"Syntheses and Characterization of ruthenium η^2-dihydrogen and η^2-silane complexes"

A Thesis Submitted to

The Department of Applied Biology and Chemical Technology

for the degree of Master of Philosophy

at

The Hong Kong Polytechnic University

by

Siu-Man, NG

July, 1998

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, 1995; 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.

Siu-Man, NG

July, 1998

Acknowledgements

I would like to express my deepest gratitude to my supervisor Dr. C. P. Lau for his advice and patience throughout the course of my study. His guidance, encouragement and devoted attitude in research has made my study a truly rewarding experience.

Thanks are also expressed to Dr. G. Jia of the Department of Chemistry, The Hong Kong University of Science and Technology for many fruitful discussions over the area of acidity of non-classical dihydrogen complexes and Dr. W. T. Wong of The University of Hong Kong for solving the crystal structures of some of the ruthenium complexes.

I am deeply in debt to Dr. C. H. Yeung for his expertise knowledge and assistance in performing the ^{29}Si NMR.

I also want to thank all my postgraduate colleagues and the undergraduate students in Dr. Lau's group, especially Mr. W. C. Chan who introduced to me the interesting chemistry of ruthenium. Sincere thanks are due to Mr. Y. Z. Chen, Mr. Y. Q. Fang, Ms. M. Y. Hung, Mr. C. C. Mak and Mr. C. Q. Yin, all of whom have made my study in FG 703 more pleasant. Special thanks are expressed to Mr. H. S. Chu for his valuable discussions and assistance.

I am obliged to the staff and the technical service crew of the Chemical Technology section of the Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University for their assistance throughout my postgraduate study, especially thanks to Mr. Y. K. Au , Ms. P. S. Chan and Mr. W. K. Kwan for their assistance in running the MS and NMR. spectra respectively.

Lastly but not the least, I am greatly indebted to my parents and the whole family for their support, forbearance, patience and concern while I was engaged in this research project.

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

Abstract of thesis entitled "Syntheses and Characterization of ruthenium η^2-dihydrogen and η^2-silane complexes"

submitted by Siu-Man. NG

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in July, 1998.

Abstract

Protonation of $[^{R}CnRuH(L)(L')]^{+}$ (^{R}Cn = 1,4,7-triazacyclononane and 1,4,7-trimethyl-1,4,7-triazacyclononane, (L)(L') = $(PPh_3)_2$, dppe, and $(CO)(PPh_3)$) and TpRuH(dppe) (Tp = hydrotris(pyrazolyl)borato) produced the corresponding dicationic dihydrogen complexes $[^{R}CnRu(H_2)(L)(L')]^{2+}$ and new monocationic dihydrogen complex $[TpRu(H_2)(dppe)]^{+}$, respectively. pK_a measurments indicate that the dicationic η^2-H_2 complexes are more acidic than their monocationic Tp and Cp counterparts. $[^{Me}CnRu(H_2)(CO)(PPh_3)]^{2+}$ was found to be more acidic than $[^{H}CnRu(H_2)(CO)(PPh_3)]^{2+}$, probably due to stronger H—H interaction in the latter complex. It is also noted that triazacyclononane and hydrotris(pyrazolyl)borato dihydrogen complexes with pseudo aqueous pK_a values well above that of H_3O^+ can be deprotonated by H_2O to form the corresponding monohydride complexes in organic/aqueous mixed solvents. It is believed that deprotonation of the dihydrogen ligands in these complexes is assisted by strong solvation of H^+ by H_2O.

No silane complex was observed in the reaction of $[TpRu(H_2)(PPh_3)_2]^{+}$ with silane, although the η^2-H_2 ligand had undoubtedly been displaced. The silane complex had probably been formed, but it was readily attacked by nucleophilic species such as the counterion BF_4^- or water in the solvent. It was found that ruthenium solvent hydride complex $[TpRuH(CH_3CN)(PPh_3)]$ reacted with silanes $HSiR_3$ (R_3 = HPh_2, HEt_2, Ph_3, Et_3, H_2Ph and $(OEt)_3$) to yield the silane complexes $[TpRuH(HSiR_3)(PPh_3)]$ which, instead of equilbrating between the η^2-silane and η^2-

H_2 tautomeric forms, interchanged the H atoms rapidly, and rendering them equivalent. The silane complex [$TpRuH(HSiR_3)(PPh_3)$] is analogous to the dihydrogen hydride complex $TpRuH(H_2)(PPh_3)$ which we have recently reported.

