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NONCLASSICAL RUTHENIUM SILYL DIHYDRIDE COMPLEXES AND THEIR CATALYTIC ACTIVITIES. CATALYTIC REACTIONS WITH ELECTROPHILIC BIPYRIDINE RUTHENIUM COMPLEXES

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Nonclassical Ruthenium Silyl Dihydride Complexes and their Catalytic Activities. Catalytic Reactions with Electrophilic Bipyridine Ruthenium Complexes

By

Ting-Yan LEE

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

January, 2011
Declaration

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_____________________
Ting-Yan LEE

January, 2011

Submitted by Ting-Yan LEE

for the degree of doctor of philosophy

at The Hong Polytechnic University

in January, 2011
Abstract

The X-ray crystallographic study showed that it is more appropriate to describe the ruthenium-silane complexes $\text{TpRu(PPh}_3\text{)^"H}_2\text{SiR}_3$" as $\text{TpRu(PPh}_3\text{)(H}_3\text{SiR}_3\text{)}$, a static structure containing H···Si···H bonding rather than a highly fluxional pair of $\sigma$-silane hydride species $\text{TpRu(PPh}_3\text{(H}_a\text{)(H}_b\text{SiR}_3\text{)}\text{)}$.

One of the complexes, $\text{TpRu(PPh}_3\text{)(H}_3\text{SiPhMe}_2\text{)}$, was used for the catalytic hydrolytic oxidation of organosilanes to silanols. A mechanism, which does not involve the usual oxidative addition of silane to the metal center to form the silyl hydride species, is proposed; it is supported by theoretical calculations.

The ruthenium-silane complex $\text{TpRu(PPh}_3\text{)(H}_3\text{SiPhMe}_2\text{)}$ was also found to effect catalytic reduction of carbon dioxide by PhMe$_2$SiH to give methoxide as the ultimate reduction product. Proton NMR study of the reaction revealed that various reduced products of carbon dioxide including formoxysilane, bis(silyl)acetal, and silyl methoxide were formed during the course of the catalysis, the identities of which were further confirmed by $^{13}$C NMR through the use of $^{13}$CO$_2$. Concurrent $^{31}$P NMR monitoring indicated that the starting complex was first converted to the carbonyl-hydride species $\text{TpRu(PPh}_3\text{(CO)}\text{)}$, probably due to decarbonylation of the
initially formed formoxysilane. The carbonyl-hydride complex was then partially converted to a new species, which we suspect to be the formate complex \( \text{TpRu}(\text{PPh}_3)(\text{CO})(\eta^1\text{-OCHO}) \) generated by protonation of the hydride complex by formic acid in the reaction. Slow formation of the dicarbonyl-hydride complex \( \text{TpRu} (\text{CO})_2 \text{H} \) from the formate complex was observed at the latter stage of the monitoring experiment. A mechanism for the reduction of carbon dioxide to the various silicon-containing products was proposed after taking into consideration the NMR monitoring results.

The air stable, dicationic bipyridine ruthenium diaquo complex \( \text{cis-}[\text{Ru}(6,6'\text{-Cl}_2\text{bpy})_2(\text{H}_2\text{O})_2] (\text{OTf})_2 \) was found to be an efficient catalyst for the \( \beta \)-alkylation of secondary alcohols with primary alcohols. On the other hand, the dimethyl analog \( \text{cis-}[\text{Ru}(6,6'\text{-Me}_2\text{bpy})_2(\text{H}_2\text{O})_2] (\text{OTf})_2 \) was found to be an efficient catalyst for the transfer hydrogenation of carbonyl compounds with 1,4-butanediol. The diol, acting as both solvent and hydrogen donor, was converted to the more thermodynamically stable \( \gamma \)-butyrolactone upon its release of hydrogen. For each catalytic reaction a mechanistic pathway was proposed. It should be noted that both catalytic systems are insensitive to oxygen and therefore do not require the use of nitrogen or argon atmosphere for protection.
Publications


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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>δ</td>
<td>Chemical shift (NMR)</td>
</tr>
<tr>
<td>η</td>
<td>Descriptor for hapticity</td>
</tr>
<tr>
<td>μ</td>
<td>Descriptor for bridging</td>
</tr>
<tr>
<td>ν</td>
<td>Frequency</td>
</tr>
<tr>
<td>e⁻</td>
<td>Electron</td>
</tr>
<tr>
<td>L</td>
<td>Generalized ligand, in particular a 2e⁻ ligand</td>
</tr>
<tr>
<td>LₙM</td>
<td>Generalized metal fragment with n ligands</td>
</tr>
<tr>
<td>[]</td>
<td>Encloses complex molecules or ions</td>
</tr>
<tr>
<td>ESI-MS</td>
<td>Electrospray ionization mass spectrometry</td>
</tr>
<tr>
<td>IR</td>
<td>Infra-red</td>
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<td>NMR</td>
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<td>THF</td>
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<td>MeOH</td>
<td>Methanol</td>
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<tr>
<td>EtOH</td>
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</tr>
<tr>
<td>DMSO</td>
<td>Dimethylsulfoxide</td>
</tr>
<tr>
<td>Tp</td>
<td>Hydrotris(1-pyrazolyl)borate</td>
</tr>
<tr>
<td>Cp</td>
<td>Cyclopentadienyl</td>
</tr>
<tr>
<td>Cp*</td>
<td>Pentamethylcyclopentadienyl</td>
</tr>
<tr>
<td>OTf</td>
<td>Trifluoromethanesulfonate</td>
</tr>
<tr>
<td>BArF</td>
<td>Tetrakis(pentafluorophenyl)borate</td>
</tr>
<tr>
<td>dmp</td>
<td>1,10-dimethylphenanthroline</td>
</tr>
<tr>
<td>bpy</td>
<td>2,2'-bipyridine</td>
</tr>
<tr>
<td>PPh₃</td>
<td>Triphenylphosphine</td>
</tr>
<tr>
<td>PCy₃</td>
<td>Tricyclohexylphosphine</td>
</tr>
<tr>
<td>dppm</td>
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<td>dppe</td>
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<tr>
<td>COD</td>
<td>1,5-Cyclooctadiene</td>
</tr>
<tr>
<td>R</td>
<td>Generalized alkyl group</td>
</tr>
<tr>
<td>X</td>
<td>Halogen group</td>
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<tr>
<td>Me</td>
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</table>
Et  Ethyl
iPr  Isopropyl
tBu  t-Butyl
nBu  n-Butyl
Ph  Phenyl
Np  Naphthyl
s  Singlet
d  Doublet
t  Triplet
q  Quartet
m  Multiplet

TpRu(PPh₃)(η³-HSiPh₃H) (1a)

TpRu(PPh₃)(η³-HSiPh₂MeH) (1b)

TpRu(PPh₃)(η³-HSiPhMe₂H) (1c)
tpRu(PPh₃)(η³-HSiEtMe₂H) (1d)

TpRu(PPh₃)(H₂)H (2)

TpRu(PPh₃)(H₂O)H (3)

TpRu(PPh₃)(H₂)OH (4)

TpRu(PPh₃)(CO)H (5)
TpRu(PPh$_3$)(CO)(η$^1$-OCHO) (6)

TpRu(CO)$_2$H (7)

TpRu(PPh$_3$)(CO)(η$^2$-HSiPhMe$_2$)(OCHO) (8)

TpRu(PPh$_3$)dppmH (9)

cis-[Ru(6,6'-Cl$_2$bpy)$_2$(H$_2$O)$_2$](OTf)$_2$ (10)
`cis-[Ru(6,6'-Me₂bpy)₂(H₂O)₂](OTf)₂ (11)`

`cis-[Ru(2,9-dmp)₂(H₂O)₂](OTf)₂ (12)`

`cis-[Ru(6,6'-Cl₂bpy)₂Cl₂] (13)`
Chapter 1  Introduction

1.1 Activation of Hydrosilanes by transition metal complexes

1.1.1 Non-classical σ-Silane complexes

Since the discovery of the first transition metal complex incorporating molecular dihydrogen ligand by Kubas et al., there has been an extensively growing interest on the studies of this type of non-classical σ-coordinated compounds [1–4]. As an analogue of dihydrogen, silanes possessing silicon–hydrogen bond (hydrosilanes) are also capable of interacting with transition metal center in a non-classical manner, giving rise to σ-silane complexes (Chart 1.1) [5].

![Chart 1.1](image)

Chart 1.1

Although the bonding mode of both M(η²-HSiR₃) and M(η²-H₂) moiety can be viewed in terms of the famous Dewar–Chatt–Duncanson model (Figure 1.1) [6], the situation regarding the extent of the oxidative addition process is more complex in the former case for 2 major reasons. Firstly, the Si–H bond is more basic than H–H bond, and is thus a better σ-donor; moreover, back donation of electron density from metal is more
prominent in the M(η²-HSiR₃) moiety since the Si–H bond is also a better π acceptor than the H–H bond. Secondly, the presence of substituents at the silicon center with different steric and electronic properties, a feature not found in hydrogen, has a significant influence on the extent of oxidative addition of Si–H bond to the metal center, directly affecting the resultant strength of Si–H interaction. For these reasons, difficulties are sometimes found in discriminating a σ-silane coordination from a silyl hydride formulation [7]. In fact, the hydrogen atom in a Si–H bond of hydrosilane interacting with a metal center could be regarded as a classical hydride ligand, involved in a σ-coordination, or having a secondary interaction with a silicon atom [8–11] (see next section). X-ray crystallographic analysis and DFT calculations are particularly useful for the assignment of these different bonding modes [8]. For ruthenium complexes, the key parameters thus concerned are not only the Si–H distances, but also the Ru–Si and Ru–H distances. The Ru–Si distance diminishes for a given series of compounds as the extent of activation of the Si–H bond increases. Typically, Si–H distances of 1.7–1.8 Å can reasonably be regarded as involving in σ-bond coordination; those in the range of 1.9–2.0 Å are more controversial.
Values up to 2.4 Å, which is still much shorter than the sum of the van der Waal’s radii of Si and H (3.4 Å), indicates a significant Si–H interaction.

Figure 1.1  Dewar–Chatt–Duncanson model for Si···H···M bonding.

1.1.2 Multicenter Si···H interactions in Silyl Polyhydride Complexes

The term interligand interaction could be applied to complexes that incorporate a supposedly η²-silane and one or more cis-coordinated hydride ligand, and in fact there is solid evidence for the presence of multiple interligand Si···H interactions in polyhydride trialkyl/aryl silyl complexes. Crabtree and co-worker reported in 1990 the syntheses of the rhenium complexes Re(PPh₃)₂H₆SiR₃ (Chart 1.2)
Although the T₁ relaxation time measured for the hydride ligands gave small values of 76–79 ms (for 259 MHz at 209 K), they rejected the assignment of the complex as having σ-coordinated dihydrogen ligand on the basis of very small isotopic perturbation of resonance. Indeed, Hartree-Fock calculations using the model complexes Re(PH₃)₂H₆SiH₃ indicated that all the H–H distances between any two cis-coordinated hydride ligands fall in nonbonding range (2.083–3.157 Å, 0.82–0.90 Å for σ-dihydrogen ligand). The Re–Si distance in Re(PPh₃)₂H₆SiR₃ was determined to be 2.474 Å. This value is considerably shorter than the sum of covalent radii of the two atoms (2.65 Å). This observation, together with the two short Si–H distances of 1.76 and 1.92 Å in the complex, led to the suggestion of a Re(η³-H₂SiR₃) moiety being present in Re(PPh₃)₂H₆SiR₃. A similar η³-H₂SiR₃ motif was also found in the related complex Re(PPh₃)₄(CO)H₂SiR₃ (Chart 1.3), which shows a rather short Re–Si distance of 2.451(3) Å and two close Si–H interactions [13].
In 1999, the research group of Sabo-Etienne and Chaudret reported the synthesis and X-ray characterization of the ruthenium complex RuH$_2$(η$^2$-H$_2$)(η$^2$-HSiPh$_3$)(PCy$_3$)$_2$, which was originally formulated as a mixed dihydrogen and silane σ-complex. However, its unusual structural features including the cis-orientation of the two bulky phosphine ligand, the close Ru–P bond lengths despite the two phosphines are lying trans to two supposedly different ligands (η$^2$-HSiPh$_3$ and hydride), and the almost-equivalent bonding of the silicon center to the two hydride units, suggest that a special type of interligand interaction is present in the complex [14]. In a separate
report, Nikonov suggested that the unusual bonding between the silicon and the hydride in RuH2(η²-H2)(η²-HSiPh3)(PCy3)2 could be viewed in terms of an interaction between the metal fragment [(PCy3)2RuH2]⁺ and the dihydrosilyl anion [H2SiPh3]⁻, resulting in the nonclassical complex [η²-H2](PCy3)2RuH(η³-H2SiR3)] [9] (Chart 1.4).

![Chart 1.4]

More recently, Nikonov and co-workers provided evidence via X-ray and DFT studies for the existence of H···Si···H bonding in the complex resulting from silane activation on the CpFe(Pr2MeP)H moiety (Chart 1.5). The compound can reasonably be formulated as CpFe(Pr2MeP)(η³-HSiR3H) [15].

![Chart 1.5]
1.1.4 Catalytic processes involving silane complexes

Several σ-coordinated silane complexes have been suggested to be involved in catalytic transformations [16]. Crabtree and Luo reported highly efficient iridium-catalyzed homogeneous silane alcoholysis to silyl ethers [17]. Direct nucleophilic attack of a \( \eta^2\)-Si–H bond rather than silyl hydride by oxygen of alcohol was proposed (Scheme 1.1). Kinetic, mechanistic, and DFT studies on an iron and a manganese catalytic systems show that the key step of the alcoholysis of silane catalyzed by these metal systems (Ir, Fe, and Mn) is the nucleophilic attack of alcohol oxygen on the silicon of \( \eta^2\)-Si–H bond.

Brookhart’s group found that the iron σ-silane complex [CpFe(CO)(PR$_3$)(HSiEt$_3$)][BAR$_5$] is an active catalyst for silane alcoholysis [18]. It was proposed that the alcohol oxygen attack the silicon-center of the \( \eta^2\)-coordinated R$_3$Si–H to give a protonated silyl ether which rapidly protonate the hydride to form a dihydrogen complex \([\text{M–H}_2]^+\). Displacement of coordinated dihydrogen regenerates the starting silane complex, completing the catalytic cycle. The displacement step was determined to be rate-determining (Scheme 1.2) [19].
Scheme 1.1  Mechanism of the $[\text{IrH}_2(\text{S})_2(\text{PPh}_3)_2]\text{SbF}_6$-catalyzed silane alcoholysis ($S = \text{solvent}$).

Scheme 1.2  Proposed mechanism for the iron-catalyzed silane alcoholysis
The cationic manganese dichloromethane complex 
[Mn(CO)$_3$(P)$_2$(CH$_2$Cl)$_2$][BAR$_F$] bearing tied-back phosphites was also found to catalyze the alcoholysis of triethylsilane with phenol, following a mechanism similar to that proposed for the Brookhart’s iron systems (Scheme 1.3) [20].

Scheme 1.3 Proposed mechanism for the manganese-catalyzed alcoholysis of HSiEt$_3$ by phenol

Sabo-Etienne's and Chaudret's groups showed that a silane complex Ru”H$_2$SiMe$_2$Cl”{(η$^3$-C$_6$H$_8$)PCy$_2$}(PCy$_3$) was generated during the silylation of ethylene with HSiMe$_2$Cl catalyzed by a bis(dihydrogen) complex RuH$_2$(η$^2$-H$_2$)$_2$(PCy$_3$)$_2$ [21, 22]. The complex was fully characterized by multinuclear NMR and X-ray spectroscopies, which indicated that the silicon is almost symmetrically bound to the two
neighboring hydrogens. It is therefore more reasonable to assign the complex as having a $\eta^3$-HSiMe$_2$ClH moiety rather than a $\eta^2$-silane hydride. Independently-synthesized Ru($\eta^3$-HSiMe$_2$ClH){($\eta^3$-C$_6$H$_8$)PCy$_2$}(PCy$_3$) was also found to be a catalyst for ethylene silylation, albeit with lower rate. NMR monitoring indicated that the silane complex remained the only detectable organometallic species in the course of catalysis (Scheme 1.4).

