Intermolecular and Intramolecular Ru-H···H-X Dihydrogen-Bonding Interaction in Some Ruthenium Complexes

A Thesis submitted to

The Department of Applied Biology and Chemical Technology

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at

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By

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Declaration

I hereby declare that this thesis summarized my own work carried out since my registration for the Degree of Master of Philosophy in September, 1998; and that has not been previously included in a thesis, dissertation or report submitted to this or any other institution for a degree, diploma or other qualification.

Yat-Fai Lam

November, 2001.

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Abstract of thesis entitled "Intermolecular and Intramolecular Ru-H···H-X Dihydrogen-Bonding Interaction in Some Ruthenium Complexes"

Submitted by Yat-Fai Lam

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in November, 2001.

Abstract

The Tp and Tpm (Tp = hydridotris(pyrazole)borate, Tpm = trispyrazolylmethane) supported ruthenium hydride complexes, $TpRu(PPh_3)_2H$ **(34)** and $[TpmRu(PPh_3)_2H](BF_4)$ **(35)**, have been examined for their abilities to form intermolecular hydrogen bonding. Acidic alcohols such as TFE, HFIP and PFTB (TFE = trifluoroethanol, HFIP = hexafluoroisopropyl alcohol and PFTB = perfluoro-*tert*-butyl alcohol) have been chosen to react with the complexes in order to investigate the existence of hydrogen-bonding interaction of the type ROH···H-M. The interaction is monitored by variable-temperature NMR spectroscopy and T_1 measurement of the hydride and η^2-dihydrogen ligands.

My work shows the presence of equilibria between the intermolecular hydrogen-bonded intermediate and η^2-dihydrogen complexes at different temperatures. The ^1H NMR hydride signal of $TpRu(PPh_3)_2H$ disappeared as excess HFIP was added at 228K while an upfield broad signal assignable to a η^2-H_2 ligand was observed. After the temperature was raised to 263K, an upfield signal assignable to the hydrogen-bonded intermediate became observable and its intensity increased with increase in temperature. This phenomenon is in line with other complexes containing dihydrogen bonds which show enhanced M-H···H-X interaction as the temperature is lowered. Since the acidity of the acidic alcohol increase from TFE, HFIP, PFTB; equilibria between the hydrogen bonded intermediate and the dihydrogen complex is observed with the addition of HFIP to **34** in variable temperature NMR (VT-NMR) spectroscopy. There are no interaction detected for **35** with any acidic alcohol in the ^1H NMR spectra.

The second part of my research concerns the chemistry of intramolecular hydrogen bonding between the pendent amino group and the hydride ligand in the aminocyclopentadienyl ruthenium complexes, and studies of their reactivities. The starting aminocyclopentadienyl ruthenium phosphite complex $CpNRu[P(OPh)_3]_2Cl$ **(40)** (CpN = [2-(N,N-dimethylamino)ethyl]cyclopentadienyl) was obtained by reflux of $CpNRu(PPh_3)_2Cl$ with triphenylphosphite in toluene solution.

The ortho-metalated complexes $[CpN\overline{Ru(P(OPh)_3)(P(OC_6H_4)}(OPh)_2]$ **(41)** was prepared by reactions of **40** with excess silver triflate in THF solution and followed by column chromatography using neutral alumina. Acidification of **41** with $HBF_4 \cdot Et_2O$ yielded the protonated ortho-metalated complex $[CpNH^+\overline{Ru(P(OPh)_3)(P(OC_6H_4)}(OPh)_2]$ **(42)**. Application of 25 bar of hydrogen pressure to **41** and **42** in chlorobenzene yielded different results. Complex **42** gave the corresponding hydride complex $[CpNH^+Ru((P(OPh)_3))_2H]$ **(43)** but no reaction for **41** was observed even with prolonged heating at elevated temperature. The complex $CpNRu(P(OPh)_3)_2H$ **(44)** was prepared by reacting **43** with KOH in ethanol solution. However, 2D-NOESY experiments show that there is no hydride-proton interaction between the Ru-H and $N\text{-}H^+$ moieties in **43.**

The catalytic activity of the CpN complex **43**, toward hydrogenation of carbon dioxide was also studied. It was found that, although similar in structure to previously reported dppm analogue $[CpNH^+Ru(dppm)H](BF_4)$ which catalyzes CO_2 hydrogenation albeit in low rate, **43** showed no catalytic activity. We attribute the lack of activity of **43** to decreased hydridicity of the hydride ligand in the complex due to the presence of the low donating phosphite ligand.

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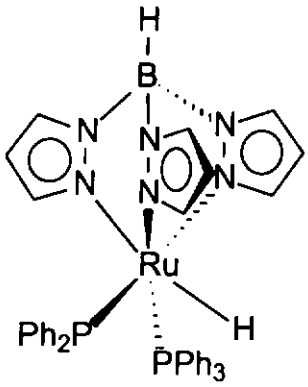
Abbreviations

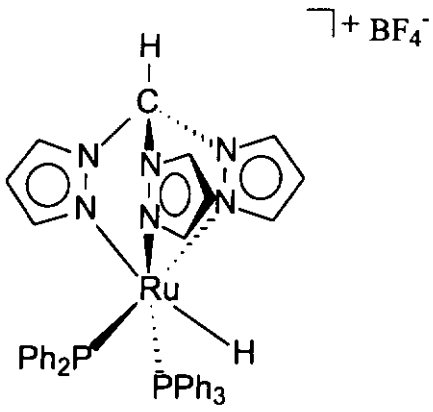
δ :	Chemical shift (NMR)
η :	Descriptor for hapticity
L :	Generalized ligand, inb particular a 2e ligand
L_nM :	Generalized metal fragment with n ligands
Tp :	Hydrotris(1-pyrazolyl)borate
Tpm :	Hydrotris(1-pyrazolyl)methane
Cp :	Cyclopentadienyl
CpN :	(2-(Dimethylamino)ethyl)cyclopentadienyl
PPh_3 :	Triphenylphosphine
$P(OPh)_3$:	Triphenylphosphite
OTf :	Trifluoromethane sulfonate
BF_4 :	Tetrafluoroborate
Me :	Methyl
EtOH :	Ethanol
Et_2O :	Diethyl ether
THF :	Tetrahydrofuran
TFE :	Trifluoroethenol
HFIP :	Hexafluoroisopropanol
PFTB :	Perfluoro-*tert*-butanol

NMR :	Nuclear magnetic resonance spectroscopy
VT-NMR :	Variable temperature nuclear magnetic resonance spectroscopy
TMS :	Tetramethylsilane
br :	Broad
s:	Singlet
d :	Doublet
t :	Triplet
m :	Multiplet

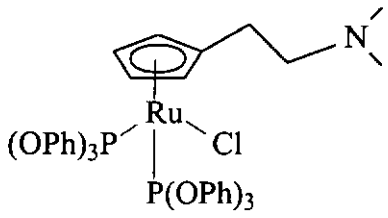
(34) : $TpRu(PPh_3)_2H$



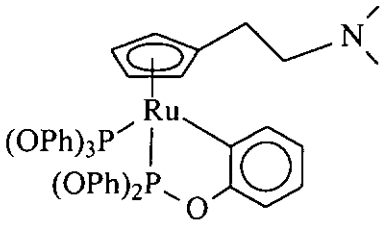
(35) : $[TpmRu(PPh_3)_2H](BF_4)$



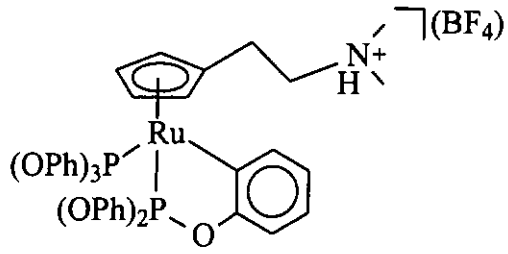
(40) : $(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2)Ru(P(OPh)_3)_2Cl$



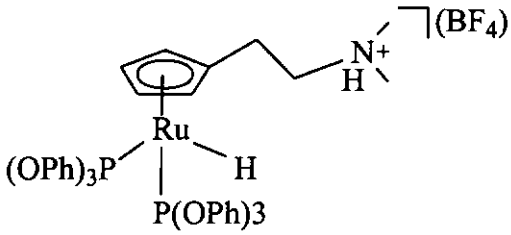
(41) : $(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2)Ru(P(OPh)_3)(P(OPh)_2OC_6H_4)$



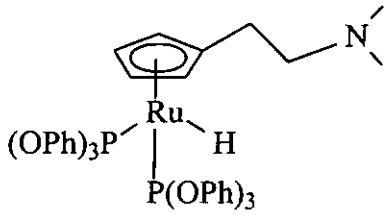
(42) : $[(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2H^+)Ru(P(OPh)_3)(P(OPh)_2(OC_6H_4))](BF_4)$



(43) : $[(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2H^+)Ru(P(OPh)_3)_2H](BF_4)$



(44) : $(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2)Ru(P(OPh)_3)_2H$



1. Introduction

1.1 *Review of hydrogen bonding in organometallic compounds*

Proton transfer reactions proceeding through hydrogen bonding are widespread and fundamental in chemistry and biochemistry [1]. The modern concepts of the nature and the structural and spectral manifestations of hydrogen bonds were formed on the basis of the large data on the interaction between organic acids and bases. Tremendous success was achieved in determining the structure of intra- and intermolecular hydrogen bonds, the energetics of ion-molecular hydrogen bonded complex formation in the gas phase, as well as in the determination of correlations between hydrogen bond characteristics and acid-basic properties [2].

In recent years, much attention has been paid to the investigation of hydrogen bonding with transition metal complexes or hydrides and its participation in proton transfer reactions. It is therefore extremely important to find out whether the numerous catalytic processes involving transition metal complexes can proceed through intermediate hydrogen-bonded complexes to explicate the reaction mechanism. Hydrogen bonds with different ligands have been examined extensively. For example, hydrogen bonds with π-ligands have been investigated since the 1970s. The large series of works by Lokshin and co-workers concerned the study of the interaction of fluorinated alcohols [3] and HCl with carbonyl and nitrosyl containing half-sandwich transition metal π-complexes was continued by Poliakoff and co-workers. These low temperature IR investigations in

liquid xenon solution enabled the detection and study of previously unknown hydrogen bonding with the oxygen atom of terminal CO- and NO- groups. Fairly strong H-bonds of proton donors with alkoxy and phenoxy ligands were studied in solutions and in the solid state. The nature of hydrogen bonds with the oxygen atom of terminal CO- and NO- groups is similar to the hydrogen bonds typical of organic bases, since lone pairs of sp-electrons of heteratoms or p-electrons of unsaturated and aromatic fragments are acting as proton acceptors [4]. Braga and co-workers, concluded that hydrogen bonded in organometallic complexes through the oxygen atom of terminal carbonyl group with proton donors have structural properties that are similar to those of related organic solids after an analysis of the structural data in the Cambridge database [5, 6].

Recently, new types of hydrogen bonds which are characteristic only of organometallic compounds were found and investigated. (Figure 1.1) These are hydrogen bonding to transition metal atoms (XH···M) (**1**). In contrast to organic bases, in this case d-electrons are proton acceptors. In (ML···HX) (**2**), the ligand of the metal complexes, which act as the proton acceptor, is the bonding site. Another surprise presented by organometallic chemistry in recent years is hydrogen bonds formed with transition metal hydrides. The particular characteristic of transition metal hydrides is their dual reactivity, i.e. they can be the source of both protons and hydride ions. Two extreme cases of hydride ligand participation in hydrogen bonding were found: acting as a proton donor ($[MH]^{+}$···B) (**3**), in the case of cationic hydrides, and as an acceptor of protons (MH···HX) (**4**). Since hydrogen has no lone pair, the hydrogen bond in **4**, is exceptional. Moreover, these new

types of hydrogen bonds are in a head-on manner, not the side-on manner of agostic interactions.

XH··M	ML··HX	([MH]$^{+}$··B)	(MH··HX)
(1)	**(2)**	**(3)**	**(4)**

Figure 1.1 Different modes of hydrogen bonding.

Since the discovery of the first dihydrogen complex by Kubas in 1984 [7] (Figure 1.2), great effort has been put into investigating the chemical, structural, thermodynamics, kinetics, acidity, and computational studies as well as characterization of this type of complexes. Dihydrogen complexes are important intermediates in a number of hydrogenation processes. This type of complexes have been extensively investigated by Kubas [8], Heinekey [9], Morris [10], Crabtree's [11] and other research groups including ours.

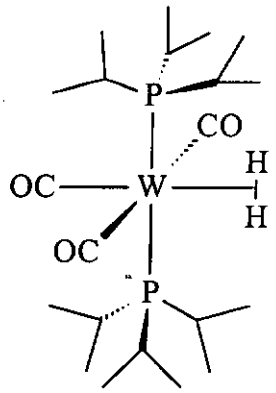


Figure 1.2 The first dihydrogen complexes discovered by Kubas *et al.*. $[W(\eta^2\text{-}H_2)(CO)_3(P\text{-}i\text{-}Pr_3)_2]$.

1.1.1 Hydrogen bonding to transition metals atoms - the XH···M type

1.1.1.1 Intermolecular hydrogen bonding

Formation of the **XH···M** hydrogen bonding has frequently been postulated as a key-step in reaction pathways in organometallic chemistry. This type of hydrogen bonding has been observed by Calderazzo *et al.* [12] and Brammer and co-workers in crystal structures [13-15].

Calderazzo *et al.* found that reaction of trialkylamines and $HCo(CO)_4$ forms 1:1 adducts, intermolecular hydrogen bonding was observed between the protonated amine and the cobalt metal [12] (Fig 1.3a). Recently, many examples of complexes having this type of hydrogen bond have been found. Poliakoff *et al.* found spectroscopic evidence for O-H···Ir bonding between cyclopentadienyl complexes $(\eta^5\text{-}C_5R_5)ML_2$ and fluoroalcohols in solution at room temperature by infrared spectroscopy [16] (Fig 1.3b).

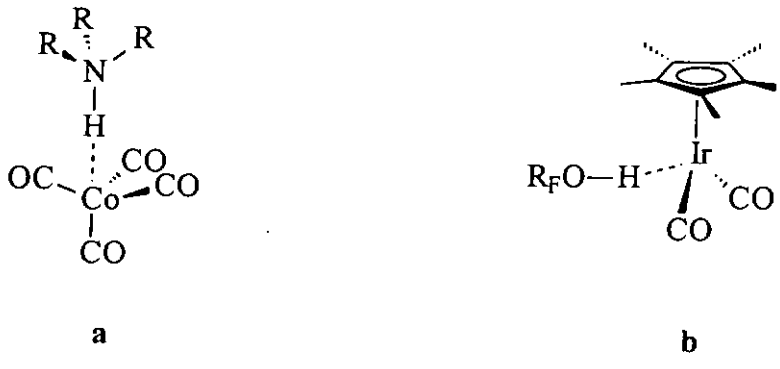
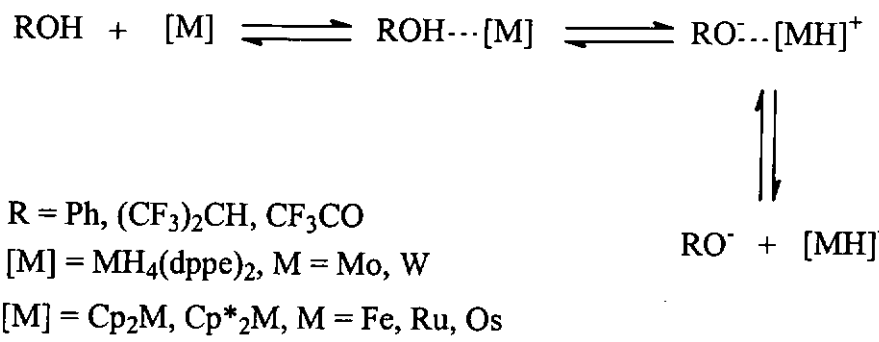


Figure 1.3 XH···M type hydrogen bonding

Epstein's group found that the intermolecular hydrogen-bonding initially formed by interaction of metallocenes and metal polyhydrides $MH_4(dppe)_2$ with proton donors is the first stage of protonation. An ionic hydrogen bonded complex of the type $MH^+\cdots O^-$ was formed as a result of proton transfer [17],[18]. The following equilibrium involving the first type hydrogen bond after proton transfer appears for all compounds investigated by Epstein's group.

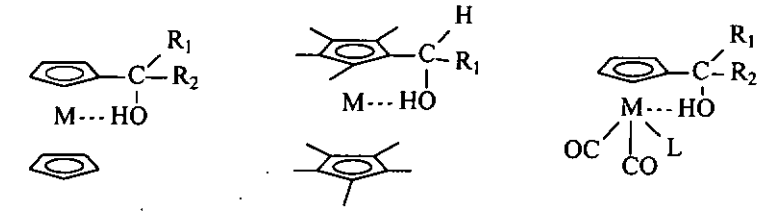


Eq. 1.1

1.1.1.2 Intramolecular hydrogen bonding

Intramolecular hydrogen bonding of the XH···M type has been observed since the 1970's. In 1986, Roundhill *et al.* found an intramolecular hydrogen bond between an amido N-H and a platinum center with a bond length in crystal structure of 2.318(22) Å. The Pt-H bond was not observed in ^1H NMR spectroscopy due to chemical shift anisotropy broadening [19].

In 1992, Epstein and co-workers observed intramolecular hydrogen-bond in α-carbinol derivatives of cyclopentadienyltricarbonyls of manganese and rhenium by IR spectroscopy [20] (Figure 1.4). They found that the stability of the hydrogen-bond depended on (i) the basicity of the metal ion, the more electron rich the transition metal center, the higher was the stability of the hydrogen bonding; (ii) the electronic effect of the ligands of the complexes, higher stability was achieved by replacing a carbonyl with a triphenylphosphine ligand; (iii) the proton donating property of the proton donor.



I

$McCR_1R_2OH$

II

Mc^9CR_1HOH

III

L = CO, PR_3

M = Fe, Ru, Os

M = Mn, Re

R_1,R_2 = H, Me, Ph, Mes, C_6F_5, ^{t}Bu

Mc = $C_5H_5MC_5H_4$; ^{9}Mc = $C_5Me_5MC_5Me_4$.

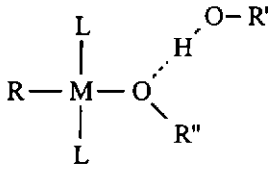
Figure 1.4 Intramolecular hydrogen bonded carbinols complexes studied by Epstein and co-workers.

1.1.2 Hydrogen bond of the [ML] ··· HX type

This type of hydrogen bonding is most common among the transition metal complexes. In 1987, Bergman's group reported that an intermolecular hydrogen bond

existed between the metal and the oxygen atom in the rhodium complex $(PMe_3)_3Rh$-OR and ROH [21]. The hydrogen bond is rather strong (ΔH = -9.7 ± 0.5 kcal/mol in benzene).

Similar hydrogen-bonding was found to be present in *trans*-PdR_2L_2 (R = CH_3, C_2H_5; L = PMe_3, PEt_3) and *trans*-NiR_2L_2 complexes by IR, NMR spectroscopy and X-ray diffraction study. The distance between the oxygen atom of the associated alcohol or phenol and the phenoxide ligand were in the range of 2.59-2.61Å. The OH hydrogen atoms were located in difference Fourier maps at distances of 1.61-1.62Å from the oxygen atom of the phenoxide ligand and at distances of 1.00-1.01Å from that of the associated phenol and alcohol. The O-H···O angles in these complexes were in the range of 165-170°, indicating that the hydrogen is close to the line connecting the two oxygen atoms [22] (Figure 1.5). Van Koten and co-workers also detected this type of hydrogen bonding between platinum, palladium phenoxide and associated phenol [23].



1. M = Ni; R = Me, R' = R" = Ph, L = PMe_3
2. M = Pd; R = Me, R' = R" = Ph, L = PMe_3
3. M = Pd, R = Ph, R" = $CH(CF_3)Ph$, L = PMe_3

Figure 1.5 Metal complexes having ML···HX type hydrogen bond.

Hydrogen bond between the bridged carbon monoxide in $[CpRu(CO)_2]_2$ and perfluorinated alcohol have been observed by Lokshin and co-workers in liquid Xe

solution [3]. Poliakoff *et al.* also investigated the hydrogen bonding in permethylated cyclopentadienyl metal carbonyls with perfluoro-*tert*-butyl alcohol (PFTB) in liquid xenon and found evidence for its existence between the metal carbonyl and the perfluorinated alcohol [4]. It is however, different from the hydrogen-bonding interactions in the solid phase.

Epstein, Caulton and co-workers had carried out theoretical calculation for the hydrogen-bond that existed between an acidic alcohol and the chloride ligand of the osmium complex $OsHCl(CO)(PtBu_2Me)_2$. The steric hindrance of the bulky ligands prevented the hydroxy group from approaching either the hydride or the metal ion and favoured its approach to the chloride [24].

