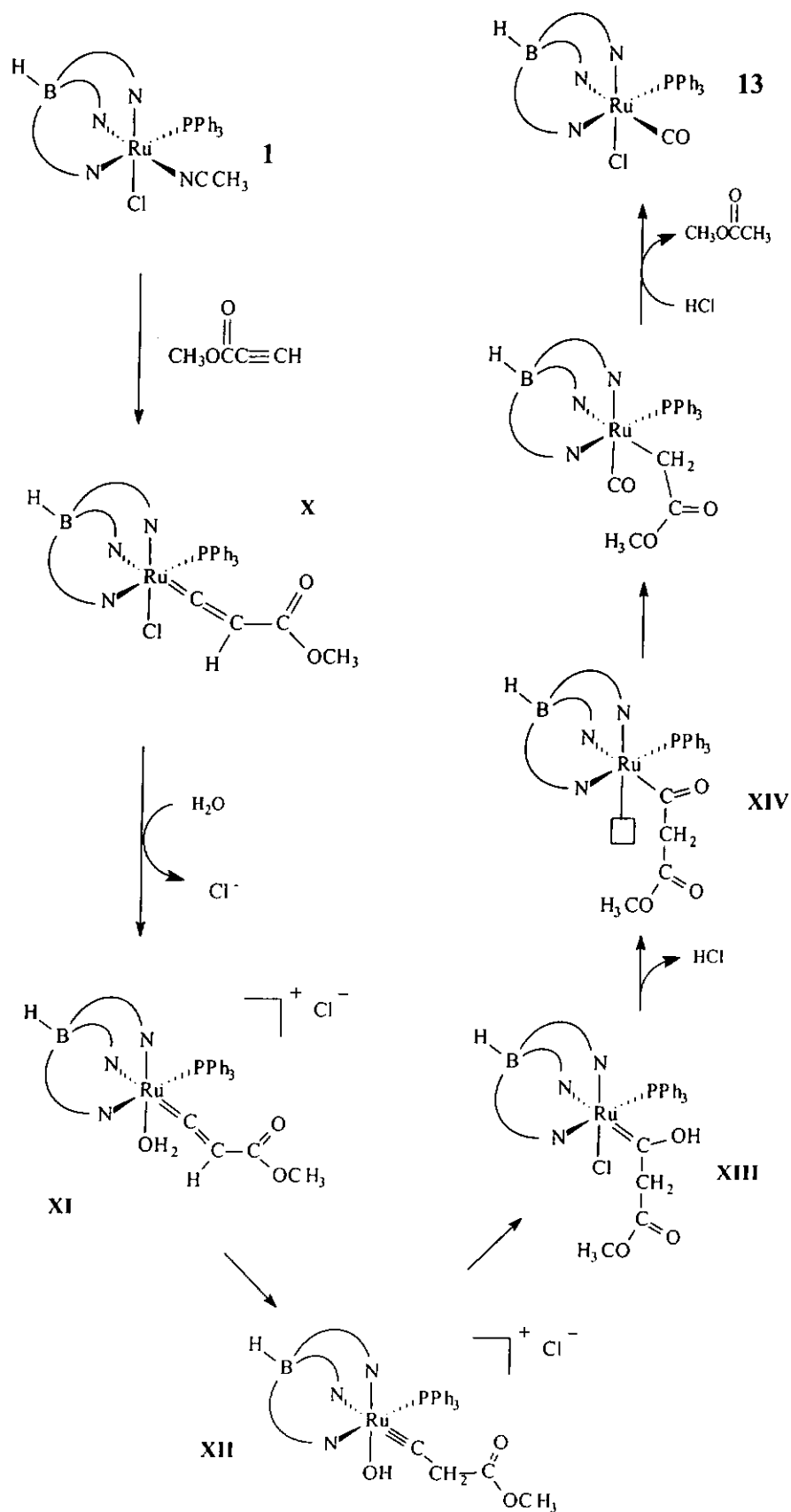
Scheme 3.4. The proposed mechanism for the formation of 13.
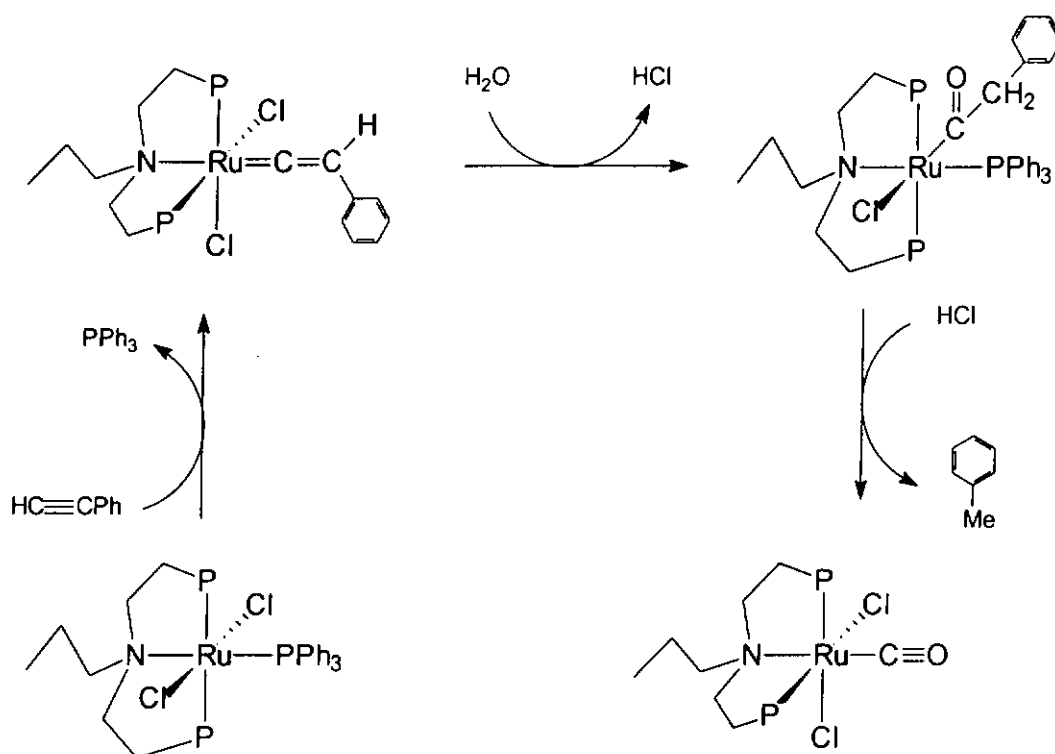
Scheme 3.5. Mechanism of the formation of carbonyl complex
proposed by Bianchini et al.

Bianchini has also mentioned that in the absence of water, the reaction between

mer,trans-(PNP)RuCl$_2$(PPh$_3$) and HC≡CPh in dried THF at 60°C gives exclusively the

vinylidene complex fac,cis-(PNP)-RuCl$_2$\{C=C(H)Ph\} [148]. However, total removal of

adventitious water molecules in solvent by P$_2$O$_5$ is difficult in our case. As a result, the

expected vinylidene complex TpRu(PPh$_3$)(Cl)(=C=CHCOOCH$_3$) X cannot be isolated

since an absolutely dried condition cannot be obtained.