Brookhart and coworkers reported the reduction of alkyl halides by triethylsilane based on a cationic iridium bis(phosphinite) pincer catalyst (POCOP)IrH$^+$ {POCOP = 2,6-[OP(tBu)$_2$]$_2$C$_6$H$_3$} [23, 24]. They originally proposed the formation of an $\eta^2$-silane complex (POCOP)Ir($\eta^2$-HSiEt$_3$)H$^+$ during the course of the catalysis. However, their later work on the X-ray crystallographic analysis of the silane complex showed that the complex is in fact an unprecedented $\eta^1$-silane complex (Scheme 1.5).
Scheme 1.4 Generation of the $\eta^2$-sialne complex
RuH($\eta^2$-HSiMe$_2$Cl)\{($\eta^3$-C$_6$H$_9$)PCy$_2$\}(PCy$_3$) during ethylene hydrosilylation by HSiMe$_2$Cl
Scheme 1.5 Proposed mechanism for the iridium-catalyzed reduction of alkyl halides by triethylsilane

Very recently Nikonov’s group reported the use of cationic ruthenium complex \([\text{Cp}(\text{P}^3\text{Pr}_3)\text{Ru}(\text{CH}_3\text{CN})_2]^+\text{BArF}^-\) for a number of silane-related transformations, such as hydrosilylation of aldehydes, ketones, and esters \[25\]. They proposed the formation of cationic silane \(\sigma\)-complexes from \([\text{Cp}(\text{P}^3\text{Pr}_3)\text{Ru}(\text{CH}_3\text{CN})_2]^+\text{BArF}^-\) during the course of the hydrosilylation of carbonyl substrates.
1.2 Hydrolytic hydrosilane oxidation to silanol

Silanols are widely utilized as building blocks for silicon-based polymeric materials [26–29] and as the nucleophilic partners in cross-coupling reactions [30–33]. Common preparative methods for silanols include hydrolysis of chlorosilanes [34–35] or reactions of siloxanes with alkali reagents. Oxidation of organosilanes with stoichiometric amounts of oxidants such as potassium permanganate [36], OsO₄ [37], and dioxiranes [38], has also been reported (Figure 1.2). The obvious shortcoming of these methods is the generation of large amounts of environmentally damaging wastes; moreover, these methods have limited scopes. Highly efficient and more environmentally friendly synthetic methods for the conversion of readily available organosilanes to silanols are therefore highly desirable. In recent years some promising homogeneous [39–43] and heterogeneous [44–46] systems that catalyze the oxidation of hydrosilane to silanol with the use of water as an oxygen source have been reported. This oxidation approach is deemed an environmentally benign one not only because of the use of water as a source of oxygen, but also the generation of molecular hydrogen as the only byproduct.
Chang’s group reported highly efficient ruthenium [40] and iridium [41] systems for the hydrolytic oxidation of hydrosilanes to silanols under very mild conditions. Dimethylphenylsilane, for instance, was hydrolyzed in the presence of \([\text{Ru}(p\text{-Cymene})_2\text{Cl}_2]\) to give high yield of dimethylphenylsilanol at 25°C in air (eq. 1.1). The same silane was also hydrolyzed to give good yield of the corresponding silanol using \([\text{IrCl(COD)})_2]\) as catalyst under very similar reaction conditions (eq. 1.2). In both catalyst systems a metal silyl hydride species was suggested to be the active species.
A very recent work on silane hydrolysis reaction using cationic \[2-(2'\text{-hydroxyphenyl})-2\text{-oxazolinato(–2)}\]oxorhenium(V) complex was reported by Abu-Omar [43]. The reaction between PhMe_2SiH and H_2O in the presence of the rhenium complex gives high yield of PhMe_2SiOH under ambient conditions (eq. 1.3). A proposed mechanism for the hydrolysis reaction was disclosed. The coordinated H_2O in the aquorhenium(V) complex was first deprotonated to generate the corresponding hydroxo species; reaction between the R_3SiH and the hydroxo ligand affords R_3SiOH and a rhenium(V) hydride. The hydride reacts with solvated H^- generated in the first step of the catalytic reaction to evolve H_2 and regenerate the cationic active catalyst (Scheme 1.6).
Scheme 1.6  Proposed mechanism for the rhenium-catalyzed hydrolytic oxidation of hydrosilanes to silanols
1.3 Carbon dioxide reduction by silane

Work on the use of carbon dioxide as a renewable source of carbon for the manufacture of chemicals has been extensively conducted in recent decades since CO₂ offers the advantages of being cheap, abundant, and non-toxic [47–48]. To date, however, industrial processes employing carbon dioxide as raw material are still very limited; carbon dioxide, the most oxidized form of carbon, is of high thermodynamic stability, large energy input such as the use of light, electricity, or high energy substances are required to overcome the obstacle imposed by the low-energy nature of carbon dioxide.

A notable example of overcoming the unfavorable thermodynamics associated with the use of carbon dioxide is to employ reducing agents such as molecular hydrogen [49–54] or hydrosilanes, R₃−ₓSiH₁₊ₓ [55–64]. We will focus our attention on the use of hydrosilanes, a class of relatively unexplored reagents for effecting CO₂ transformation. Silicon–hydrogen bond is of high reactivity and therefore might transfer its energy to CO₂ through the formation of the more stable Si–O bond. A number of catalytic systems were reported in recent decades for the reduction of carbon dioxide using hydrosilanes as reducing agent.
Early in the 1980’s, ruthenium [55, 56] and iridium [57] complexes were known to be catalysts for the hydrosilylation of carbon dioxide. Eisenberg et al. reported the reduction of carbon dioxide by alkylsilanes catalyzed by the iridium complex Ir(CN)(CO)dppe at ambient temperature and pressures [57]; carbon dioxide reacts with Me₂SiH₂, Et₂SiH₃, and Me₃SiH to yield silyl methoxides as the ultimate reduction products. Monitoring of the reaction through the use of ^13CO₂ revealed that several reduced carbon intermediates such as formoxysilane (FOS), bis(silyl)acetals (BSA), silyl methoxides (SMO), and disiloxane (DSO) are formed during the course of the reaction (Scheme 1.7 using Me₃SiH as an example).

Scheme 1.7 Ir(CN)(CO)dppe-catalyzed reduction of carbon dioxide by Me₃SiH
Matsuo and Kawaguchi reported in 2006 that the reduction of carbon dioxide by hydrosilanes under mild conditions to afford methane was catalyzed by the zirconium–borane complexes [60]. An outline of a proposed mechanism had been described; the zirconium cationic complex first forms an adduct with CO$_2$; the activated CO$_2$ then reacts with hydrosilanes to yield BSA, CH$_2$(OSiR$_3$)$_2$, as initial reduction product. Subsequently, B(C$_6$F$_5$)$_3$, generated by slow decomposition of the counter-anion [PhCH$_2$B(C$_6$F$_5$)$_3$]$^-$ during the reaction, catalyzes the reduction of the BSA by HSiR$_3$ to afford methane and (R$_3$Si)$_2$O (DSO) (Scheme 1.8).

Scheme 1.8 Conversion of carbon dioxide to methane catalyzed by zirconium complex
In 2007 Deglmann reported the hydrosilylation of carbon dioxide by PhMe$_2$SiH catalyzed by the ruthenium nitrile complexes $mer$-(RuX$_3$(MeCN)$_3$) and $cis/ trans$-(RuX$_2$(MeCN)$_4$), with X = Cl, Br [61]. The major steps of the catalytic cycle were shown by theoretical calculation to be the transfer of the trimethylsilyl moiety from Me$_3$SiH to a coordinated halide ligand, leading to the formation of a L$_n$RuH–(XSiMe$_3$) intermediate, carbon dioxide coordination to Ru center in a side-on manner, transfer of trimethylsilyl group to carbon dioxide, and finally, reductive elimination of the silyl fomate product HCOOSiMe$_3$. The step involving the silyl transfer from the R$_3$SiCl ligand to the oxygen of the coordinated carbon dioxide was found be the highest point in the energy pathway (Scheme 1.9).

In 2009 Ying reported conversion of carbon dioxide into methanol with silanes using N-heterocyclic carbene (NHC) catalysts under ambient conditions [62]. The reactions between CO$_2$ and diarylsilane in the presence of 1,3-bis(2,4,6-trimethylphenyl)imidazolium carboxylate (Imes-CO$_2$) yield silyl methoxides (SMO) as the final reduction product. Various reduced carbon intermediates such as FOS and BSA were identified during the course of the catalytic reaction using $^{13}$CO$_2$ as a source of carbon. Density functional theory
study of the catalytic reduction of carbon dioxide by the NHC catalysts reported by Wang’s group in an independent article revealed that formaldehyde, not detected in Ying’s work but is believed to have been generated from the dissociation of BSA (Scheme 1.10), should be an inevitable intermediate [65]. When NHC catalyzes the reduction of CO\textsubscript{2}/FOS/formaldehyde by silane, it prefers to activate Si–H bonds of silane and push electron density to the hydrogen atoms in favor of prior coordination to the electrophilic carbonyl carbon of CO\textsubscript{2}/FOS/formaldehyde. Scheme 1.11 depicts the predicted mechanism of the whole catalytic cycle. It should be noted that methanol, the target reduction product from carbon dioxide, is obtained by treatment of the methoxysilanes with aqueous NaOH.
Scheme 1.9 Calculated mechanism of the ruthenium-catalyzed hydrosilylation of carbon dioxide
Scheme 1.10 Decomposition of bis(silyl)acetal (BSA) to give disiloxane (DSO) and formaldehyde

Scheme 1.11 Detailed mechanism for the N-heterocyclic carbene-catalyzed reduction of carbon dioxide by silane.
Very recently Piers reported the reduction of carbon dioxide to methane catalyzed by a tandem catalyst comprising of an ion pair \([\text{TMPH}]^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-\) (\(\text{TMP} = \text{2,2,6,6-tetramethylpiperidine}\)) and a Lewis acidic borane \(\text{B}(\text{C}_6\text{F}_5)_3\) \([64]\). Carbon dioxide is first activated by the ion pair \([\text{TMPH}]^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-\) to afford the formatoborate species \([\text{TMPH}]^+[\text{HCOOB}(\text{C}_6\text{F}_5)_3]^-\) (Scheme 1.12). In the presence of \(\text{B}(\text{C}_6\text{F}_5)_3\) and triethylsilane, an adduct \([\text{Et}_3\text{Si}]^+\text{HB}^+(\text{C}_6\text{F}_5)_3\] is formed, the formatoborate rapidly transfer its \(\text{CO}_2\) moiety to the adduct to give \(\text{FOS}\) and regenerate \([\text{TMPH}]^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-\). The reactive formoxysilane is then readily reduced by the borane/triethylsilane system to afford \(\text{CH}_4\) via \(\text{BSA}\) and \(\text{SMO}\), with the formation of the \(\text{DSO} \ (\text{Et}_3\text{Si})_2\text{O}\) as byproduct.
Scheme 1.12 Reduction of carbon dioxide to methane catalyzed by a frustrated acid-base pair $[\text{TMPH}]^+[\text{HB(C}_6\text{F}_5)_3]^-$
1.4 Electrophilic transition-metal complexes for catalytic reactions

The design and synthesis of electrophilic transition-metal complexes has been an important area of research in organometallic chemistry catalysis [66, 67]. Several types of catalytic reactions such as alkene hydrogenation [68, 69], alkene metathesis [70], and 1,3-butadiene polymerization [71] were found to have rate enhancement with increased electrophilicity of the metal centers achievable by going from neutral to cationic catalyst complexes. Brookhart’s cationic dimine complexes [Pd(Me)(sol)(Ar$_2$DAB)]$^+$ (Ar$_2$DAB = diaryldiazabutadiene, sol = coordinated solvent) (Chart 1.6) for ethylene and olefin polymerization represents an impressive example of utilizing electrophilic late transition metal for olefin polymerization [72–74]. On the other hand, Sen’s early work on reactions such as alkene polymerization, promoted by electrophilic palladium(II) species [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ (Chart 1.7) and other electrophilic solvent complexes have also contributed to the development of electrophilic transition–metal catalysis [75, 76].

Chart 1.6
It is suggested that with the use of the above-mentioned catalysts, the electrophilicity of the coordinated alkenes can be strongly enhanced by increasing the net positive charge, resulting in high carbocationic properties. This concept of increasing the positive charge on the complex is believed to be useful for the development of catalysts for reactions where activation of alkenes or other unsaturated compounds are involved.

1.5 Activation of alcohols via borrowing hydrogen methodology

Alcohols are generally of limited reactivity unless activated by several means, including the conversion to a nucleophilic alkoxide by addition of a base, or to an electrophilic species by the addition of an acid. Alternatively, they can be temporarily oxidized into the corresponding aldehydes or ketones, taking advantages of the latter being able to participate in nucleophilic addition reactions as well as acting as nucleophiles by themselves (in the form of the corresponding enol or enolate). This activation mode can become a catalytic
process when the oxidation product is subsequently subjected to reduction under the reaction conditions. **Scheme 1.13** shows the major reactions in which this mode of alcohol activation, named borrowing hydrogen methodology, was employed. The greater reactivity of the ketone over that of the alcohol is utilized for (i) imine formation and its subsequent reduction to an amine, (ii) alkene formation and its reduction to a carbon–carbon bond and (iii) enolisation with electrophile and subsequent reduction to afford a functionalized alcohol. It should be emphasized that, in all the cases mentioned above there is no net hydrogen loss or gain during the reaction.

Recent research on the area of borrowing hydrogen methodology had benefited from the advancement in transfer hydrogenation chemistry [109–112]. Late transition complexes have been shown to affect imine and alkene reduction using alcohol as hydrogen donor.
Scheme 1.13  Activation of alcohols by borrowing hydrogen methodology
1.5.1 β-functionalization of alcohols

As discussed, when an alcohol is temporarily oxidized to the corresponding aldehyde or ketone, nucleophilic addition process can take place more readily and, with amine or Wittig reagent as nucleophile, imine and alkene can be formed respectively which were then reduced to give C–N and C–C bonds. Another possible manipulation of this temporary oxidation of an alcohol to a carbonyl compound is reacting the carbonyl compound via enol/enolate chemistry. The possibility for the β-functionalisation of alcohols by temporarily oxidation using borrowing hydrogen methodology is shown in Scheme 1.14. The alcohol oxidation is followed by addition of an electrophile to the generated enol or enolate, and this allows the overall reaction to proceed. This β-functionalisation strategy has been applied to the bromination of alcohols [113]. Thus, in the presence of an aluminium alkoxide and pyridium tribromide, bromination occurred giving 2-bromo-1-phenylethanol as the product (eq. 1.7). The reaction conditions also result in some irreversible oxidation of the alcohol by its direct interaction with the brominating agent.
The activation of a primary alcohol and a secondary alcohol simultaneously by borrowing hydrogen methodology can result in an interesting C–C bond coupling process [114–120]. Such processes are believed to involve temporary oxidation of both alcohols to the corresponding ketone and aldehyde, which undergo an aldol condensation in the presence of base to give an \( \alpha,\beta \)-unsaturated ketone.
Reduction of this ketone affords the saturated alcohol as the final product (Scheme 1.15).

\[
\begin{align*}
R\text{OH} + R'\text{OH} &\rightarrow R\text{OH} + R'\text{OH} \\
\text{R} + \text{R'} &\rightarrow \\
\text{R} - \text{H}_2 + \text{R'} - \text{H}_2 + 2\text{H}_2 \\
\end{align*}
\]

\[\text{Aldol condensation} \]

**Scheme 1.15 Carbon-carbon bond formation between two alcohols.**

Cho et al. reported in 2003 the first example of one-pot β-alkylation of secondary alcohol with primary alcohol [114]. The coupling process involves the addition of 1-dodecene as a sacrificial hydrogen acceptor, which allows 1-phenylethanol to be β-alkylated by benzyl alcohol giving high yield of product (eq. 1.8). In 2005 Yamaguchi reported the β-alkylation of secondary alcohols with primary alcohols using the dimeric iridium complex \([\text{Cp*IrCl}_2]\) as catalyst [115]. As an example, the reaction between 1-phenylethanol
and a slight excess of $n$-butanol afforded 1-phenyl-1-hexanol in good yield (eq. 1.9). Ramon and Yus reported in 2006 the use of dimethylsulfoxide ruthenium complex $\text{RuCl}_2(\text{DMSO})_4$ as a catalyst for the coupling reaction between primary alcohol and secondary alcohol [116]. For instance, 1-phenylethanol was successfully $\beta$-alkylated with 2-furfuryl alcohol in the presence of KOH to give 3-(2-furyl)-1-phenylethanol in 98% yield, although a relatively longer reaction time is required (eq. 1.10). In the report they suggested a mechanism for the coupling reaction (Scheme 1.16). The alcohols are first oxidized to the corresponding aldehyde and ketone, which then undergo an aldol condensation in the presence of base to afford an unsaturated ketone. Subsequent reduction of the ketone gives the saturated alcohol as the final product.
Scheme 1.16 Proposed mechanism for the RuCl$_2$(DMSO)$_4$-catalyzed $\beta$-alkylation of secondary alcohols with primary alcohols
The most efficient $\beta$-alkylation of secondary alcohols with primary alcohols to date is reported in 2009 by Crabtrees and coworkers using iridium complexes supported by chelating N-Heterocyclic carbenes [120]. As an example, 1-phenylethanol reacted with 4-chlorobenzyl alcohol in refluxing toluene to afford 96% conversion to 3-(4-chlorophenyl)-1-phenylethanol (eq. 1.11).

\begin{equation}
\text{Ph} \text{OH} + 4\text{-ClPh} \text{OH} \xrightarrow{\text{KOH (100 mol\%), toluene, 110\degree C, 3h}} \text{Ph} \text{4-ClPh OH}
\end{equation}

96% (1.11)
1.6 Transfer hydrogenation of carbonyl compounds

Transfer hydrogenation refers to a process in which a hydrogen donor releases its hydrogen to an unsaturated bond, such as C=C, C=O, and C=N. The reaction is now widely investigated in both academic and industrial sectors since the use of potentially hazardous pressurized hydrogen can be avoided. Many transition-metal complexes of rhodium, iridium and ruthenium have been found to be active in catalyzing transfer hydrogenation of polar functional groups [77–80]. In particular, ruthenium(II) complexes supported by either tridentate, cyclometalated PCP- [81–84], NCN- [81], CNN-[85, 86], NNN- [87, 88] pincer, or bidentate PC- [89], NC- [90, 91], and NN-[92] ligands are found to be highly active for such reaction.