1.1.3 Hydrogen bonding of the MH···HX type

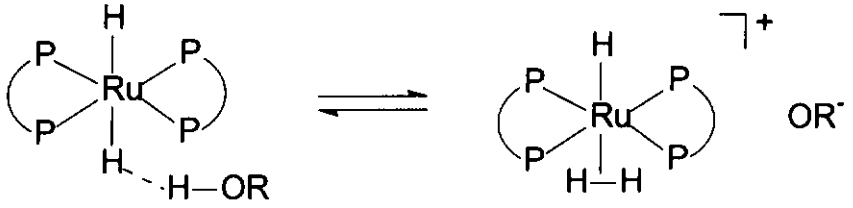
1.1.3.1 Intermolecular hydrogen bonding

Epstein and Berke reported spectroscopic evidence for intermolecular hydrogen-bonding of the type M-H···H-OR in a series of tungsten hydride complexes in acidic alcohol solutions. The tungsten hydride complex, $WH(CO)_2(NO)L_2$ (L = PMe_3, PEt_3, $P(O^iPr)_3$, PPh_3) was used as the proton acceptor, while acidic alcohols PhOH, $(CF_3)_2CHOH$ (HFIP), and $(CF)_3COH$ (PFTB) function as the proton donors. Hydrogen bonds formed between the acidic alcohol and the metal hydride in hexane, toluene-d_8, and CD_2Cl_2

solutions [25]. Similar hydrogen-bonding interaction was found in rhenium hydrides $ReH_2(CO)_2(NO)L_2$ (L = PMe_3, PEt_3, $P(O^iPr)_3$) within acidic alcohols but the interaction is weaker than those in the tungsten complexes[26].

Recently, Berke, Epstein and co-workers have found that other than the hydrides in $ReH_2(CO)_2(NO)L_2$ and $ReHCl(CO)(NO)(PMe_3)_2$ (L = PMe_3, PEt_3, $P(O^iPr)_3$), ligands such as NO, CO, Cl are also potential hydrogen-bonding sites [27, 28]. Very recently, the same group has also discovered M-H···H-OR type of hydrogen bond in complexes with facial ligands. Evidence from in situ IR and low temperature variable-temperature NMR spectroscopies show that interaction of the hydride ligand with various proton donors is the first step of the protonation reaction [29-31].

Chaudret *et al.* have conducted similar experiments by adding the metal hydride $Ru(dppm)_2H_2$ to acidic alcohols. They found that a dynamic equilibrium was established between the hydrogen-bonded species and a η^2-dihydrogen complex [32] (Eq. 1.2). The same group carried out experiments to measure quantum mechanical exchange couplings, which provide evidence for the formation of hydrogen bonds between the hydride and different proton donors by adding different proton donors to $Cp^*RuH_3(PCy_3)$ in deuterated toluene [33]. Recently, protonations of $Cp^*RuH_3(PCy_3)$ with different acidic alcohols in freon mixture $CDCl_2F/CDF_3$ (2:1) have been carried out. The novel cationic complex $[Cp^*RuH_4(PCy_3)]^+[A\cdots H\cdots A]^-$ had been observed at low temperatures as the intermediate species, but it was too unstable to be isolated at room temperature [34].



Eq. 1.2

Crabtree *et al.* detected the presence of three-centered hydrogen-bond between indole and metal polyhydrides ($[ReH_5(PPh_3)_3]$, $[ReH_7(dppe)]$, and $[WH_4(PMePh_2)_4]$) in solid crystalline structures and solid films. They found that the bond angles of the $ReH_2\cdots HN$ (97.2(3) and 118.9(4)) are strongly bent (Fig. 1.6). Therefore, it was suggested that the hydrogen-bonding is in a side-on manner [35], not the usual linear A-H···B type [36, 37]. Very recently, it was discovered that hydrogen-bond exists between the N-H of imidazole and a hydride ligand of $ReH_7(PPh_3)_2$ [38].

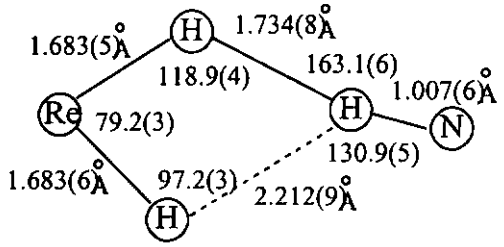


Figure 1.6 The detailed structure of the $NH\cdots H_2Re$ in $[ReH_5(PPh_3)_3]\cdot C_8H_6NH\cdot C_6H_6$.

Morris and co-workers have identified intermolecular hydride-proton interaction in metal polyhydrides and crown ether as ion pairs: $[K(Q)][MH_5(P^iPr_3)_2]$ (M = Os, Ru; Q = 18-crown-6, 1-aza-18-crown-6, 1,10-diaza-18-crown-6). Intermolecular proton-hydride interactions between the hydrides of the anions and the NH moieties of the cation (Fig. 1.7) cause the self assembly of one-dimensional networks of pentagonal

bipyramidal $[MH_5(P^iPr_3)_2]^-$ anions and $[K(diaza\text{-}18\text{-}crown\text{-}6)]^+$ cations. For complexes containing cation with one aza-group, one-dimensional chains formed with hydrogen-bonding interactions presented in MH···HN and weak MH···HC manner [39].

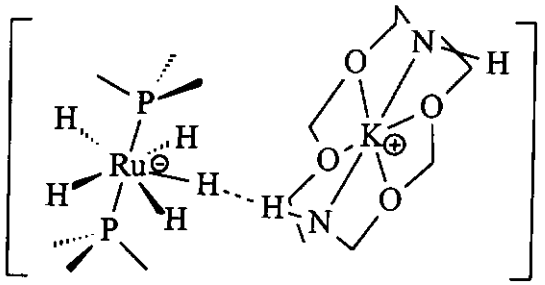


Figure 1.7 Proton-hydride interaction in $[K(1,10\text{-diaza-}18\text{-crown-}6)][RuH_5(P^iPr_3)_2]$

Lau *et al.* found interesting results when acidifying $[tpmRu(PPh_3)_2H]BF_4$ with excess aqueous HBF_4 or aqueous triflic acid in THF-d_8. Variable temperature ^1H- and ^{31}P-NMR studies revealed that the aqueous acid did not fully protonate the metal hydride to form the dihydrogen complex, but a hydrogen bonded species was formed. The special feature of this species is that the strength of its Ru-H···H-$(H_2O)_m$ interaction decreases with temperature; this phenomenon is unusual because other complexes containing dihydrogen bonds usually show enhanced M-H···H-X interaction as the temperature is lowered. Decrease of the dihydrogen-bond strength with temperature in the present case can be attributed to the decline of acidity that results from the formation of larger $H^+(H_2O)_n$ (n>m) clusters at lower temperature; steric hindrance of these large clusters also contributes to the weakening of the dihydrogen bonding interactions [40].

1.1.3.2 Intramolecular hydrogen bonding

In 1990, an early example of weak intramolecular M-H···XH interaction was confirmed in $[IrH(OH)(PMe_3)_4]^+$ [41]. The hydroxy ligand is having a bent conformation close to the metal hydride. The comparatively small bond angle of Ir-O-H (104.4°) indicates an attractive interaction between the hydridic Ir-H and the electron-deficient OH proton, in effect an $H(\delta^+)\cdots H(\delta^-)$ interaction.

Crabtree's group described intramolecular hydrogen-bonding in transition metal hydrides with a pendant side-arm ligands [42]. A series of iridium complexes containing pendant amino ligands were synthesized and crystallographic data suggested that hydrogen bonding existed between hydride ligands and the pendant amino and aldehyde groups [43, 44] [45] (Chart 1.1). Core potential ab initio studies were carried out for $IrH_2Y(pyNH_2)(PPh_3)_2$ and it was found that the N-H···H-Ir hydrogen bond strength is in the range of 5.7-7.1 kcal/mol, assuming that the intrinsic C-N rotation barrier is the same in free and coordinated 2-$C_5H_4NH_2$. Factors causing such strong hydrogen bonds are (i) a favorable geometry which allows NH and IrH to approach very close to one another and (ii) the facility with which Ir-H may be polarized in the sense $Ir^{\delta+}$-$H^{\delta-}$ on the approach of the N-H bond [46]. The same group also found that the formation of the N-H···H-Ir interaction depends on the basicity of the surrounding ligands of the metal complexes as well [47]. The pendent arm in the complexes studied above not only acts as proton donor but also stabilizes other ligands such as fluoride ions and ketones [48, 49].

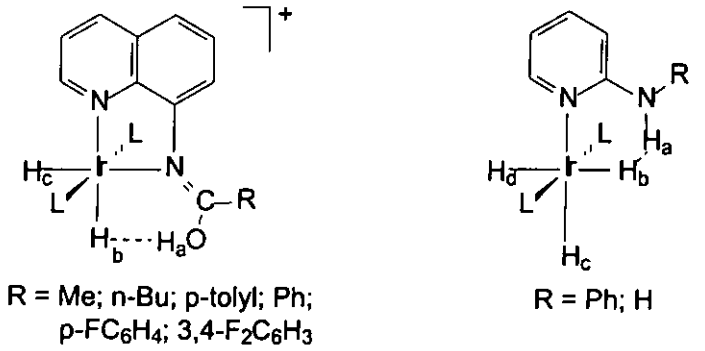


Chart 1.1 Examples of intramolecular hydrogen bonding complexes.

Morris *et al.* reported intramolecular hydrogen bonding in iridium complexes with 2-pyridiniumthiolate ligands coordinated in a monodentate fashion via the sulfur atom [50, 51]. Hoffmann and co-workers used this complex for the study of the intramolecular hydrogen-hydrogen interaction with extended Huckel method and found that the interaction is weakly attractive [52]. Recently, Morris's group identified linear and bifurcated hydrogen bonds between iridium complexes and tetrafluoroborate ions in crystal structures and in CD_2Cl_2 solutions [53, 54] (Fig. 1.8).

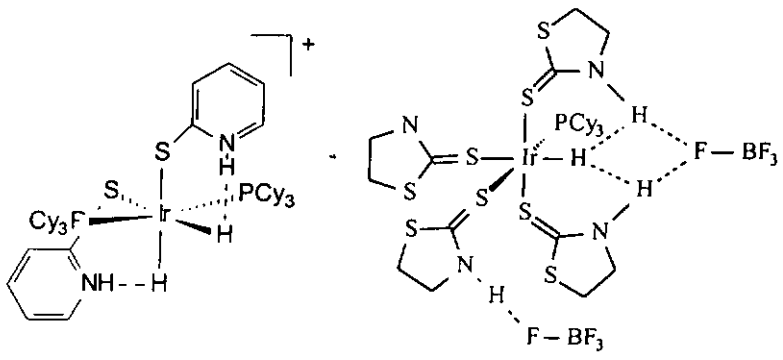


Figure 1.8 Linear and bifurcated MH···HX type hydrogen bonds.

Lau *et al.* have synthesized intramolecularly Ru-H···H-N dihydrogen-bonded ruthenium complexes with pendant (2-(dimethylamino)ethyl)cyclopentadienyl and (3-(dimethylamino)propyl)cyclopentadienyl ligands [55]. When the complexes were exposed to H_2/CO_2 (40 atm /40 atm) at 80°C for 16h, formic acid was formed in low yield. The formation of formic acid is best explained by a mechanism which involves intramolecular heterolytic cleavage of the bound H_2 to generate $[(\eta^5\text{-}C_5H_4(CH_2)_nNMe_2H^+)RuH(dppm)]BF_4$, followed by CO_2 insertion into the Ru-H and then N-H protonation of the formato ligand.

Chaudret *et al.* have synthesized similar ruthenium complexes with the η^5-cyclopentadienyl-amino ligand [56]. They found that addition of 1 equiv of $HBF_4.Et_2O$ to (Cp-N)$RuH(PPh_3)_2$ (Cp-N = $C_5H_4CH_2CH_2NMe_2$) yielded, after the elimination of H_2, $[(\eta^5:\eta^1\text{-Cp-N})Ru(PPh_3)_2](BF_4)$ containing a chelating amino-cyclopentadienyl ligand. Addition of excess HPF_6 leads to the dicationic derivative $[(Cp\text{-}NH)RuH_2(PPh_3)_2](PF_6)_2$ in which both the metal and the amino substituent are protonated. Intramolecular hydrogen bonds were suggested between the hydride and the protonated pendant amino side arm.

Not only mononuclear species contain XH···HM hydrogen bonding, metal cluster may also have intramolecular hydrogen bonding. Aime *et al.* have found this type of interaction between osmium hydride and coordinated imine ligand in $H(\mu\text{-}H)Os_3(CO)_{10}(HN{=}CHCH_3)$ [57].

1.2 *Introduction to cyclopentadienyl complexes containing amino side-arms*

Cyclopentadienyl complexes have been intensively studied during the past 40 years. During the last decade, the introduction of functional groups at the C_5 perimeter of a cyclopentadienyl (Cp) fragment has become an interesting tool to modify drastically the chemical and physical properties of classical Cp complexes of s-, p-, d- and f- block elements. The coordination of a tethered donor fragment to a metal center is thermodynamically favored when compared with the coordination of a free donor molecule. Furthermore, intramolecular coordination is generally preferred to intermolecular coordination. However, increase in ring strain of the chelating ligand and decrease in solubility might enforce the formation of coordination polymers (Fig. 1.9).

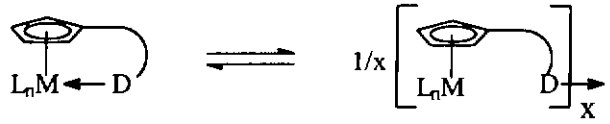


Figure 1.9 Relationship of intermolecular and intramolecular coordination affected by ring strain and solubility

In cyclopentadienyl complexes of transition metals, the Cp ligand is known to stabilize metal fragments in both low and high oxidation states and is usually regarded as substitutionally inert. The effect of an additional donor group, however, strongly depends on the nature of the metal and of the donor group. The strength of the interaction can be estimated on the basis of Pearson's HSAB concept that 'hard' ligands combine preferentially with 'hard' metal centers, and 'soft' ligands favor the interaction with 'soft' metal centers. Interesting reactivity due to change of electronic effect at the metal center is achieved when unfavored 'hard-soft' combinations are used. These unfavored

combinations are stabilized to a certain extent by the chelate effect. Of course, the side-chain donor can be easily substituted in such types of complexes. This results in a hemilabile behavior [58], where the side-chain functionally can either act as donor or as a spectator ligand (Figure 1.10).

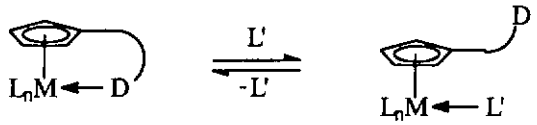


Figure 1.10 Hemilabile behavior of the side-chain donor complexes

The hemilabile situation is expected in compounds where a 'hard' donor, such as an amino or alkoxy group, coordinates to a 'soft' metal center, as present in complexes with a late transition metal in low oxidation states. Vice versa, hemilability is anticipated when a 'soft' donor, such as phosphino, thio, or alkenyl group, interacts with a 'hard' center, as present in complexes with early transition metals in high oxidation states. Of course, there exist many 'borderline' bonding situations, where the donor-acceptor interaction is difficult to predict. A substitutionally labile group is capable of temporarily blocking a coordination site and therefore allows turning-on of the reactivity of the metal center. The fluxional 'opening and closing' character provides interesting perspectives in terms of stabilization of reactive, unsaturated species, of substrate activation, of chemical sensing, and of homogenous catalysis.

Many examples of dialkylaminoalkyl-substituted Cp complexes with s-, p-, d-, and f-block elements have been described in the literature [59, 60]. A representative selective is collected in Figure 1.11.

Jutzi's group has synthesized the metallocenes **1** and **2**. The coordination of the amino side-chain prevents association to oligomers. In a similar manner, compounds **3** and **4**, achieved intramolecular stabilization and were prevented from association into oligomers. The monomeric lanthanum complex **3**, reported by Herrmann and co-workers, contains three dimethylaminoethyl substituted cyclopentadienyl groups; two of the amino groups coordinate to the metal center and thus circumventing the formation of oligomers. Lanthanoid complexes of type **4**, reported by Schumann *et al.*, are more stable towards air and moisture than the parent compounds; unfortunately, they do not catalyze ethylene polymerization reaction [61].

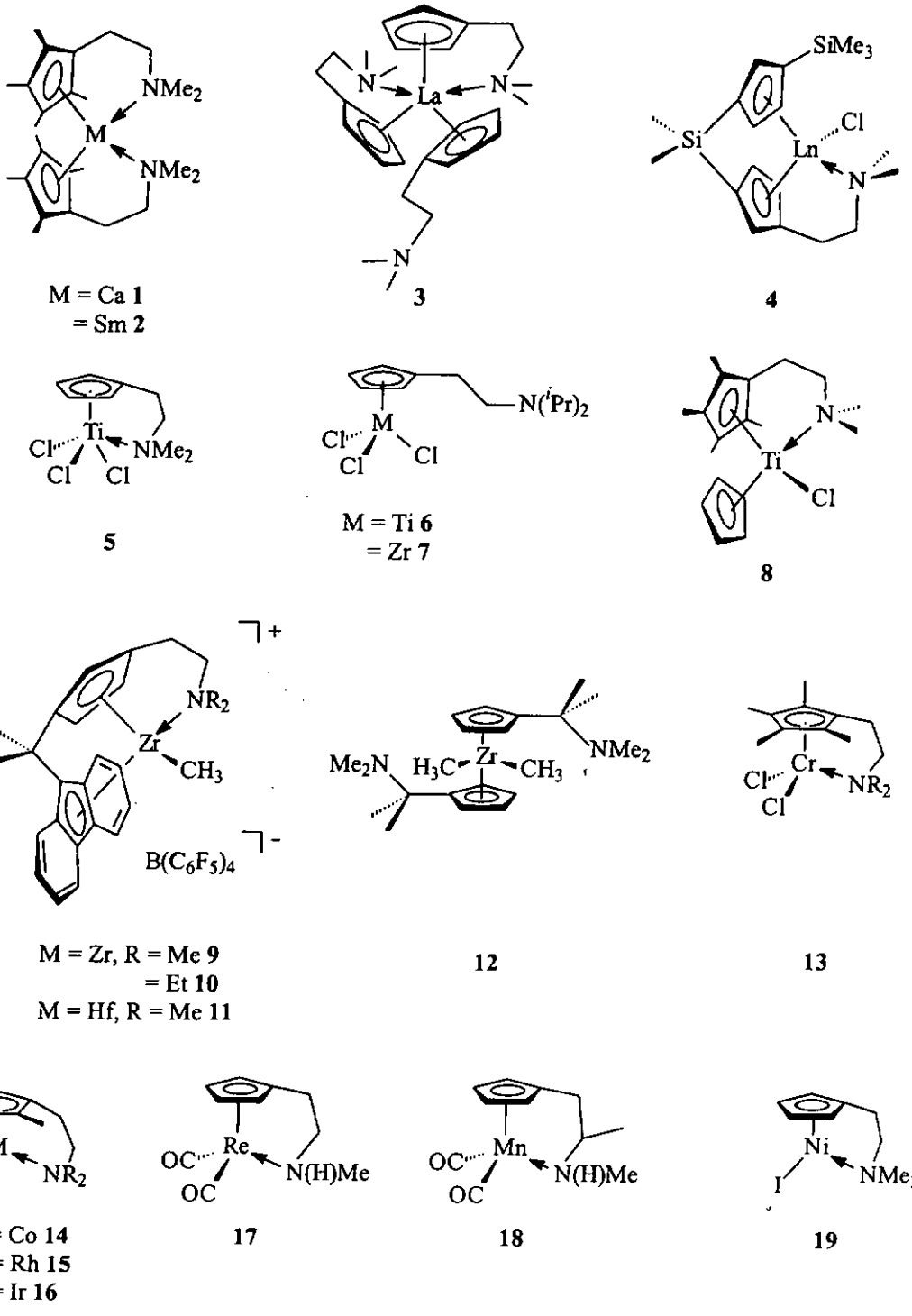
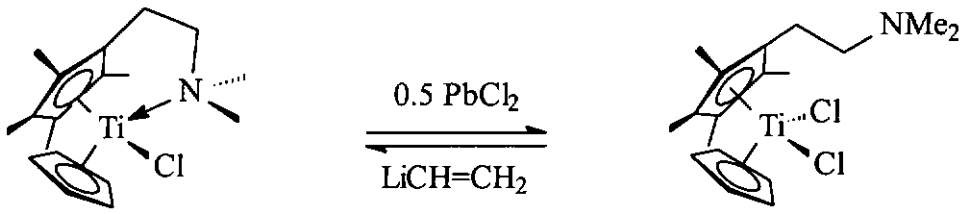


Figure 1.11 Representative selection of dialkylaminoalkyl-substituted Cp complexes

The alkyl substituents at the amino groups in complex **5-7** are different. The titanium half-sandwich complex **5**, as described by Rausch and co-workers, is monomeric

in the solid state and in solution [62]. Analogous to the parent compound $CpTiCl_3$, **5** in combination with methylaluminoxane (MAO) is a very active catalyst for the polymerization of ethylene; the role of the dimethylamino group in the polymerization process has not been elucidated yet. Jutzi's group has prepared complexes **6** and **7** [63], with diisopropylamino groups on the side chain. These compounds prefer an intermolecular coordination, which resulted in the formation of coordination polymers. Influence of the oxidation state of the central metal on the coordination behavior was studied by Beckhaus *et al.* [64]. Experimental result showed that oxidation of **8** to **20** (Eq. 1.3) is accompanied by decomplexation. Although **20** is a 16-valence-electron early transition metal complex, intramolecular coordinations of the amino-side arm to obtain an 18 electron species has not been reported. But, addition of $LiCH{=}CH_2$ to **20** yields the starting compound **8** with the amino group coordinated at the metal center.