Vinylidene complexes have been recognized as active species in dimerization of terminal alkynes. A ruthenium vinylidene intermediate is likely the crucial species in the dimerization of terminal alkynes to butatriene[82] or enynes.[8] In this part of the research program, we sought to investigate catalytic activities of ruthenium(II) complexes towards alkyne dimerization. The complex [TpRu(PPh$_3$)$_2$(CH$_3$CN)]BF$_4$ (**8**) was found to be an active catalyst for the dimerization of phenylacetylene in the presence or absence of a base. The results are summarized in table 3.1. The major products present in the final mixture are the head-to-head dimers trans-1,4-diphenyl-1-buten3-yne and cis-1,4-diphenyl-1-buten-3-yne, which are shown in structure 3.1, along with some unreacted phenylacetylene.
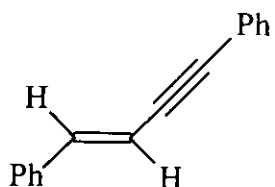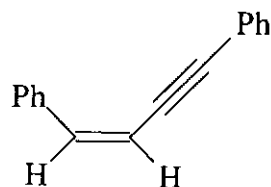
trans-1,4-diphenyl-1-buten3-yne   cis-1,4-diphenyl-1-buten3-yne

Structure 3.1. Structures of the major dimerization products of phenyl acetylene

Table 3.1. Dimerization of phenylacetylene with $[(Tp)Ru(PPh_3)_2CH_3CN](BF_4)$ (8) as catalyst [a]

Run	Additive	% conversion[b]
1	Nil	38.46
2	Et_3N[c]	87.94

a. Complex 8 (0.01mmol) and phenylacetylene (1:500) were dissolved in 5 mL of THF, the reaction mixture was heated at 90°C for 48 h.

b. Based on the substrate used. The products were trans- and cis-1,4-diphenyl-1-buten-3-yne.

c. 0.5 mmol added

71

Scheme 3.6 shows a proposed mechanism for the dimerization of phenylacetylene catalyzed by **8**, in the presence of the base Et_3N. The catalytic cycle is initiated by the loss of a CH_3CN ligand and the formation of a coordinatively unsaturated species **XV**. Addition of $HC\equiv CPh$ leads to the formation of the cationic vinylidene intermediate **XVI**. It is likely that the $PhC\equiv CH$ is initially bound to the ruthenium center in a side-on fashion. A 1,2-hydrogen shift subsequently occurs to give the vinylidene intermediate. The presence of the base Et_3N resulted in β-carbon deprotonation and the generation of σ-acetylide intermediate **XVII.** Yang et al. [154] have shown that $[Ru(Me_3tacn)(PMe_3)(O_2CCF_3)\{C=CH(Ph)\}]PF_6$ and $[Ru(Me_3tacn)(PMe_3)(O_2CCF_3)\{C=CH(p\text{-tolyl})\}]PF_6$ (Me_3tacn = 1,4,7-trimethyl-1,4,7,-triazacyclononane) are stable in refluxing methanol. Deprotonation of the vinylidene ligand is observed upon reaction with primary and secondary amines, leading to the formation of the σ-acetylide complexes. Coordination of the second $HC\equiv CPh$, followed by 1,2 hydrogen shift gave the σ-alkyne-vinylidene intermediate **XVIII**. 1,2-migratory insertion of the acetylide gives the η^3-butenyny intermediate **XIX** followed by proton shift to yield intermediate **XX**. Yang et al. [154] reported the synthesis and proposed mechanism of similar η^3-butenyny complex shown in scheme 3.7. Several literature reports have mentioned 1,2-migratory insertion of acetylide to give a η^3-butenyny intermediate followed by proton shift. [82, 163-170] Coordination of the third $HC\equiv CPh$ and subsequent σ-bond metathesis between the Ru-C bond and the terminal C-H bond of the coordinated alkyne, via a 4-center transient species **XXI**, yields the dimer product and completes the catalytic cycle. This step involves the C-H bond activation of the phenylacetylene. Even though the C-H bond activation by insertion of metal center into

C-H bond, i.e. oxidative addition, is commonplace [26, 44, 45, 47-55, 67], such process can probably be ruled out in the present case.

Kirchner has proposed a similar mechanism for the dimerization of alkyne, as shown in scheme 3.1. In this scheme, the active species contained a chloride ligand as an internal base to abstract the β-hydrogen of the vinylidene ligand to yield the alkylidene intermediate.

PPh₃

[Ru]⟍PPh₃   **8**

S

⇅ -S

[Ru]— PPh₃   **XV**

PPh₃

[Ru] = TpRu(II)
S = CH₃CN
B = Et₃N

⇅ ≡—Ph

PPh₃

[Ru]⟍C=C⟍Ph   **XVI**

H

⇅ B

BH⁺

Ph ≡ Ph

PPh₃

[Ru]⟍   **XVII**

Ph

≡—Ph

PPh₃

[Ru]⟍

Ph—≡   Ph

PPh₃

[Ru]=C   **XVIII**

C

H Ph   Ph

[Ru]

H   C   C

C=C   C—Ph

Ph   Ph

XIX

PPh₃   Ph

[Ru]⟍   ≡

Ph   **XX**

≡—Ph

PPh₃   Ph

[Ru]--- ≡

Ph   **XXI**

Ph—C≡C----H
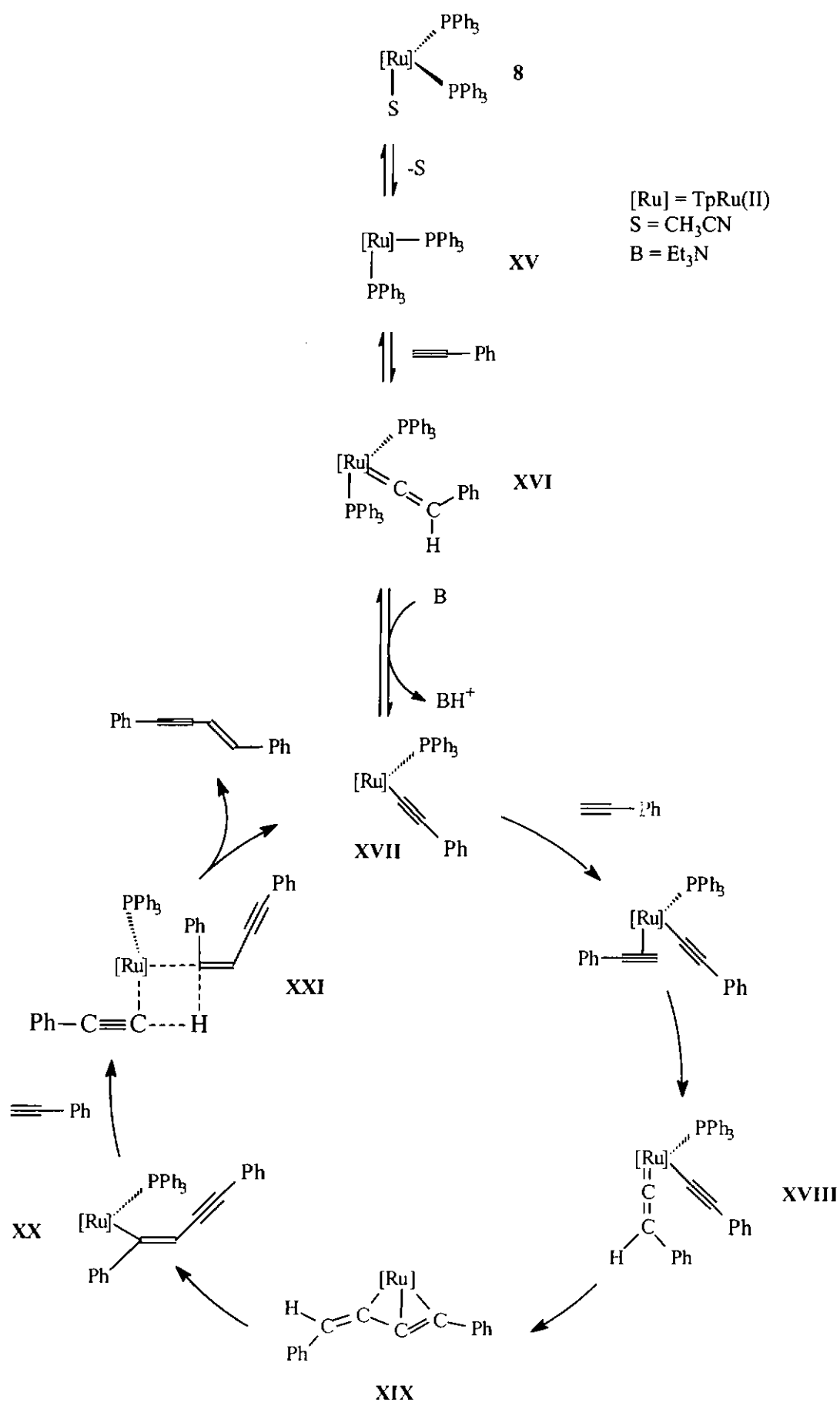
Scheme 3.6. Proposed mechanism for the dimerization of
phenyl acetylene by **8**

74

[Ru] = Ru(Me$_3$tacn)(PMe$_3$)