1.6.1 Mechanisms of transition metal-catalyzed transfer hydrogenation

Generally, transition-metal complexes catalyze transfer hydrogenation of unsaturated compounds through the formation of metal monohydride or dihydride as key intermediates [79, 93–94]. In some cases, the hydride species are stable enough to be isolated or observed spectroscopically. The RuCl₂(PPh₃)₃-catalyzed reduction of carbonyl compounds reported in the 1960s represents an early example of
transition metal-catalyzed hydrogen transfer reaction [95–97]. In the presence of base, the rate of the transfer reaction was found to be enhanced dramatically [98, 99] and this was later shown by Backvall to be a result of the formation of a highly active dihydride species RuH$_2$(PPh$_3$)$_2$ (Scheme 1.13) [100].

Noyori reported the use of metal-ligand bifunctional catalysts, such as (η$^6$-arene)RuH((S,S)-H$_2$NCHRCHRNTs), for the asymmetric transfer hydrogenation of unsaturated compounds [101–103]. They suggested that the key feature of these catalysts is the presence of a basic site in the ligand, which interacts with the alcohol or other hydrogen donor through hydrogen bond and thereby facilitates the hydride transfer (from the hydrogen donor to the metal). The proposed mechanism of the transfer hydrogenation of ketones in 2-propanol catalyzed by these complexes involves a concerted transfer of the proton and the hydride from the catalyst to the substrate via a cyclic six-membered transition state to give the alcohol and (η$^6$-arene)Ru((S,S)-HNCHRCHRNTs) (Scheme 1.14). The proton and the hydride from 2-propanol are then transferred to the nitrogen and metal, respectively, forming acetone and
regenerating the active catalyst. It is noted that the catalytic reaction is suggested to proceed without coordination of either alcohol or ketone to the metal. Other examples of metal-ligand bifunction catalysts for transfer hydrogenation reactions include

\[ \text{RuH(NHCOMe)(OHCHMe_2)(PCy_3)_2(CO)} \] (Chart 1.8) reported by Yi [104] and \[ ((\text{Ph}_4\text{C}_4\text{COHOC})\text{C}_4\text{Ph}_4)(\mu-\text{H})(\text{CO})_4\text{Ru}_2] \) (Chart 1.9) by Shvo [105].
Scheme 1.17 Proposed mechanism of the transfer hydrogenation of carbonyl compounds involving a dihydride intermediate
Scheme 1.18 Catalytic cycle of (η^6-arene)RuH((S,S)-H2NCHRCHRNTs) via a concerted six-membered transition state.

Chart 1.8

Chart 1.9
1.4.2 Choices of hydrogen donors

It is well known that 2-propanol is conventionally used as a hydrogen donor in hydrogen transfer reactions because of its valuable properties: it is of high stability, easy to handle, non-toxic, environmentally benign, inexpensive, and is good solvent for most organic compounds [106]. The oxidized product acetone has a low boiling point and is therefore readily removable. However, due to the very similar thermal stabilities of the 2-propanol and acetone, large excess of the former is required in order to push the hydrogen transfer reaction to the product. Therefore, an alternative hydrogen donor other than 2-propanol is desirable.

William has investigated the possibility of using 1,4-butanediol as an alternative source of hydrogen donor in ruthenium-catalyzed transfer hydrogenation of unsaturated compounds. The diol, after its double hydrogen release, is converted irreversibly to a lactone, rendering stiochiometric reduction possible (Scheme 1.19). In addition to aldehydes and ketones, imines and alkenes were also successfully reduced with 1 equivalent of 1,4-butanediol under similar reaction conditions (eq. 1.12-1.14) [107, 108].
Scheme 1.19 Lactonization of 1,4-butanediol

(1.12)

(1.13)

(1.14)
Chapter 2  Nonclassical Ruthenium Silyl Dihydride Complexes

TpRu(PPh₃)(η³-HSiR₃H) (Tp = Hydrotris(pyrazolyl)borate).

Catalytic Hydrolytic Oxidation of Organosilanes to Silanols with TpRu(PPh₃)(η³-HSiR₃H)

2.1 Introduction

Our research group has previously reported the syntheses of a series of ruthenium complexes TpRu(PPh₃)“H₂SiR₃” (Tp = hydrotris(pyrazolyl)borate); on the basis of NMR and DFT studies, we formulated these complexes as the σ-silane hydride species which rapidly exchange between the two forms:

\[ \text{TpRu(PPh₃)(H₃)H₂SiR₃} \rightleftharpoons \text{TpRu(PPh₃)(H₃)H₂SiR₃} \]  [121]. We have now successfully obtained single crystals of three of these complexes and carried out X-ray crystallographic studies, the results of which are more consistent with a static structure TpRu(PPh₃)(η³-HSiR₃H) containing H····Si····H bonding. In addition to the X-ray structures of three Ru–(η³-HSiR₃H) complexes, we report here catalytic hydrolytic oxidation of organosilanes to silanols with one of these complexes.
2.2 Experimental section

2.2.1 Materials and Instrumentation

All manipulations were carried out under an inert nitrogen atmosphere using standard Schlenk techniques. Solvents were dried, degassed, and distilled prior to use: THF, 1,4-dioxane, and diethyl ether from Na benzophenone ketyl, n-hexane and toluene from Na, acetonitrile and dichloromethane from CaH₂. All chemicals were commercially available (Aldrich, Acros, Strem and International Laboratory) and used without further purification. The chiral silane R-(+)-Me(α-Np)PhSiH (98% ee) [122], and the complexes TpRu(PPh₃)(CH₃CN)H [123] and TpRu(PPh₃)(η³-HSiPh₃H) [121] were prepared according to literature methods. Deuterated NMR solvents, purchased from Armar and Cambridge Isotope Laboratories, were dried with P₂O₅ prior to use. ¹H NMR spectra were obtained from a Varian (500 MHz) or Bruker DPX (400 MHz) spectrometer; chemical shifts were reported relative to residual protons of the deuterated solvents. ¹³C NMR spectra were recorded with a Bruker DPX 400 spectrometer at 100.61 MHz; chemical shifts were internally referenced to CD₂Cl₂ (δ = 53.8 ppm). ³¹P NMR spectra were recorded on a Bruker DPX 400 spectrometer at 161.70 Mz; chemical shifts were externally referenced to 85% H₃PO₄ in D₂O (δ =
$^{29}\text{Si}$ NMR spectra were obtained from a Bruker DPX 400 spectrometer at 79.50 MHz; chemical shifts were externally referenced to Me$_4$Si in CDCl$_3$ ($\delta = 0.00$ ppm). Infrared spectra were obtained from a Bruker Vector 22 FT-IR spectrophotometer. Optical rotations were recorded on a Perkin-Elmer 341 polarimeter in a 10 cm cell. Electrospray ionization mass spectrometry was carried out with a Finnigan MAT 95S mass spectrometer with the samples dissolved in dichloromethane. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

### 2.2.2 Syntheses and Reactions

#### 2.2.2.1 Synthesis of TpRu(PPh$_3$)(η$_3$-HSiPh$_2$MeH)

A sample of TpRu(PPh$_3$)(CH$_3$CN)H (0.20 g, 0.32 mmol) was loaded into a 50 mL two-necked pear-shaped flask, which was evacuated and filled with nitrogen for four cycles. Freshly distilled toluene (10 mL) and Ph$_2$MeSiH (0.8 mL, 4 mmol) were then added to the flask via syringes, and the resulting solution was heated at 90°C with stirring for 4 h. The solution was cooled to room temperature, the volume of which was reduced to 1 mL in vacuo, and 10 mL of pre-cooled hexane was added to precipitate out the product as orange solid. The solid was collected and washed with
pre-cooled hexane (5 mL), it was dried under vacuum. Yield: 0.14 g (55%).

Anal. Calcd (%) for C_{46}H_{40}BN_{6}PRuSi: C 61.93, H 5.20, N 10.83. Found: C 61.93, H 5.25, N 10.85. IR (KBr): \( \nu (\text{Ru–H}) = 1942 \, (\text{m}) \), \( \nu (\text{B–H}) = 2468 \, (\text{m}) \).

\(^1\text{H} \text{NMR} \) (400.13 MHz, CD_{2}Cl_{2}, 25°C): \( \delta = -9.93 \, (d, \, 2H, \, \text{Ru–H}, \, ^1J_{\text{SiH}} = 25.0 \, \text{Hz}) \), \( ^2J_{\text{HP}} = 22.6 \, \text{Hz} \); 0.70 (s, 3H, Si–CH_{3}); 5.48 (t, 1H of Tp), 5.77 (t, 2H of Tp), 7.52 (d, 1H of Tp), 7.68 (d, 2H of Tp), 7.82 (d, 1H of Tp), 8.35 (d, 2H of Tp), 6.93–7.60 (m, 25H of Ph). \(^{13}\text{C} \{ ^1\text{H} \} \) NMR (100.61 MHz, CD_{2}Cl_{2}, 25°C): \( \delta = 9.49 \, (s, \, \text{Si–CH}_{3}) \). \(^{31}\text{P} \{ ^1\text{H} \} \) NMR (161.7 MHz, CD_{2}Cl_{2}, 25°C): \( \delta = 70.3 \). \(^{29}\text{Si} \{ ^1\text{H} \} \) NMR (79.50 MHz, CD_{2}Cl_{2}, 25°C): \( \delta = 16.8 \) (s). ESI-MS (m/z): 576, [M – Ph_{2}MeSiH]^+.

**2.2.2.2 Synthesis of TpRu(PPh_{3})(\eta^3-\text{HSiPhMe}_{2}H) (1c)** This complex was synthesized by using the same procedure as for the preparation of 1b, except that PhMe_{2}SiH was used in place of Ph_{2}MeSiH. Yield: 0.11 g (48%).

Anal. Calcd (%) for C_{35}H_{38}BN_{6}PRuSi: C 58.90, H 5.37, N 11.78. Found: C 58.91, H 5.41, N 11.80. IR (KBr): \( \nu (\text{Ru–H}) = 2013 \, (\text{m}) \), \( \nu (\text{B–H}) = 2464 \, (\text{m}) \).

\(^1\text{H} \text{NMR} \) (400.13 MHz, CD_{2}Cl_{2}, 25°C): \( \delta = -11.06 \, (d, \, 2H, \, \text{Ru–H}, \, ^1J_{\text{SiH}} = 19.2 \, \text{Hz}) \), \( ^2J_{\text{HP}} = 22.8 \, \text{Hz} \); 0.36 (s, 6H, Si(\text{CH}_{3})_{2}); 5.33 (t, 1H of Tp), 5.77 (t, 2H of Tp), 5.88 (d, 1H of Tp), 7.58 (d, 2H of Tp), 7.66 (d, 1H of Tp), 7.93 (d,
2H of Tp), 6.03–7.30 (m, 20H of Ph). $^{13}$C{¹H} NMR (100.61 MHz, CD$_2$Cl$_2$, 25°C): δ 13.05 (s, Si(CH$_3$)$_2$). $^{31}$P{¹H} NMR (161.7 MHz, CD$_2$Cl$_2$, 25°C): δ 71.0. $^{29}$Si{¹H} NMR (79.50 MHz, CD$_2$Cl$_2$, 25°C): δ 15.1 (s). ESI-MS (m/z): 576, [M – PhMe$_2$SiH]$^+$. 

2.2.2.3 General Procedures for the Hydrolysis of Silanes Catalyzed by TpRu(PPh$_3$)(η$_3$-H$_2$SiPhMe$_2$) (1c).

The catalyst 1c (7.1 mg, 0.01 mmol) was loaded into a 25 mL two-necked pear-shaped flask, which was then evacuated and flushed with nitrogen for four cycles. Silane (0.5 mmol), water (0.36 mL, 20 mmol), and 1,4-dioxane (2 mL) were then added to the flask via syringes and needles (In the case of Ph$_3$SiH, the solid was loaded into the flask prior to system evacuation and nitrogen-flushing), and the resulting solution was stirred under constant nitrogen flow in a preheated 90°C silicone oil bath for the pre-designated times. At the end of the reaction, the flask was cooled to room temperature; a 0.1 mL aliquot of the solution was withdrawn and analyzed by $^1$H NMR spectroscopy (in CD$_3$COCD$_3$ or CD$_3$CN). Conversions were determined by comparison of the integrations of the characteristic peaks of the product and the unreacted silane.
2.2.2.4 Monitoring of 1c-Catalyzed Hydrolytic Oxidation of PhMe₂SiH to PhMe₂SiOH with NMR spectroscopy. A sample of 1c (31.2 mg) was loaded into a J. Young valved NMR tube. The tube was evacuated and filled with nitrogen for four cycles. PhMe₂SiH (33 μL, 5 equiv), water (157 μL, 200 equiv), and 1,4-dioxane-d₈ (1 mL) were added via syringes and needles. The resulting solution was heated to 90°C. At different time intervals, the tube was cooled to room temperature. ¹H and ³¹P NMR spectra of the solution were then taken.

2.2.2.5 Monitoring of the Reaction Between 1c and EtMe₂SiH. A sample of 1c (31.2 mg) was loaded into a J. Young valved NMR tube. The tube was evacuated and filled with nitrogen for four cycles. EtMe₂SiH (28 μL, 5 equiv) and 1,4-dioxane-d₈ (1 mL) were added via syringes and needles. The solution was heated to 90°C for 3h. The tube was cooled to room temperature, ¹H and ³¹P NMR spectra of the solution were taken.
Crystallographic Structure Analysis of TpRu(PPh₃)(η³-HSiPh₃H) (1a),

TpRu(PPh₃)(η³-HSiPh₂MeH) (1b), and

TpRu(PPh₃)(η³-HSiPhMe₂H)·3CH₂Cl₂ (1c).

Orange crystals of 1a-c suitable for X-ray diffraction study were obtained by layering of n-hexane on a dichloromethane solution of the complexes. A suitable crystal of 1a with dimensions 0.32 × 0.3 × 0.28 mm, or 1b with dimensions 0.50 × 0.48 × 0.32 mm, or 1c with dimensions 0.42 × 0.36 × 0.30 mm was mounted on a Bruker CCD area detector diffractometer and subjected to Mo Kα radiation (λ = 0.71073 Å) from a generator operating at 50kV and 30 mA. The intensity data of 1a, 1b, and 1c were collected in the range θ = 1.94–27.39°, 2.09–27.33°, and 1.17–27.46°, respectively, with oscillation frames of Ψ and ω and in the range 0–180°. A total of 1728 frames in 1a, 800 in 1b, and 988 in 1c, were taken in four shells. An empirical absorption correction of the SADABS (Sheldrick, 1996) program based on Fourier coefficient fitting was applied. The crystal structures were solved by Patterson function methods and expanded by difference Fourier synthesis, and refined by full-matrix least-squares on F2 using the Bruker smart and Bruker SHELXTL program packages. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in ideal positions.
and refined as rigid atoms. The \( R \) and \( R_w \) values of 1a, 1b and 1c are 0.0335 and 0.0528, 0.0320 and 0.0758, and 0.0437 and 0.1069, respectively.