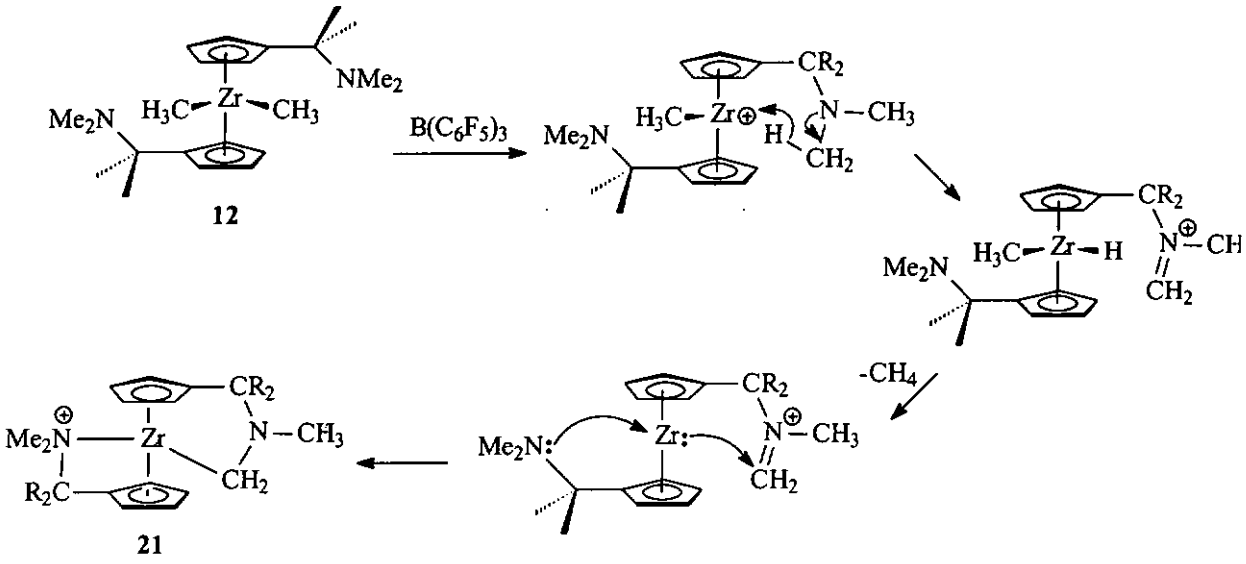


8 **20**

Eq. 1.3

Very recently, Jutzi's group have synthesized compounds **9-11,** NMR spectral studies showed those complexes to have the amino groups coordinated to the metal centers [65]. Surprisingly, the amino group is bonded to the metal center rather strongly, therefore preventing hemilability. Upon addition of aluminum trialkyl to **9** and **10**, active catalysts for the polymerization of ethylene was obtained. It is probably due to the coordination of the Lewis acidic aluminum alkyl to the amino group and the activation of

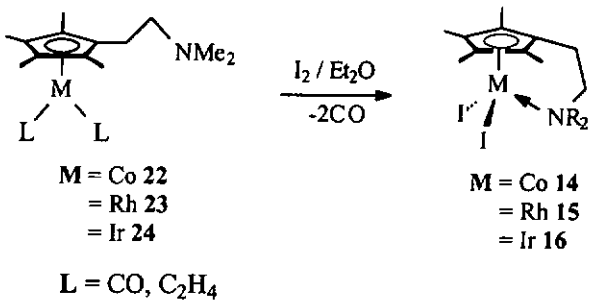
the dormant catalytically active site [66]. An interesting aspect concerning the effect of space length has been reported by Erker and co-workers [67]. Treatment of **12**, in which the Cp rings are substituted by dimethylaminomethyl groups, with the strong Lewis acidic tris(pentafluorophenyl)-borane leads to an ionic intermediate, which undergoes a surprising reaction sequence: C-H activation under loss of methane instead of coordination of the second dimethylamino group, yields the spiro-metallocene **21** (Scheme 1.1).



Scheme 1.1 Proposed mechanism for the formation of the spiro-metallocene, 21

Jolly *et al.* reported the chromium half-sandwich complex **13**. It is a highly active catalyst when combined with MAO for the polymerization of ethylene. Unfortunately, the reaction mechanism remains unknown. Late transition metal complexes bearing functionalized cyclopentadienyl ligands have been extensively studied by Jutzi *et al.* [68, 69]. The amino side-chains do not coordinate in complexes **22-24** (L = CO, C_2H_4; M = Co, Rh, Ir). However, oxidation of the complexes with I_2 leads to the formation of

complexes **14-16,** each having the amino group coordinated to metal center in the oxidation state of +III (Eq. 1.4).



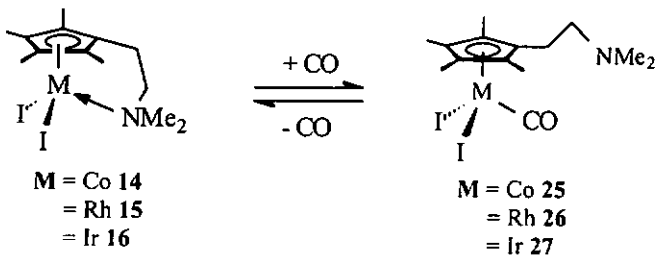
M = Co **22**
= Rh **23**
= Ir **24**

L = CO, C_2H_4

M = Co **14**
= Rh **15**
= Ir **16**

Eq. 1.4

Moreover, application of CO pressure to **14-16** gives the unarmed complexes **25-27** (Eq. 1.5).

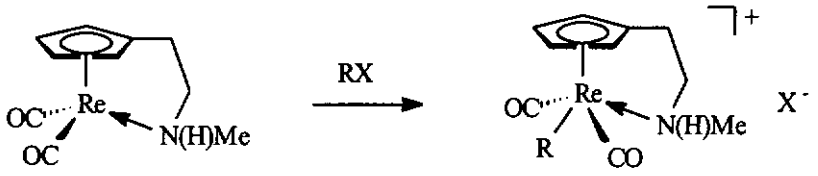


M = Co **14**
= Rh **15**
= Ir **16**

M = Co **25**
= Rh **26**
= Ir **27**

Eq. 1.5

Wang *et al.* have contributed significantly to the area of amino-substituted Cp ligands [70-72], for example, they have synthesized compound **17**, in which the 'hard' amino group is coordinated to a 'soft' Re(I) center. The enhanced nucleophilicity of the metal now enables alkylation with substrates RX (Eq. 1.6) [73]. The same group also presented complex **18**, in which chelating effect supported N-donor coordination to the mono-valent metal center.

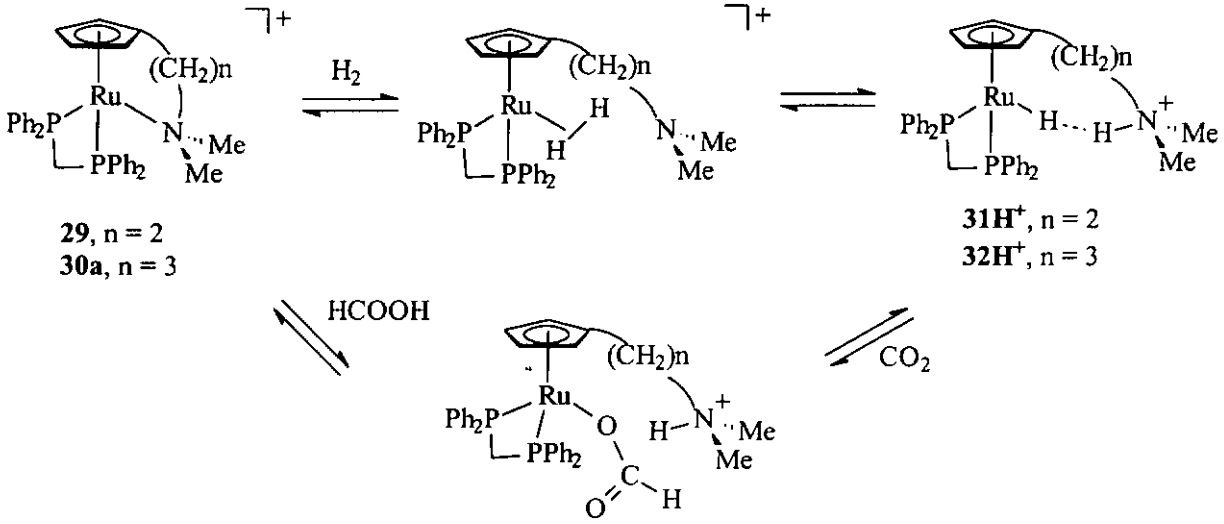


17 **28**

RX = CH_3I, CH_3Br, $C_6H_5CH_2Br$, C_3H_3Br, $MeO_2C_2H_2Br$, $EtO_2C_2H_2Br$, $NCCH_2Br$

Eq. 1.6

Lau *et al.* synthesized ruthenium complexes **29**, **30** containing cyclopentadienyl ligand with amino sidearms, and found that **29** and **30** catalyzed hydrogenation of CO_2 to formic acid, albeit in low yields [55]. The formation of formic acid can be explained by intramolecular heterolytic cleavage of the bound H_2 to generate $[(\eta^5\text{-}C_5H_4(CH_2)_nNMe_2H^+)RuH(dppm)]BF_4$ (n = 2, **31H**$^+$; = 3, **32H**$^+$), followed by CO_2 insertion into the Ru-H and then N-H protonation of the formato ligand (Scheme 1.2).

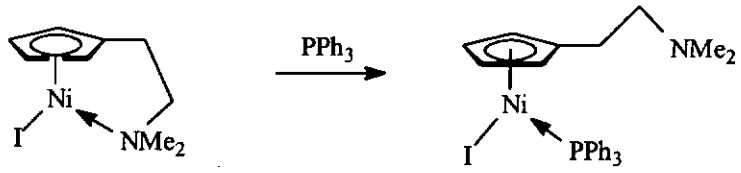


29, n = 2
30a, n = 3

31H$^+$, n = 2
32H$^+$, n = 3

Scheme 1.2 Proposed mechanism of hydrogenation of CO_2 to formic acid by $[(\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2NMe_2)Ru(dppm)](BF_4)$

Another example consisting of intramolecular coordination of amino sidearm to a Group 10 element has been reported by Fischer and co-workers [74]. The labile dimethylaminoethyl group in the nickel (II) complex **19** can easily be displaced by a triphenylphosphine ligand (Eq. 1.7).



19 **33**

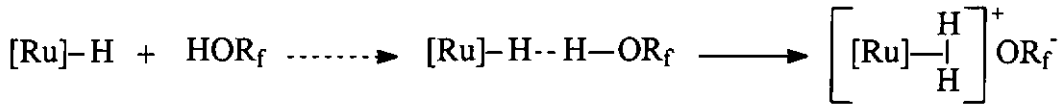
Eq. 1.7

2 Intermolecular M-H•••H-OR Hydrogen bonding of Ruthenium hydride complexes with acidic alcohols

2.1 *Introduction*

The protonation reaction of transition metal hydrides with acids to yield the corresponding η^2-H_2 complexes is well known and common. [8-11, 75] It has recently been reported that protonation may proceed via intermediate species containing unusual intramolecular [42, 44, 46, 50, 51] or intermolecular [25, 26, 36, 37] dihydrogen bonds M-H···H-X, a special kind of hydrogen bond in which the proton acceptor is a metal hydride. Shubina et al [25] reported that intermolecular W-H···H-OR dihydrogen bonding was formed between acidic alcohols and the tungsten hydride complex $WH(CO)_2(NO)L_2$; hydridicity of the metal hydride and the proton donating ability of the acidic alcohol are factors affecting the strength of the intermolecular dihydrogen bonding.

In this work, reactions of various proton donors (trifluoroethanol, TFE; hexafluoroisopropanol, HFIP and perfluoro-*tert*-butanol, PFTB) with ruthenium hydride complexes [$TpRu(PPh_3)_2H$ **(34)** and $[TpmRu(PPh_3)_2H](BF_4)$ **(35)**] have been studied in deuterated dichloromethane solution by in-situ NMR spectroscopy. The aim of this work is to show that the intermediate in the protonation reaction is the dihydrogen-bonded species **II**.



I II III

Eq. 2.1

2.2 *Experimental*

2.2.1 Materials and instrumentation

Ruthenium trichloride, $RuCl_3.xH_2O$ was obtained from Johnson Matthey and Pressure Chemical Co. Pyrazole, triphenylphosphine, sodium tetrafluoroborate, potassium borohydride were purchased from Aldrich. Fluorinated alcohols were purchased from ACROS and used without further purification. The complexes, $Ru(PPh_3)_3Cl_2$ [76], $RuHCl(PPh_3)_3$ [77], $TpRu(PPh_3)_2H$ [78] and $[TpmRu(PPh_3)_2H](BF_4)$ [79] were prepared according to literature methods.

NMR spectra were recorded with a Bruker DPX-400 spectrometer. ^1H NMR spectra were measured at 400.13 MHz, chemical shifts were reported relative to residual protons of deuterated solvents. $^{31}P\{1H\}$ NMR spectra were measured at 161.70 MHz, chemical shifts were relative to 85% H_3PO_4 in D_2O (0 ppm) as an external reference. Standard Bruker software was used for measuring the longitudinal relaxation times, T_1,

using the 180° inversion recovery method. The reactions of acidic alcohol with the various ruthenium hydride complexes were carried out in CD_2Cl_2 solutions at 223 K in 5 mm NMR tubes. The NMR spectra were first measured at low temperature with pre-cooled probe-heads (223K), and then measured at increasing temperature.

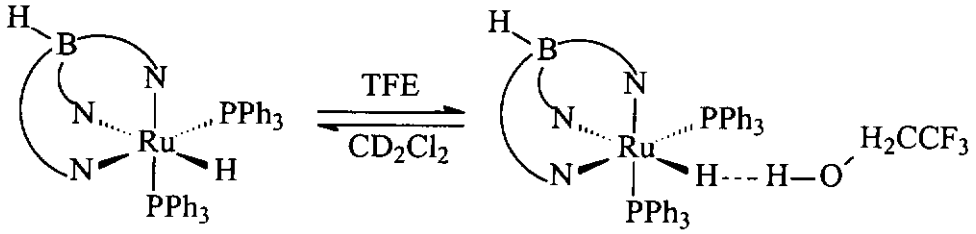
2.2.2 General procedure of reaction of a ruthenium hydride with an acidic alcohol

A sample of 15 mg of ruthenium hydride complex was weighed into a 5 mm NMR tube which was then sealed with a rubber septum. The tube was purged and filled with nitrogen. Degassed deuterated dichloromethane (0.35 ml) was added. The tube was then placed in the pre-cooled probe and was allowed to stand for 5 minutes. The pre-cooled NMR tube was then lifted up for the addition of 10 equiv of an acidic alcohol by a micro-syringe. The mixture was allowed to stand for 15 minutes for the reaction to proceed. The ^{1}H, ^{31}P NMR spectra and T_1 relaxation time were then measured. The temperature was increased by 10 degree and the solution was allowed to equilibrate for 10 minutes before taking the measurements. These NMR measurements were taken for the temperature range of 223K to 293K.

2.3 *Results and Discussion*

2.3.1 Reaction of $TpRu(PPh_3)_2H$ with trifluoroethanol (TFE)

After 10 equiv of TFE was added to $TpRu(PPh_3)_2H$ (**34**) in CD_2Cl_2 solution at 223K, the ^1H NMR spectrum showed a small upfield shift ($\Delta\delta$ = 0.27 ppm) of the hydride signal. The ^{31}P NMR signal of the equivalent phosphine ligands also showed a similar shift from δ 74.83 ppm to δ 73.72 ppm. Moreover, decrease of the longitudinal relaxation time T_1(min) of the hydride signal was observed. For the hydride complex in CD_2Cl_2 solution, the T_1(min) is 304 ms (400 MHz) at 246 K, and after addition of 10 equiv of TFE, the T_1(min) dropped to 266 ms at 238 K. The decrease in T_1(min) was caused by weak interaction between the metal hydride **34** and the proton of TFE (Eq. 2.2). Similar observation was made by Chaudret *et al* when excess phenol was added to a solution of $Ru(dppm)_2H_2$ in C_7D_8 at room temperature. The ^1H NMR signals of both the hydrogen-bonded adducts of the *cis*- and *trans*- isomers of $Ru(dppm)_2H_2$ were found shifted upfield and the T_1(min) were shortened [32].



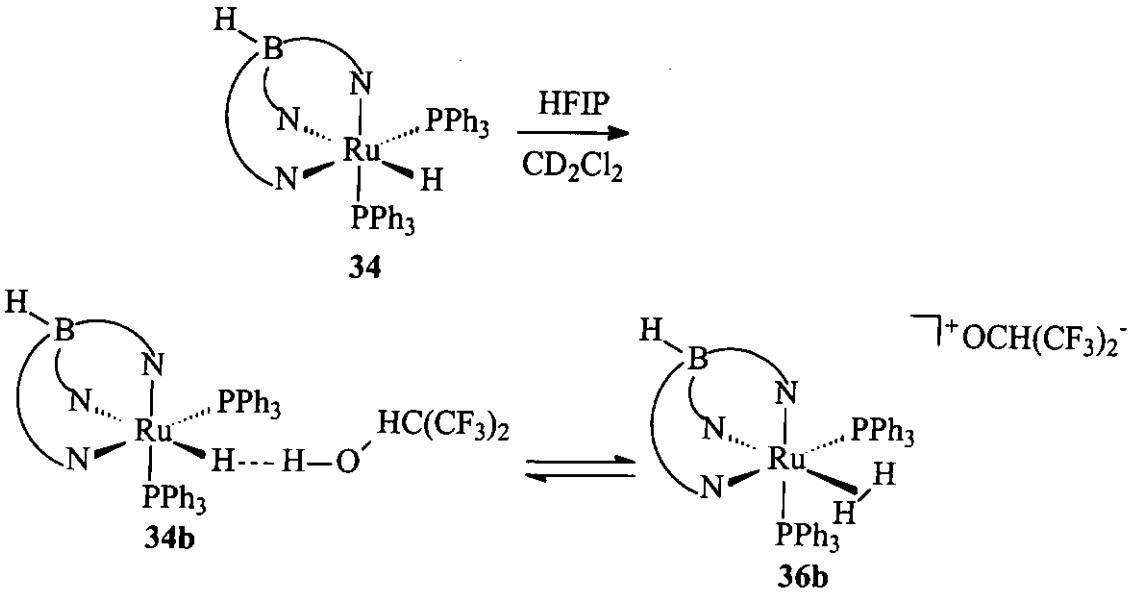
34 **34a**

Eq. 2.2

Proton NMR monitoring of the reaction of **34** with TFE shows no sign of formation of the dihydrogen complex $[TpRu(PPh_3)_2(H_2)]^+$, indicating that complete proton transfer for TFE to the complex has not occurred; it may be due to the fact that acidity of trifluoroethanol (TFE) is lower than that of $[TpRu(PPh_3)_2(H_2)]^+$. In view of this, a more acidic alcohol was then employed for the study of intermolecular dihydrogen bonding between **34** and the alcohol.

2.3.2 Reaction of $TpRu(PPh_3)_2H$ with hexafluoroisopropanol (HFIP)

Since little reaction was observed between **34** and TFE, a more acidic alcohol, hexafluoroisopropanol (HFIP) was then employed for the study. Addition of 10 equiv of HFIP to a solution of **34** in CD_2Cl_2 at 223 K led to the immediate disappearance of the hydride signal in ^1H NMR spectroscopy. A new broad singlet at δ –8.44 ppm, integrating to two hydrogens and assignable to the $Ru(\eta^2\text{-}H_2)$ was observed. The assignment was based on comparison to the η^2-dihydrogen NMR signal of $[TpRu(PPh_3)_2(H_2)]^+(BF_4)^-$ formed by acidification of **34** with $HBF_4.Et_2O$ in dichloromethane [78]. The literature values of the chemical shift of the $\eta^2\text{-}H_2$ peak and T_1(min) of $[TpRu(PPh_3)_2(H_2)]^+(BF_4)^-$ are –8.20 ppm and 21 ms (240 K) in CD_2Cl_2, respectively. In the reaction of **34** with HFIP, the chemical shift of the $\eta^2\text{-}H_2$ peak and T_1(min) were found to be –8.44 ppm and 18 ms (242 K), respectively.



Eq. 2.3

When the temperature was increased from 223 K to 293 K, the signal of η^2-H_2 ligand shifted slightly upfield ($\Delta\delta$ = 47 ppb). At 263 K, in addition to the η^2-H_2 signal, a small peak was observed at –14.08 ppm, the intensity of which increased with temperature, and eventually it became clearly visible and appeared as a broad triplet with ^2J(HP) of 26.4 Hz. This triplet was attributable to the hydrogen bonded intermediate, **34b**. The formation of **34b** resulted from weakening of the H-H bond of **36b** as temperature increased. Apparently, increase in temperature shifted the equilibrium to the left. The assignment of **34b** is supported by upfield shift of the hydride signal to δ –14.06 ppm relative to that of **34** at δ – 13.96 ppm in the absence of alcohol at 293 K. The intermolecularly-hydrogen bonded complex **34b** was formed as temperature increased at the expense of the η^2-dihydrogen complex **36b**. The variable temperature ^{1}H NMR measurements are totally reversible (Figure 2.1).