η^3

p-Tolylacetylene
KOH

Rearrangement

C-C coupling
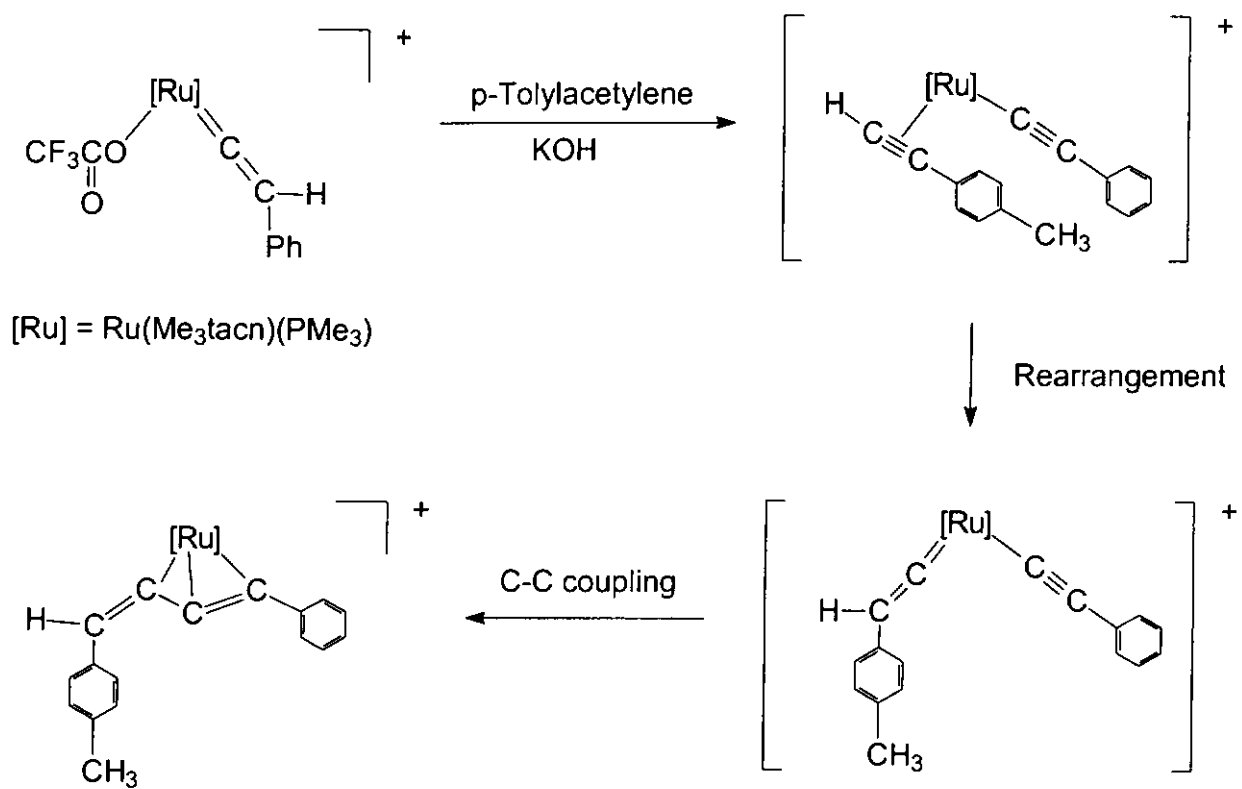
Scheme 3.7. Proposed mechanism for the formation of η^3-butenynyl complexes by Yang et al.

Table 3.1 shows that **8** also is capable of catalyzing the dimerization of phenylacetylene in the absence of a base, although the yield is much lower than that of the base-promoted catalytic reaction. In the absence of a base, the dimerization mechanism depicted in scheme 3.6 is probably not in operation. Since the dimerization of alkynes by cationic solvento complexes without addition of base is uncommon, we are interested in studying the activities of ruthenium complexes toward dimerization of alkynes in the absence of base, and to elucidate the mechanism of these reactions. Table 3.2 shows the results of the dimerization of terminal alkynes using **8** as the catalyst in the absence of base.

Table 3.2. Dimerization of alkynes with **8** as the catalyst in the absence of base [a]

Run	Substrate	Product(% conversion) [b]
1	Phenylacetylene	**i** (38) / **ii** (3) [c]
2	Methyl propiolate	Trace
3	3,3-dimethylbutyne	Nil
4	1-hexyne	Nil
5	Trimethylsilylethyne	Nil
6	Methyl butylnoate	Nil

a. Complex **8** (0.01mmol) and phenylacetylene (1:200) were dissolved in 5 mL of THF, the reaction mixture was heated at 90°C for 48 h.

b. Based on the substrate used

c. **i** = trans-1,4-diphenyl-1-buten3-yne and **ii** is cis-1,4-diphenyl-1-buten3-yne

Table 3.2 shows that measurable conversion was achieved only with phenylacetylene, although trace amounts of dimerization products were detected using methyl propiolate as the substrate. No dimerization product was formed with the other alkynes.

The Tpm supported complex [TpmRu(PPh$_3$)$_2$(CH$_3$CN)](BF$_4$)$_2$ (7) showed activity similar to that of 8, and Table 3.3 shows the results of the dimerization of the alkynes. Only 12 % conversion to trans-1,4-diphenyl-1-buten3-yne and about 2 % of conversion to cis-1,4-diphenyl-1-buten3-yne were observed with the substrate phenylacetylene. Again, no dimerization was observed for the other alkynes.

Table 3.3. Dimerization of alkynes with 9 as the catalyst in the absence of base. [a]

Run	Substrate	Product(% conversion)[b]
1	Phenylacetylene	**i** (12) / **ii** (2)[c]
2	Methyl propiolate	None
3	3,3-dimethylbutyne	None
4	1-hexyne	None
5	Trimethylsilylethyne	None
6	Methyl butylnoate	None

a.   Complex 9 (0.01mmol) and substrate (1:200) were dissolved in 5 mL of THF, the

reaction mixture was heated at 90°C for 48 h.

b.   Based on the substrate used

c.   **i** = trans-1,4-diphenyl-1-buten3-yne and **ii** is cis-1,4-diphenyl-1-buten3-yne

The dimerization reaction seems to work better with the triphos complex

$[(\text{Triphos})\text{Ru}(\text{CH}_3\text{CN})_3](\text{CF}_3\text{SO}_3)_2$ (Triphos = $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$) (10). Table 3.4 shows

the results of dimerization and trimerization of alkynes with 10. The percent conversion

for methyl propiolate in this case was much better than those using other cationic

complexes. Cyclic trimers and dimers of methyl propiolate were formed (run 2, table

3.4). Phenylacetylene gave only dimer, with an overall percent conversion of about 70%

(run1, table 3.4). The formation of cyclic trimers will be discussed later in this chapter.

The structures of the cyclic trimers are shown in structure 3.2.

and

where R = —$\overset{\displaystyle O}{\overset{\displaystyle \|}{\text{C}}}$—O—CH$_3$
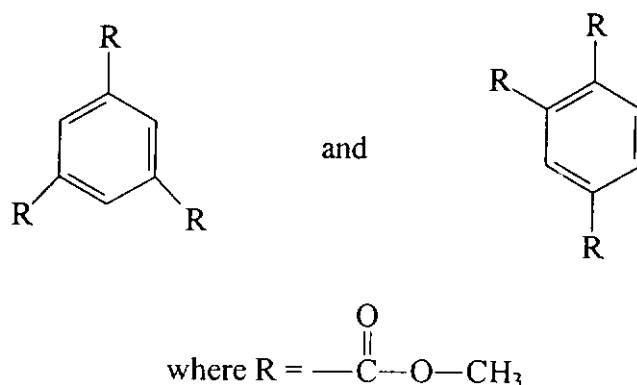
Structure 3.2. Products of the cyclic trimerization of
methyl propiolate catalyed 8

Table 3.4. Dimerization of alkynes with **10** as the catalyst in the absence of base. [a]

Run	Substrate	Product(% conversion) [b]
1	Phenylacetylene	**i** (66) / **ii** (4)
2	Methyl propiolate	**iii** (43) / **iv** (25)[c] / **v** (12)
3	3,3-dimethylbutyne	Nil
4	1-hexyne	Nil
5	Trimethylsilylethyne	Nil
6	Methyl butylnoate	Nil

a. Complex **10** (0.01mmol) and substrate (1:200) were dissolved in 5 mL of THF, the reaction mixture was heated at 90°C for 48 h.

b. **i** = trans-1,4-diphenyl-1-buten3-yne, **ii** is cis-1,4-diphenyl-1-buten3-yne

iii =

and **iv** =

v = R━━━━╱╲━R

where R = —C(=O)—O—CH₃
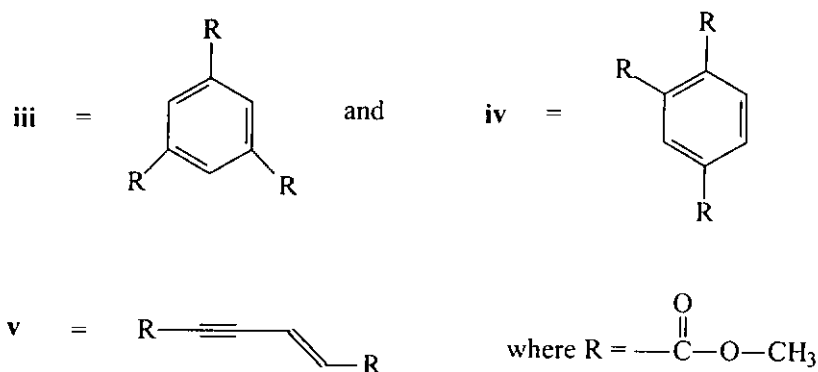
The proposed mechanism, depicted in scheme 3.8, shows the possibility that a cationic

ruthenium complex may be the active species in the dimerization of alkyne involving

vinylidene intermediate.