CCDC-763941 (1a), CCDC-763942 (1b) and CCDC-763943 (1c) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

### 2.2.2.7 Computational Details

Molecular geometries of the model complexes were optimized without constraints via DFT calculations using the mPW1K [124] functional. Frequency calculations at the same level of theory have also been performed to identify all the stationary points as minima (zero imaginary frequencies) or transition states (one imaginary frequency). Transition states were located using the Berny algorithm. Intrinsic reaction coordinates (IRC) [125, 126] were calculated for the transition states to confirm that such structures indeed connect two relevant minima. The effective core potentials (ECPs) of Hay and Wadt with double-\( \zeta \) valence basis sets (LanL2DZ) [127] were used to describe Ru, P and Si. Polarization functions were also added for Ru (\( \zeta_{\text{f}} = 1.235 \)), P (\( \zeta_{\text{d}} = 0.387 \)), Si (\( \zeta_{\text{d}} = 0.284 \)).[128, 129] The 6-311G (d,
p) Pople basis set was used for water molecule and those H atoms that were
directly bonded to the metal center.[130] The 6-311G basis set was used forall the other atoms.[131–133] All of the DFT calculations were performed
with the Gaussian 03 package.[134]

2.3 Results and Discussion

2.3.1 Synthesis and X-ray Crystallographic Study of TpRu(PPh3)“H2SiR3”

The complex TpRu(PPh3)“H2SiPh3” (1a) is one of the members of the
series of complexes TpRu(PPh3)“H2SiR3” which we had previously
reported [121]. Complexes TpRu(PPh3)“H2SiPh2Me” (1b) and
TpRu(PPh3)“H2SiPhMe2” (1c) are new members of the series; they were
synthesized according to our previously reported procedure, i.e. by reacting
the solvent hydride precursor TpRu(PPh3)(CH3CN)H with the
corresponding organosilanes (eq 1). Similar to those of other complexes in
the series, the 1H NMR spectra of 1b and 1c each shows a doublet hydride
signal, which integrates for two hydrogens and does not show sign of
decoalescence down to –100°C in the upfield region (for 1b, at δ –9.93 ppm,
J(HP) = 22.6 Hz; for 1c, at δ –11.06 ppm, J(HP) = 22.8 Hz). The hydride
signals of 1b and 1c are flanked by 29Si satellites; the observed J(SiH) value
for 1b is 25.0 Hz and that for 1c is 19.2 Hz. These values are comparable to those of the other complexes in the series.

\[
\text{TpRu(PPh}_3\text{)(CH}_3\text{CN)H} + R_3\text{Si} \rightarrow \text{TpRu(PPh}_3\text{)}"H_2\text{SiR}_3\text{"} \\
1a, R_3 = \text{Ph}_3 \\
1b, R_3 = \text{Ph}_2\text{Me} \\
1c, R_3 = \text{PhMe}_2
\]  

Crystals of 1a-c suitable for X-ray crystallographic studies were obtained by layering \(n\)-hexane on dichloromethane solutions of the complexes. The molecular structures of 1a-c are shown, respectively in Figures 1-3. The crystal data and refinement details are given in Table 1. Selected bond distances and angles are listed in Table 2. It is noted that the two hydrogen atoms HM1 and HM2 in each of the structures are located and refined. A common feature of the structures of 1a-c is that the silicon atom interacts almost symmetrically with the two hydrogen atoms HM1 and HM2; the Si–H bond distances lie at the long end of the 2 Å limit normally admitted for \(\sigma\)-Si–H bonds [135, 136]. The ruthenium-hydrogen (Ru-HM1 and Ru-HM2) bond lengths (1.49 Å–1.568 Å) are within the normal range of classical ruthenium-hydride bond distances. In addition, the two H–Ru–Si angles in each of the complexes are very close to each other (53.9° and
structures of 1a-c therefore reveal that these complexes are more appropriately formulated as TpRu(PPh₃)(η³-HSiR₃H) containing a nearly symmetrical H···Si···H bonding in the [HSiR₃H]⁻ moiety. On the basis of our model previously used in the B3LYP calculations, it was shown that the rapidly interchanging σ-silane hydride enantiomeric pair TpRu(PPh₃)(H₃)(η²-H₆SiR₃) → TpRu(PPh₃)(H₆)(η²-H₃SiR₃) are slightly lower in energy (2.1 kJ/mol) than the corresponding symmetrical structure, which was regarded as the transition state for the interchange of the enantiomeric pairs. The B3LYP calculation was performed on a model complex in which the Tp, PPh₃, and SiR₃ moieties were replaced by (H₂C=NNH)₃BH, PH₃, and SiH₃, respectively [121].
Figure 2.1 ORTEP view (30% probability) of TpRu(PPh₃)(η³-HSiPh₃H) showing the atom-labeling scheme.
Figure 2.2 ORTEP view (30% probability) of TpRu(PPh₃)(η³-HSiPh₂MeH)
showing the atom-labeling scheme.
Figure 2.3 ORTEP view (30% probability) of TpRu(PPh$_3$)(η$^3$-HSiPhMe$_2$H) showing the atom-labeling scheme.
<table>
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<th><strong>Table 2.1</strong> Crystal Data and Structure Refinement of TpRu(PPh₃)(η³-HSiPh₃H)</th>
</tr>
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<td><strong>Empirical formula</strong></td>
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<tr>
<td><strong>Formula weight</strong></td>
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<tr>
<td><strong>Temperature / K</strong></td>
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<tr>
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<tr>
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<tr>
<td><strong>Space group</strong></td>
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<tr>
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</tr>
<tr>
<td>b = 12.2111(2)Å</td>
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<tr>
<td>c = 21.2219(4)Å</td>
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<tr>
<td><strong>Density (calculated) / g cm⁻³</strong></td>
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<td><strong>Goodness-of-fit on F²</strong></td>
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<td><strong>Final R indices [I &gt; 2σ(I)]</strong></td>
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<td><strong>R indices (all data)</strong></td>
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<td><strong>Largest diff. peak and hole / e Å⁻³</strong></td>
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</table>
Table 2.2  Selected bond Distance (Å) and Angles (°) for TpRu(PPh₃)(η³-HSiPh₃H) (1a)

| Bond distances (Å) |  |  |  |
|--------------------|-----------------------------|-----------------------------|
| Ru(1)–N(1)        | 2.2087(13)                 | Ru(1)–HM(2)                 | 1.502(15) |
| Ru(1)–N(3)        | 2.1668(16)                 | Si(1)–HM(1)                 | 2.016(14) |
| Ru(1)–N(5)        | 2.1576(15)                 | Si(1)–HM(2)                 | 1.928(14) |
| Ru(1)–P(1)        | 2.2973(4)                  | Ru(1)–Si(1)                 | 2.3816(5) |
| Ru(1)–HM(1)       | 1.491(15)                  |  |  |

| Bond angles (°) |  |  |  |
|-----------------|-----------------------------|-----------------------------|
| N(5)–Ru(1)–N(3)| 88.81(6)                   | N(3)–Ru(1)–HM1              | 173.6(5) |
| N(5)–Ru(1)–N(1)| 80.45(5)                   | N(1)–Ru(1)–HM1              | 97.1(5)  |
| N(3)–Ru(1)–N(1)| 82.32(5)                   | P(1)–Ru(1)–HM1              | 87.1(5)  |
| N(5)–Ru(1)–P(1)| 90.69(4)                   | Si(1)–Ru(1)–HM1             | 57.3(5)  |
| N(3)–Ru(1)–P(1)| 92.54(4)                   | N(5)–Ru(1)–HM2              | 168.7(5) |
| N(1)–Ru(1)–P(1)| 169.81(4)                  | N(3)–Ru(1)–HM2              | 81.5(6)  |
| N(5)–Ru(1)–Si(1)| 137.33(4)                  | N(1)–Ru(1)–HM2              | 103.8(5) |
| N(3)–Ru(1)–Si(1)| 128.81(4)                  | P(1)–Ru(1)–HM2              | 84.0(5)  |
| N(1)–Ru(1)–Si(1)| 85.19(4)                   | Si(1)–Ru(1)–HM2             | 53.9(5)  |
| P(1)–Ru(1)–Si(1)| 104.829(18)                | HM1–Ru(1)–HM2               | 104.9(8) |
| N(5)–Ru(1)–HM1  | 84.8(5)                    |  |  |
Table 2.3  Crysta1 Data and Structure Refinement of TpRu(PPh3)(η^3-HSiPh3MeH)

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Table 2.4  Selected bond Distance (Å) and Angles (°) for TpRu(PPh₃)(η³-HSiPh₂MeH) (1b)

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Table 2.6  Selected bond Distance (Å) and Angles (°) for TpRu(PPh₃)(η³-HSiPhMe₂H).3CH₂Cl₂ (1c)

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<td>N(1)–Ru(1)–HM1</td>
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2.3.2 Catalytic hydrolytic oxidation of organosilanes to silanols with

\[ \text{TpRu(PPh_3)(\eta^3-HSiPhMe_2H)} \] (1c).

Complexes 1a-1c can be readily synthesized; we suspect that it would make no difference using any one of them for the catalytic hydrolytic oxidation of silanes (eq 2). Table 3 shows the results of the 1c-catalyzed hydrolytic oxidation of silanes to silanols. The reactions did not proceed at room temperature and were performed at 90°C. Trialkyl silanes (entries 4–9) were oxidized more readily than the silanes bearing aryl substituents (entries 1-3, 10). In all the reactions reported, disiloxanes resulting from condensation of silanols were basically not detected (See appendices). Formation of undesirable side products such as disiloxane and polymeric siloxanes were often observed in the catalytic hydrolytic oxidation of hydrosilanes reported in the literature. It is important to note that the optically active silane \[ R-(+)-\text{Me(\alpha-Np)PhSiH} \] (98% ee) was hydrolyzed to yield \[ S-(+)-\text{Me(\alpha-Np)PhSiOH} \] with retention (entry 11 & eq. 2.1).
Table 2.7 Hydrolytic Oxidation of Organosilanes to Silanols with 
TpRu(PPh₃)(η³-HSiPhMe₂H) (1c).[a]

<table>
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<tr>
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<td>99</td>
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<tr>
<td>3</td>
<td>PhMe₂SiH</td>
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<td>96</td>
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<td>tBuMe₂SiH</td>
<td>4</td>
<td>96</td>
</tr>
<tr>
<td>5</td>
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<td>97</td>
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<tr>
<td>6</td>
<td>CyMe₂SiH</td>
<td>2</td>
<td>94</td>
</tr>
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<td>7</td>
<td>CH₃(CH₂)₁₆CH₂Me₂SiH</td>
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<td>94</td>
</tr>
<tr>
<td>8</td>
<td>Et₃SiH</td>
<td>4</td>
<td>97</td>
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<tr>
<td>9</td>
<td>Et₂MeSiH</td>
<td>4</td>
<td>85</td>
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<td>10</td>
<td>1,4-(SiMe₂H)C₆H₄</td>
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<td>65</td>
</tr>
<tr>
<td>11</td>
<td>R-(-)-Me(α-Np)PhSiH</td>
<td>24</td>
<td>91[c]</td>
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</tbody>
</table>

[a] Reaction conditions: silane (0.5 mmol), H₂O (40 equivalents), 1c (10 μmol, 2 mol% with respect to silane), 1,4-dioxane (2 mL), 90°C, under nitrogen flow. [b] Determined by ¹H NMR spectroscopy. [c] product : S-(-)-Me(α-Np)PhSiOH, isolated yield, 90 % ee.

![Chemical structure](image)
2.3.3 NMR monitoring of the 1c-catalyzed hydrolytic oxidation of PhMe₂SiH to PhMe₂SiOH.

Five equiv of PhMe₂SiH and 200 equiv of water were added to a 1,4-dioxane-$d_8$ solution of 1c in a J. Young valved NMR tube and the tube was heated in an oil bath at 90 °C. Figure 4 shows the $^{31}$P{^1}H and ^1H NMR spectra of the solution taken at different times; the column at the far right shows the percent conversions (estimated from the integrations of the methyl peaks of the PhMe₂SiH and PhMe₂SiOH in the ^1H NMR spectra) to the products. The $^{31}$P{^1}H NMR spectrum of the solution taken after 10 min of heating showed that 1c was present as the overwhelming species; around 2% of the dihydrogen-hydride complex TpRu(PPh₃)(H₂)H (2) [137] was also formed. As the reaction proceeded, the amount of 2 increased at the expense of that of 1c; at the end of the reaction, 1c was nearly all converted to 2. The presence of 1c and 2 and the variation of their amounts at different times were corroborated by the ^1H NMR spectra of the solution which showed the hydride signals of 1c and 2 in the upfield region. It should be pointed out that in this experiment, the H₂ by-product was trapped in the NMR tube.
Figure 2.4  NMR study of 1c-catalyzed hydrolysis of PhMe₂SiH to PhMe₂SiOH
2.3.4 Relative stability of TpRu(PPh₃)(η³-HSiPhMe₂H) (1c) and TpRu(PPh₃)(η³-HSiEtMe₂H) (1d)

In the course of growing single crystals for X-ray crystallographic studies, we learned that the complexes containing trialkyl silanes are less stable than those containing silanes with aryl groups; the trialkyl silane complexes undergo decomposition more readily; and we have not been able to obtain single crystals of them. We therefore carried out ligand substitution of 1c with HSiEtMe₂ (eq. 2.2) to gain a more quantitative comparison of the thermal stability of 1c and 1d. It was learned that after heating a 1,4-dioxane-д₈ solution of 1c in the presence of 5 equiv of HSiEtMe₂ at 90 °C for 3h, the relative equilibrium concentrations of 1c : 1d was ~ 50 : 50; the equilibrium constant Kₑq is estimated to be 1.1 × 10⁻¹. This experiment therefore shows that the thermal stability of 1c is about 9 times that of 1d.

The [H₂SiR₃]⁻ moiety, in bonding to the metal fragment, transfers electron-density from the occupied orbitals ψ₁ and ψ₂ to the metal-center orbitals; on the other hand, the metal back-donates a lone pair into the empty ψ₃ orbital of [H₂SiR₃]⁻ [9, 138] Here, ψ₁ is the all-in-phase combination of the two H 1s orbitals and the SiR₃ sp³-hybridized orbital, ψ₂ is the out-of-phase combination of the two H 1s orbitals only, and ψ₃ is the
all-out-of-phase combination of the two $1s$ orbitals and the $\text{SiR}_3$ sp$^3$-hybridized orbital. The higher stability of $1c$ vs $1d$ is probably due to the phenyl group of the silane ligand in the former being able to invite more back-donation from the metal.

$$
\text{TpRu(PPh}_3)(\eta^3\text{-HSiPhMe}_2\text{H}) + \text{EtMe}_2\text{SiH} \quad 1c
\leftrightarrow \quad \text{TpRu(PPh}_3)(\eta^3\text{-HSiEtMe}_2\text{H}) + \text{PhMe}_2\text{SiH} \quad 1d
$$

2.3.5 Proposed mechanism for the catalytic hydrolytic oxidation of silanes to silanols

The NMR monitoring experiment above shows that in the course of catalysis, the silane complex $1c$ and $\text{TpRu(PPh}_3)(\text{H}_2)\text{H}$ (2) were the only detectable organometallic complexes; these two complexes are interconvertible via ligand exchange. We believe that $1c$ is the key species reacting directly with water to generate the silanol. The fact that hydrolytic oxidation of the chiral silane $R$-(+)-Me($\alpha$-Np)PhSiH to give the silanol product $S$-(+)-Me($\alpha$-Np)PhSiOH with retention is a strong indication that the water molecule attacks the silicon center in a manner shown in Scheme
2.1. Dihydrogen-bonding interaction between the proton of the attacking water molecule and the hydride of the \((\text{H}_2\text{Si}(\text{Me})(\alpha\text{-Np})\text{Ph})^-\) moiety is expected to be present. We have reported similar dihydrogen-bonding interaction between the hydride ligand and the proton of the attacking water molecule in hydration of nitriles catalyzed by Ru-H complexes [139, 140].

![Scheme 2.1](image)

**Scheme 2.1** Attack of water on \([\text{H}_2\text{Si}(\text{Me})(\alpha\text{-Np})\text{Ph}]^-\) moiety.

Scheme 2.2 shows a possible mechanism for the hydrolytic oxidation of silanes to silanols. We propose the existence of dihydrogen-bonding interaction between one of the hydrides of the \([\text{H}_2\text{SiR}_3]^-\) moiety and a water proton during nucleophilic attack of the water molecule at the silicon center. Several studies of metal-silane interactions indicate that silane is a strong \(\sigma^*\)-accepting ligand because of the weaker H—Si \(\sigma\)-bonding. The metal \((d\pi)\)-to-silane \((\sigma^*)\) back-bonding is deemed very important for the metal-(\(\eta^2\)-silane) interaction [141–143]. The lower activity of the aryl
silanes in comparison to the trialkyl silanes in the hydrolytic oxidation reactions can be explained in terms of the diminished electrophilicity of the silicon center resulting from more back bonding from the metal and the stronger Ru–Si bond in A when R₃ contains one or more phenyl groups. The lower electrophilicity at the silicon center renders the nucleophilic attack by the water more sluggish, and the strong Ru–Si bond would slow down the extrusion of the silanol product from the metal center.

![Scheme 2.2 Proposed mechanism for the hydrolytic oxidation of organosilanes to silanols](image)

**Scheme 2.2**  Proposed mechanism for the hydrolytic oxidation of organosilanes to silanols

To study the feasibility of the proposed reaction mechanism shown in Scheme 2.2 for the catalytic hydrolytic oxidation of silanes, DFT
calculations were performed to examine the catalytic cycle using 
TpRu(PMe$_2$)(η$_3$-HSiHMe$_2$H) (1A) as the model catalyst. The potential 
ergy profile is shown in Figure 2.5 with the calculated relative electronic 
energies. The reaction of 1A with water occurred by a nucleophilic attack of 
the water oxygen on the silicon center of the η$_2$-silane ligand in a 
six-membered-ring transition state to give silanol and the dihydrogen 
complex 2A. From the dihydrogen complex 2A, a ligand substitution with 
silane occurs to regenerate 1A and release a dihydrogen molecule, 
completing the catalytic cycle. The overall reaction barrier shown in Figure 
2.5 is 90.0 kJ/mol and the hydrolysis reaction is thermodynamically 
favorable. These results support the proposed mechanism discussed above.