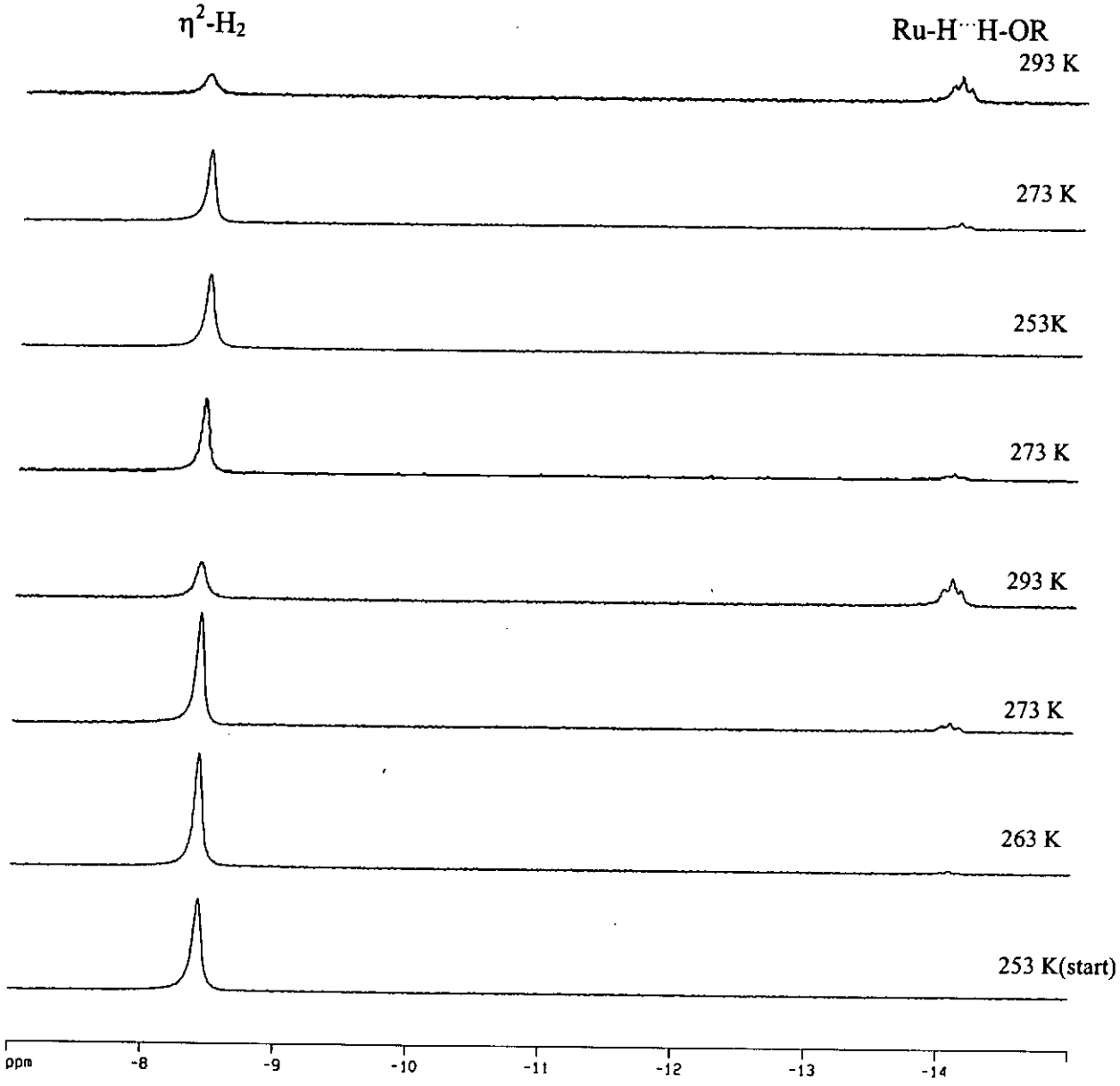
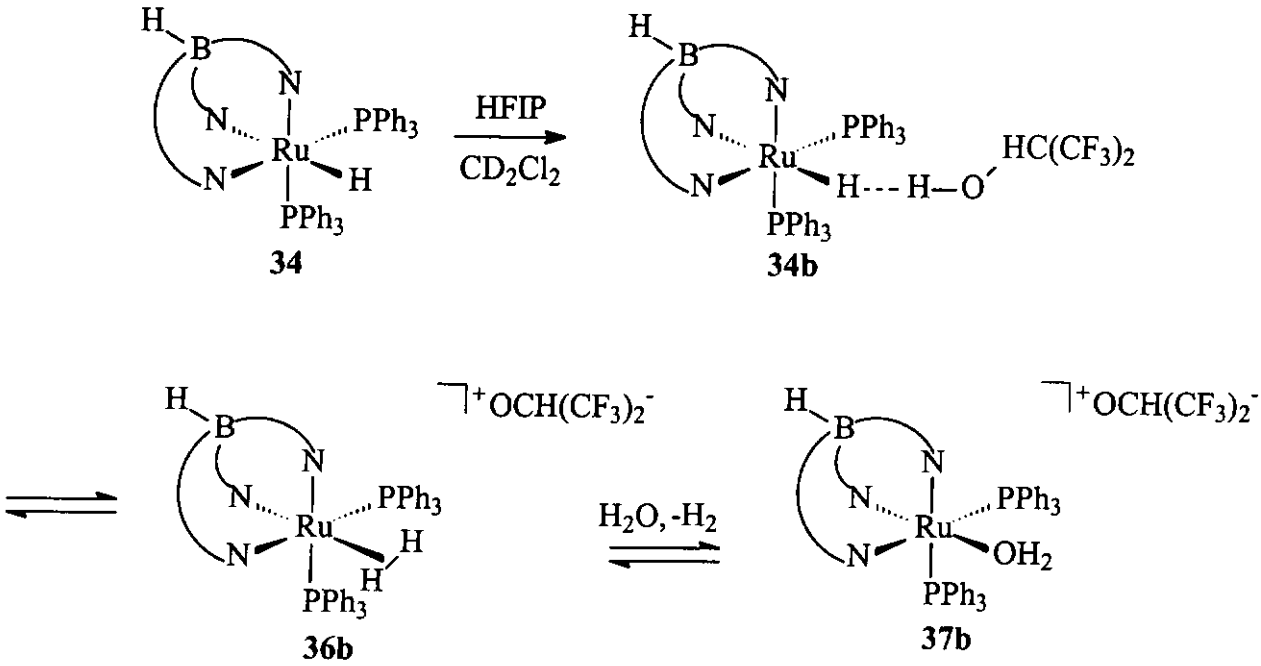


Figure 2.1 Variable temperature ^{1}H NMR spectra (upfield region) of $TpRu(PPh_3)_2H$ + HFIP in CD_2Cl_2

The variable temperature ^{1}H NMR study showed that an equilibrium existed between **34b** and **36b**. The upfield hydride signal of **34b** was broad when compared to that

of **34**; broadening of the hydride signal indicates that hydrogen bond interaction is present between the hydride ligand of **34** and the proton of HFIP. Measurement of the T_1(min) of **34b** was attempted, but it was thwarted by the shifting of the equilibrium (Eq. 2.3) to the far right at lower temperatures, at which **34b** was no longer detectable.

^{31}P NMR study showed that after addition of 10 equiv of HFIP at 223 K to **34** in CD_2Cl_2, the phosphine signal at δ 74.8 ppm disappeared, and new peaks were found at δ 51.9 and 42.9 ppm, with integral ratio of about 9:1. The peak at δ 51.9 ppm was assignable to the product of complete proton transfer, **36b** while the other peak at δ 42.9 ppm was due to the chloro-complex, $TpRu(PPh_3)_2Cl$, which was formed by reaction of **34** with the dichloromethane. When the temperature was increased to 263 K, two more new signals appeared at δ 74.6 and 48.8 ppm. The peak at δ 74.6 ppm was due to the dihydrogen-bonded intermediate, **34b**. The other signal at δ 48.8 ppm was assigned to be the aquo complex, $[TpRu(PPh_3)_2(H_2O)](OCH(CF_3)_2)$, **37b** (Eq. 2.4); similar signal was assignable to the $[TpRu(PPh_3)_2(H_2O)]BF_4$ in $CDCl_3$ by reacting $TpRu(PPh_3)_2H$ with $HBF_4.Et_2O$ in dichloromethane followed by addition of H_2O [78].



Eq. 2.4

The formation of **37b** resulted from cleavage of the labile dihydrogen ligand and coordination of adventitious water. The intensities of the two new peaks at δ 74.6 and 48.8 ppm further increased with increased temperature, while the intensity of the signal of the dihydrogen complex at 51.9 ppm decreased. This observation is reversible when temperature was decreased. The intensities of the signals corresponded to **37b** and **34b** decreased when the temperature decreased while the signal of the dihydrogen complex, **36b,** increased. The signal for the intermolecular hydrogen bonded intermediate, **34b** disappeared completely at 253 K or below, it became detectable again as temperature was raised to 263 K or above.

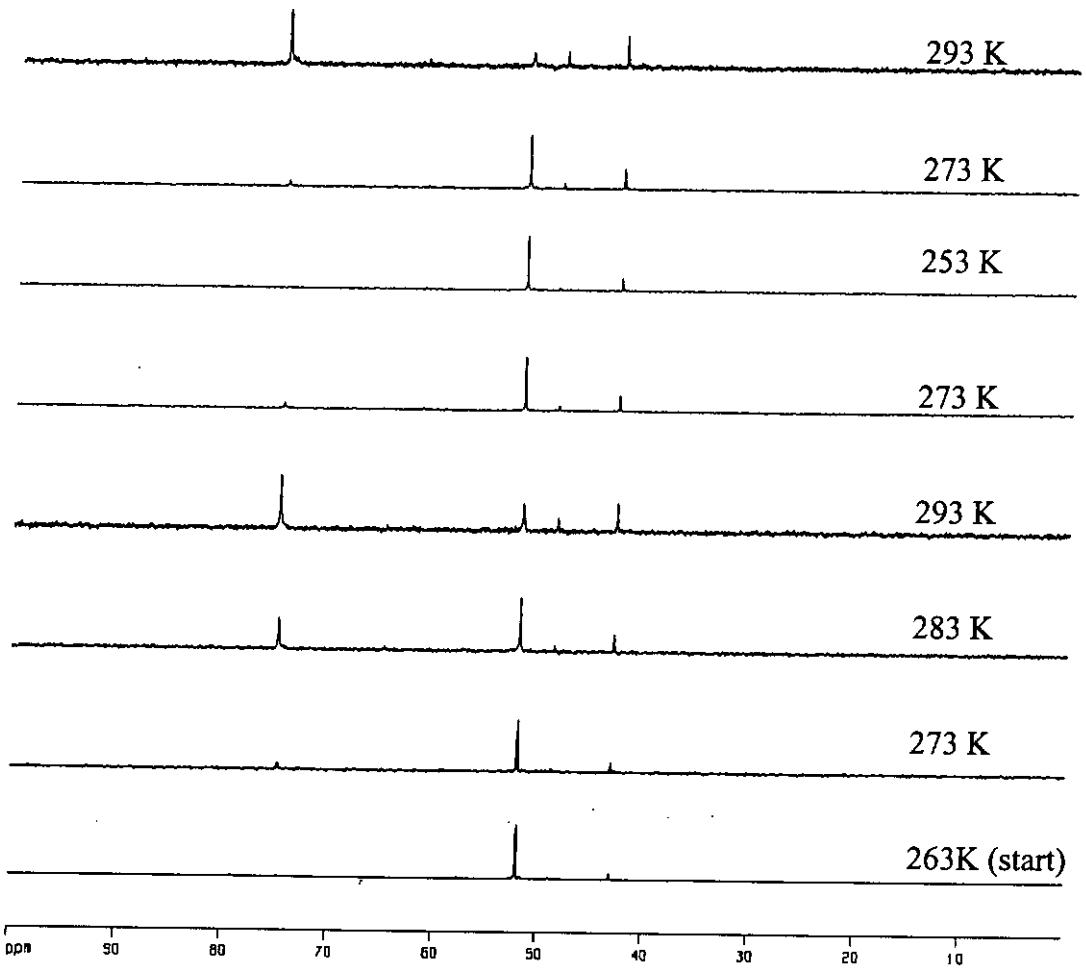


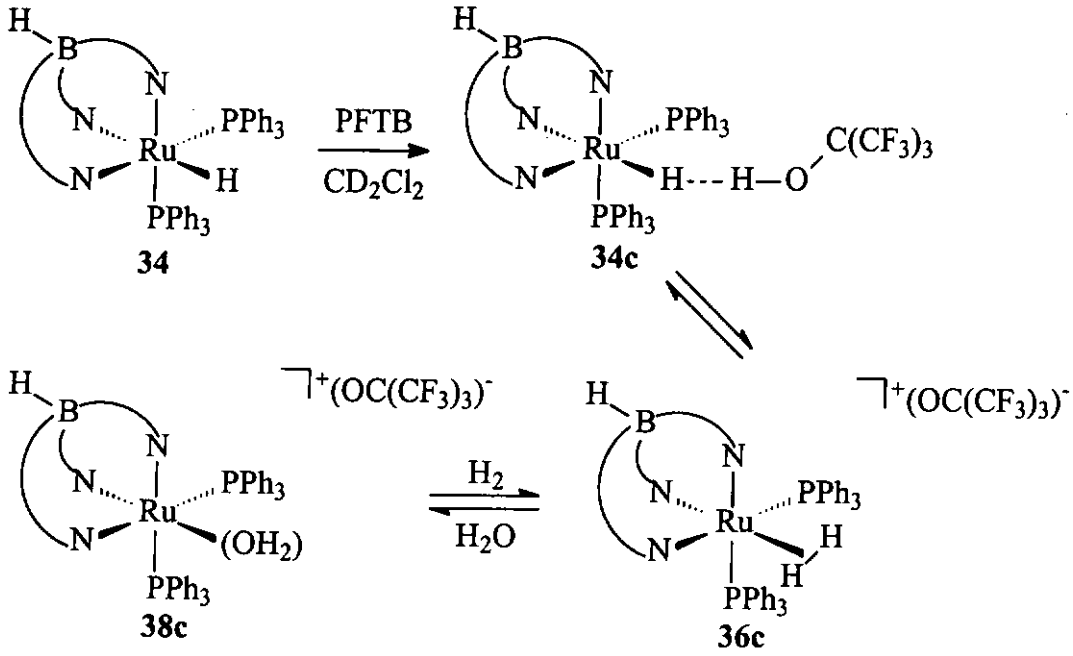
Figure 2.2 Variable temperature ^{31}P NMR spectrum of mixture of $TpRu(PPh_3)_2H$ and excess HFIP in CD_2Cl_2

2.3.3 Reaction of $TpRu(PPh_3)_2H$ with perfluoro-*tert*-butanol (PFTB)

The interaction of ruthenium hydride with the more acidic proton donor, PFTB was monitored by ^1H NMR spectroscopy. When ten equivalents of PFTB were added to a solution of **34** in CD_2Cl_2 at 223K, the hydride signal at δ –13.76 ppm

disappeared immediately and a broad peak at δ –8.2 ppm appeared. This peak was attribute to the η^2-H_2 of the product of proton transfer, **36c** (Eq. 2.5). Since the aciditiy of PFTB was the strongest among the three acidic alcohols chosen, net proton transfer was expected. Variable temperature NMR measurement monitored between 223 K and 293 K did not show signal of the intermolecular hydrogen bonded intermediate, **34c**. The T_1(min) of the dihydrogen peak (δ -8.2 ppm) was measured to be 20 ms(400 MHz) at 245 K.

Other than the broad peak found at the upfield region, free H_2 was also observed as a small peak at 4.57 ppm in ^{1}H NMR spectrum after the addition of PFTB. The free dihydrogen at δ 4.57 ppm can be explained, in terms of the cleavage of the labile η^2-H_2 ligand and its replacement by adventitious water. For example, Epstein and Berke showed that cleavage of η^2-H_2 followed by coordination of the alkoxo group of acidic alcohol gave the final product of the reaction between $WH(CO)_2(NO)L_2$ (L = PMe_3, PEt_3, $P(O^iPr)_3$, PPh_3) and HFIP [25]. Moreover, the same group observed the cleavage of H_2 when [(triphos)$Re(CO)_2H$] reacted with excess PFTB and eventually forming the alkoxo complex [29].



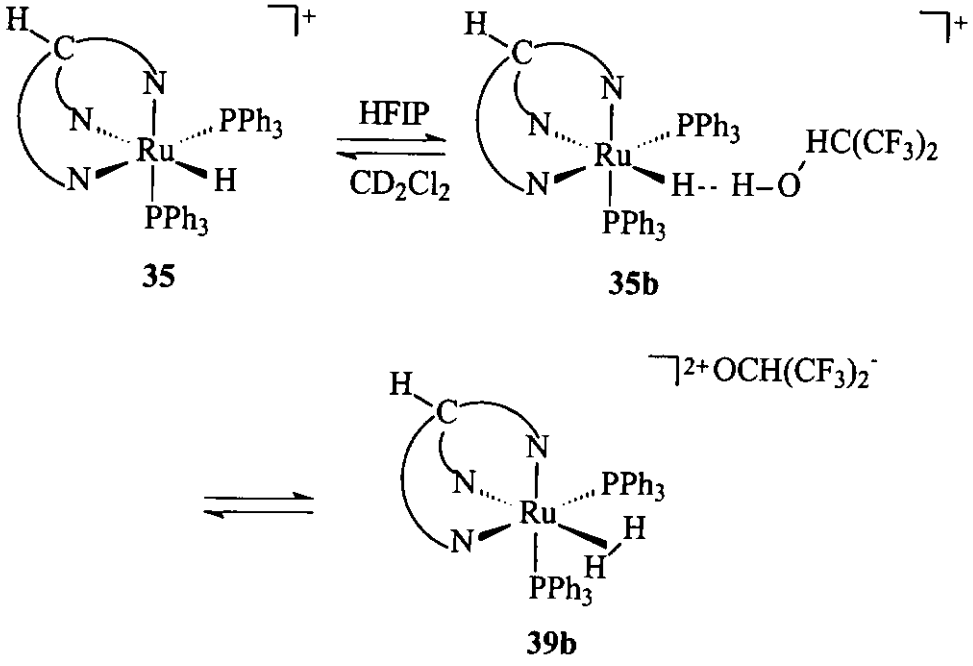
Eq. 2.5

2.3.4 Reaction of $[TpmRu(PPh_3)_2H](BF_4)$ towards hexafluoroisopropanol (HFIP)

The strength of intermolecular hydrogen bonding between the metal hydride and the acidic alcohol depends on the proton donating ability of the alcohol and also the hydridicity of the metal hydride. After studying the effect of variation of proton donating ability of the acidic alcohols on the strength of proton-hydride interaction between **34** and different alcohols, we turn our attention to the effect of changing hydridicity of the metal hydride on the strength of the dihydrogen bond.

Ten equiv of HFIP was added to a CD_2Cl_2 solution of $[TpmRu(PPh_3)_2H](BF_4)$ **(35)** and the reaction was monitored by low-temperature ^1H NMR spectroscopy. The hydride region in the ^1H NMR spectrum, recorded at 223 K (400 MHz), showed no significant change. As the temperature was increased from 223 K to 293 K, no new peaks were observed in the upfield region. This implied that there was no evidence for interaction between **35** and HFIP in the ^1H NMR spectrum. However, very weak interaction between **35** and HFIP was supported by the T_1(min) measuremnets. T_1(min) measured for the hydride peak at –13.76 ppm in the reaction of **35** to HFIP from 223 K to 293 K was found to be 302 ms at 257 K, in comparison to a solution of **35** in CD_2Cl_2 without alcohol gave a T_1(min) of 319 ms at 253 K for the hydride signal.

In the ^{31}P NMR spectrum, there were no other signals observed except the singlet at δ 73.61 ppm of **35** from 223 K to 297 K. The very weak interaction between **35** and HFIP may be due to the high acidity of the product of the proton transfer reaction, $[TpmRu(PPh_3)_2(H_2)]^{2+}$, **39b**, ($pK_a = 2.8$) [40] (Eq. 2.6). Such high acidity of the dihydrogen complex shifted the equilibrium to the far left. As a result, very little reaction of **35** with HFIP was observed. Alternatively, lack of dihydrogen bonding between **35** and HFIP may be explained in terms of the low hydridicity of the hydride ligand in the former. Lower hydridicity of the hydride ligand in **35** relative to that of the hydride ligand in the Tp analogue **34** is due to the extra charge of the metal center in the former.



35 **35b** **39b**

Eq. 2.6

2.3.5 Reaction of $[TpmRu(PPh_3)_2H](BF_4)$ towards perfluoro-*tert*-butanol (PFTB)

Since experimental result implied very weak interaction between **35** and HFIP, the more acidic proton donor PFTB was employed to see if proton-hydride interaction between **35** and the alcohol would become detectable. Upon addition of 10 equiv of PFTB to **35** in CD_2Cl_2 at 223 K, the ^1H NMR spectrum of the mixture again showed no noticeable change, no new peaks were observed as the temperature was increased from 223 K to 293 K.

The very weak interaction between PFTB and **35** was also supported by the T_1(min) measurement. The T_1(min) for the hydride signal at –13.76 ppm of the mixture of

PFTB and **35** was measured to be 309 ms at 263 K. This T_1(min) was very close to that of the hydride ligand of **35** in CD_2Cl_2 (319 ms at 253 K). Although a more powerful proton donating alcohol was used, still no dihydrogen-bonding interaction has observable between **35** and the alcohol.

3 Synthesis, Characterization and Study on the Intramolecular Hydrogen Bonding of Tethered Cyclopentadienyl Ruthenium Complexes

3.1 *Introduction*

Cyclopentadienyls are one of the most widely used classes of ligands in organometallic chemistry and homogeneous catalysis [80]. Many studies concerning functionalized cyclopentadienyl have also been reported. Cyclopentadienyls with tethered amino groups (CpN) have been used for coordination with various transition metals. Surprisingly, ruthenium complexes bearing these ligands are not too many. In view of the fact that intramolecular hydrogen bonding was found in the complex $CpNH^{+}Ru(PPh_3)_2H$ [55], studies of dihydrogen bonding in aminocyclopentadienyl ruthenium hydride complexes and the catalytic activity of these complexes in CO_2 hydrogenation were continued. We choose to study the influence of decreased basicity of the metal center on the strength of the Ru-H···H-N dihydrogen bond and the efficiency of CO_2 hydrogenation. Thus, it is the purpose of this chapter to fine-tune the intramolecular dihydrogen bond by changing ligands from electron donating to electron withdrawing, viz. from triphenylphosphine to triphenylphosphite.