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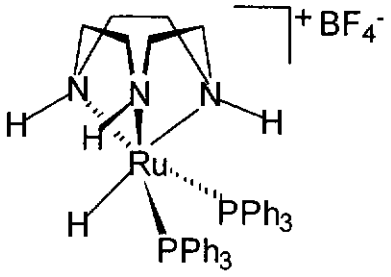
Abbreviations

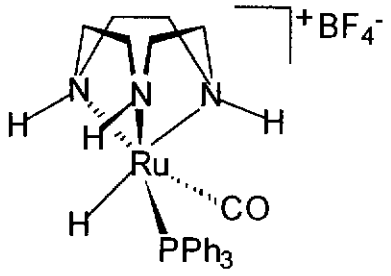
Me :	methyl
Et :	ethyl
^{i}Pr :	isopropyl
^{n}Pr :	n-propyl
^{n}Bu :	n-butyl
CH_3CN :	acetonitrile
EtOH :	ethanol
NEt_3 :	triethylamine
THF :	tetrahydrofuran
Cp :	cyclopentadienyl
Cp* :	pentamethylcyclopentadienyl
COD :	1,5-cyclooctdiene
pz :	pyrazole
$H_2Bpz_2^-$:	dihydrobis (1-pyrazolyl) borate
Tp :	hydrotris (1-pyrazolyl) borate
$^{3,5\text{-Me}}$Tp :	hydrotris [1-(3,5-dimethylpyrazolyl] borate
$^{3,5\text{-tBu}}$Tp :	hydrotris [1-(3-t-butylpyrazolyl]borate
^{R}Cn :	1,4,7-triazacyclononane derivatives
^{Me}Cn :	1,4,7-trimethyl-1,4,7-triazacyclononane.
^{H}Cn :	1,4,7-triazacyclononane
PMe_3 :	trimethylphsophine
PEt_3 :	triethylphsophine
$P(OMe)_3$:	trimethylphsophite
$PMePh_2$:	methyldiphenylphsophine
PPh_3 :	triphenylphsophine
PCy_3 :	tricyclohexylphsophine
$P^{i}Pr_3$:	tri-isopropylphsophine
dppe:	1,2-bis(diphenylphosphino)ethane
dppp:	1,3-bis(diphenylphosphino)propane
bpy :	2,2-bipyridine
phen :	1,10-phenanthroline
IR :	infra-red
FT-IR :	Fourier transform infra-red
NMR :	nuclear magnetic resonance spectroscopy
EI-MS :	electron impact mass spectroscopy
FAB-MS :	fast atom bombardment mass spectroscopy
nba :	3-nitrobenzylacohol

TMS :	tetramethylsilane
sh :	sharp
br :	broad
vs :	very strong
med :	medium
w :	weak
s :	singlet
d :	doublet
t :	triplet
m :	multplet

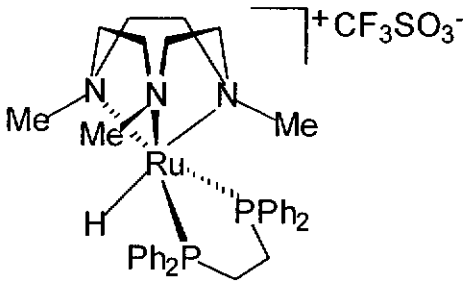
(1) : $[^{H}CnRuH(PPh_3)_2]BF_4$



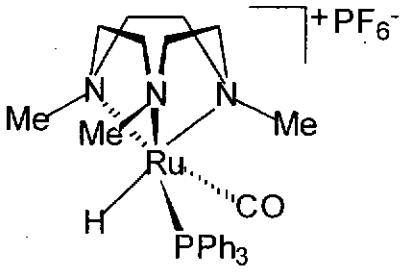
(2) : $[^{H}CnRuH(CO)(PPh_3)]BF_4$



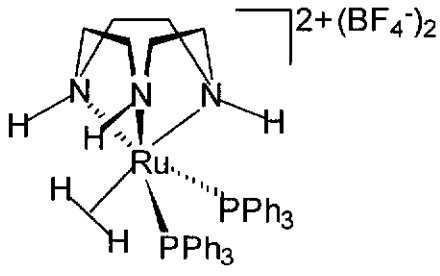
(3) : $[^{Me}CnRuH(dppe)]CF_3SO_3$



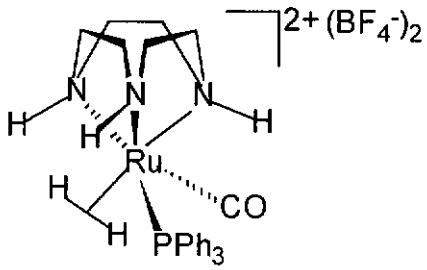
(4) : $[^{Me}CnRuH(CO)(PPh_3)]PF_6$



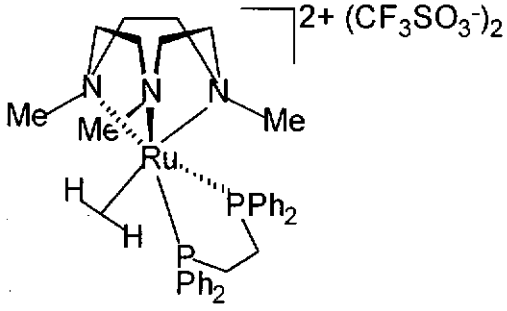
(5) : $[^{H}CnRu(H_2)(PPh_3)_2](BF_4)_2$