Figure 2.6 presents the optimized structures with selected structural 
parameters for the species shown in Figure 2.5. The bond distances 
calculated for the Ru–Si, Si–H and Ru–H bonds in 1A are similar to those 
in TpRu(PPh$_3$)(η$_3$-HSiR$_3$H) determined experimentally. In 1A, both hydride 
ligands maintain strong interaction with the silicon center of the silyl ligand, 
indicating the hypervalency around the silicon center [136]. The double 
silyl-hydrido interactions have been also found in Cp(Pr$^i$$_2$MeP)FeH$_2$SiR$_3$
reported recently [15]. 2A is a dihydrogen complex with an H–H distance of 0.90Å. The transition structure TS\textsubscript{A(1-2)} displays a strong dihydrogen bonding with an H---H distance of 1.29 Å.

Figure 2.5 Energy profile calculated for the hydrolysis reaction of HSiHMe\textsubscript{2} catalyzed by TpRu(PMe\textsubscript{3})(η\textsubscript{3}-HSiHMe\textsubscript{2}H) (1A). The calculated relative electronic energies are given in kJ/mol.
Figure 2.6 Optimized structures for the species involved in the hydrolysis reaction of HSiHMe₂ catalyzed by TpRu(PMe₃)(η¹-HSiHMe₂H) (1A) (Figure 5). Bond distances are given in angstrom.
An alternate mechanism for the 1-catalyzed hydrolytic oxidation of silanes is shown in Scheme 2.3. The cycle begins with the generation of the aquo-hydride complex 3 via H2O/silane exchange, 3 then generates the hydroxo species 4, probably via σ-bond metathesis [144–150]. Displacement of the dihydrogen ligand in 4 by silane, and subsequent intramolecular hydroxylation of the silane ligand yields the product and metal hydride. Although we have not observed the aquo-hydride complex 3 in the NMR monitoring experiment, we cannot, however, exclude the possibility that it might be present in trace amount therefore eluding NMR detection.

Our theoretical calculations show that the substitution of HSiHMe2 by a water molecule is endothermic (eq. 2.3). 3A is less stable than 1A by 36.4 kJ/mol, consistent with the experiment results that the aquo-hydride complex 3A was not observed. The energy required to dissociate a silane molecule from 1A was estimated to be 124.3 kJ/mol, indicating that the substitution of water for silane is relatively difficult to occur.
Scheme 2.3 Alternative mechanism for the hydrolytic oxidation of organosilanes to silanols

\[
\text{Tp(PMe}_3\text{)RuSiMe}_2\text{H} + \text{H}_2\text{O} \xrightarrow{\Delta E = 36.4 \text{ kJ/mol}} \text{Tp(PMe}_3\text{)RuOH} + \text{HSiMe}_2\text{H} \quad (2.3)
\]
3.1 Introduction

Our group had previously reported the water-promoted hydrogenation of carbon dioxide to formic acid catalyzed by ruthenium solvento-hydride complex TpRu(PPh₃)(CH₃CN)H [151]. It is proposed that the key species, an aquo hydride species TpRu(PPh₃)(H₂O)H, is generated by ligand displacement reaction of TpRu(PPh₃)(CH₃CN)H with H₂O; the aquo hydride complex acts as a metal ligand bifunctional catalyst, transferring the hydride and a proton of the H₂O ligand in a concerted manner to CO₂ to yield formic acid, and itself being converted to a transient hydroxo species, which is reverted to TpRu(PPh₃)(H₂O)H by reaction with H₂ (Scheme 3.1).

Several years later, we reported that alcohols also exhibit a promoting effect in the TpRu(PPh₃)(CH₃CN)H-catalyzed CO₂ hydrogenation reactions [152]. It is believed that the active species in the catalysis is the analogous alcohol-hydride TpRu(PPh₃)(ROH)H; the reaction proceeds via a reaction sequence similar to that shown in Scheme 3.1.

We have learned that the solvento-hydride complex TpRu(PPh₃)(CH₃CN)H reacts with silanes HSiR₃ (R₃ = Ph₃, Ph₂Me, PhMe₂) to yield non-classical silyl
dihydride complexes TpRu(PPh₃)(η³-HSiR₃H). It is of interested to investigate if the electrophilic silyl group and the hydridic hydrogen in the complex can also be transferred in a concerted manner to CO₂ to yield a silyl formate HCOOSiPhMe₂. Several catalytic reductions of carbon dioxide by silane have been reported in recent decades as means of CO₂-transformation [55–64]. Reported here is a study of the reduction of carbon dioxide by PhMe₂SiH in the presence of the complex TpRu(PPh₃)(η³-HSiPhMe₂H). The initial product silyl formate HCOOSiPhMe₂ was found to be further reduced by PhMe₂SiH to give silyl methoxide as the ultimate reduction product.
Scheme 3.1 Proposed mechanism for the TpRu(PPh₃)(CH₃CN)H-catalyzed hydrogenation of carbon dioxide to formic acid
3.2 Experimental Section

3.2.1 Materials and Instrumentation

All manipulations were carried out under an inert nitrogen atmosphere using standard Schlenk techniques. Solvents were dried, degassed, and distilled prior to use: THF, 1,4-dioxane, and diethyl ether from Na benzophenone ketyl, n-hexane and toluene from Na, acetonitrile and dichloromethane from CaH₂. All chemicals were commercially available (Aldrich, Acros, Strem and International Laboratory) and used without further purification. The complex TpRu(PPh₃)(η³-HSiPhMe₂H) was synthesized using the method reported in section 2.2.2.1. The complexes TpRu(PPh₃)(CO)H [153] and TpRu(dppm)H [123] were prepared according to literature methods. Deuterated NMR solvents, purchased from Armar and Cambridge Isotope Laboratories, were dried with P₂O₅ prior to use. ¹H NMR spectra were obtained from a Varian (500 MHz) or Bruker DPX (400 MHz) spectrometer; chemical shifts were reported relative to residual protons of the deuterated solvents. ¹³C NMR spectra were recorded with a Bruker DPX 400 spectrometer at 100.61 MHz; chemical shifts were internally referenced to CD₂Cl₂ (δ = 53.8 ppm). ³¹P NMR spectra were recorded on a Bruker DPX 400 spectrometer at 161.70 MHz; chemical shifts were externally referenced to 85% H₃PO₄ in D₂O (δ = 0.00 ppm).
3.2.2 Reactions

3.2.2.1 NMR-monitoring of the reaction between CO$_2$ and TpRu(PPh$_3$)(η$^3$-HSiPhMe$_2$H) in 1,4-dioxane-d$_8$

The complex TpRu(PPh$_3$)(η$^3$-HSiPhMe$_2$H) (0.016 g, 26 μmol) was dissolved in 1,4-dioxane-d$_8$ (0.4 mL) in a pressure-valved NMR tube, which was then pressurized with 9 bar of CO$_2$. At different time intervals, the tube was cooled to room temperature and $^1$H and $^{31}$P NMR spectra of the solution were taken.

3.2.2.2 NMR-monitoring of the reaction between CO$_2$ and PhMe$_2$SiH in the presence of TpRu(PPh$_3$)(η$^3$-HSiPhMe$_2$H) 1c in 1,4-dioxane-d$_8$

The complex TpRu(PPh$_3$)(η$^3$-HSiPhMe$_2$H) (0.016 g, 26 μmol) and PhMe$_2$SiH (70 μL, 5 equivalence) were dissolved in 1,4-dioxane-d$_8$ (0.4 mL) in a pressure-valved NMR tube. The resulting solution was heated at 110°C under 9 bar of CO$_2$. At different time intervals, the tube was cooled to room temperature and $^1$H and $^{31}$P NMR spectra of the solution were taken.

3.2.2.3 In Situ Preparation of TpRu(PPh$_3$)(CO)(η$^1$-OCHO) (6)

The complex TpRu(PPh$_3$)(CO)H (0.016 g, 26 μmol) was loaded into a 5 mm pressure-valved NMR tube, which was then evacuated and flushed with nitrogen
for four cycles. 1,4-dioxane-$d_8$ (0.2 mL) and formic acid (0.2 mL) were added to the tube via syringes and needles. The tube was sealed and heated at 100°C in a silicone oil bath for 30 mins; it was cooled down to room temperature, and subjected to NMR analysis. $^1$H NMR (400.13 MHz, 1,4-dioxane-$d_8$, 25°C): δ 7.87 (s, 1H, −OCHO) 7.74 (d, 1H; Tp-H), 7.71 (d, 1H; Tp-H), 7.60 (d, 1H; Tp-H), 7.58 (d, 1H; Tp-H), 7.27–7.31 (m, 3H; PPh$_3$−H), 7.14–7.18 (m, 6H; PPh$_3$−H), 7.10 (d, 1H; Tp-H), 6.93–6.97 (m, 6H; PPh$_3$−H), 6.28 (d, 1H; Tp-H), 6.08 (t, 1H; Tp-H), 5.87 (t, 1H; Tp-H), 5.80 (t, 1H; Tp-H). $^{31}$P$	extit{^1}$H NMR (161.7 MHz, 1,4-dioxane-$d_8$, 25°C): δ 44.4 ppm. $^{13}$C$	extit{^1}$H NMR (100.61 MHz, 1,4-dioxane-$d_8$, 25°C): δ 205.10 (d, $^2$J$_{p-C}$ = 15.1 Hz, Ru−CO), δ 167.83 (d, $^1$J$_{C-H}$ = 197 Hz, Ru−OCHO)
3.3 Results and Discussion

3.3.1 NMR monitoring of the reaction between TpRu(PPh₃)(η³-HSiPhMe₂H) (1c) and CO₂ in 1,4-dioxane-d₈

The reaction between the complex TpRu(PPh₃)(η³-HSiPhMe₂H) (1c) and CO₂ was first studied. It is learned that the structurally analogous solvent hydride complex TpRu(PPh₃)(CH₃CN)H reacts with CO₂ to give a solvent formate species TpRu(PPh₃)(CH₃CN)(η¹-OCHO) by insertion of CO₂ into the Ru–H bond [151]; we are curious if CO₂-insertion also occurs for the structurally-similar complex 1c with CO₂.

A 1,4-dioxane-d₈ solution of 1c in a 5-mm Wilmad pressure-valved NMR tube was pressurized with 9 bar CO₂. After heating the tube for 5 mins, the ¹H NMR spectrum of the solution revealed that the methyl peak of TpRu(PPh₃)(η³-HSiPhMe₂H) at δ 0.30 ppm was diminished (Figure 3.1). Two signals were observed at δ 0.55 and 0.28 ppm; they were identified as the methyl peaks of formoxysilane, HCOOSiPhMe₂ and silanol, HOSiPhMe₂. The concurrent ³¹P NMR spectrum indicated that small amounts of hydrido-dihydrogen complex TpRu(PPh₃)(H₂)H (2) and carbonyl-hydride complex TpRu(PPh₃)(CO)H (5) were formed; 1c, however, remained the most abundant metal-containing species in the reaction. Trace amount of H₂ was
generated as evidenced by the observation of a very small signal at δ 4.58 ppm in the 1H NMR spectrum. After heating the solution for another 5 mins, more HCOOSiPhMe2 and HOSiPhMe2 were formed; the amounts of both complexes 3 and 5 increase at the expense of 1c, with the rate of increase of 5 being more prominent. Further heating the solution for 5 mins, not only was the amount of 1c decreased but also that of HCOOSiPhMe2, and HOSiPhMe2 became the most abundant silicon containing species. More hydrogen was produced at this stage.

Trace amount of formic acid HCOOH was also observed. At the end of the heating process, 1c and HCOOSiPhMe2 totally disappeared and HOSiPhMe2 was the only detectable silicon containing species. The major ruthenium containing species is 5.

The results of the NMR monitoring experiment show that 1c is probably the active species in the hydrosilylation of carbon dioxide by HSiPhMe2 to HCOOSiPhMe2 (see next section). The CO2 reacts with the Si–H bond in 1c without prior coordination to the Ru center (Cycle A, Scheme 3.2). In other words, 1a may act as a bifunctional catalyst, transfering its hydride and SiMe2Ph moiety in a concerted manner, respectively, to the carbon and oxygen of CO2 to afford HCOOSiPhMe2. Another route that might be operative is that the CO2 might have displaced silane in 1c and coordinate to ruthenium center and
inserted into the Ru–H bond to form a ruthenium formate. Re-coordination of silane and σ-metathesis between the η^3^-silane and formate ligand results in the formation of HCOOSiPhMe₂ (Cycle B, Scheme 3.2).
Figure 3.1. $^1$H NMR monitoring of the reaction between 1c and carbon dioxide in 1,4-dioxane-$d_8$
Scheme 3.2 Suggested pathways for the reaction between 1c and CO$_2$ to give HCOOSiPhMe$_2$. 
The formoxysilane HCOOSiPhMe$_2$, which has never been isolated, is probably a highly reactive species. Its –CHO group reacts further with the TpRu(PPh$_3$)H fragment to give the carbonyl hydride complex 5, and itself is converted into a silanol HOSiPhMe$_2$ (eq. 3.1). Decarbonylation of formyl group by transition metal complexes to form carbonyl complexes is well-established [154-160]. The identity of HOSiPhMe$_2$ was confirmed by adding an authentic sample of the silanol into the reaction mixture at the end of the monitoring experiment. The mechanism of the decarbonylation of –CHO group in HCOOSiPhMe$_2$ might be similar to the one proposed by our group in an earlier report for the reaction between TpRu(PPh$_3$)(CH$_3$CN)H and aldehyde (RCHO) to give TpRu(PPh$_3$)(CO)R (Scheme 3.3) [137]. We propose in Scheme 3.4 a possible pathway for the decarbonylation of HCOOSiPhMe$_2$ by TpRu(PPh$_3$)H to give HOSiPhMe$_2$ and 5. The hydrogen produced during the carbonylation of TpRu(PPh$_3$)H by HCOOSiPhMe$_2$ to give 5 might react with TpRu(PPh$_3$)H to give small amount of the hydrido-dihydrogen species 2 (eq. 3.2). In the reaction, the formic acid produced may be due to the reduction of CO$_2$ by H$_2$ catalyzed by TpRu(PPh$_3$)(η$_3$-HSiPhMe$_2$H) or TpRu(PPh$_3$)H fragment.
Scheme 3.3  Proposed mechanism for the decarbonylation of aldehyde with TpRu(PPh₃)(CH₃CN)H

Scheme 3.4  Proposed mechanism for the decarbonylation of HCOOSiPhMe₂ by TpRu(PPh₃)H

\[
\text{Tp(PPh₃)Ru-H} + \text{HC=O} \rightarrow \text{Tp(PPh₃)Ru-H} + \text{HOSiPhMe₂} \quad (3.1)
\]

\[
\text{Ru=H} \quad \text{O=O} \quad \text{Ru-H} \quad \text{Ru-H} \rightarrow \text{Ru-OSiPhMe₂} \rightarrow \text{Ru-OSiPhMe₂} \rightarrow \text{Ru-H} + \text{HOSiPhMe₂} \quad (3.2)
\]

\[
\text{Tp(PPh₃)Ru-H} + \text{H₂} \rightarrow \text{Tp(PPh₃)Ru(H₂)H} \quad (3.2)
\]
The overall equation for the reaction between complex 1c and carbon dioxide is represented in eq. 3.3. Noteworthy of this reaction is to view it as transfer of an oxygen atom from CO$_2$ to PhMe$_2$SiH (coordinated) to afford HOSiPhMe$_2$; the CO$_2$ is reduced to CO (coordinated). It is believed that such a reaction (eq. 3.4) might be turned into a catalytic process if appropriate catalytic system was employed. Zhang et. al. reported organocatalytic oxidation of aldehydes to carboxylic acids using carbon dioxide as a source of oxygen [161]; the CO$_2$ is reduced to CO.

\[
\text{Tp(PPh$_3$)Ru} \begin{array}{c} \text{H} \\ \text{H}^- \text{SiPhMe}_2 \end{array} + \begin{array}{c} \text{O} \\ \text{C} \end{array} \xrightarrow{\text{cat.}} \text{Tp(PPh$_3$)Ru} \begin{array}{c} \text{H} \\ \text{CO} \end{array} + \text{HOSiPhMe}_2
\]

(3.3)

\[
\text{R}_3\text{Si} \begin{array}{c} \text{H} \\ \text{C} \end{array} \xrightarrow{\text{cat.}} \text{R}_3\text{SiOH} + \text{CO}
\]

(3.4)
3.3.2 NMR monitoring of the catalytic reduction of CO₂ by PhMe₂SiH with 1c.

The monitoring experiment in the previous section implies the possibility of using 1c as a catalyst for the hydrosilylation of carbon dioxide by PhMe₂SiH. We therefore monitored the reaction between PhMe₂SiH and CO₂ in the presence of 1c. Surprisingly, it is learned that, the CO₂ reduction did not stop at the formoxysilane stage, further reduced products were also observed, despite low turnover.