3.2 *Experimental*

3.2.1 Materials and instrumentation

Ruthenium trichloride, $RuCl_3.xH_2O$ was obtained from Johnson Matthey and Pressure Chemical Co. All other chemicals were obtained from Aldrich except dicyclopentadiene and deuterated NMR solvents, which were purchased from BDH and Armar, respectively. The ligand $C_5H_5(CH_2)_2NMe_2$ [81], the complexes $Ru(PPh_3)_3Cl_2$ [76] and $(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2)Ru(PPh_3)_2Cl$ [55] were prepared according to literature methods.

Solvents were distilled under dry nitrogen atmosphere with the appropriate drying agents: (solvent/ drying agent) methanol/ Mg-I_2, ethanol/ Mg-I_2, tetrahydrofuran/ Na benzophenone ketyl, diethyl ether/ Na, n-hexane/ Na, toluene/ Na, chlorobenzene/ P_2O_5. All reactions were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. High-purity hydrogen gas was supplied by Hong Kong Oxygen.

Elemental analyses were performed by M-H-W laboratories, Phoenix, Arizona, USA. NMR spectra were recorded with a Bruker DPX-400 spectrometer. ^1H NMR spectra were measured at 400.13 MHz, chemical shifts were reported relative to residual protons of deuterated solvents. $^{31}P\{^1H\}$ NMR spectra were measured at 161.70 MHz, chemical shifts of these spectra were relative to 85% H_3PO_4 in D_2O (0 ppm) as an external reference. $^{13}C\{^1H\}$ NMR spectra were measured at 100.63 MHz, the chemical shifts of these spectra were referenced to the solvent peaks of the deuterated solvent.

Relaxation time T_1 measurements were carried out at 400 MHz by the inversion-recovery method using the standard 180°–τ–90° pulse sequence. High-pressure studies were carried out in a commercial 5mm Wilmad pressure-valved NMR tube.

3.3 *Syntheses and Characterization*

3.3.1 $(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2)Ru(P(OPh)_3)_2Cl$ (**40**)

A solution containing $(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2)Ru(PPh_3)_2Cl$ (1.00 g , 1.12 mmol) and triphenylphosphite (1.02 mL, 3.92 mmol) in toluene (50 mL) was refluxed for 48 h. Upon removal of the solvent under vacuum, 20 mL of ether was added to the residual paste with vigorously stirring to produce a yellow sticky solid which was then washed with hexane (2 x 20 mL) and dried in *vacuo*. Yield 0.87 g, (86%).

Anal. Calcd. for $C_{45}H_{44}ClNO_6P_2Ru$: C, 60.50; H, 4.96; N 1.58; Found: C, 59.36; H, 5.01; N 1.61.

^{1}H NMR ($CDCl_3$, 400 MHz, 20°C): δ1.84(2H, br s, -*CH*$_2$-N), 2.21(2H, m, Cp-*CH*$_2$), 2.28(6H, s, *NMe*$_2$), 3.54(2H, br s, Cp ring), 3.93(2H, br s, Cp ring), 6.81-7.33(30H, m, $P(OPh)_3$), $^{31}P\{^1H\}$NMR: δ138.3 (s).

3.3.2 $(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2)Ru(P(OPh)_3)(P(OPh)_2OC_6H_4)$ (**41**)

A sample of **40** (0.25g, 0.28 mmol) was added to excess $AgSO_3CF_3$ in THF (20 mL), the resulting solution was stirred at room temperature for 2 days. The solution was filtered to remove the silver chloride, and the solvent of the filtrate was removed by vacuum to yield a brown oily liquid. Elution of this oily compound through a neutral alumina column (1 cm x 10 cm) with toluene followed by ethanol gave, after evaporation of solvent, the pure complex as a tacky yellow solid. Yield 0.12 g, (50%).

The complex can also be prepared by an alternative method: a sample of **40** (0.12 g, 0.13 mmol) was added to a solution of sodium methoxide (1.25 g, 23.10 mmol) in methanol (30 mL), the resulting solution was allowed to reflux for 24 h. It was then filtered and the solvent was removed by vacuum to yield a yellow oil. The oily product was purified by elution through neutral alumina column (1 cm x 10 cm) with toluene followed by ethanol. Removal of solvent by vacuo yielded the product as sticky yellow solid. Yield 0.08 g, (33%).

Anal. Calcd. for $C_{45}H_{43}NO_6P_2Ru$: C, 63.08; H, 5.06; N, 1.63 ; Found: C, 62.06; H, 5.84; N, 1.67.

^{1}H NMR (acetone-d_6, 400 MHz, 20°C): δ1.86(2H, m, -*CH*$_2$-N), 2.03(6H, s, *NMe*$_2$), 2.06(2H, m, Cp-*CH*$_2$), 4.08(1H, br s, Cp ring), 4.09(1H, br s, Cp ring), 4.37(1H, br s, Cp ring), 4.86(1H, br s, Cp ring), 6.89-7.52(29H, m, $P(OPh)_3$), $^{31}P\{^1H\}$NMR: 144.3(d, $P(OPh)_3$, $^2J(PP)$=100Hz), 170.9(d, $P(OPh)_2(OC_6H_4)$, $^2J(PP)$=100Hz). $^{13}C\{^1H\}$NMR: 111.10(d, Ru-C, $^2J(PC)$=16.0 Hz).

3.3.3 $[(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2H^+)Ru(P(OPh)_3)(P(OPh)_2OC_6H_4)](BF_4)$ (**42**)

To a sample of **41** (0.10 g, 0.12 mmol) in 15 mL of tetrahydrofuran was added 1.2 equiv of tetrafluoroboric acid in etheral solution ($HBF_4 Et_2O$ 54%) (19 μL, 0.14 mmol), the resulting solution was allowed to stir for 1 h. It was then concentrated to 1-2 mL, and 20 mL of hexane was added to precipitate the product. The solution was filtered and the product was washed with diethyl ether (2 x15 mL) and dried in *vacuo* to yield a sticky yellowish brown solid. Yield 0.08 g, (73%).

Anal. Calcd. for $C_{45}H_{44}BF_4NO_6P_2Ru$: C, 57.22; H, 4.69; N, 1.48 ; Found: C, 57.54; H, 4.59; N, 1.57.

^{1}H NMR ($CDCl_3$, 400 MHz, 20°C): δ2.39(2H, m, -*CH*$_2$-N), 2.60(3H, d, NH$^+$*Me*$_2$, J=4.3Hz), 2.70(3H, d, NH$^+$*Me*$_2$, J=4.3Hz), 2.87(2H, m, Cp-*CH*$_2$-), 5.04(1H, br s, Cp ring), 5.20(1H, br s, Cp ring), 5.45(1H, br s, Cp ring), 5.66(1H, br s, Cp ring), 6.95-7.38(29H, m, $P(OPh)_3$), 8.17 (1H, br, *H*N$^+$Me). $^{31}P\{^1H\}$NMR: 144.2 (d, $P(OPh)_3$, $^2J(PP)$=89Hz), 172.9(d, $P(OPh)_2(OC_6H_4)$, $^2J(PP)$=89Hz). $^{13}C\{^1H\}$NMR: 111.21(d, Ru-C, $^2J(PC)$=16.1 Hz).

3.3.4 $[(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2H^+)Ru(P(OPh)_3)_2H](BF_4)$ (**43**)

A solution of **42** (0.20 g, 0.21 mmol) in chlorobenzene (15 mL) was stirred at room temperature under 25 bar of H_2 in a stainless steel autocleave for 16 h. The reactor was carefully vented and the solvent of the resulting solution was removed by vacuum. The product was washed with 3 x 20 mL portions of hexane and 20 mL of diethyl ether to yield a sticky pale brown solid. Yield 0.15 g, (75%).

Anal. Calcd. for $C_{45}H_{46}BF_4NO_6P_2Ru$: C, 57.09; H, 4.90; N, 1.48 ; Found: C, 57.64; H, 5.04; N, 1.53.

^1H NMR (benzene-d_6, 400 MHz, 20°C): δ -11.83 (1H, t, $^2J(HP)$=26.0 Hz, RuH), 2.33 (2H, br s, -*CH*$_2$-N), 2.55 (6H, d, J=4.8 Hz, -*NMe*$_2$), 2.89 (2H, br s, Cp-*CH*$_2$-), 4.48(2H, s, Cp ring), 5.49(2H, s, Cp ring), 7.23-7.60(30H, m, $P(OPh)_3$), 8.43(1H, br s, Me_2N^+H). $^{31}P\{^1H\}$NMR: 149.7 (s).

3.3.5 $(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2)Ru(P(OPh)_3)_2H$ (**44**)

A sample of **43** (0.15g, 0.16 mmol) was added to a suspension of excess powdered potassium hydroxide in ethanol (20 mL). The mixture was allowed to stir overnight at room temperature. It was filtered to remove the unreacted KOH, and the solvent of the filtrate was removed in *vacuo* to yield a black oily liquid, which was extracted with 4 x 20mL portions of hexane. The solvent of the extract was removed by vacuum, and a very sticky brown solid was obtained. Yield 0.09 g, (65%).

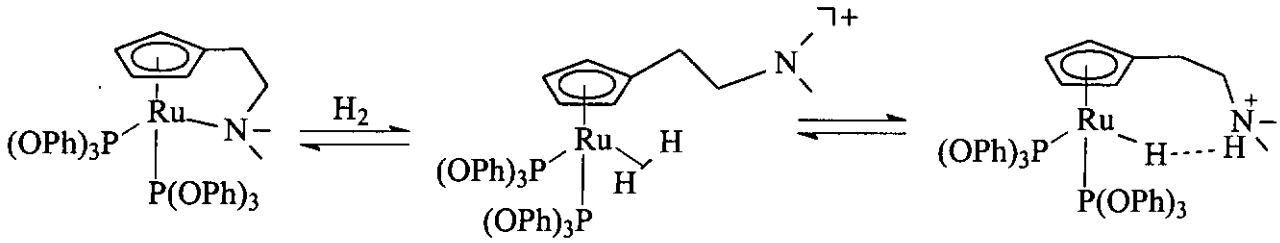
Anal. Calcd. for $C_{45}H_{45}NO_6P_2Ru$: C, 62.93; H, 5.28; N, 1.63; Found: C, 62.91; H, 5.25; N, 1.43.

^1H NMR (benzene-d_6, 400 MHz, 20°C): δ -11.54 (1H, t, $^2J(HP)$=36.0 Hz, RuH), 2.21 (2H, br s, -*CH*$_2$-N), 2.29(8H, br s, Cp-*CH*$_2$- overlapped with -*NMe*$_2$), 4.44(2H, s, Cp ring), 4.50(2H, s, Cp ring), 7.10-7.63(30H, m, $P(OPh)_3$). $^{31}P\{^1H\}$NMR: 143.7 (s).

3.4 *Results and Discussion*

3.4.1 Synthesis and characterization of ortho-metalated amino-cyclopentadienyl ruthenium complexes

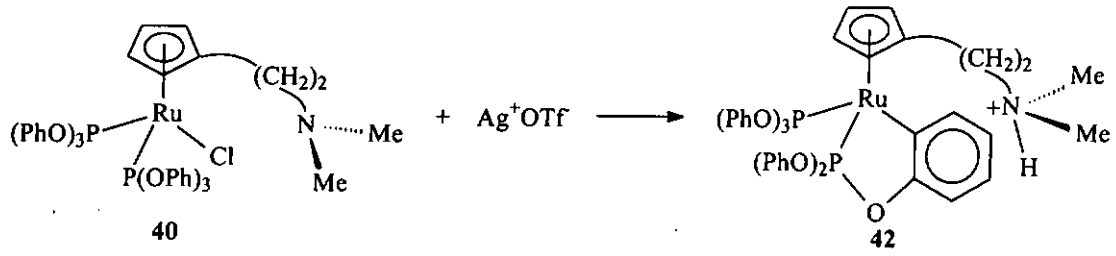
We intended to prepare the triphenylphosphite analogue of $[(\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2NMe_2)Ru(dppm)]^+$, **29** and then react the complex with pressurized H_2 to obtain $(\eta^5\text{-}C_5H_4(CH_2)_nNMe_2H^+)Ru(P(OPh)_3)_2H$, the phosphite analogue of $[(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2H^+)Ru(dppm)H]$ **(31)**, with which we would study the strength of its Ru-H···H-N interaction. Comparisons in terms of H-bond strength and reactivity of this complex with those of **31** could then be made. (Scheme 3.1)



Scheme 3.1 Proposed mechanism of the reaction of $[(\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2N(Me_2))Ru[P(OPh)_3]_2]$ towards H_2

The chloro precursor $(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2)Ru(P(OPh)_3)_2Cl$ **(40)** was prepared by refluxing a solution of $(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2)Ru(PPh_3)_2Cl$ with triphenylphosphite in toluene. We reacted the chloro complex **40** with AgOTf, anticipating

that removal of the chloro ligand would create a vacant site, which would be occupied by the amine sidearm, thus producing the desired complex. But apparently, instead of sidearm coordination, proximal generation of a vacant coordination site at the cationic ruthenium center induced cyclometalation of one of the triphenylphosphite ligands and produced the ortho-metalated complex $[(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2H^+)Ru(P(OPh)_3)(P(OPh)_2OC_6H_4)]^+OTf$ **(42-OTf)** (Eq 3.1).



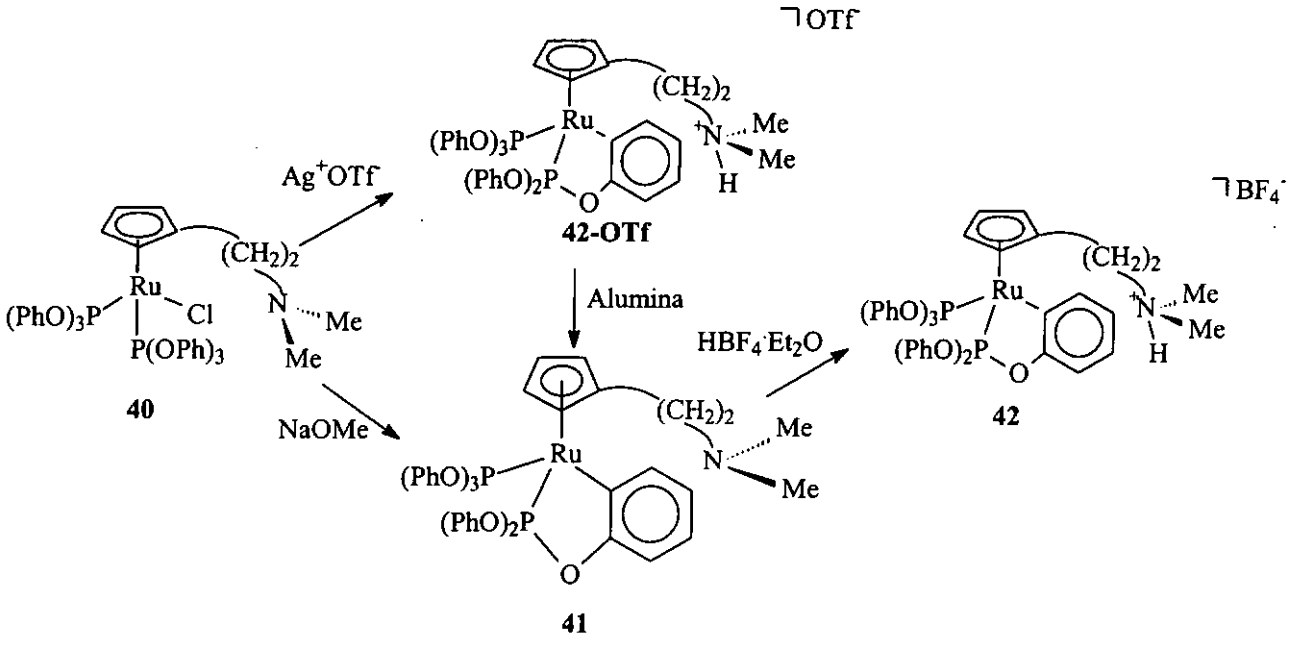
Eq. 3.1

Formation of **42** is not surprising, since it is known that the unsubstituted Cp complex $(\eta^5\text{-}C_5H_5)Ru(PPh_3)(P(OPh)_3)Cl$ reacts with AgOTf in the presence of piperidine at room temperature to give the ortho-metalated complex $(\eta^5\text{-}C_5H_5)(PPh_3)(\eta^2\text{-}P(OPh)_2OC_6H_4)$ [82]. Ortho-metalated Cp ruthenium and osmium complexes are well-documented [70, 71], [82]. Complex **42** was characterized by NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum showed two doublets corresponding to the two inequivalent phosphites at δ 144.2 and 172.9 ppm (J(PP) = 89 Hz). The sharp AX pattern indicates that there is no interconversion of the two phosphites at room temperature by reversible metalation/demetalation of ortho-hydrogens on the two different phosphites. Exchange of the two phosphines has been observed in the ortho-metalated iridium complex $IrH(C_2Ph)(P^tBu_2Ph)(\eta^2\text{-}C_6H_4P^tBu_2)$ [83]. The doublet signal at δ 111.2 ppm (J(CP) = 16.1

Hz) in the ^{13}C NMR spectrum of **42** is diagnostic of metalated ortho-carbon atom Ru-C. Signals with similar chemical shifts and P-C coupling constants also appear in ^{13}C NMR spectra of similar ortho-metalated Ru(II) complexes [70],[82]. The amine group in the sidearm was protonated. Evidence for amine protonation was provided by ^{1}H NMR spectrum of **42**, it showed the N-methyl protons as two doublets at δ 2.60 (J(HH) = 4.4 Hz) and 2.70 (J(HH) = 4.3 Hz) ppm, which were downfield-shifted from the N-methyl proton signal of the free ligand $C_5H_5(CH_2)_2NMe_2$ (δ 2.27 ppm). Similar downfield shifts of the N-methyl protons have been observed in **31** and its chloro analogue [79], in molybdenum [70, 71] and rhodium [83] complexes containing similar ligands. Protonation of the amine group in **42** was also supported by observation of the broad singlet signal of N-H at δ 8.20 ppm. It is also noteworthy that the N-methyl groups are inequivalent, probably due to restricted rotation of the C-N bond.

It is difficult to obtain analytically pure sample of **42** by the silver triflate reaction (Eq. 3.1), probably due to difficulty in completely removing the silver salts from the product, which is a sticky semi-solid. We attempted to purify **42** by column chromatography using neutral alumina, but the product collected was the deprotonated form of **42**, i.e. (η^5-$C_5H_4(CH_2)_2NMe_2$)Ru($P(OPh)_3$)(η^2-$P(OPh)_2OC_6H_4$) (**41**). The $^{31}P\{^{1}H\}$ NMR spectrum of **41** is similar to that of **42**, showing two doublets at δ 144.3 (J(PP) = 99.9 Hz) and 170.9 (J(PP) = 99.9 Hz) ppm. The ^{13}C NMR spectrum of **41**, similar to that of **42**, also contains a doublet in the downfield region at δ 111.1 ppm (J(CP) = 16.0 Hz), due to Ru-C. However, the ^{1}H NMR spectrum of **41**, shows, instead of a pair of downfield-shifted doublets for the N-methyl protons, a relatively upfield singlet, which integrates to 6

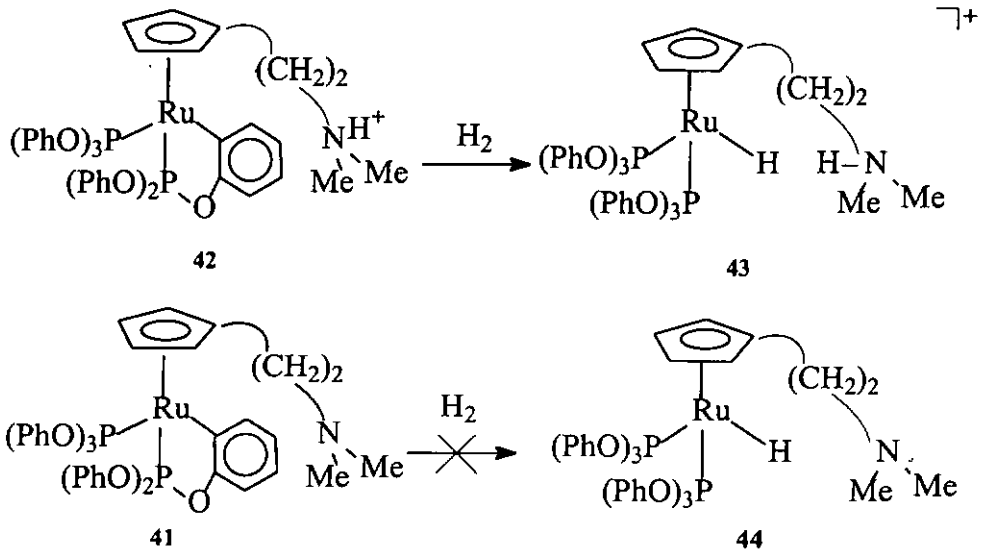
hydrogens, at δ 1.90 ppm. No N-H signal is observable in the downfield region. Acidification of **41** with tetrafluoroboric acid in etheral solution gives **42** of acceptable purity. Complex **41** can also be prepared by refluxing **40** with sodium methoxide in methanol (Scheme 3.2). Similar ortho-metalation has been achieved for $(\eta^5\text{-}C_5H_5)Ru(P(OPh)_3)_2Cl$ by refluxing the complex with methoxide ion in methanol [70]. However, the complexes $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl$ and $(\eta^5\text{-}C_5H_5)Ru(PPh_3)(P(OPh)_3)Cl$ cannot be ortho-metalated under the same experimental conditions [82].