[Ru] = TpRu$^+$ (8), [TpmRu]$^{2+}$ (9),
or [(Tripod)Ru]$^{2+}$ (10)

L = CH$_3$CN, or PPh$_3$

S = CH$_3$CN

σ-bond metathesis

XXII

XXIII

XXIV

XXV

XXVI

XXVII
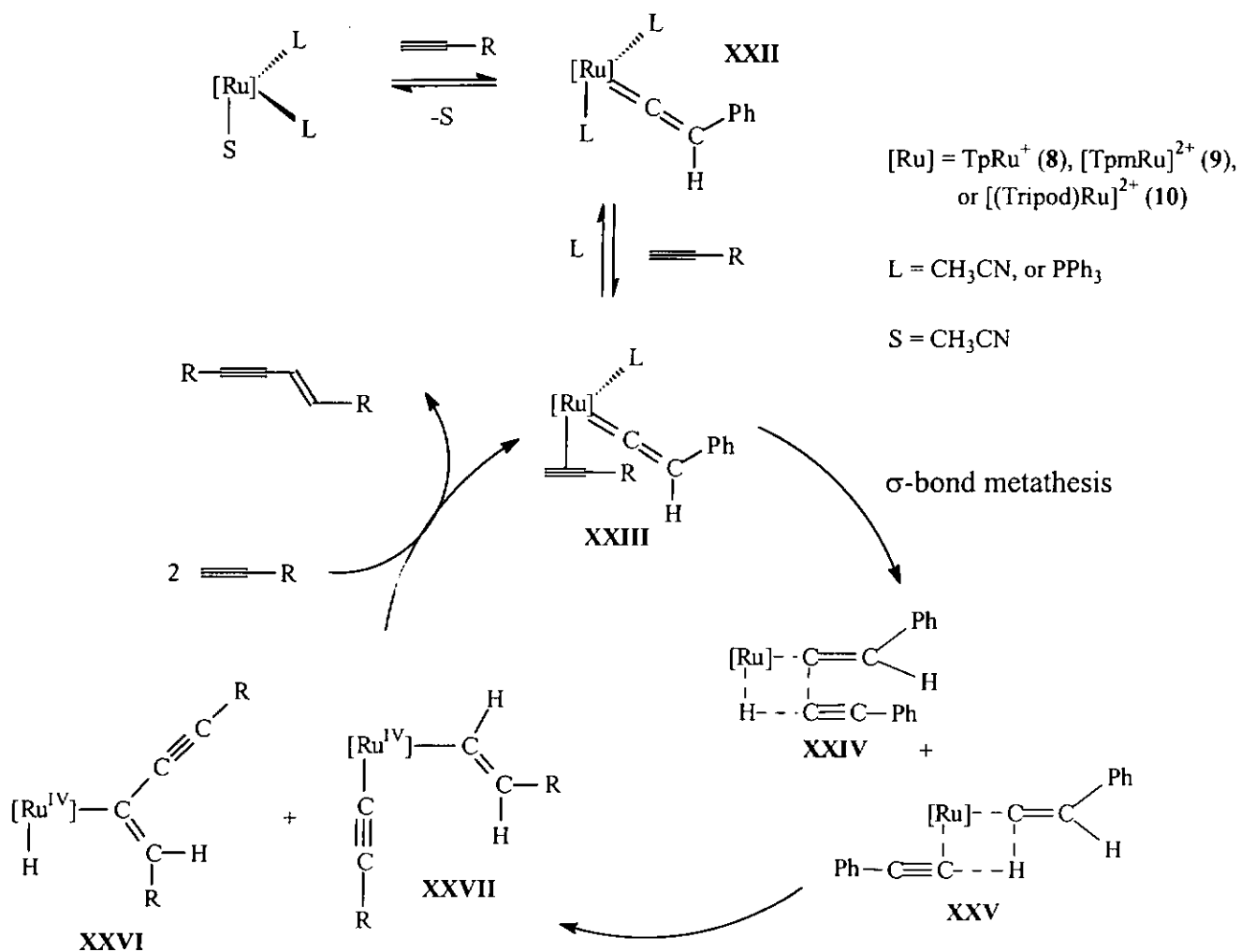
Scheme 3.8. Proposed mechanism for the dimerization of terminal
terminal alkyne in the absence of base

As showed in scheme 3.8, the incoming alkyne substrate displaces the relatively loosely coordinated acetonitrile ligand to form the vinylidene intermediate **XXII**. Yang et al. [154] have studied the stepwise mechanism for the formation of vinylidene complexes, they have learned that [Ru(Me$_3$tacn)(PMe$_3$)$_2$(O$_2$CCF$_3$)]PF$_6$ reacted with PhC≡CH in refluxing 1,2-dichloroethane to give the vinylidene complex [Ru(Me$_3$tacn)(PMe$_3$)(O$_2$CCF$_3$){C=CH(Ph)}]PF$_6$ (dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$). On the other hand, no reaction was found between [Ru(Me$_3$tacn)(dmpe)(O$_2$CCF$_3$)]PF$_6$ and PhC≡CH after refluxing in 1,2-dichloroethane for 24 h. The chelating dmpe ligand in [Ru(Me$_3$tacn)(dmpe)(O$_2$CCF$_3$)]PF$_6$ was expected to resist dissociation and prevent subsequent reaction with the PhC≡CH. Hence dissociation of CH$_3$CN to generate a coordination vacancy is presumably the first step in the catalytic cycle. Then coordination of the second alkyne substrate yeilds **XXIII**. It then undergoes σ-bond methathesis via **XXIV** or **XXV** to yeild intermediates **XXVI** or **XXVII** respectively. Wakatsutiand and coworkers[82] proposed a similar mechanism for the dimerization of terminal alkyne. They also prepared a model complex to demonstrate the migration of the alkynyl ligand to the vinylidene α-carbon to give a complex with a but-1-en-3-ny-2-yl ligand. The coupling reaction between the vinylidene and σ-alkynyl ligands is a downhill process, which has many precedents in the literature, particularly for ruthenium compounds.[8, 82, 167, 171, 172] Thorn[173, 174] has also reported this type of intramolecular migration (hydride to vinylidene and σ-alkyne to vinylidene), and several papers, establishing carbon-carbon bond formation of this type, have been published.[175-177] Finally, reductive elimination of both **XXVI** and **XXVII** gives the dimerized products and

coordination of the incoming 2 alkynes followed by rearrangement completes the catalytic cycle.

As is evident from Tables 3.2, and 3.3, 3.4, a higher percentage conversion (12-66%) can be measured only with phenylacetylene as substrate for dimerization. It is probably due to the necessity of conversion of acetylene to vinylidene as the first step of the dimerization reaction. This step is, however, known to be sluggish for nonaromatic alkyne.[146] Yang et al. [154] also reported a similar phenomenon during the synthesis of the vinylidene complexes [Ru(Me$_3$tacn)(PMe$_3$)(O$_2$CCF$_3$){C=CH(Ph)]PF$_6$ and [Ru(Me$_3$tacn)(PMe$_3$)(O$_2$CCF$_3$){p-tolyl}]PF$_6$ from the reactions of [Ru(Me$_3$tacn)(PMe$_3$)$_2$(O$_2$CCF$_3$)]PF$_6$ with PhC≡CH and p-tolylC≡CH in refluxing 1,2-dichloroethane respectively. However, no desired products are obtained using alkylacetylenes such as 2-methyl-3-butyn-2-ol, $tert$-butylacetylene, (trimethylsilyl)acetylene, or 1-hexyne.