A solution of 1c and PhMe₂SiH (20 equiv relative to 1c) in 1,4-dioxane-\(d_8\) was pressurized with 9 bar of CO₂. The \(^1\)H NMR spectrum taken after heating the solution at 110°C for 15 mins revealed that approximately 25% of PhMe₂SiH was converted to HCOOSiPhMe₂ (15%) and HOSiPhMe₂ (10%), also present were hydrogen gas and formic acid. About 90% of 1c was converted to the carbonyl-hydride complex 5 as indicated in the concurrent \(^{31}\)P\{\(^1\)H\} spectrum. A small phosphorus peak at \(\delta\) 41.2 ppm was also seen. The solution was then heated for a further 45 mins. At the end of this period the conversion of PhMe₂SiH to HCOOSiPhMe₂ and HOSiPhMe₂ were increased to about 25% and 15%, respectively. Except for the unknown species which showed the signal at \(\delta\) 41.2 ppm in the \(^{31}\)P\{\(^1\)H\} spectrum, 5 was the only detectable metal-containing
species. After heating the solution for further 60 mins, the $^1$H and $^{13}$C NMR spectra of the resulting solution showed the formation of a new ruthenium species (appearance of a new set of Tp peaks) and a silyl methoxide PhMe$_2$SiOCH$_3$ (~5%). Also observed were trace amounts of formaldehyde, bis(silyl)acetal (PhMe$_2$SiO)$_2$CH$_2$, hemi(silyl)acetal PhMe$_2$SiOCH$_2$OH, and methanol. The NMR chemical shifts and splitting patterns of all the organic species generated in this experiment are tabulated in Table 3.1. $^{31}$P$_1$$^1$H NMR spectrum indicated that about half of 5 was converted to a new species 6 showing a signal at $\delta$ 44.4 ppm. Analysis of the NMR spectra of the solution taken at different time indicated that the amount of silyl methoxide PhMe$_2$SiOCH$_3$ gradually increased, while the quantity of HCOOSiPhMe$_2$ remains fairly constant; and those of HCOOH and PhMe$_2$SiH decrease slowly. The peaks due to (PhMe$_2$SiO)$_2$CH$_2$, PhMe$_2$SiOCH$_2$OH, and methanol were kept visible, although in minute amounts. A new phosphorus peak at $\delta$ –5.7 ppm characteristic of free PPh$_3$ was observed and grew in intensity, accompanied by diminish of the amount of 6 and development of a new ruthenium species 7 which exhibits a new set of six peaks due to Tp ligand and a singlet hydride signal at $\delta$ –10.1 ppm in the $^1$H spectrum. At the end of the monitoring experiment, the amount of PhMe$_2$SiOCH$_3$ was increased to about 20%; the phosphorus peak at $\delta$ 44.4 ppm
due to 6 almost vanished; 5 and 7 are the two dominant ruthenium-containing species in the reaction mixture. The conversion to Figure 3.1 shows the $^{31}$P-$^1$H{NMR spectra of the reaction solution taken at different time interval.

Table 3.1 NMR-data of the organic compounds generated in the reaction between CO$_2$ and PhMe$_2$SiH in the presence of 1c in 1,4-dioxane-$d_8$.

<table>
<thead>
<tr>
<th>organic compounds</th>
<th>NMR data</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhMe$_2$Si–OH</td>
<td>$^1$H: δ 0.28 ppm, s, 3H; Si–CH$_3$</td>
</tr>
<tr>
<td></td>
<td>$^{13}$C: δ 160.7 ppm, Si–OCHO, split into a doublet ($^1$J$_{C-H}$ = 224.3 Hz) in $^1$H-coupled spectrum</td>
</tr>
<tr>
<td>formoxysilane</td>
<td></td>
</tr>
<tr>
<td>PhMe$_2$SiO—CH$_2$</td>
<td>$^1$H: δ 5.05 ppm, s, 2H; O–CH$_2$–O</td>
</tr>
<tr>
<td></td>
<td>$^{13}$C: δ 84.3 ppm, O–CH$<em>2$–O, split into a triplet ($^1$J$</em>{C-H}$ = 162.3 Hz) in $^1$H-coupled spectrum</td>
</tr>
<tr>
<td>bis(silyl)acetal</td>
<td></td>
</tr>
<tr>
<td>PhMe$_2$SiO–OCH$_3$</td>
<td>$^1$H: δ 3.39 ppm, s, 3H; Si–OCH$_3$</td>
</tr>
<tr>
<td>Silyl methoxide</td>
<td>$^{13}$C: δ 49.8 ppm, Si–OCH$<em>3$, split into a quartet ($^1$J$</em>{C-H}$ = 141.0 Hz) in $^1$H-coupled spectrum</td>
</tr>
<tr>
<td>PhMe$_2$SiO—CH$_2$–OH</td>
<td>$^1$H: δ 4.78 ppm, d, $^3$J = 6 Hz, 2H; O–CH$_2$–OH</td>
</tr>
<tr>
<td>hemi(silyl)acetal</td>
<td>$^{13}$C: δ 91.0 ppm, O–CH$<em>2$–O, split into a triplet ($^1$J$</em>{C-H}$ = 160.0 Hz) in $^1$H-coupled spectrum</td>
</tr>
<tr>
<td>HCOOH</td>
<td>$^1$H: δ 7.93 ppm, s, 1H; HCOOH</td>
</tr>
<tr>
<td></td>
<td>$^{13}$C: δ 161.6 ppm, split into a doublet in 1H-coupled spectrum ($^1$J$_{C-H}$ = 218.0 Hz),</td>
</tr>
<tr>
<td>HCHO</td>
<td>$^1$H: δ 9.50 ppm, s, 1H; HCHO</td>
</tr>
<tr>
<td></td>
<td>$^{13}$C: δ 194.7 ppm, split into a triplet in $^1$H-coupled spectrum ($^1$J$_{C-H}$ = 177.2 Hz), HCHO</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>$^1$H: δ 3.29 ppm, d, $^3$J = 6 Hz, 3H; CH$_3$OH</td>
</tr>
</tbody>
</table>
Figure 3.2 $^{31}$P NMR monitoring of the 1c-catalyzed reduction of carbon dioxide by PhMe$_2$SiH in 1,4-dioxane-$d_8$
The monitoring result showed that the reduction of carbon dioxide by PhMe₂SiH in the presence of 1c leads to the formation of silyl methoxide PhMe₂SiOCH₃ as the ultimately-reduced product. The silyl formate HCOOSiPhMe₂ and bis(silyl)acetal (PhMe₂SiO)₂CH₂ were the intermediates in the sequential reduction of CO₂ (Scheme 3.5).

![Scheme 3.5 Sequential reduction of CO₂ by PhMe₂SiH to PhMe₂SiOCH₃](image)

In the first hour of the monitoring experiment carbon dioxide reacts with PhMe₂SiH to afford about 25% of HCOOSiPhMe₂ in the presence of 1c (See Scheme 3.2). The HCOOSiPhMe₂ then reacts with [Ru]–H to give quantitative yield of the silanol HOSiPhMe₂ and Tp(PPh₃)Ru(CO)H (5), which alone did not catalyze CO₂ hydrosilylation. It is proposed that the reaction sequence depicted
in Scheme 3.4 lead to the formation of the silanol and 5. The formation of hydrogen gas might be a result of the decarbonylation of HCOOSiPhMe$_2$ by Tp(PPh$_3$)RuH moiety. The generated H$_2$ then reduces CO$_2$ in the presence of 1c to formic acid. It should be noted that, the amount of the silanol PhMe$_2$SiOH detected in this period, which should be the same as that of 1c, was slightly higher than expected and this is probably a result of the oxidation of PhMe$_2$SiH by trace amount of water in the presence of 1c as we reported in the previous section. Decarbonylation of –CHO group forming metal-carbonyl species often causes catalyst deactivation [162-164], and this resulted in low conversion of PhMe$_2$SiH to HCOOSiPhMe$_2$ in our catalytic system. To investigate the possibility of raising the yield of HCOOSiPhMe$_2$, we repeated our monitoring experiment under identical reaction conditions except the addition of an equivalent amount (relative to 1c) of a bis(diphenylphosphino)methane complex TpRu(dppm)H 9, which does not undergo deactivation by carbonylation due to chealting effect of the bidentate dppm ligand. The new monitoring experiment showed that the conversion of PhMe$_2$SiH to HCOOSiPhMe$_2$ was increased to about 80%.

Complex 6, observed after heating the solution for 2 hrs, is suggested to be
a ruthenium carbonyl formate species $\text{TpRu(PPh}_3(\text{CO})(\eta^1\text{-OCHO})$. The $^1\text{H}$ NMR spectrum of the solution taken after this 2-hr period showed, in addition to the peaks pertaining to the Tp ligand of 6, a singlet at $\delta$ 7.88 ppm integrated for 1H. This peak could be ascribed to a formate hydrogen. In the $^{13}\text{C} \{^1\text{H}\}$ NMR spectrum of the solution using labeled $^{13}\text{CO}_2$, a singlet signal is observed at $\delta$168 ppm, and is splitted into a doublet with $^{1}J_{\text{C-H}} = 197.0$ Hz in the $^1\text{H}$-coupled spectrum. This signal is assignable to the formate carbon. In addition, a doublet was observed at 205.1 ppm; this peak is attributable to the carbon of a CO ligand. The doublet nature of the peak is a result of the coupling of the carbon with the phosphorus of the PPh$_3$ ligand ($^{2}J_{\text{C-P}} = 15.1$ Hz). Formation of the formate complex 6 is probably due to protonation of the carbonyl hydride complex 5 by formic acid (eq. 3.5). Although attempt to isolate 6 was frustrated by its decarboxylation back to 5 during workup, the formate complex was obtained in a highly pure form in solution by treatment of 5 with a large excess of formic acid and is characterized by $^1\text{H}$ and $^{31}\text{P}$ NMR spectroscopies. The fact that the further-reduced products of CO$_2$, i.e. (PhMe$_2$SiO)$_2$CH$_2$ and PhMe$_2$SiOCH$_3$, were observed as long as 6 was present might imply that the formate complex 6, or species derived from it but not visible in the NMR spectra, is the active catalyst for the further-reduction of HCOOSiPhMe$_2$ by PhMe$_2$SiH.
Complex 7 is likely to be a ruthenium dicarbonyl-hydride TpRu(CO)$_2$H [165]. The proton NMR spectrum taken in the monitoring experiment showed a set of six peaks due to Tp ligand, which implies that two of the three legs trans to the Tp ligand in an octahedral configuration are equivalent. In addition to these Tp-peaks, a singlet hydride signal at δ –10.1 ppm was also observed. The fact that this singlet hydride signal is splitted into a triplet when $^{13}$CO$_2$ is used strongly rents support to the identity of 7. Formation of the dicarbonyl-hydride complex 7 is probably a result of dissociation of the PPh$_3$ ligand in the formate complex 6 followed by carbonylation. The source of the second CO ligand is probably formaldehyde generated in the reaction. Scheme 3.6 depicts the suggested pathway for the carbonylation reaction. Complete conversion of 6 to 7 takes days, and this suggest that the PPh$_3$ ligand in 6 is not so substitutionally labile.

$$\text{Tp(PPh}_3\text{)Ru} + \text{HCOOH} \rightarrow \text{Tp(PPh}_3\text{)Ru(OCHO) + H}_2$$

(3.5)
Scheme 3.6. Suggested mechanism for the conversion of the carbonyl formate complex (6) to dicarbonyl hydride complex (7).

3.3.3 Suggested Mechanism of Formoxysilane Reduction

There is no information from NMR spectra on how the carbonyl-formate complex 6 catalyzes the reduction of HCOOSiPhMe₂ by PhMe₂SiH, we can therefore only speculate the route by which the reduction takes place. The formate ligand might have been displaced by silane to give a cationic silane complex [TpRu(PPh₃)(CO)(η²-HSiPhMe₂)](OCHO) (8) (eq. 3.6). The highly electrophilic silicon center in this complex might be having some interaction with the oxygen of the formate anion. We suggest that the cationic silane
complex 8 catalyzes the reduction of HCOOSiPhMe$_2$ via a 4-center intermediate as proposed in Scheme 3.7; transfer of the hydride and silyl group of the silane to, respectively, the carbon and oxygen of the carbonyl group in HCOOSiPhMe$_2$ affords bis(silyl)acetal (PhMe$_2$SiO)$_2$CH$_2$. The suggested mechanism is similar to that of the rhenium-catalyzed hydrosilylation of aldehydes/ketones proposed by Abu-Omar [166]. In this reaction, the silane coordinates to the metal in an $\eta^2$ fashion and is then attacked by the aldehyde/ketone to give silyl ether; coordination of the carbonyl compound to the metal center is not required.

\[
\text{Tp(PPh}_3\text{)RuOCHO} + \text{HSiPhMe}_2 \overset{\text{6}}{\longrightarrow} \text{Tp(PPh}_3\text{)RuH}^+ \text{SiPhMe}_2^- \text{OCHO} \quad (3.6)
\]
Scheme 3.7 Suggested mechanism for the 8-catalyzed reduction of HCOOSiPhMe₂ to (PhMe₂SiO)₂CH₂

The ability of the bis(silyl)acetal (PhMe₂SiO)₂CH₂ to undergo further reduction by PhMe₂SiH to methoxide PhMe₂SiOCH₃ is probably a result of its decomposition to formaldehyde along with disiloxane (PhMe₂Si)₂O (eq. 3.7). The formaldehyde was then hydrosilylated by PhMe₂SiH to PhMe₂SiOCH₃ with the carbonyl-formate complex 6 (eq. 3.8), presumably via the formation of the cationic silane species 8 and a mechanism similar to that for the reduction of HCOOSiPhMe₂ by PhMe₂SiH (Scheme 3.8). Hydrosilylation of aldehydes to silyl ethers is a well-known reaction and is catalyzed by large number of transition metal complexes. Although we were unable to identify the disiloxane
in the reaction mixture because its methyl peak probably overlaps with that of PhMe₂SiOCH₃ (identified by the more upfield Si–OCH₃ but not Si–CH₃) in the \(^1\)H NMR spectrum, we did confirm the presence of formaldehyde by observation of its characteristic peaks in the \(^1\)H and \(^{13}\)C NMR spectra (see Table 4.1). The density function theory study performed by Wang et al. for the N-heterocyclic carbene-catalyzed reduction of CO₂ into methanol with silane revealed that formaldehyde is an indispensable intermediate in the course of reduction [65]. We believe that we are the first group to detect formaldehyde during the reduction of carbon dioxide by silane.

\[
\begin{align*}
\text{PhMe}_2\text{SiO} & \quad \text{C} \quad \text{OSiMe}_2\text{Ph} \quad \text{O} \\
\text{H} \quad \text{H} & \quad \text{H} \quad \text{H} \\
\text{bis(silyl)acetal} & \quad \text{disiloxane} (3.7)
\end{align*}
\]

\[
\begin{align*}
\text{H} \quad \text{H} & \quad \text{H} \quad \text{SiPhMe}_2 \\
\text{O} & \quad \text{H} \quad \text{H} \quad \text{H} \\
\text{methoxysilane} & \quad \text{H}_3\text{CO} \quad \text{SiPhMe}_2 (3.8)
\end{align*}
\]
Scheme 3.8. Suggested mechanism for the 8-catalyzed reduction formaldehyde to PhMe₂SiOCH₃

The formation of trace amount of hemiacetal PhMe₂SiOCH₂OH might be due to the reduction of HCOOSiPhMe₂ by hydrogen in the reaction mixture (eq. 3.9), whereas the formation of methanol might be a result of the reduction of formaldehyde by hydrogen (eq. 3.10).

\[
\begin{align*}
\text{PhMe}_2\text{SiOCH}_2\text{OH} \quad \text{formation trace amount} \\
\text{PhMe}_2\text{SiOCH}_3 \quad \text{methanol formation}
\end{align*}
\]

(eq. 3.9)
The PPh$_3$ dissociated from 1c may be responsible for the consumptions of HCOOH and PhMe$_2$SiH at the later stage of the NMR monitoring experiment [167]. Independently performed experiment confirmed that HCOOH reacts with PhMe$_2$SiH to form HCOOSiPhMe$_2$ in the presence of PPh$_3$ in 1,4-dioxane (eq. 3.11).

$$\begin{align*}
\text{HCOOH} + \text{HSiPhMe}_2 & \xrightleftharpoons[\text{PPh}_3]{\text{eq. 3.11}} \text{HCOOSiPhMe}_2 + \text{H}_2
\end{align*}$$
Chapter 4  Electrophilic Ruthenium-complexes-catalyzed $\beta$-Alkylation of Secondary Alcohols with Primary Alcohols and Transfer Hydrogenation of Carbonyl Compounds with 1,4-Butanediol

4.1 Introduction

Transition metal-catalyzed transfer hydrogenation of carbonyl compounds and $\beta$-alkylation of secondary alcohols with primary alcohols are two actively investigated reactions [77–80, 109–112]. Known catalytic systems for affecting these organic transformations are mainly based on electroneutral complexes; the use of electrophilic complexes for these reactions are, however, relatively unexplored [77–92, 114–120]. Continuing our interest on the use of Lewis acidic ruthenium complexes for catalytic reactions, we report here that the air-stable, bipyridine supported dicationic ruthenium complexes $\textit{cis}$-$\text{[Ru}(6,6-X_2\text{bpy})_2(\text{H}_2\text{O})_2]\text{OTf}_2 \ (X = \text{Cl, Me})$ are active catalysts towards $\beta$-alkylation of secondary alcohols with primary alcohols and transfer hydrogenation of carbonyl compounds with 1,4-butanediol. Both catalytic processes require no inert atmosphere for protection as a result of the high air stabilities of the complexes.
4.2 Experimental Section

4.2.1 Materials and Instrumentation

All syntheses of complexes were carried out under an inert nitrogen atmosphere using standard Schlenk techniques. Solvents were dried, degassed, and distilled before using: diethyl ether from Na/benzophenone, n-hexane and toluene from Na. All organic and inorganic compounds were commercially available (Aldrich, Acros, Strem and International Laboratory) and used without further purification. The complex \( \text{cis-}[\text{Ru}(6,6'-\text{Cl}_2\text{bpy})_2(\text{H}_2\text{O})_2](\text{OTf})_2 \) was prepared according to literature methods [168]. The complex \( \text{cis-}[\text{Ru}(6,6'-\text{Me}_2\text{bpy})_2(\text{H}_2\text{O})_2](\text{OTf})_2 \) was synthesized using the same method as for the synthesis of \( \text{cis-}[\text{Ru}(6,6'-\text{Cl}_2\text{bpy})_2(\text{H}_2\text{O})_2](\text{OTf})_2 \) except 6,6’-Me_2bpy was used instead of 6,6’-Cl_2bpy. Deuterated NMR solvents, purchased from Armar and Cambridge Isotope Laboratories, were dried with P_2O_5 prior to use. 