Scheme 3.2 Reaction pathways for the preparation of ortho-metalated aminocyclopentadienyl ruthenium complexes

3.4.2 Synthesis and characterization of hydrido aminocyclopentadienyl ruthenium complexes

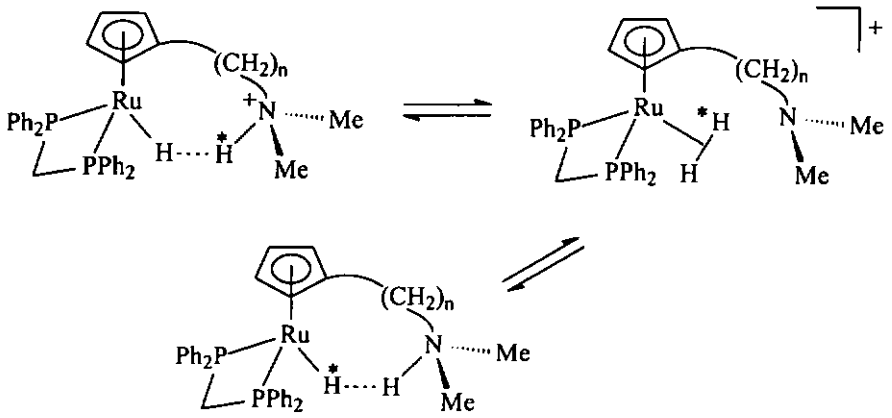
Study of reactivity of **42** and **41** toward pressurized dihydrogen gave interesting results. Complex **42** reacted, as expected, with H_2 (10 atm) in chlorobenzene at room temperature to yield our targeted complex $[(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2H^+)Ru(P(OPh)_3)_2H]^+$ (**43**) (Eq. 3.2). Under identical experimental conditions, **41** is, however, inert to H_2. We expect **41**, in analogous to **42**, to react with H_2, forming the deprotonated form of **43**, i.e. $(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2)Ru(P(OPh)_3)_2H$ (**44**). It was later found out that **44** could be obtained by deprotonation of **43** with aqueous KOH in ethanol.



Eq. 3.2

In the ^1H NMR spectrum of **43**, the hydride signal is a sharp triplet (J(HP) = 26.0 Hz) at δ −11.83 ppm. Similar to its precursor **42**, complex **43** shows a downfield

shifted signal (δ 2.61 ppm) for its N-methyl protons, but the signal is a singlet rather than a pair of doublets as observed for the N-methyl protons of **42**. The N-H of **43**, which does not split the N-methyl signal, appears as a broad peak at δ 8.47 ppm. The $^{31}P\{^{1}H\}$ NMR spectrum of **43** shows a singlet at δ 149.7 ppm, indicating that the two phosphorous atoms are equivalent. Several attempts to obtain single crystals of **43** for x-ray structural determination have not been successful; in fact, this complex, and other phosphite complexes reported in this work, are sticky solids, they all resist single crystal formation.



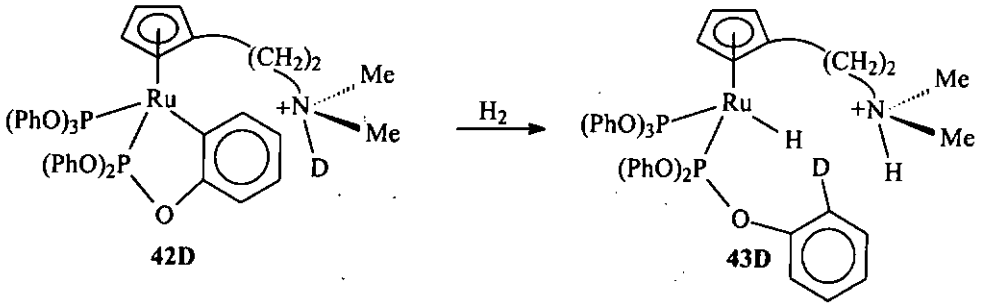
Scheme 3.3 Proposed mechanism for the rapid and reversible hydride proton exchange via η^2-tautomer in $[(\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2NMe_2)Ru(dppm)]^+$

Sharpness of the hydride signal of **43** indicates that H···H interaction between the hydride ligand and N-H on the pendant amine arm is very weak, if exists at all. On the contrary, complex **31**, the dppm analogue of **43**, which shows a broad hydride signal, exhibits considerably strong Ru-H···H-N dihydrogen-bonding interaction, the two hydrogen atoms undergo rapid exchange via the intermediacy of a η^2-dihydrogen species [79] (Scheme 3.3). Broadening of the hydride signal of $WH(CO)_2(NO)(PMe_3)_2$ was

observed in the presence of acidic alcohol, due to the formation of intermolecular M-H···H-OR dihydrogen bond [25]. Significant broadening of the hydride signals of both *cis* and *trans* isomers of $RuH_2(dppm)_2$ were also observed upon addition of excess phenol [32]. Lack of Ru-H···H-N dihydrogen-bonding interaction in **43** was also supported by the fact that practically no NOE was detected between Ru-H and N-H. Variable temperature T_1 measurements for the hydride ligand of **43** yielded a T_1(min) of 890 ms (at 400 MHz and 290 K), this value is very similar to that of the hydride ligand of **44** (T_1(min) = 900 ms at 400 MHz and 248 K); similarity of T_1(min) values of the hydride ligands of **43** and **44** lends further support to the notion that intramolecular dihydrogen-bonding interaction in the former is minimal. It is obviously true that the less donating triphenylphosphite ligands lower the basicity of the metal center in **43**, which, in turn decreases the hydridicity of the hydride ligand to such an extent that the Ru-H···H-N dihydrogen bond is no longer stable. M-H···H-X dihydrogen bond is a hydride-proton interaction, and its bond strength can be modulated by tuning the nucleophilicity of M-H and/or electrophilicity of H-X [39, 40, 46, 84]. Epstein, Berke, and co-workers have reported that the strengths of the dihydrogen bonds in the tungsten hydride-alcohol complexes $W(CO)_2(NO)(L)_2H\cdots HOR$ increase with the donor abilities of the ligand L ($PPh_3 < P(P^iPr)_3 < PEt_3 < PMe_3$) [25].

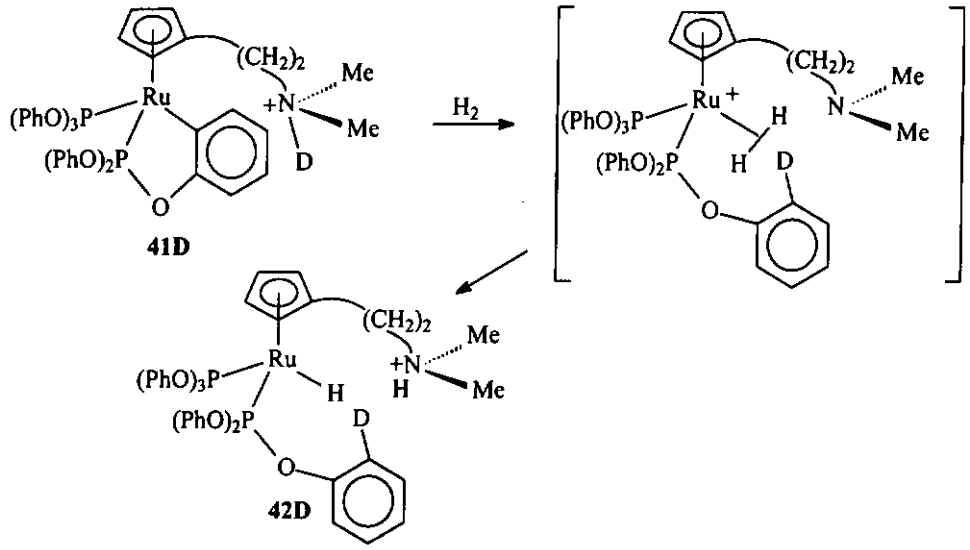
Unlike the dppm analogue **31**, **43** is stable towards H_2 loss even after reflux in THF or heating at 90 °C in chlorobenzene for 2 days. This is not unexpected since lack of Ru-H···H-N dihydrogen bonding in **43** precludes the possibility of eliminating H_2 via the intermediacy of a η^2-H_2 species.

To learn more about the reaction of **42** with H_2, we reacted $[(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2D^+)Ru(P(OPh)_3)(P(OPh)_2OC_6H_4)]^+OTf^-$ (**42D**), the deuterated form of **42** in which the amine sidearm was deuterated, with H_2 and studied the distribution of deuterium in the product. A combination of ^1H and ^2H NMR spectroscopic studies clearly indicated that all the deuterium atoms had been transferred to the triphenylphosphite ligand, and the Ru-H and N-H groups were deuterium-free (Eq. 3.3).



Eq. 3.3

The result of the labeling experiment is in consonance with the proposed reaction mechanism depicted in Scheme 3.4. The crucial step of the hydrogenolysis of **42** with H_2 seems to be protonation of the ortho-carbon in Ru-C by the ammonium proton. It is therefore not surprising to find that **41**, which is devoid of an ammonium proton, is unreactive towards H_2.



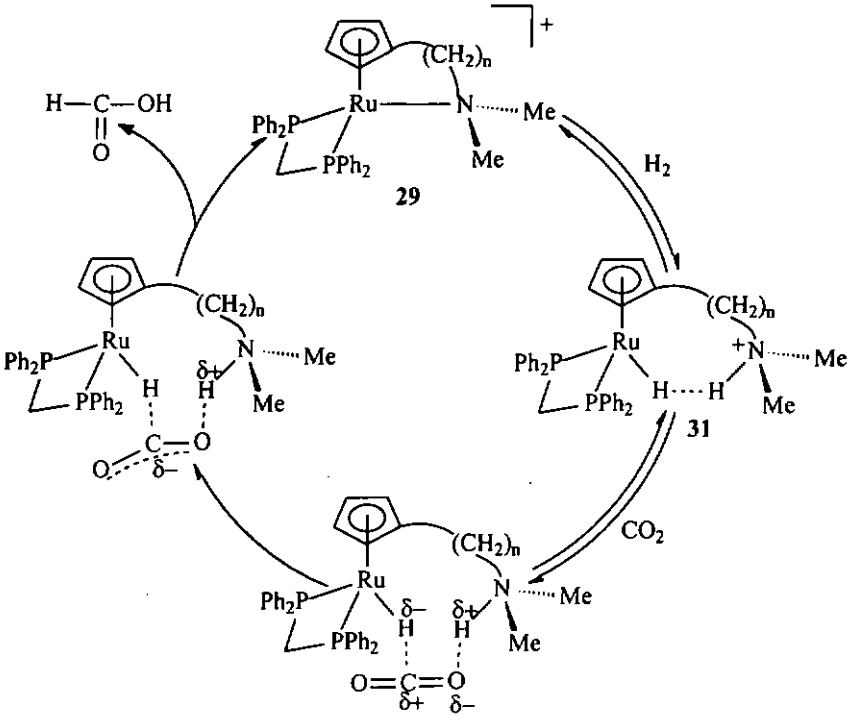
Scheme 3.4 Proposed reaction pathway of the deuterium labeling experiment

As expected, the ^{1}H NMR spectrum of **44** shows a relatively upfield singlet signal for its non-protonated amine group (δ 2.29 ppm), and no N-H signal is observable in the downfield region. The two equivalent phosphite ligands of **44** appear as a singlet at δ 143.7 ppm in the $^{31}P\{^1H\}$ NMR spectrum.

3.4.3 Reactivities of $[(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2H)Ru(P(OPh)_3)_2H]^+$ towards H_2/CO_2.

Since complex **31**, the dppm analogue of **43**, is believed to play a crucial role in reduction of CO_2 to formic acid catalyzed by its precursor complex **29** (Scheme 3.5), we are thus interested in studying the catalytic activity of **43** (or its precursor **42**) in CO_2 hydrogenation. No catalytic activity was, however, found. Lack of activity in **43** is attributable to low hydridicity of the hydride ligand. In **43**, although the protonated amine

sidearm, like that of **31**, can H-bond with one of the oxygen atoms of an incoming CO_2 molecule and thus enhancing the electrophilicity at the carbon, the hydride ligand is unfortunately not hydridic enough to allow its abstraction by the electrophilic carbon center.



Scheme 3.5 Proposed mechanism for the hydrogenation of carbon dioxide by $[(\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2NMe_2)Ru(dppm)]^+$

4. Conclusion

Intermolecular and intramolecular hydrogen bonding is crucial in many chemical reactions including proton transfer reactions. The hydrogen bond strength depends on the proton donating ability of the proton donor and the proton accepting ability of the proton acceptor. Choosing different proton donors or acceptors can vary the strength of the hydrogen bond. The proton transfer reaction between different acidic alcohols; trifluoroethanol (TFE), hexafluoroisopropanol (HFIP) and per-*tert*-fluorobutanol (PFTB) and ruthenium complexes; $TpRu(PPh_3)_2H$ and $[TpmRu(PPh_3)_2H](BF_4)$ were investigated. Intermolecular hydrogen bonded species was detected in variable temperature ^1H NMR spectra when $TpRu(PPh_3)_2H$ reacted with acidic alcohol only. Moreover, with HFIP the intermolecularly hydrogen-bonded intermediate was in equilibrium with the η^2-H_2 complex, the product of proton transfer reaction. The stability of the intermolecular hydrogen bond depends on both the proton accepting power of the metal hydride and also the proton donating ability of the acidic alcohols.

For the reaction of TFE with $TpRu(PPh_3)_2H$, the low acidity of TFE led to the formation of hydrogen bonded species as the only product. The product of complete proton transfer, the dihydrogen complex was not detected. When a more acidic alcohol, HFIP was employed, variable temperature ^1H NMR experiment showed an equilibrium between the hydrogen bonded species and the η^2-H_2 complex. Unfortunately, T_1(min) of the hydrogen-bonded hydride ligand cannot be measured since it boardened into the baseline at temperature lower than 263 K. For the reaction of the most acidic alcohol PFTB

with $TpRu(PPh_3)_2H$, the high acidity of PFTB ensured complete proton transfer yielding the η^2-H_2 complex as the only species detected throughout the variable temperature ^1H NMR experiment.

Changing from the neutral ruthenium complex $TpRu(PPh_3)_2H$, to the mono-cationic complex, $[TpmRu(PPh_3)_2H](BF_4)$, no intermolecular hydrogen bonding interaction with any acidic alcohol was observed. The reason of the absence of such interaction with acidic alcohol is attributable to diminished hydridicity of the hydride ligand in the complex. The net positive charge of the metal center is responsible for the low hydridicity.

Intramolecular Ru-H···H-N dihydrogen bond was previously detected in $CpNH^+Ru(dppm)H$ **(31)** (CpN = [2-(N,N-Dimethylamino)ethyl]cyclopentadienyl) by our group, in continuing our studies of dihydrogen bonding in aminocyclopentadienyl ruthenium hydride complexes and catalytic activity of these complexes in CO_2 hydrogenation, I have studied the effect of decreased the basicity of the metal center on the strength of the Ru-H···H-N dihydrogen bond. The basicity of the metal center in the aminocyclopentadienyl ruthenium complex was decreased by replacement of the dppm ligand in **31** or **29** with triphenylphosphite.

The complex $CpNRu(P(OPh)_3)_2Cl$ was synthesized by refluxing its precursor $CpNRu(PPh_3)_2Cl$ with triphenylphosphite in toluene. Treatment of $CpNRu(P(OPh)_3)_2Cl$ with silver triflate yielded the ortho-metalated complex, $[(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2H^+)Ru(P(OPh)_3)(P(OPh)_2OC_6H_4)]^+OTf^-$ **(42-OTf)** with the side arm

protonated. This complex was obtained in impure form due to difficulty in completely removing the silver salts for the product. Eluting a sample of **42-OTf** through neutral alumina yielded the deprotonated ortho-metalated complex, (η^5-$C_5H_4(CH_2)_2NMe_2$)Ru(P(OPh)$_3$)(P(OPh)$_2$OC$_6$H$_4$), **(41)**. Acidification of **41** by $HBF_4{\cdot}Et_2O$ yielded pure $[(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2H^+)Ru(P(OPh)_3)(P(OPh)_2OC_6H_4)]^+(BF_4)^-$ **(42).** Application of hydrogen pressure (25 atm) to **41** and **42** yielded different results, **42** reacted with hydrogen to yield the hydride complex, $[(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2H^+)Ru(P(OPh)_3)_2H](BF_4)$ **(43)**, which is analogous to **31** while **41** did not react with hydrogen gas. The amine sidearm deprotonated hydride, (η^5-$C_5H_4(CH_2)_2NMe_2$)Ru(P(OPh)$_3$)$_2$H **(44)** was synthesized by stirring **43** with KOH in ethanol. NOE experiments for **43** were carried out but no Ru-H···H-N dihyrogen-bonding interaction was detected between the protonated amine sidearm and the ruthenium hydride. It is obviously true that the less donating triphenylphosphite ligands lower the basicity of the metal center in **43**, which, in turn decreases the hydridicity of the hydride ligand to such an extent that the Ru-H···H-N dihydrogen bond is no longer stable.

Finally, catalytic activity of **43** towards catalytic hydrogenation of carbon dioxide to formic acid was examined. However, no catalytic activity was detected. Lack of activity is attributed to the low hydridicity of the hydride ligand in **43**. Though the protonated amine sidearm can H-bond with one of the oxygen atoms of an incoming CO_2 molecule and thus enhancing the electrophilicity at the carbon, the hydride ligand is unfortunately not hydridic enough to allow its abstraction by the electrophilic carbon center.

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Appendix

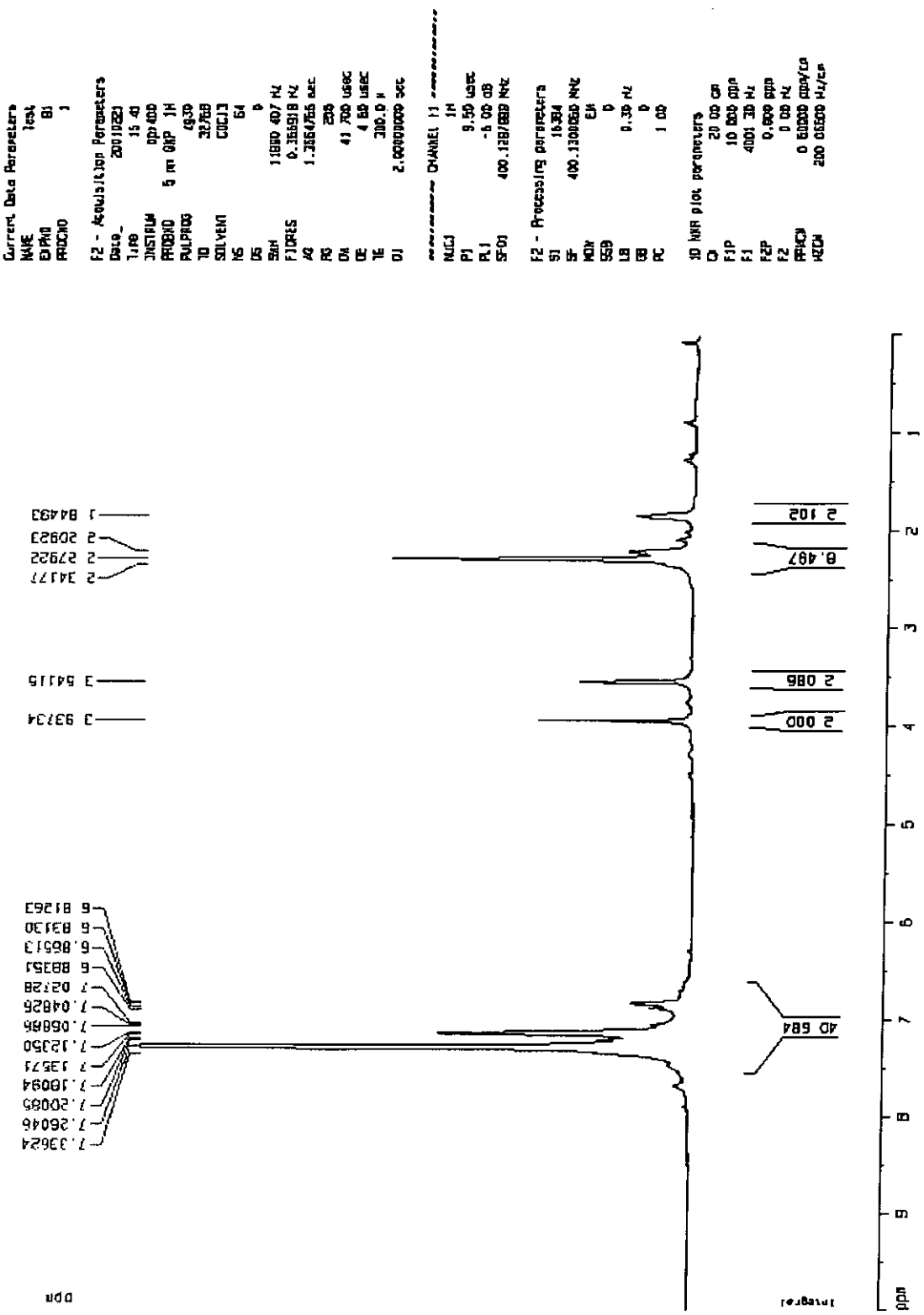

Figure 3.1 400 MHz 1H NMR spectrum of $CpNRu[P(OPh)_3]_2Cl$ (40)