According to tables 3.2, 3.3 and 3.4, 10 shows the best catalytic activity. In comparing the trans effect among the 3 facial ligands of the complexes, trispyrazolylborate and trispyrazolylmethane are N-donor ligands, hence their trans effect are similar but weaker than that of the triphos ligand. The stronger trans effect of triphos renders the complex more facile towards the reactions. Besides, as depicted in scheme 3.8, 2 vacant sites are required to form the intermediate **XXIII**. Dissociation of the

coordinated PPh$_3$ ligand to provide the third vacant site for **8** and **9** is more difficult than the dissociation of a CH$_3$CN ligand from the triphos complex **10** due to the stronger coordination power of PPh$_3$ ligand. As a result, triphos complex **10** gave the best catalytic activity toward dimerization of alkynes among the 3 catalysts.

Chapter 4

Conclusion

The activation of H-H bond and Si-H bond by ruthenium complexes have been studied by our research group. These previous research experiences prompt us to study the activation of C-H bond by ruthenium complexes.

The catalytic activity of the hydrido ruthenium complexes $TpRu(PPh_3)_2H$ (**2**) and $TpRu(PPh_3)(CH_3CN)H$ (**4**) toward activation of both aromatic and activated aliphatic C-H bonds have been studied. The activation of C-H bonds of the organic solvents are confirmed by H/D exchange between H_2 and the deuterated solvents and further evidenced by the H/D exchange among H_2, D_2O, and the non-deuterated solvents. At low temperature, only $TpRu(PPh_3)(H_2)H$ (**5**) is formed from **4** via displacement of the solvent ligand by H_2, and no C-H bond activation occurs.

The f_H, fraction of hydrogen atom in solvents for the H/D exchange between H_2 and deuterated solvents, and f_D, fraction of deuterium atom in solvents for the H/D exchange among H_2, D_2O and solvents (non-deuterated), values reveal that the C-H activation reactions are enhanced by increasing the acidity of the aryl hydrogens. Acidic aryl hydrogen is more capable of generating the aryl η^2-dihydrogen complex intermediate, which is formed via σ-metathesis between the Ru-H and the C-H of substrates.

Therefore, electron-withdrawing substituents on the aromatic rings, which increase the acidity of the aryl hydrogens, enhance the C-H activation.

Regio-selectivity in C-H bonds activation was observed in THF, toluene and diethylether. Only the aromatic C-H bonds are activated in toluene. In the case of THF, α-C-H bond activation predominates, on the other hand preferential C-H bond activation occurs at the β-positions in diethylether.

The second part of this thesis concerns the chemistry of vinylidene and alkynyl complexes of ruthenium. The vinylidene complex, [TpRu(=C=CHPh)(dppe)](BF$_4$) (11) was prepared by reacting the complex TpRu(dppe)H (3) with one equiv. of HBF$_4$ and followed by the addition of PhC≡CH. And the alkynyl complex. TpRu(C≡C-Ph)(PPh$_3$)(CH$_3$CN) (12) was prepared by reacting the complex TpRu(=C=CHPh)(PPh$_3$)(CH$_3$CN) (7) with excess Et$_3$N followed by the addition of acetonitrile.

The reactivity of TpRu(C≡C-Ph)(PPh$_3$)(CH$_3$CN) (12) with H$_2$ has been examined, it reacts with the later to yield the TpRu(PPh$_3$)(H$_2$)H (5). We believe that the η^2-H$_2$ species TpRu(PPh$_3$)(C≡C-Ph)(H$_2$) and the η^2-alkyne species TpRu(PPh$_3$)(HC≡CPh)H are the transient species for the formation of 5 from 12.

Vinylidene complexes have been recognized as active species in the dimerization of terminal alkynes. The complexes [TpRu(PPh$_3$)$_2$(CH$_3$CN)]BF$_4$ (**8**), [TpmRu(PPh$_3$)(CH$_3$CN)](BF$_4$)$_2$ (**9**), and [(triphos)Ru(CH$_3$CN)$_3$](CF$_3$SO$_3$)$_2$ (**10**) are found to be active toward dimerization of terminal alkynes in the absence of base. They show the best result with phenylacetylene as the substrate for dimerization. It is probably due to the necessity of conversion of the acetylene to the vinylidene as the first step of the dimerization reaction. This step is, however, known to be sluggish for nonaromatic alkynes.

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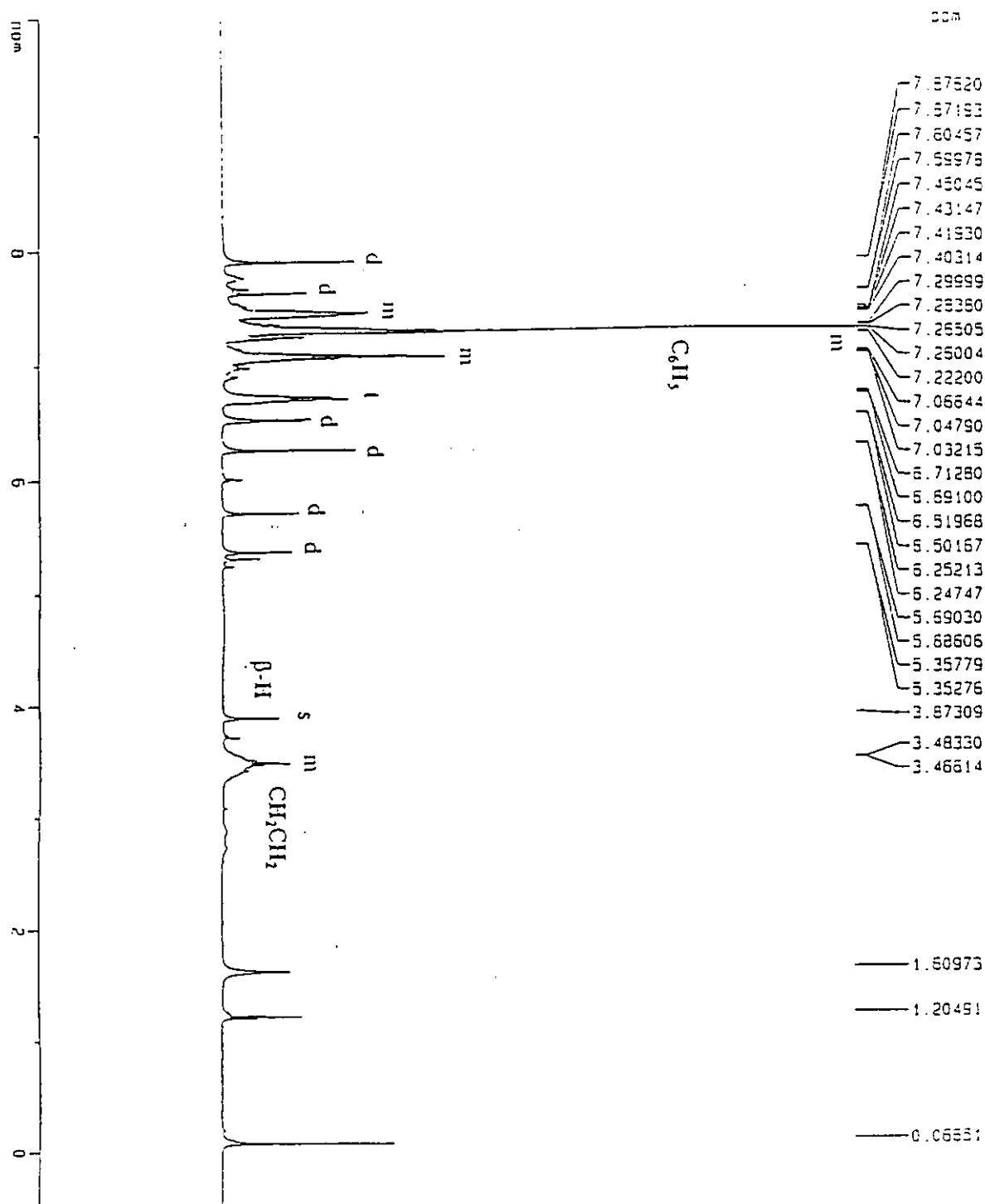
Appendix

ppm

7.87520
7.87193
7.60457
7.59976
7.45045
7.43147
7.41930
7.40314
7.29999
7.28360
7.26505
7.25004
7.22200
7.06644
7.04790
7.03215
6.71280
6.69100
6.51968
6.50167
6.25213
6.24747
5.69030
5.68606
5.35779
5.35276
3.87309
3.48330
3.46614
1.60973
1.20491
0.06661