\(^1\)H NMR spectra were obtained from a Varian (500 MHz) or Bruker DPX (400 MHz) spectrometer; chemical shifts were reported relative to residual protons of the deuterated solvents. Electrospray ionization mass spectrometry was carried out with a Finnigan MAT 95S mass spectrometer with the samples dissolved in dichloromethane.
4.2.2 Reactions

4.2.2.1 General Procedure for catalytic β-Alkylation of Secondary Alcohols with Primary Alcohols

The reactions were carried out in 11-mm Schlenk tubes equipped with Teflon screw caps. In a typical run, ruthenium complex (0.005 mmol) and NaOH (0.25 mmol) were loaded into the tube equipped with a magnetic stirrer. Secondary alcohol (1.25 mmol) and primary alcohol (1.5 mmol) were then added to the tube via syringes. The tube was sealed with the screw cap and the solution was stirred in a 120°C silicon oil bath for 24 h. At the end of the reaction, the tube was cooled to room temperature; a 0.1 mL aliquot of the solution was removed and analyzed by proton NMR spectroscopy (in CDCl₃). Comparison of the integrations of the characteristic peaks of the product and the unreacted secondary alcohol gave the conversion of the reaction. In cases where the products are new compounds, they were isolated by flash column chromatography on silica gel or with preparative thin layer chromatography (silica gel).
4.2.2.2 3-(2-methoxyphenyl)-1-phenylpropan-1-ol:

\[
\text{OH} \quad \begin{array}{c}
\text{H}_3\text{CO} \\
\end{array}
\]

pale yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.38-6.87 (m, 9H), 4.64 (t, \(J = 6\) Hz, 1H), 3.84 (s, 1H), 2.80-2.76 (t, \(J = 8\) Hz, 2H), 2.49 (s, 1H), 2.11-2.01 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 157.4, 144.7, 130.1, 128.4, 127.4, 127.3, 126.0, 120.7, 110.4, 73.6, 55.4, 39.4, 26.5; HRMS (+ESI): \(m/z\) calcd for \(C_{16}H_{18}O_2Na^+\): 265.1204; found: 265.1216 [M+Na]\(^+\).

4.2.2.3 3-(3,4-dimethoxyphenyl)-1-phenylpropan-1-ol:

\[
\text{OH} \quad \begin{array}{c}
\text{OCH}_3 \\
\end{array} \begin{array}{c}
\text{OCH}_3 \\
\end{array}
\]

pale yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.38-7.30, 6.82-6.76 (m, 8H), 4.68 (t, \(J = 6\) Hz, 1H), 3.86 (s, 6H), 2.90 (s, 1H), 2.74-2.65 (m, 2H), 2.15-2.04 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 148.8, 147.1, 144.8, 134.5, 128.4, 127.5, 126.0, 120.3, 111.9, 111.4, 73.7, 55.9, 55.8, 40.7, 31.7; HRMS (+ESI): \(m/z\) calcd for \(C_{17}H_{20}O_3Na^+\): 295.1310; found: 295.1313 [M+Na]\(^+\).
4.2.2.4 3-(4-fluorophenyl)-1-phenyl-propan-1-ol:

\[
\text{colorless oil; } ^1\text{H NMR (400 MHz, CDCl}_3) \delta 7.37-6.94 \text{ (m, 9H), 4.61 (t, } J = 6\text{Hz, 1H), 2.69-2.60 \text{ (m, 2H), 2.48 (s, 1H), 2.08-1.95 \text{ (m, 2H); } ^{13}\text{C NMR (100 MHz, CDCl}_3) \delta 162.5, 160.1, 144.5, 137.5, 137.4, 129.8, 128.6, 127.7, 126.0, 115.2, 115.0, 73.7, 40.6, 31.2; HRMS (+ESI): m/z: calcd for C}_{15}\text{H}_{15}\text{OFNa}^+: 253.1005; found: 253.1017 [M+Na]^+.}
\]

4.2.2.5 1-cyclohexyl-1-phenylpropan-1-ol:

\[
\text{white solid; } ^1\text{H NMR (400 MHz, CDCl}_3) \delta 7.36-7.25 \text{ (m, 5H), 4.62 (t, } J = 6\text{Hz, 1H), 1.88 (s, 1H), 1.73-1.67 \text{ (m, 6H), 1.26-1.13 \text{ (m, 7H), 0.87-0.85 \text{ (m, 2H); } ^{13}\text{C NMR (100 MHz, CDCl}_3) \delta 145.6, 129.1, 127.9, 126.6, 75.7, 38.3, 37.0, 34.1, 34.0, 27.3, 27.0. HRMS (+ESI): m/z: calcd for C}_{15}\text{H}_{22}\text{ONa}^+: 241.1568; found: 241.1559 [M+Na]^+.}
\]
4.2.2.6 3-(furan-2-yl)-1-phenylpropan-1-ol:

\[
\text{OH} \quad \text{O}
\]

pale yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34-7.27 (m, 6H), 6.28 (d, $J = 2$ Hz, 1H), 5.99 (d, $J = 2$ Hz, 1H), 4.65 (t, $J = 6$ Hz, 1H), 2.72-2.67 (m, 2H), 2.40 (s, 1H), 2.09-2.02 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.6, 144.4, 141.0, 128.5, 127.7, 126.0, 110.2, 105.1, 73.6, 37.1, 24.4. HRMS (+ESI): $m/z$: calcd for C$_{15}$H$_{22}$ONa$: 241.1568$; found: 241.1559 [M+Na$]^+$. 

4.2.2.7 1-phenyl-(3-thiophen-2-yl)-propan-1-ol:

\[
\text{OH} \quad \text{S}
\]

colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35-7.27 (m, 5H), 7.13 (d, $J = 5$ Hz, 1H), 6.93 (dd, $J = 5$, 3 Hz, 1H), 6.81 (d, $J = 3$ Hz, 1H), 4.67 (t, $J = 6$ Hz, 1H), 2.94-2.88 (m, 2H), 2.46 (s, 1H), 2.18-2.05 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.7, 144.4, 128.6, 127.7, 126.9, 126.0, 124.4, 123.2, 73.5, 40.7, 26.3. HRMS (+ESI): $m/z$: calcd for C$_{13}$H$_{14}$ONaS$: 241.0663$; found: 241.0663 [M+Na$]^+$. 
4.2.2.8 General Procedures for the transfer hydrogenation of ketones and aldehydes with 1,4-butanediol

The reactions were carried out in Schlenk tubes equipped with Teflon screw caps. In a typical run, ruthenium complex (0.01 mmol) and NaOH (0.25 mmol) were loaded into the tube equipped with a magnetic stirrer. The carbonyl compound (1 mmol) was then added to the tube (via syringe in case the compound is a liquid), followed by addition of 1,4-butanediol (0.089 mL, 1 mmol) and toluene (1 mL) via syringes. The tube was sealed with the screw cap and the solution was refluxed in a silicon oil bath for 24 h. At the end of the reaction, the tube was cooled to room temperature; a 0.1 mL aliquot of the solution was removed and analyzed by proton NMR spectroscopy (in CDCl₃). Comparison of the integrations of the characteristic peaks of the product and the unreacted carbonyl compound gave the conversion of the reaction.
4.3 Results and Discussion

4.3.1 β-Alkylation of Secondary Alcohols with Primary Alcohols catalyzed by cis-[Ru(6,6’-Cl₂bpy)₂(H₂O)₂](OTf)₂ (10)

We first studied the catalytic β-alkylation of 1-phenylethanol with benzyl alcohol to give 1,3-diphenyl-1-propanol with bipyridine ruthenium complexes. It can be seen from Table 4.1 that the dichloro-substituted bpy-ruthenium complex cis-[Ru(6,6’-Cl₂bpy)₂(H₂O)₂](OTf)₂ 10 demonstrates higher catalytic activity towards the alkylation reaction than the analogous dimethyl bpy-ruthenium complex cis-[Ru(6,6’-Me₂bpy)₂(H₂O)₂](OTf)₂ 11 under identical reaction conditions (entries 1–2). The closely related 2,9-dimethylphenanthroline complex cis-[Ru(2,9-dmp)₂(H₂O)₂](OTf)₂ 12 was also found to be less active than the dichloro bpy complex (entry 3). cis-[Ru(6,6’-Cl₂bpy)₂Cl₂] 13, the precursor complex of 10, also shows lower catalytic activity. Among the bases examined NaOH was found to give the highest yield of product (entries 5–6). The reaction proceeds at a faster rate under solventless condition (entries 7–9). Performing the reaction at lower temperatures resulted in significant reduction of product conversions (entries 10–12).
Table 4.1. Optimization of β-alkylation of secondary alcohols with primary alcohols

![Chemical structure](image)

<table>
<thead>
<tr>
<th>entry</th>
<th>Catalyst</th>
<th>base</th>
<th>solvent</th>
<th>conversion[^b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>cis-<a href="OTf">Ru(6,6'-Cl2bpy)2(H2O)2</a>2</td>
<td>NaOH</td>
<td>none</td>
<td>87(7)</td>
</tr>
<tr>
<td>2</td>
<td>cis-<a href="OTf">Ru(6,6'-Me2bpy)2(H2O)2</a>2</td>
<td>NaOH</td>
<td>none</td>
<td>45(2)</td>
</tr>
<tr>
<td>3</td>
<td>cis-<a href="OTf">Ru(2,9-dmp)2(H2O)2</a>2</td>
<td>NaOH</td>
<td>none</td>
<td>34(0)</td>
</tr>
<tr>
<td>4</td>
<td>cis-[Ru(6,6' -Cl2bpy)2Cl2]</td>
<td>NaOH</td>
<td>none</td>
<td>55(23)</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>Cs2CO3</td>
<td>none</td>
<td>35(2)</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>KO'Hbu</td>
<td>none</td>
<td>78(4)</td>
</tr>
<tr>
<td>7</td>
<td>10</td>
<td>NaOH</td>
<td>toluene[^c]</td>
<td>80(4)</td>
</tr>
<tr>
<td>8</td>
<td>10</td>
<td>NaOH</td>
<td>dioxane[^c]</td>
<td>42(5)</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
<td>NaOH</td>
<td>THF[^c]</td>
<td>40(5)</td>
</tr>
<tr>
<td>10[^d]</td>
<td>10</td>
<td>NaOH</td>
<td>none</td>
<td>3(2)</td>
</tr>
<tr>
<td>11[^e]</td>
<td>10</td>
<td>NaOH</td>
<td>none</td>
<td>28(2)</td>
</tr>
<tr>
<td>12[^f]</td>
<td>10</td>
<td>NaOH</td>
<td>none</td>
<td>68(2)</td>
</tr>
</tbody>
</table>

[^a] Reaction conditions: catalyst (0.005 mmol, 0.4 mol% relative to 2° alcohol), 2° alcohol (1.25 mmol), 1° alcohol (1.5 mmol), NaOH (0.25 mmol, 20 mol% referred to 2° alcohol), 120°C, 24 h.

[^b] Conversion (based on 1-phenylethanol) determined by 1H NMR spectroscopy. Values in parenthesis indicate the conversion of corresponding ketone.

[^c] 0.3 mL of solvent was used.

[^d] The reaction was performed at 60°C.

[^e] The reaction was performed at 80°C.

[^f] The reaction was performed at 100°C.

Subsequently, we apply the optimized reaction conditions to a variety of secondary alcohols and primary alcohols, and the results are listed in Table 4.2. In a few cases (entries 2, 4–7, 12) where the β-alkylation
products are new compounds, they were isolated and characterized, and their yields are reported. Aryl methyl carbinols can be alkylated with various primary alcohols. The reactions with benzyl alcohols and heterocyclic alcohols (entries 2–7) give higher conversions than with primary aliphatic alcohols (entries 8–12). The lowering of the conversion in alkylation reactions with primary alkyl alcohols is not attributable to self-condensation of these alcohols because no self-condensation products were detected in the reactions; it might be the result of the diminished electrophilicity of the carbonyl carbon atoms of the aldehydes generated via oxidation of the primary alkyl alcohols. Alkyl methyl carbinols seem to be less active than their aryl analogues toward the alkylation reaction (entries 15–17). 1-Phenyl-1-propanol, however, does not undergo alkylation. The dichloro bpy complex is basically inactive for the β-alkylation of alkyl methyl carbinols with primary alkyl alcohols (entries 20–21). Alkylation of 1,2,3,4-tetrahydro-1-napthol gives mixtures of diastereomers (entries 18–19).
<table>
<thead>
<tr>
<th>entry</th>
<th>2° alcohol</th>
<th>1° alcohol</th>
<th>product</th>
<th>conversion (%)&lt;sup&gt;[b]&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td>92 (8)</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td>89(11) [83]</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td>88(8)</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td>86(14) [83]</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td>86(9) [76]</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td>84(13) [76]</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td></td>
<td>90(6) [85]</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td>88(9)</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td></td>
<td></td>
<td>75(4)</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td>46(3)</td>
</tr>
</tbody>
</table>
11 \[
\text{Ph} \quad \text{HO} \quad \text{Ph} \quad \text{OH} \quad 32(7)
\]

12 \[
\text{Ph} \quad \text{HO} \quad \text{C}_8 \quad \text{OH} \quad 77(23) \ [71]
\]

13 \[
\text{H}_2\text{CO} \quad \text{Ph} \quad \text{HO} \quad \text{Ph} \quad 64(29)
\]

14 \[
\text{Cl} \quad \text{Ph} \quad \text{HO} \quad \text{Ph} \quad 86(10)
\]

15 \[
\text{Ph} \quad \text{HO} \quad \text{Ph} \quad \text{Ph} \quad 72(9)
\]

16 \[
\text{C}_8 \quad \text{HO} \quad \text{Ph} \quad \text{OH} \quad 64(14)
\]

17 \[
\text{C}_8 \quad \text{HO} \quad \text{Ph} \quad \text{AH} \quad 60(8)
\]

18 \[
\text{C}_8 \quad \text{HO} \quad \text{C}_8 \quad \text{OH} \quad 63(21) \ (Z:E = 40:60)
\]

19 \[
\text{C}_8 \quad \text{HO} \quad \text{Ph} \quad \text{C}_8 \quad 70(27) \ (Z:E = 44:56)
\]

20 \[
\text{Ph} \quad \text{OH} \quad \text{C}_8 \quad \text{OH} \quad \text{trace}
\]

21 \[
\text{Ph} \quad \text{OH} \quad \text{C}_8 \quad \text{OH} \quad \text{trace}
\]

[a] Reaction conditions: catalyst (0.005 mmol, 0.4 mol% referred to 2° alcohol), 2° alcohol (1.25 mmol), 1° alcohol (1.5 mmol), NaOH (0.25 mmol, 20 mol% referred to 2° alcohol), 120°C, 24 h.

[b] Conversion (based on 2° alcohol) determined by $^1$H NMR spectroscopy. Values in parenthesis indicate the conversion of corresponding ketone, whereas those in square bracket indicate the isolated yield of the higher alcohol.
It is seen from Table 4.2 that the dichloro-bpy complex 10 is capable of catalyzing the \( \beta \)-alkylation of secondary alcohols to give good yield of higher alcohols in many cases, and in fact its catalytic activity is superior to most of the other systems reported in the literature. The catalytic system comprising 10, however, does not render much information regarding the mechanistic pathway of the reaction. Complex 10 is devoid of phosphine ligand, and it is therefore not possible to monitor the 10-catalyzed reactions with \(^{31}\text{P}\) NMR spectroscopy. In addition, the \(^1\text{H}\) NMR spectrum of the recovered complex after catalysis exhibits many unidentified and chaotic peaks, which further frustrated our mechanistic investigation on this catalytic system. Depicted in Scheme 4.1 is a possible mechanism for the alkylation reaction that is parallel to those reported in the literature.