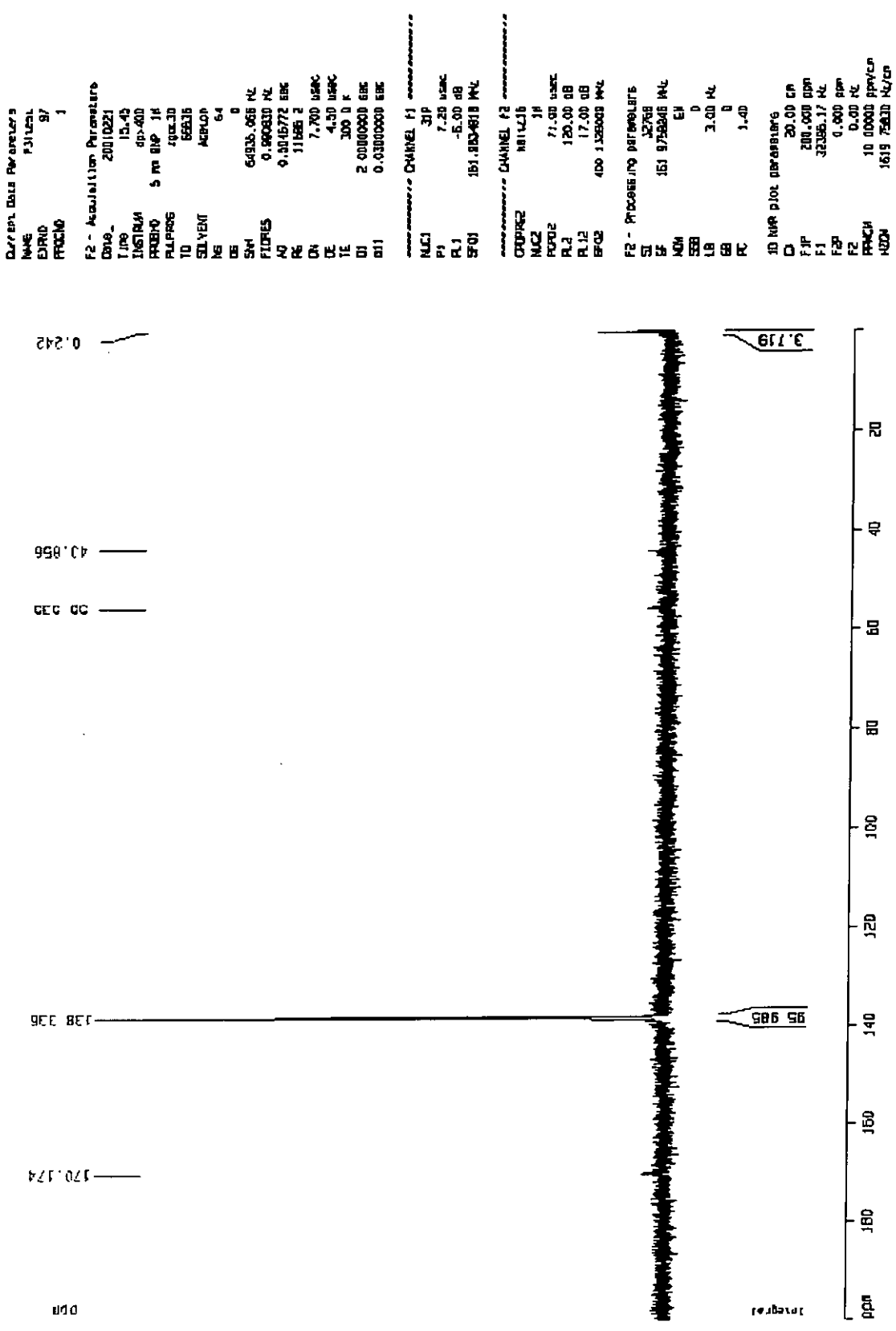

Figure 3.2 161.7 MHz $^{31}P\{^{1}H\}$ NMR spectrum of $CpNRu[P(OPh)_3]_2Cl$ (40)

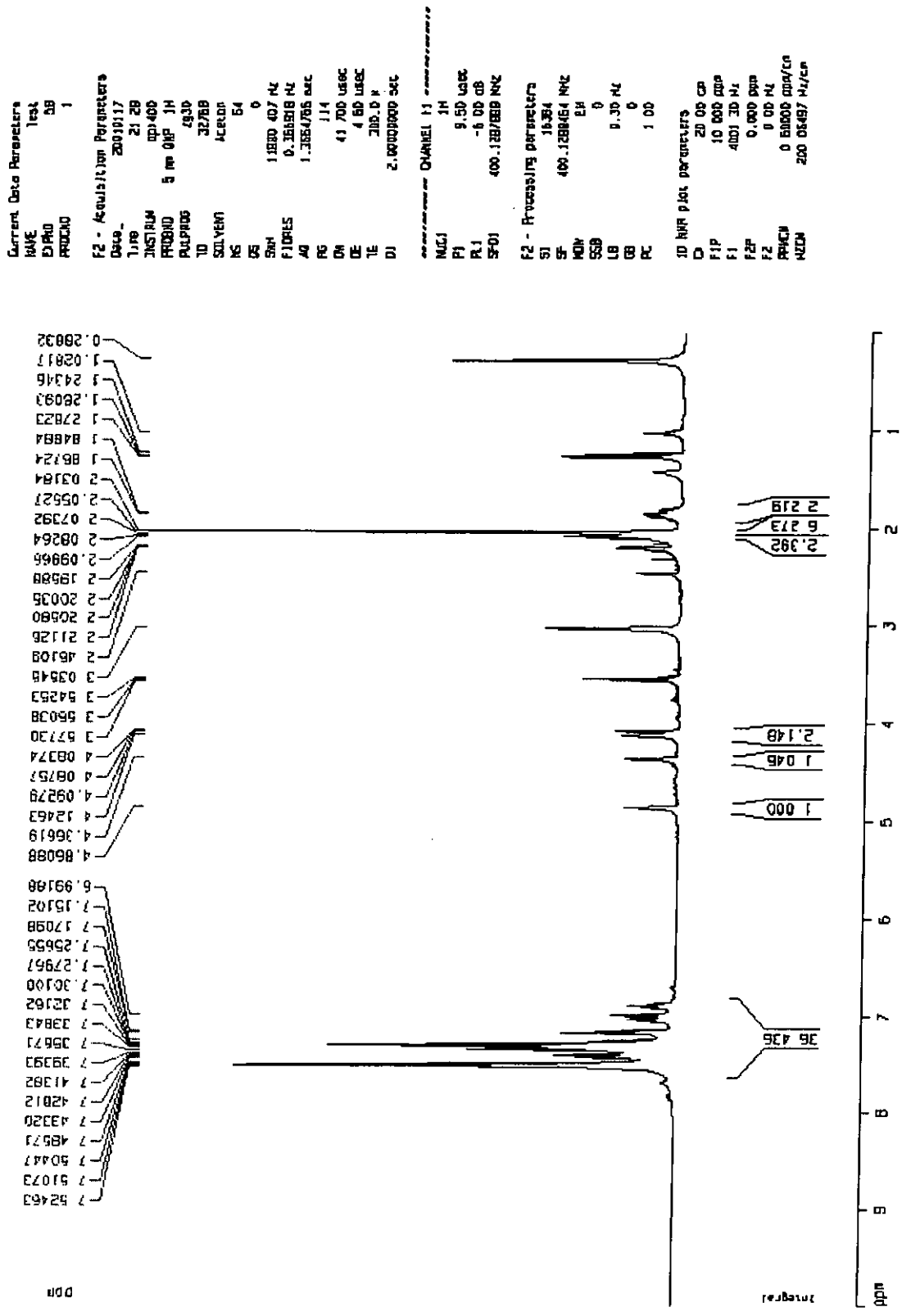

Figure 3.3 400 MHz ^{1}H NMR spectrum of CpNRu[P(OPh)$_3$][(OPh)$_2$P(OC$_6$H$_4$)] (41)

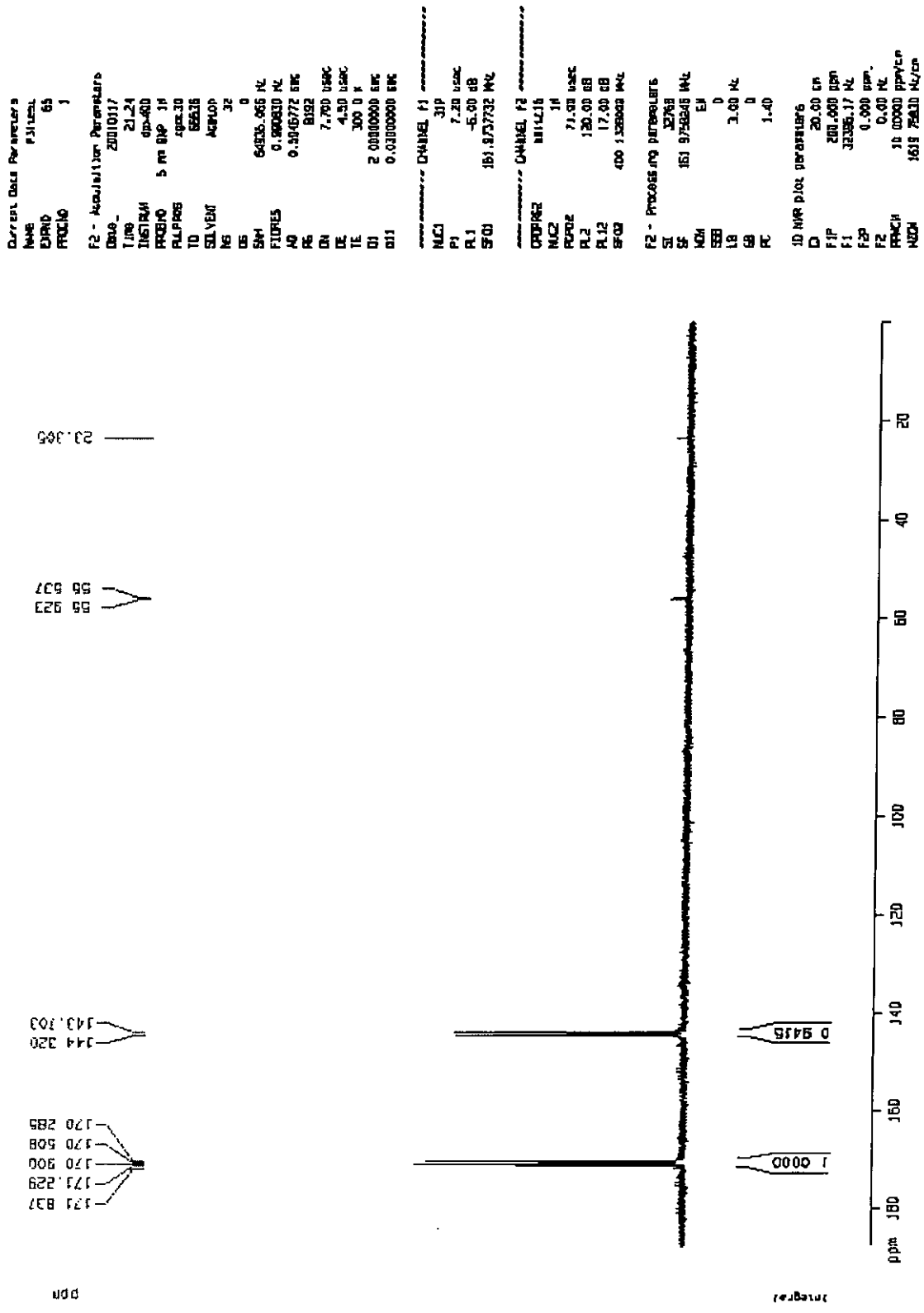

Figure 3.4 161.7 MHz $^{31}P\{^{1}H\}$ NMR spectrum of $CpNRu[P(OPh)_3][(OPh)_2P(OC_6H_4)]$ (41)

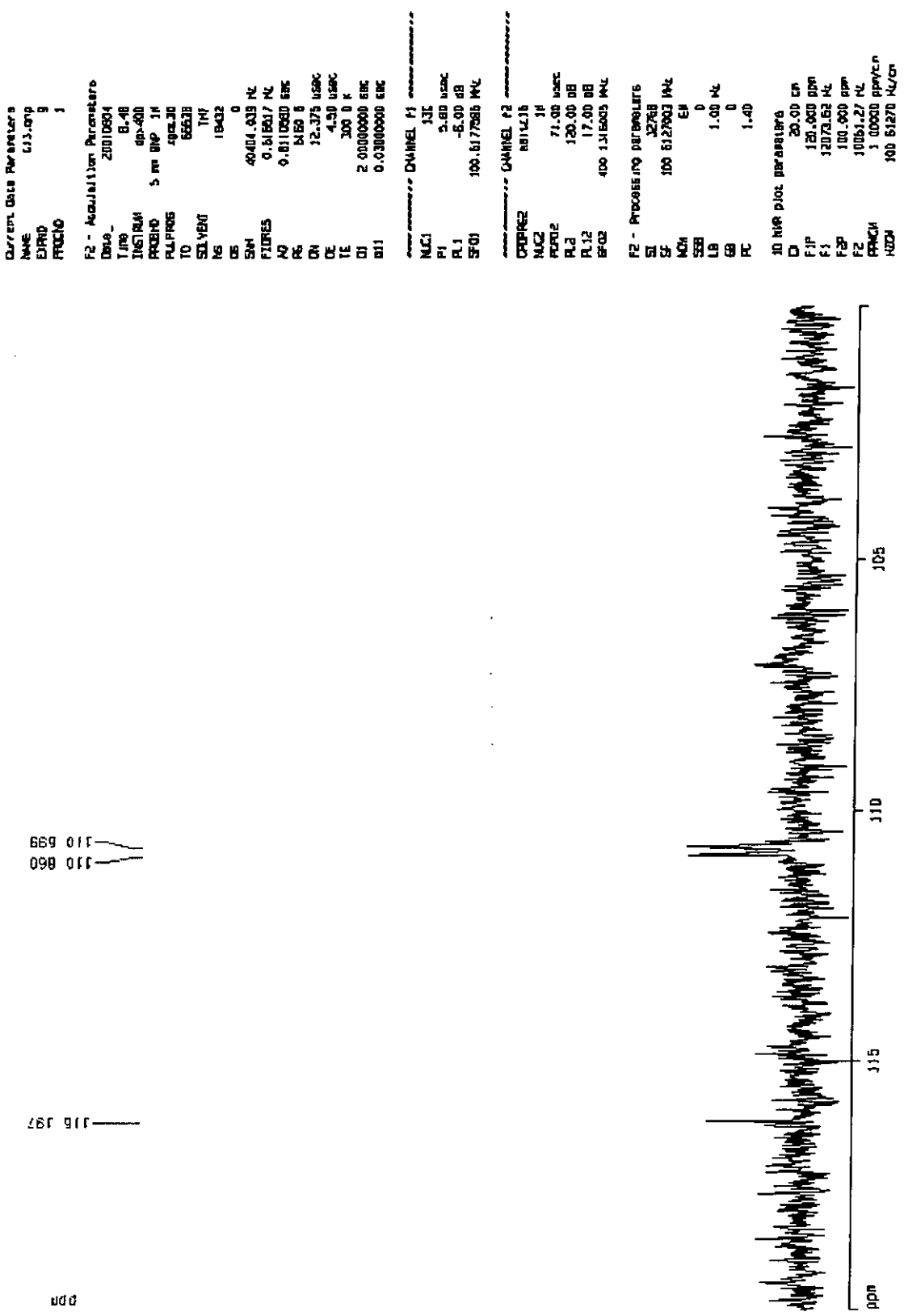

Figure 3.5 100.6 MHz $^{13}C\{1H\}$ NMR spectrum of CpNRu[P(OPh)$_3$][(OPh)$_2$P(OC$_6$H$_4$)] (41)

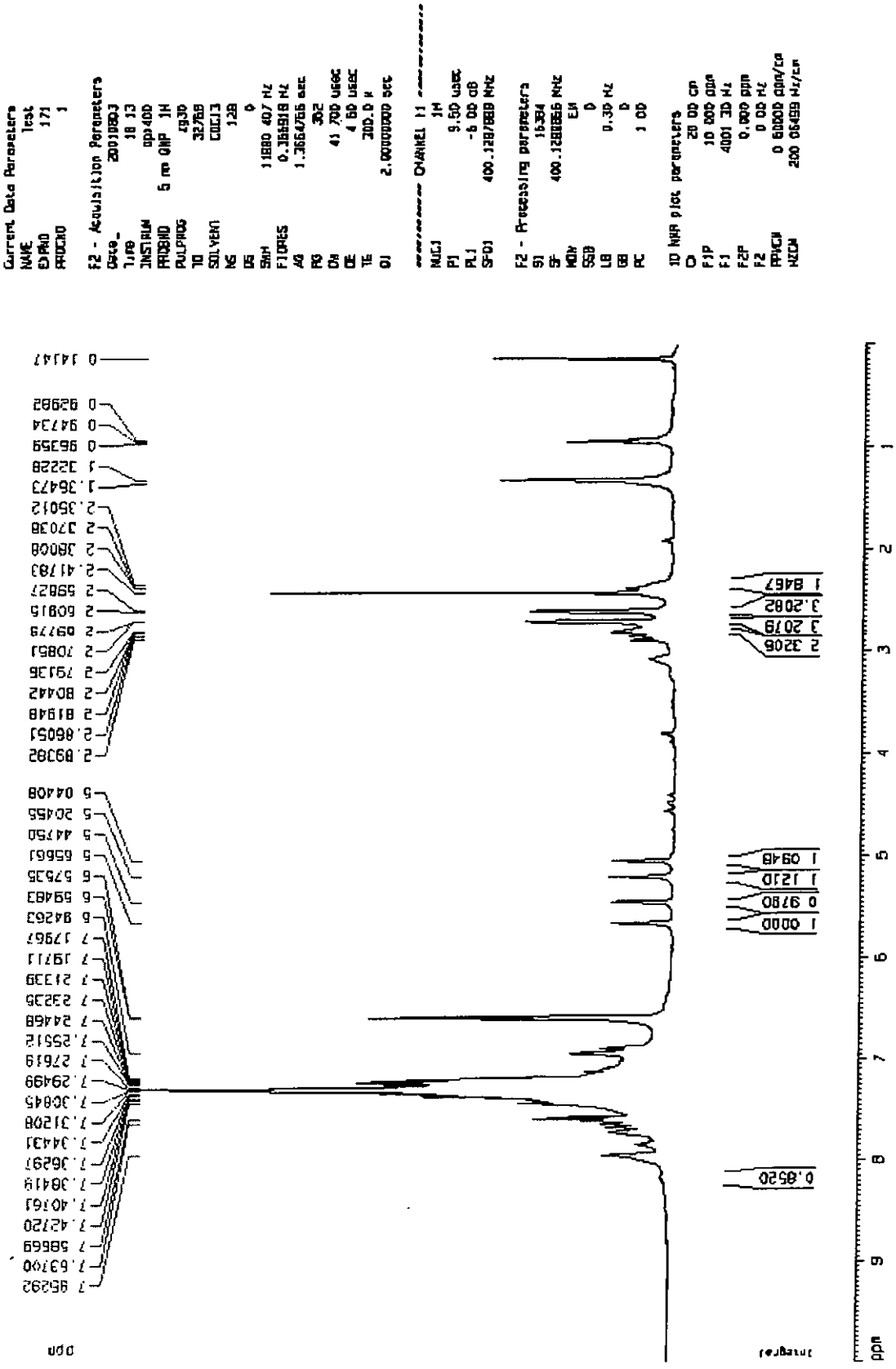

Figure 3.6 400 MHz ^{1}H NMR spectrum of $\{CpNH^+Ru[P(OPh)_3][(OPh)_2P(OC_6H_4)]\}(BF_4)$ (42)

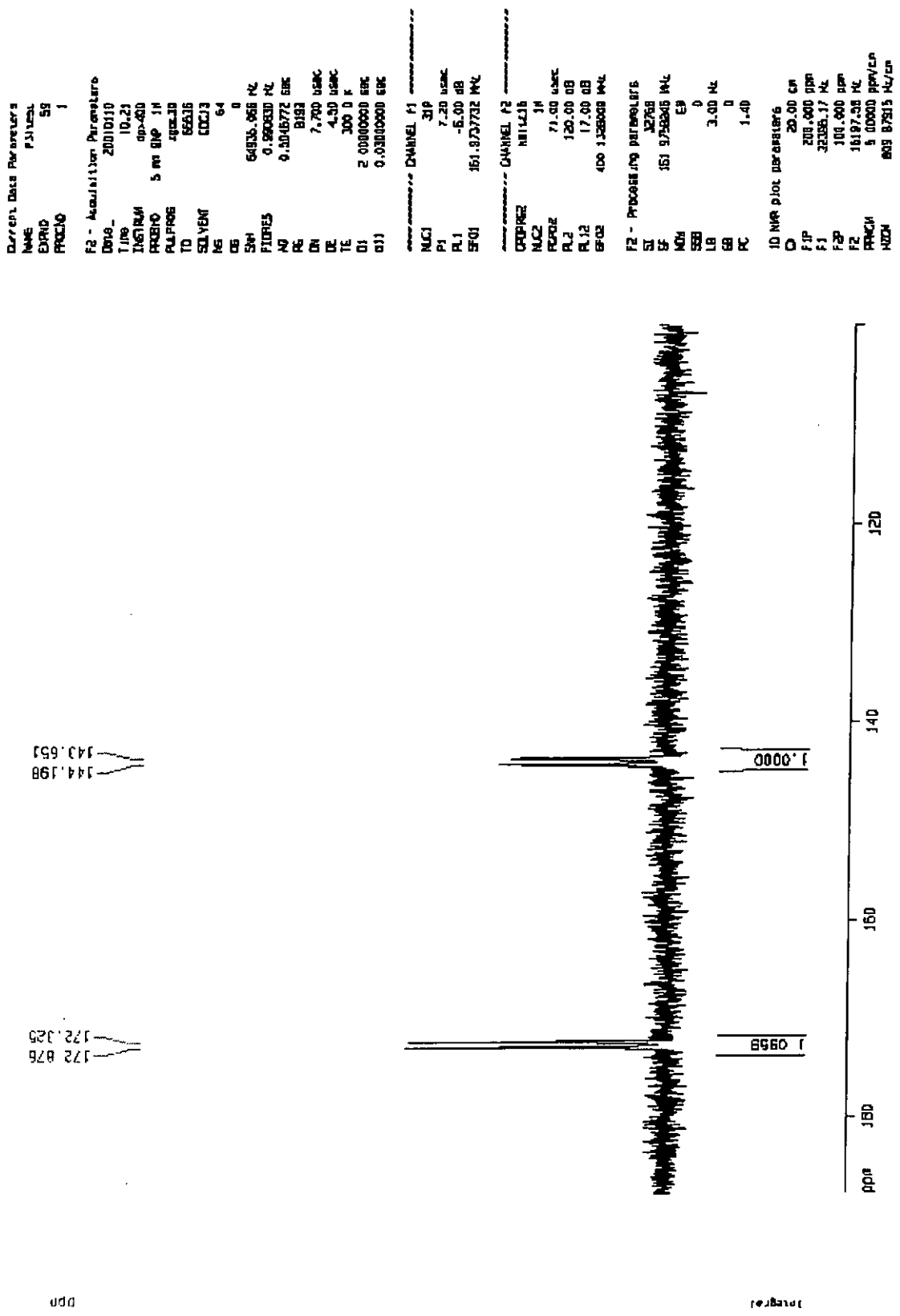

Figure 3.7 161.7 MHz $^{31}P\{^{1}H\}$ NMR spectrum of $\{CpNH^{+}Ru[P(OPh)_3][(OPh)_2P(OC_6H_4)]\}(BF_4)$ (42)