Figure 3.1. 400MHz ^{1}HNMR Spectrum of TpRu(dppe)(=C=CHPh) (11)

ppm

———72.1609
———69.8331

———54.7964
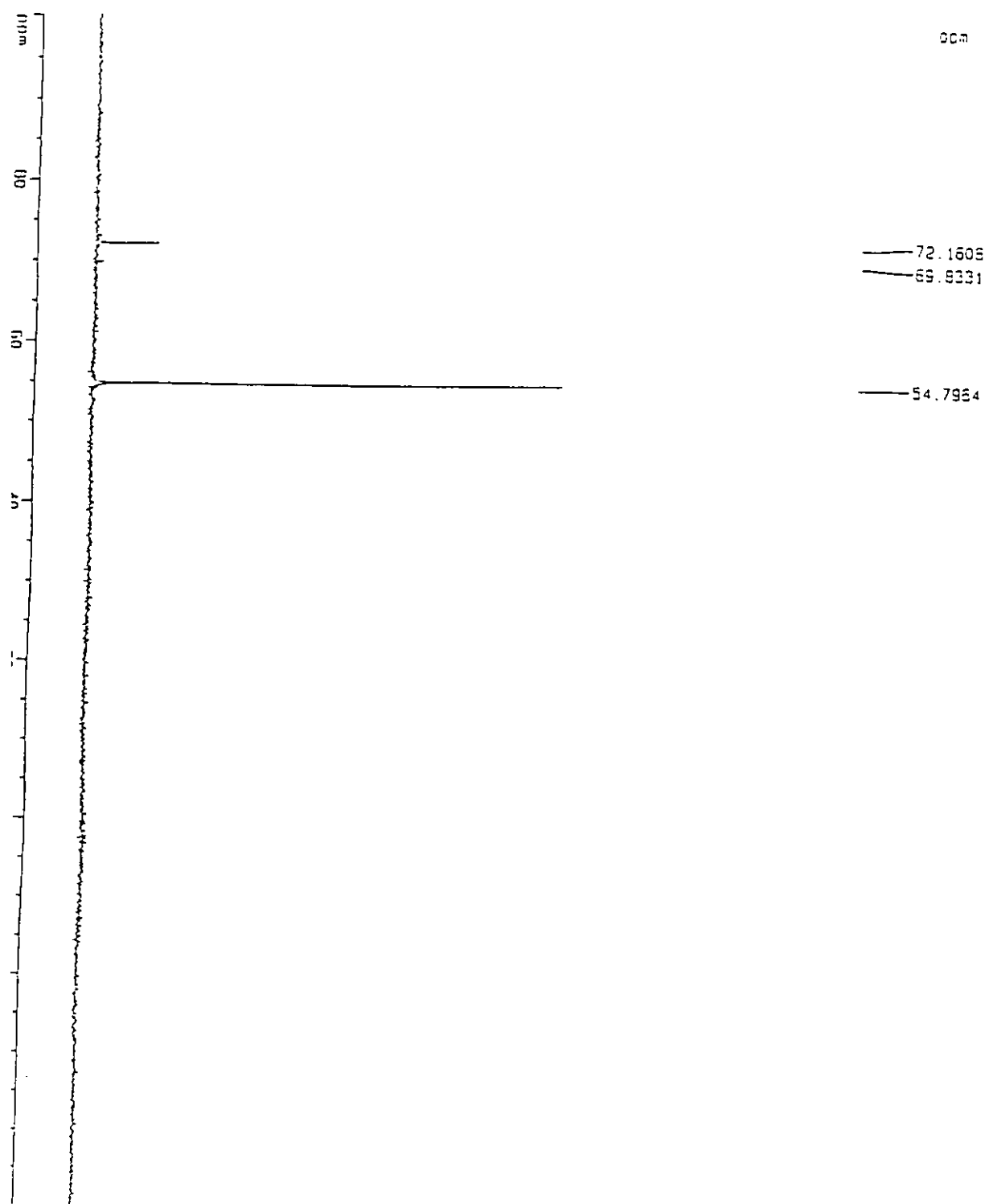
Figure 3.2. 161.9MHz $^{31}P\{^1H\}$ NMR Spectrum of TpRu(dppe)(=C=CHPh) (11)
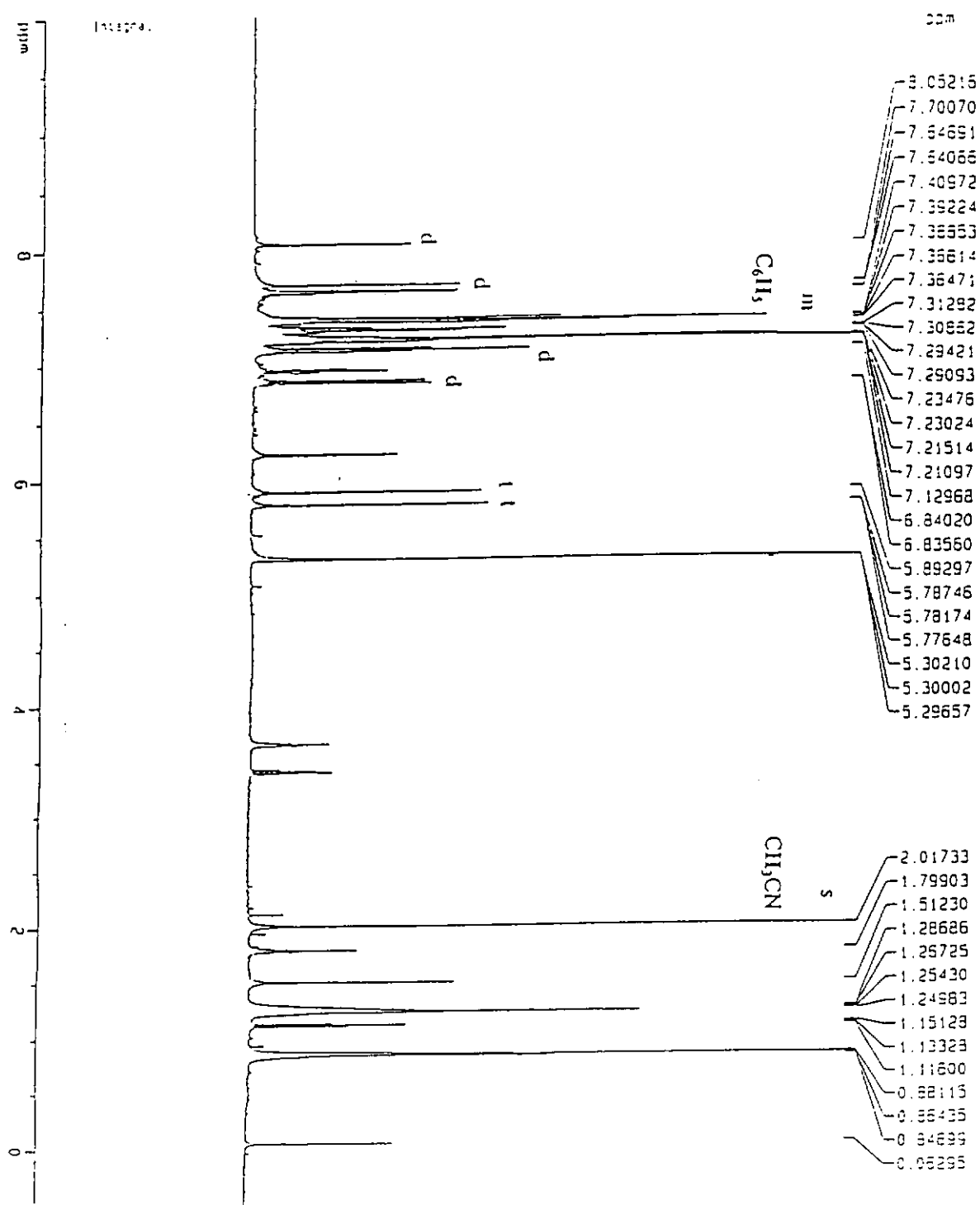
Figure 3.3. 400MHz ^{1}H NMR Spectrum of TpRu(C≡CPh)(PPh$_3$)(Cl)) (12)
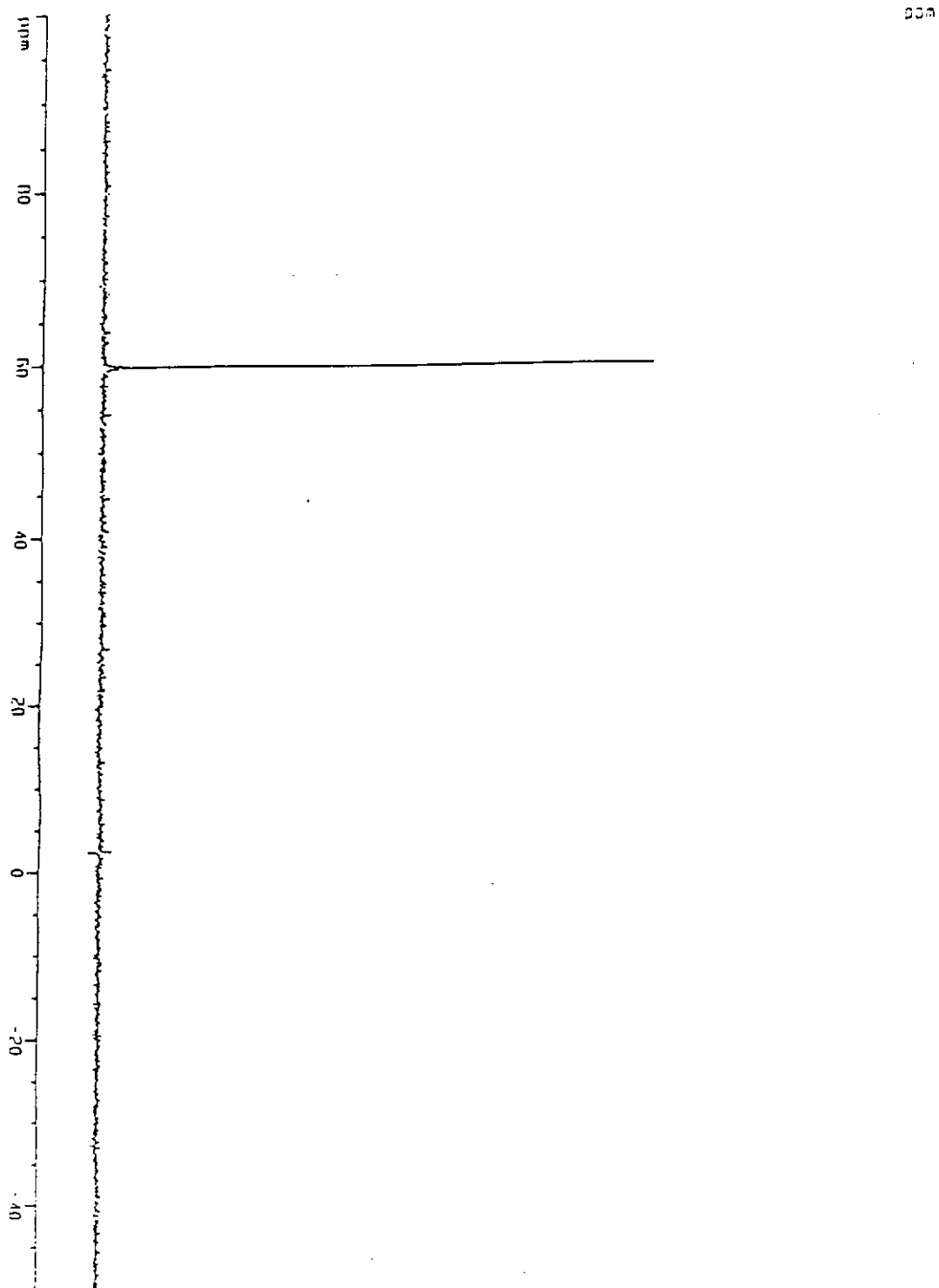
Figure 3.4. 161.9MHz ^{31}P{^{1}H} NMR Spectrum of TpRu(C≡CPh)(PPh$_3$)(Cl)) (12)