The primary and secondary alcohols were temporarily oxidized in the presence of catalyst and base to the corresponding aldehyde and ketone, respectively; they undergo an aldol condensation in the presence of base to give an \( \alpha,\beta \)-unsaturated ketone. Reduction of the ketone by the ruthenium-hydride species generated affords the saturated alcohol as the final product.
Scheme 4.1. Proposed mechanism for the 10-catalyzed $\beta$-alkylation of secondary alcohols with primary alcohols
Catalytic transfer hydrogenation is a widely employed method for the reduction of aldehydes and ketones to their corresponding alcohols. 2-Propanol is one of the most frequently used hydrogen donor for this reaction, but is required in large excess to shift the reduction equilibrium to the product side (Scheme 4.2). It is therefore desirable to identify an alcohol that releases hydrogen irreversibly and thus overcomes the equilibrium problem. 1,4-Butanediol has recently been demonstrated by Willam et al. to be a stoichiometric hydrogen donor due to its irreversible conversion to γ-butyrolactone upon release of hydrogen (Scheme 1.19, page 42) [107–108].
It is learned from the previous section of bpy-ruthenium-complexes-catalyzed alkylation reaction that transfer hydrogenation might be a step in the catalytic process for giving saturated alcohol as the final product. We therefore anticipated that the bpy complexes are active in catalyzing reduction of carbonyl compounds, and we investigated the reaction using these complexes and with 1,4-butanediol as hydrogen donor. Optimization of the reaction conditions were found using 3-pentanone as a model substrate, and the results are shown in Table 4.3. The controlled experiment, in which no complex was present, shows that transfer hydrogenation of 3-pentanone only proceeds to a small extent. Among the complexes investigated the dimethyl substituted bpy-ruthenium complex $\text{cis-[Ru(6,6'-Me}_2\text{bpy)}_2(\text{H}_2\text{O})_2](\text{OTf})_2$ was found to exhibit the highest catalytic activity towards the transfer hydrogenation reaction. Toluene is the preferred choice of solvent, although the catalysis also proceeds but at slower rate in 1,4-dioxane or water.
### Table 4.3 Catalytic transfer hydrogenation of 3-pentanone with 1,4-butanediol\[a\]

![Catalytic transfer hydrogenation of 3-pentanone with 1,4-butanediol](image)

<table>
<thead>
<tr>
<th>entry</th>
<th>Catalyst</th>
<th>base</th>
<th>solvent</th>
<th>conversion (%)[b]</th>
</tr>
</thead>
<tbody>
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<td>–</td>
<td>NaOH</td>
<td>toluene</td>
<td>33</td>
</tr>
<tr>
<td>2</td>
<td>cis-<a href="OTf">Ru(6,6'-Cl2bpy)2(H2O)2</a>2 10</td>
<td>NaOH</td>
<td>toluene</td>
<td>82</td>
</tr>
<tr>
<td>3</td>
<td>cis-<a href="OTf">Ru(6,6'-Me2bpy)2(H2O)2</a>2 11</td>
<td>NaOH</td>
<td>toluene</td>
<td>92</td>
</tr>
<tr>
<td>4</td>
<td>cis-<a href="OTf">Ru(2,9-dmp)2(H2O)2</a>2 12</td>
<td>NaOH</td>
<td>toluene</td>
<td>66</td>
</tr>
<tr>
<td>5</td>
<td>11</td>
<td>–</td>
<td>Toluene</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>11</td>
<td>NaOH</td>
<td>dioxane</td>
<td>55</td>
</tr>
<tr>
<td>7</td>
<td>11</td>
<td>NaOH</td>
<td>water</td>
<td>37</td>
</tr>
<tr>
<td>8</td>
<td>11</td>
<td>KOtBu</td>
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<td>49</td>
</tr>
<tr>
<td>9</td>
<td>11</td>
<td>Cs2CO3</td>
<td>toluene</td>
<td>7</td>
</tr>
<tr>
<td>10[e]</td>
<td>11</td>
<td>NaOH</td>
<td>toluene</td>
<td>41</td>
</tr>
<tr>
<td>11[d]</td>
<td>11</td>
<td>NaOH</td>
<td>toluene</td>
<td>74</td>
</tr>
<tr>
<td>12[e]</td>
<td>11</td>
<td>NaOH</td>
<td>toluene</td>
<td>78</td>
</tr>
</tbody>
</table>

[a] Unless otherwise noted, the reactions were carried out with 3-pentanone (1.0 mmol), 1,4-butanediol (1.0 mmol), catalyst (1.0 mol% with respect to 3-pentanone), and base (0.2 mmol) in 1 mL solvent under reflux for 20 h.

[b] 2,9-dmp: 2,9-dimethyl-1,10-phenanthroline

c] The reaction was carried out at 100°C

[d] 16 h reaction time

e] The reaction was carried out using 0.5 mol% catalyst.
The catalytic transfer hydrogenation of carbonyl compounds with 1,4-butanediol was examined for more substrates in the presence of NaOH in refluxing toluene, and the results are listed in Table 4.4. Acetophenone, benzophenone, and acetonaphthone were reduced to give good yields of their corresponding alcohols (entries 1, 4, 9). The presence of electron-releasing group made the substrates more thermodynamically stable due to resonance effect; they give poorer results in the reduction process (entries 3, 7). Sterically hindered substrates also give less satisfactory results (entries 10-11). Aliphatic and heterocyclic ketones were reduced to give moderate to good yields of alcohols (entries 13-16). Catalytic reduction of aldehydes to primary alcohols was also found to be successful using complex 11 as the catalyst (entries 17-18).

A possible mechanism of the transfer hydrogenation reaction is depicted in Scheme 4.2. A ruthenium hydride complex, which is believed to be the active species, is generated from 11 and 1,4-butanediol in the presence of base. The ketone substrate coordinates to the metal center and undergoes insertion into the Ru–H bond. Protonation of the alkoxide by new 1,4-butanediol (or the lactol
formed from cyclization of 4-hydroxybutanal) afford the alcohol product.

Table 4.4 Transfer hydrogenation of carbonyl compounds with 1,4-butanediol catalyzed by cis-[Ru(6,6′-Me2bpy)2(H2O)2](OTf)2 11[a]

<table>
<thead>
<tr>
<th>entry</th>
<th>ketone</th>
<th>alcohol</th>
<th>time</th>
<th>conversion (%)[^b]</th>
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</thead>
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<td><img src="https://via.placeholder.com/150" alt="image" /></td>
<td>20</td>
<td>94</td>
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<td><img src="https://via.placeholder.com/150" alt="image" /></td>
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<td>98</td>
</tr>
<tr>
<td>3</td>
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<td><img src="https://via.placeholder.com/150" alt="image" /></td>
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<td>89</td>
</tr>
<tr>
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<td><img src="https://via.placeholder.com/150" alt="image" /></td>
<td><img src="https://via.placeholder.com/150" alt="image" /></td>
<td>20</td>
<td>89</td>
</tr>
<tr>
<td>5</td>
<td><img src="https://via.placeholder.com/150" alt="image" /></td>
<td><img src="https://via.placeholder.com/150" alt="image" /></td>
<td>20</td>
<td>87</td>
</tr>
<tr>
<td>6</td>
<td><img src="https://via.placeholder.com/150" alt="image" /></td>
<td><img src="https://via.placeholder.com/150" alt="image" /></td>
<td>20</td>
<td>97</td>
</tr>
<tr>
<td>7</td>
<td><img src="https://via.placeholder.com/150" alt="image" /></td>
<td><img src="https://via.placeholder.com/150" alt="image" /></td>
<td>40</td>
<td>70</td>
</tr>
<tr>
<td>8</td>
<td><img src="https://via.placeholder.com/150" alt="image" /></td>
<td><img src="https://via.placeholder.com/150" alt="image" /></td>
<td>20</td>
<td>89</td>
</tr>
</tbody>
</table>
Reaction conditions: catalyst (0.01 mmol, 1 mol% referred to carbonyl substrate), NaOH (0.25 mmol, 20% referred to carbonyl substrate), 1,4-butanediol (1 eqv. referred to carbonyl substrate), toluene (1 mL), reflux.  
Conversion determined by $^1$H NMR spectroscopy.
Scheme 4.2. Proposed mechanism for the 11-catalyzed transfer hydrogenation of carbonyl compounds with 1,4-butandiol
Conclusion

Based on the X-ray crystallographic structures of 1a-c, it is more appropriate to describe this class of Ru–silane complexes TpRu(PPh₃)“H₂SiR₃” as having a static structure TpRu(PPh₃)(η³-H₃SiR₃H) containing H···Si···H bonding, rather than a highly fluxional pair of σ-silane hydride complexes TpRu(PPh₃)(Hₖ)(η²-HₖSiR₃)

$$\text{TpRu(PPh₃)(Hₖ)(HₗSiR₃).}$$

The complex TpRu(PPh₃)(η³-H₃SiPhMe₂H) (1c) was used to catalyze the hydrolytic oxidation of silanes to silanols. Although the catalytic activity of 1c might not be as high as some of the catalytic systems reported by others, we have, however, been able to present a much clearer picture of the mechanistic aspects of the reaction. More importantly, this is a rare example employing complex, which contains the [H₂SiR₃]⁻ moiety, for catalytic study. For most of the previously studied catalytic systems, the reaction mechanisms had not been studied in detail; it was generally suggested that the catalysis involves oxidative addition of the silane molecule to the metal to form the silyl hydride species. In our study, a new mechanism was revealed. Theoretical calculations show that the crucial step of the catalytic process is the nucleophilic attack of water oxygen at the silicon center of the [H₂SiR₃]⁻ moiety; strong dihydrogen-bonding interaction between one of the hydrides of [H₂SiR₃]⁻ and a water proton is present in the transition state. This work not only provides experimental evidence, which is still scarce, for the presence of the
[H$_2$SiR$_3$]$^{-}$ ligand, it also establishes a unique mechanism for the transition metal-catalyzed hydrolytic oxidation of silanes to silanols. An alternative mechanism, which involves intramolecular hydroxo attack at the silane ligand is also proposed. However, theoretical calculations indicate that this alternative mechanism is less favorable.

We have also demonstrated that the silane complex 1c is capable of catalyzing the reduction of carbon dioxide by hydrosilane to give silyl methoxide as the ultimate reduction product. Although the turnovers of the catalytic system comprising 1c are not as high as those reported in the literature, we are able to identify most the chemical species generated in the catalytic reaction, including the CO$_2$-reduction products such as formoxysilane and bis(silyl)acetal, as well as the ruthenium complexes TpRu(PPh$_3$)(CO)H (5), TpRu(PPh$_3$)(CO)(η$^1$-OCHO) (6), and TpRu(CO)$_2$H (7). In addition, we are probably the first group to detect formaldehyde, an indispensable intermediate according to density function theory study, during the CO$_2$-reduction by silane. This work also gives a demonstration of the possibility of using hydrosilane as a reducing agent for affecting CO$_2$-transformation.

The dicationic bpy-ruthenium complexes were found to be active catalysts for
$\beta$-alkylation of secondary alcohols with primary alcohols and transfer hydrogenation of aldehydes and ketones with 1,4-butanediol. The work demonstrated a relatively rare example of using electrophilic transition-metal complexes for the two reactions. Moreover, the use of stoichiometric amount of 1,4-butandiol in transfer hydrogenation reaction provides an alternative for the reduction of carbonyl compounds.
Appendices

Figure 2.7. 1H NMR spectrum of TpRu(PPh₃)(η³-HSiPh₂MeH)-1b
Figure 2.8 $^1^3$C NMR spectrum of TpRu(PPh$_3$)(η$_3$-HSiPh$_2$MeH)-1b
Figure 2.9 $^{29}$Si NMR spectrum of TpRu(PPh$_3$)(η$_3$-HSiPh$_2$MeH)-1b
Figure 2.10 $^{31}$P NMR spectrum of TpRu(PPh$_3$)(η$_3$-HSiPh$_2$MeH)-1b
Figure 2.11 Infrared spectrum of TpRu(PPh₃)(η³-HSiPh₂MeH)-1b
Figure 2.12 $^1$H NMR spectrum of TpRu(PPh$_3$)(η$^3$-HSiPhMe$_2$H)-1c
Figure 2.13 $^{13}$C NMR spectrum of $\text{TpRu(PPh}_3\text{)}(\eta^3-\text{HSiPhMe}_2\text{H})-1c$
Figure 2.14 $^{29}$Si NMR spectrum of TpRu(PPh$_3$)(η$^3$-HSiPhMe$_2$H)-1c
Figure 2.15 $^{31}$P NMR spectrum of TpRu(PPh$_3$)(η$_3$-HSiPhMe$_2$H)-1c
Figure 2.16 Infrared spectrum of TpRu(PPh₃)(η³-HSiPhMe₂H)-1c
Figure 2.17  $^1$H NMR spectrum of the reaction mixture of 1c-catalyzed hydrolytic oxidation of Ph$_3$SiH.

Ph$_3$SiOH

Ph$_3$SiH

phenyl protons of Ph$_3$SiOH

phenyl protons of Ph$_3$SiH
Figure 2.18 $^1$H NMR spectrum of the reaction mixture of 1c-catalyzed hydrolytic oxidation of $\text{Ph}_2\text{MeSiH}$
Figure 2.19 $^1$H NMR spectrum of the reaction mixture of 1c-catalyzed hydrolytic oxidation of PhMe$_2$SiH
Figure 2.20 $^1$H NMR spectrum of the reaction mixture of 1c-catalyzed hydrolytic oxidation of BuMe$_2$SiH.
Figure 2.21 1H NMR spectrum of the reaction mixture of 1-catalyzed hydrolytic oxidation of EtMe2SiH
Figure 2.22 $^1$H NMR spectrum of the reaction mixture of 1c-catalyzed hydrolytic oxidation of CyMe$_2$SiH
Figure 2.23. $^1$H NMR spectrum of the reaction mixture of 1-catalyzed hydrolytic oxidation of CH$_3$(CH$_2$)$_{16}$CH$_2$Me$_2$SiH.
Figure 2.24 $^1$H NMR spectrum of the reaction mixture of 1c-catalyzed hydrolytic oxidation of Et$_3$SiH
Figure 2.25: 1H NMR spectrum of the reaction mixture of 1c-catalyzed hydrolytic oxidation of Et2MeSiH.
Figure 2.26. $^1$H NMR spectrum of the reaction mixture of 1-catalyzed hydrolytic oxidation of 1,4-(SiMe$_2$H)$_2$C$_6$H$_4$. 

1,4-(Si(CH$_3$)$_2$H)$_2$C$_6$H$_4$ 

1,4-(Si(CH$_3$)$_2$OH)$_2$C$_6$H$_4$
Figure 2.27 $^1\text{H}$ NMR spectrum of the reaction mixture of 1c-catalyzed hydrolytic oxidation of $(\pm)$-$(R)$-Me($\alpha$-Np)PhSiH
Figure 3.3 $^1$H NMR spectrum of TpRu(PPh$_3$)(CO)(η$^1$-OCHO)-8 in 1:1 formic acid and dioxane
Figure 3.4 $^{31}$P NMR spectrum of TpRu(PPh$_3$)(CO)(η$^1$-OCHO)-8 in 1:1 formic acid and dioxane
Figure 4.1 $^1$H NMR spectrum of 3-(2-methoxyphenyl)-1-phenylpropan-1-ol
Figure 4.2 13C NMR spectrum of 3-(2-methoxyphenyl)-1-phenylpropan-1-ol
Figure 4.3 1H NMR spectrum of 3-(3,4-dimethoxyphenyl)-1-phenylpropan-1-ol
Figure 4.4 13C NMR spectrum of 3-(3,4-dimethoxyphenyl)-1-phenylpropan-1-ol
Figure 4.5 1H NMR spectrum of 3-(4-fluorophenyl)-1-phenylpropan-1-ol
Figure 4.6 13C NMR spectrum of 3-(4-fluorophenyl)-1-phenyl-propan-1-ol
Figure 4.7 $^1$H NMR spectrum of 1-cyclohexyl-1-phenylpropan-1-ol
Figure 4.8 13C NMR spectrum of 1-cyclohexyl-1-phenylpropan-1-ol.
Figure 4.9 1H NMR spectrum of 3-(furan-2-yl)-1-phenylpropan-1-ol
Figure 4.10: $^{13}$C NMR spectrum of 3-(furan-2-yl)-1-phenylpropan-1-ol.
Figure 4.11 $^1$H NMR spectrum of 1-phenyl-(3-thiophen-2-yl)-propan-1-ol
Figure 4.12 13C NMR spectrum of 1-phenyl-3-(2-thiophen-2-yl)propan-1-ol.
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