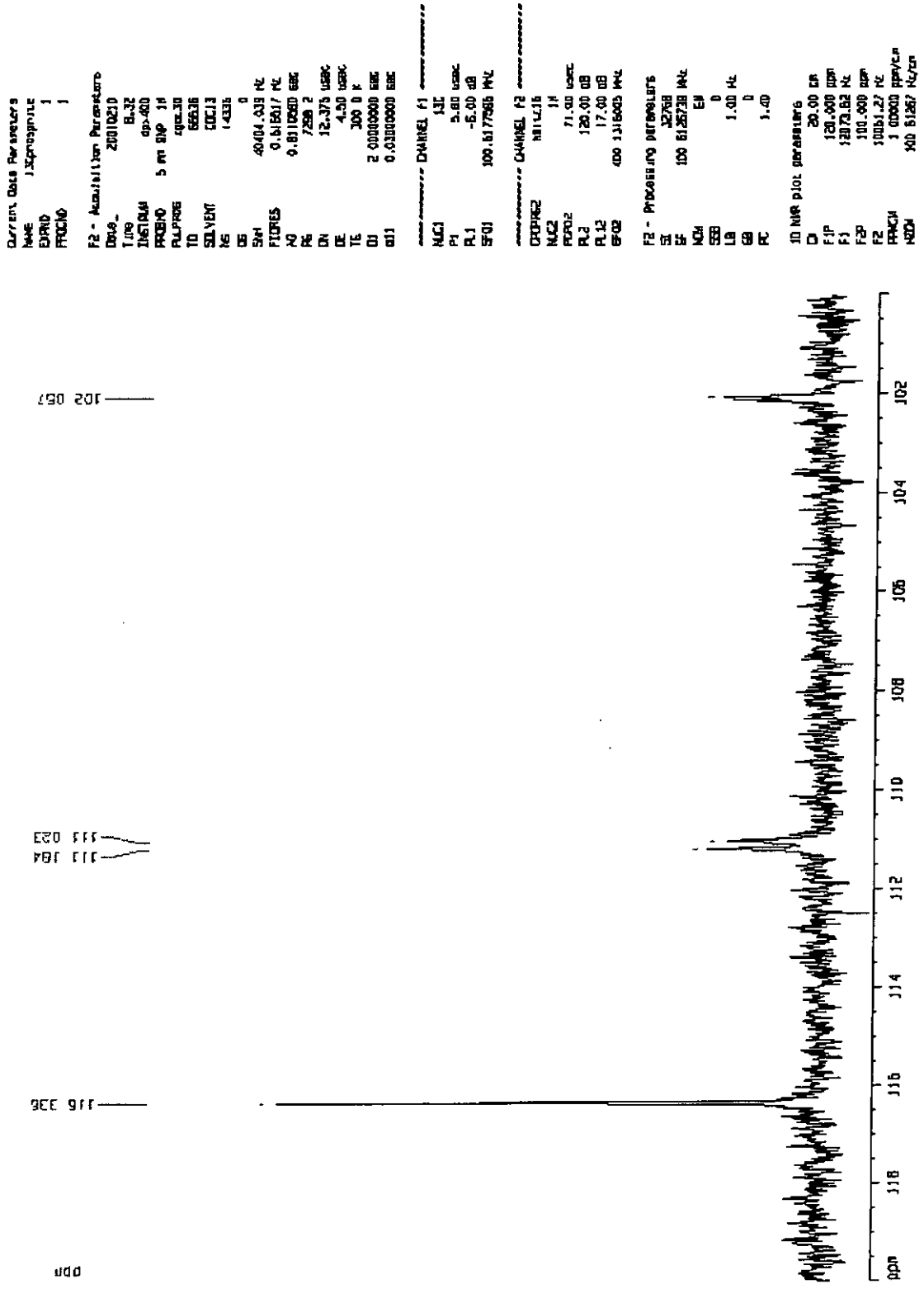

Figure 3.8 100.6 MHz $^{13}C\{1H\}$ NMR spectrum of $\{CpNH^{+}Ru[P(OPh)_3][(OPh)_2P(OC_6H_4)]\}(BF_4)$ (42)

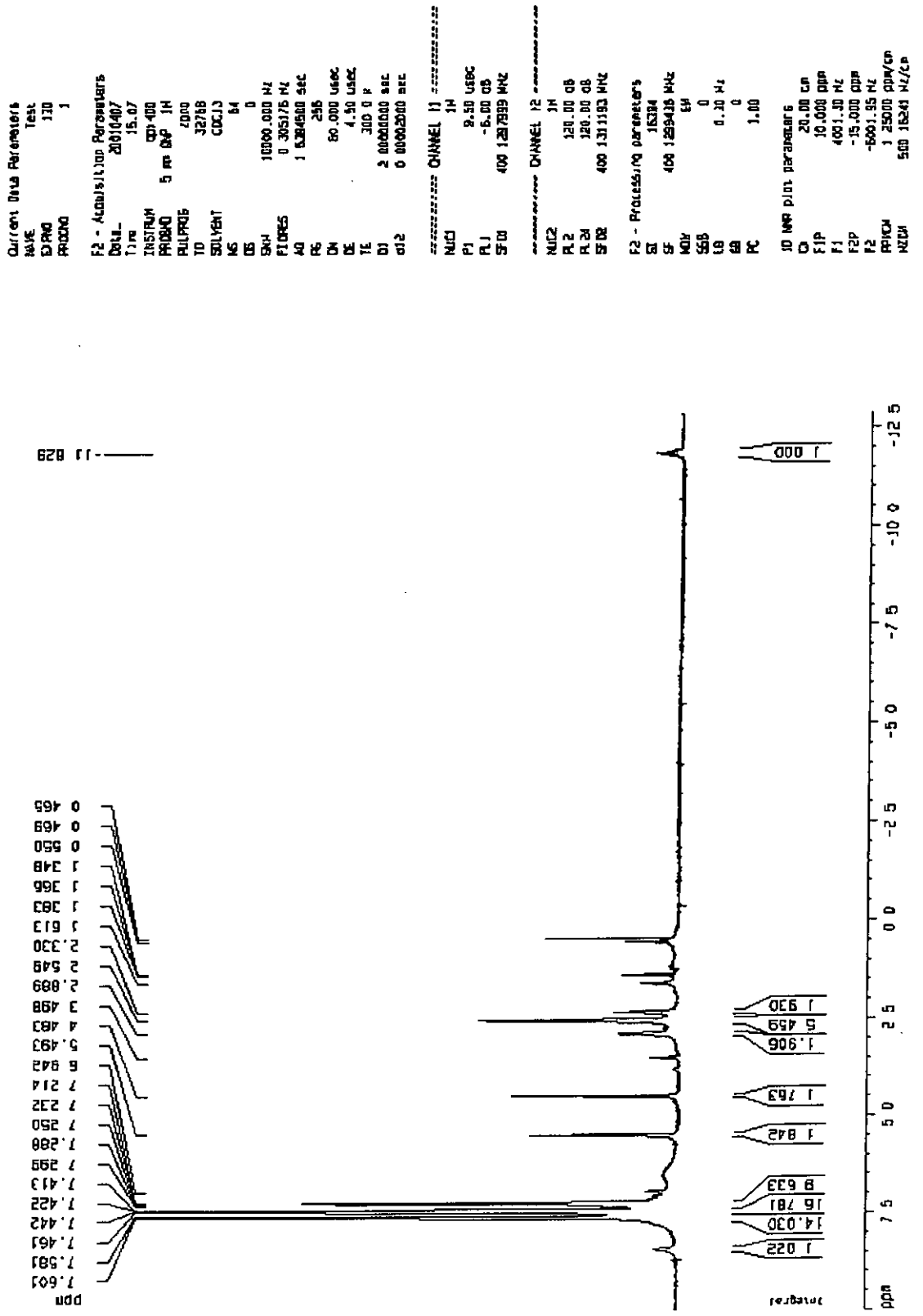

Figure 3.9 400 MHz ^{1}H NMR spectrum of $\{CpNH^+Ru[P(OPh)_3]_2H\}(BF_4)$ (43)

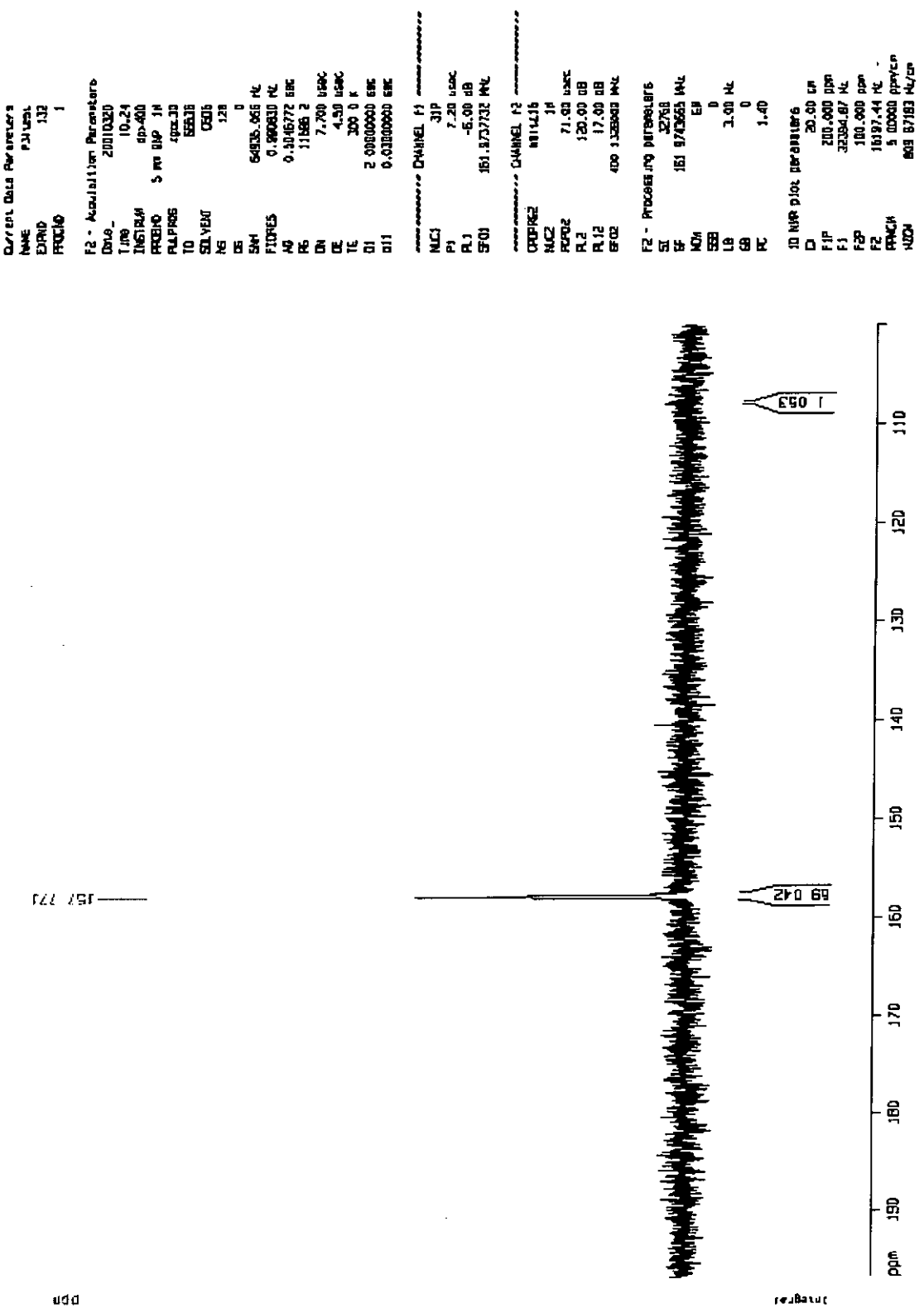

Figure 3.10 161.7 MHz $^{31}P\{^{1}H\}$ NMR spectrum of $\{CpNH^{+}Ru[P(OPh)_3]_2H\}(BF_4)$ (43)

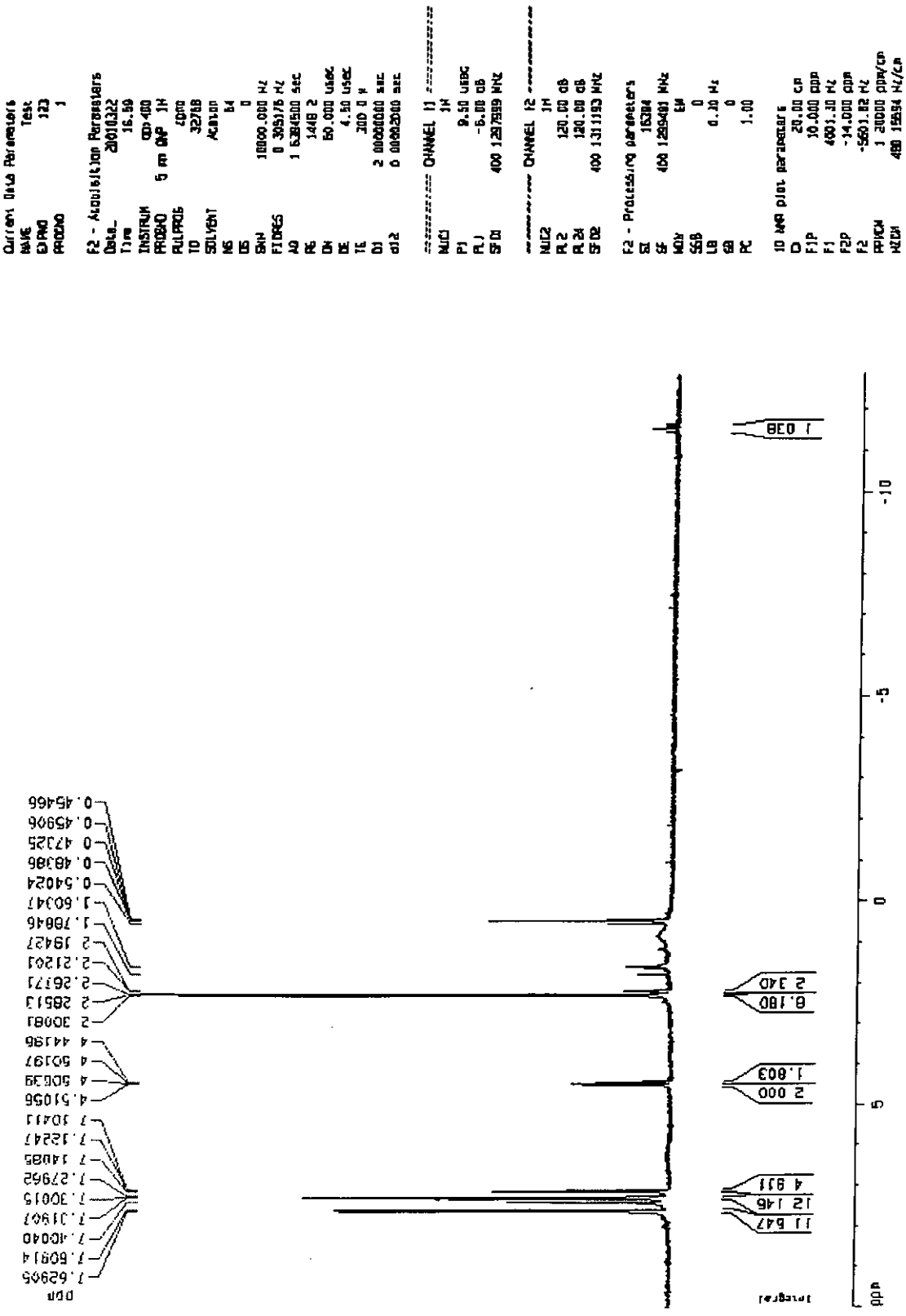

Figure 3.11 400 MHz ^{1}H NMR spectrum of CpNRu[P(OPh)$_3$]$_2$H (44)

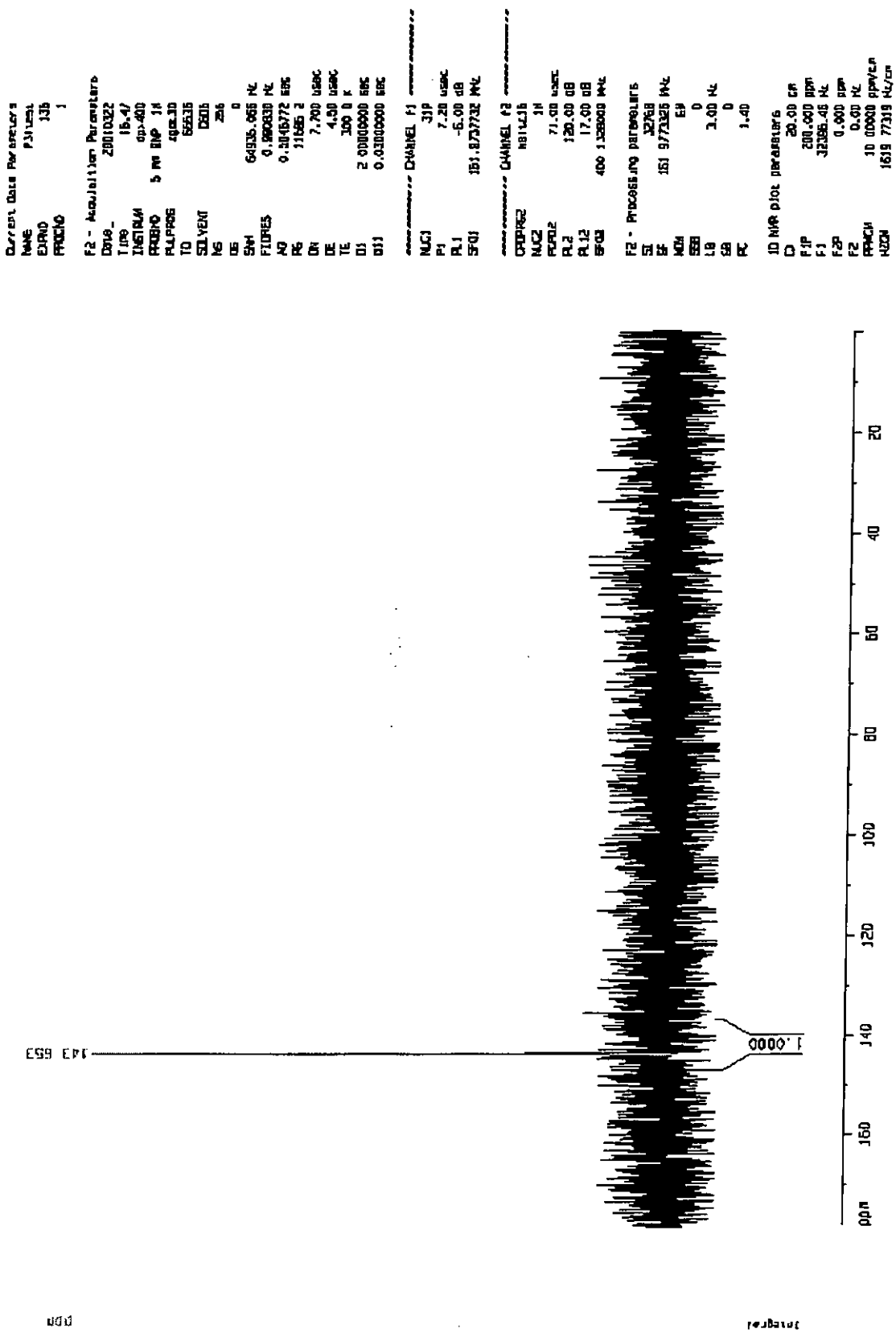

Figure 3.12 161.7 MHz $^{31}P\{^{1}H\}$ NMR spectrum of $CpNRu[P(OPh)_3]_2H$ (44)