ppm

7.9786
7.6971
7.6736
7.6677
7.6339
7.6229
7.5573
7.4643
7.4036
7.3817
7.3626
7.3392
7.3167
7.2990
7.2782
7.2629
7.2575
7.2352
6.9054
6.3161
6.1861
5.8992
5.8923
5.7518
5.7453
3.8483
3.8381
3.8051
3.7986
3.7468
3.6669
2.8989
2.1048
2.0605
2.0000
1.8518
0.0707
-0.0002

C_6H_5

m

p
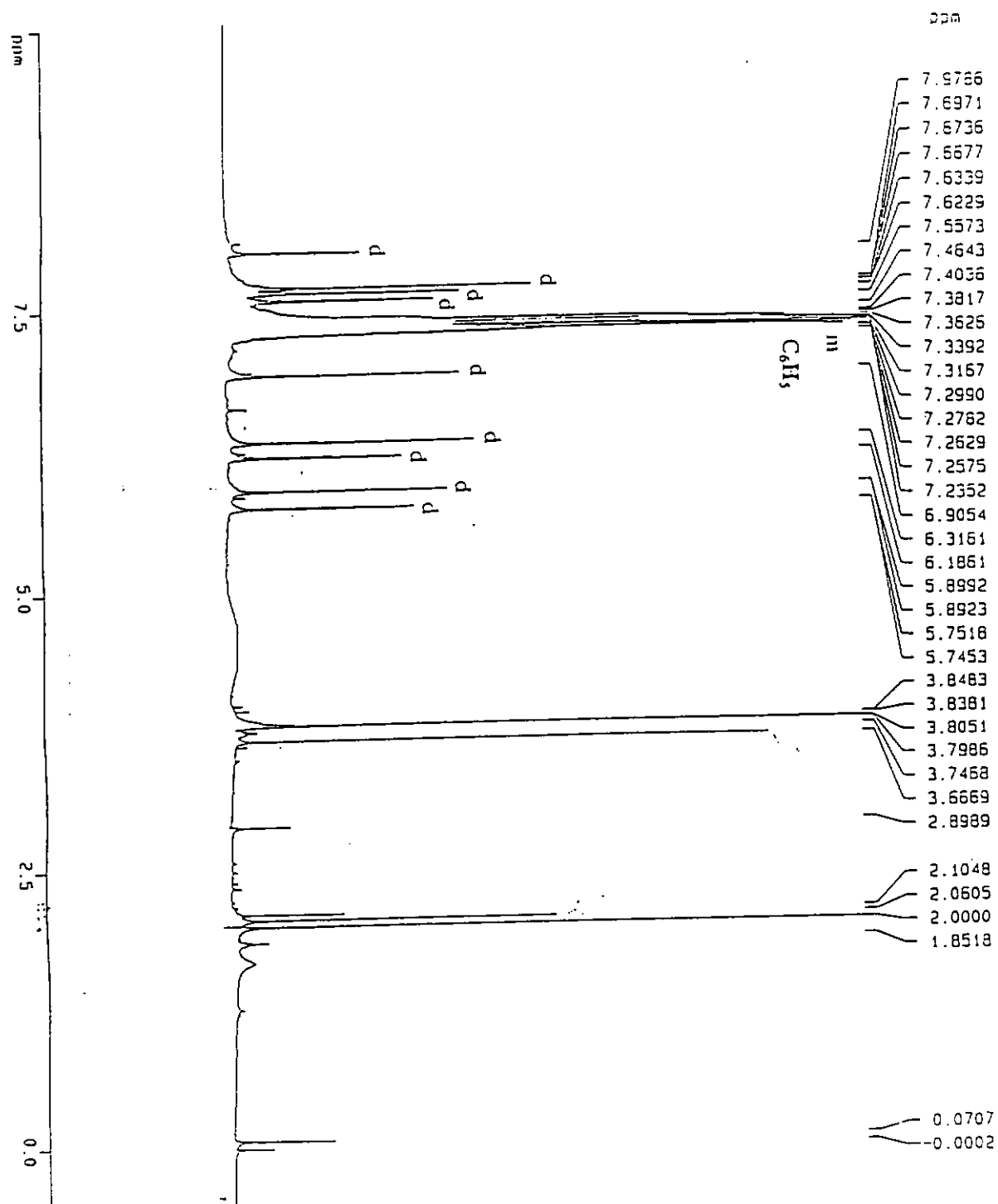
Figure 3.5. 400MHz ^{1}H NMR Spectrum of TpRu(CO)(PPh$_3$)(Cl) (13)
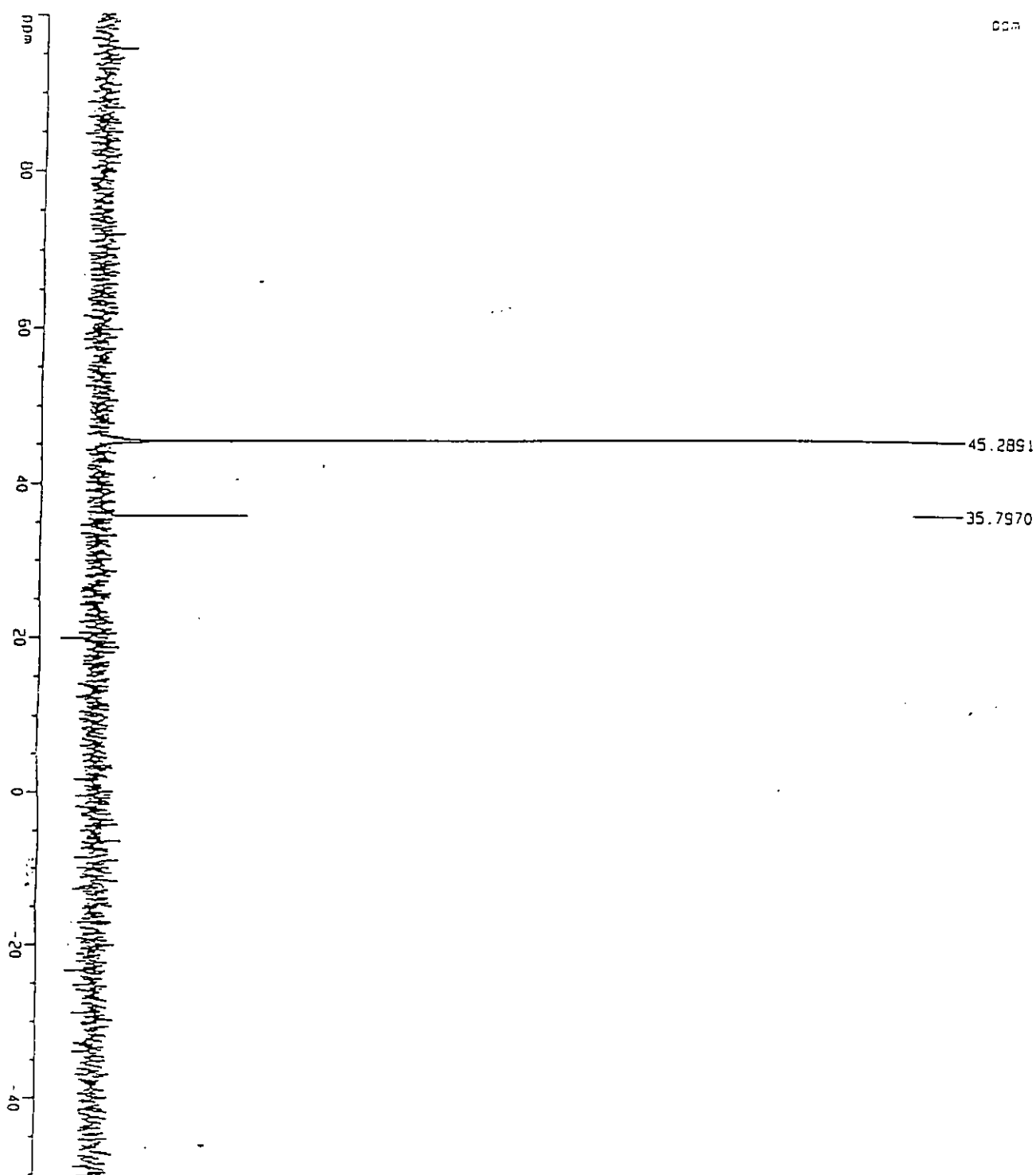
Figure 3.6. 161.9MHz ^{31}P{^{1}H} NMR Spectrum of TpRu(CO)(PPh$_3$)(Cl) (13)

ppm

204.244
204.091

CO

146.519
144.267
143.982
136.859
135.791
135.248
134.934
134.842
133.013
132.569
130.686
128.813
128.716

106.659
106.535
106.308

78.013
77.899
77.697
77.379

32.248

23.317

14.785

ppm
200
175
150
125
100
75
50
25
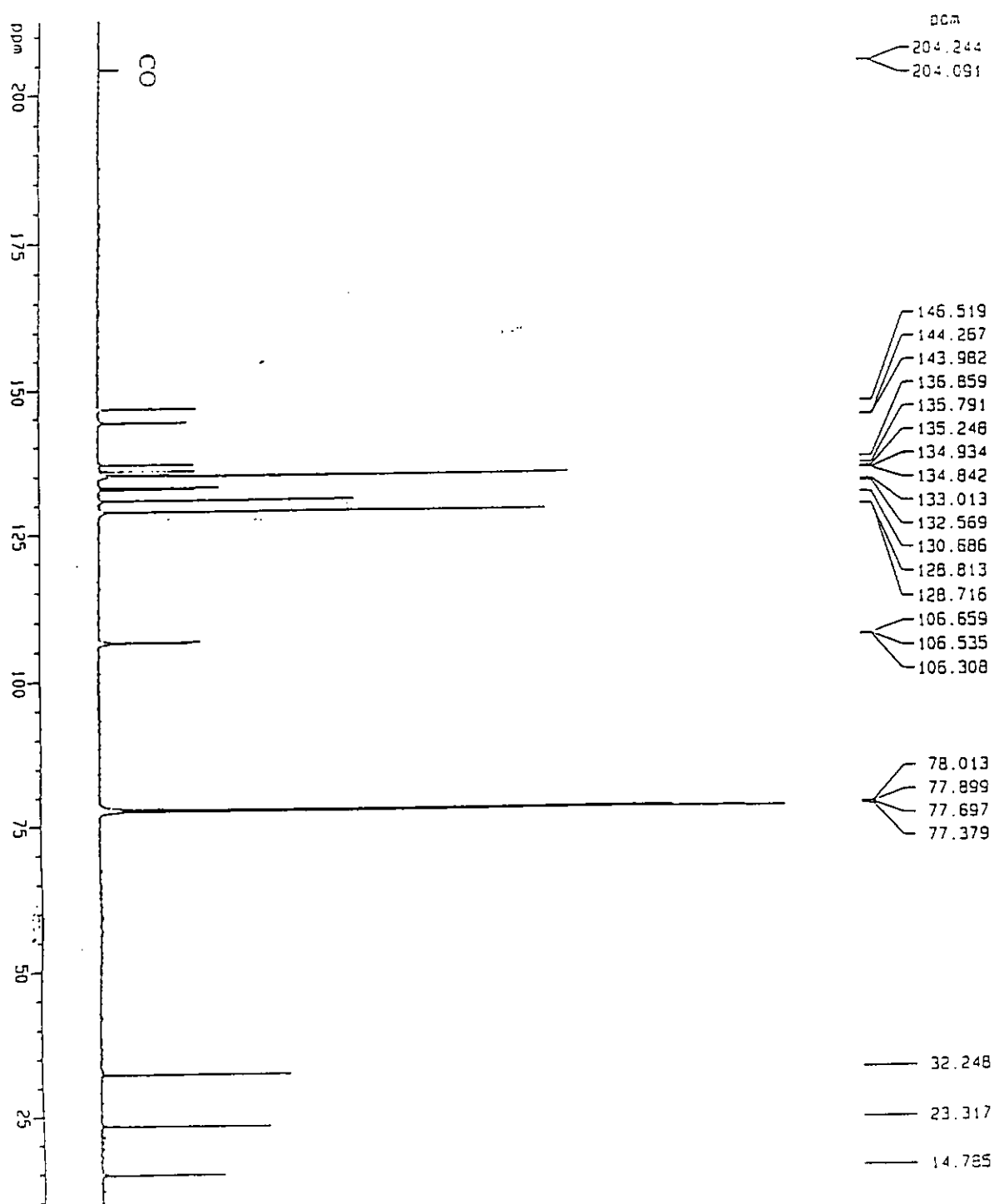
Figure 3.7. 400MHz ^{13}C{^{1}H} NMR Spectrum of TpRu(CO)(PPh$_3$)(Cl) (13)

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