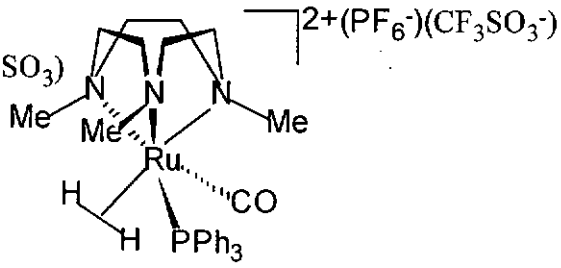
(6) : $[^{H}CnRu(H_2)(CO)(PPh_3)](BF_4)_2$



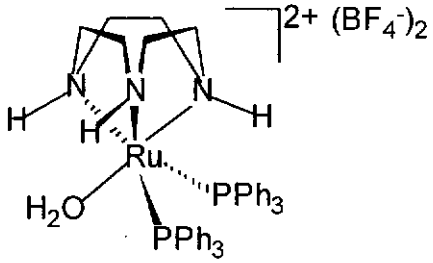
(7) : $[^{Me}CnRu(H_2)(dppe)](CF_3SO_3)_2$



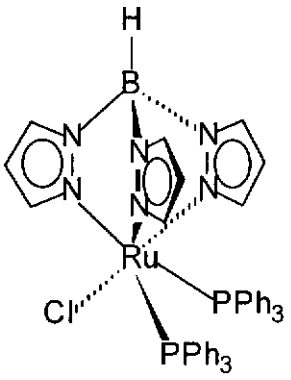
(8) : $[^{Me}CnRu(H_2)(CO)(PPh_3)](PF_6)(CF_3SO_3)$



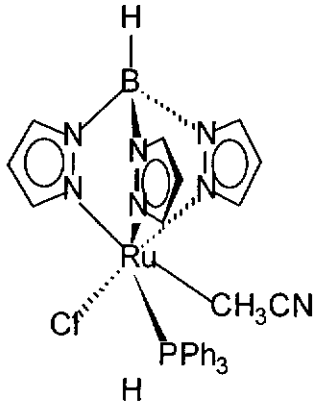
(9) : $[^{H}CnRu(H_2O)(PPh_3)_2](BF_4)_2$



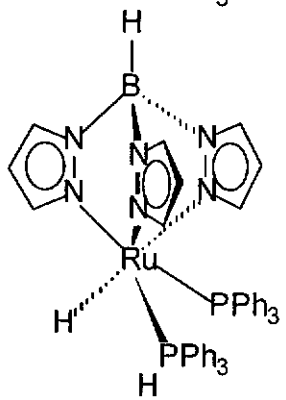
(10) : $TpRuCl(PPh_3)_2$



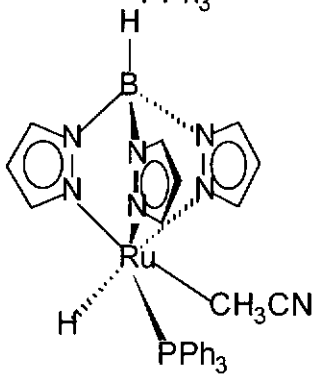
(11) : $TpRuCl(CH_3CN)(PPh_3)$



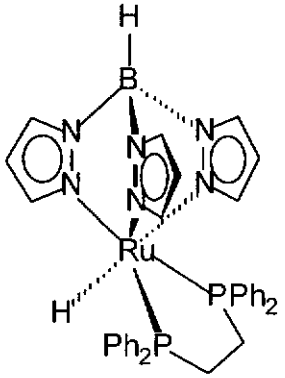
(12) : $TpRuH(PPh_3)_2$



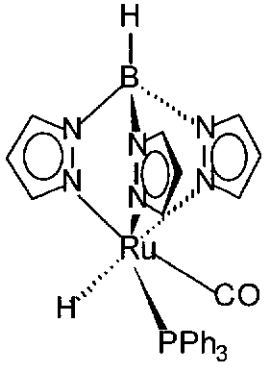
(13) : $TpRuH(CH_3CN)(PPh_3)$



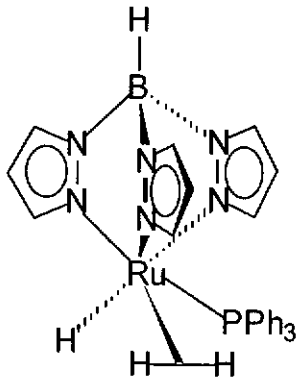
(14) : TpRuH(dppe)



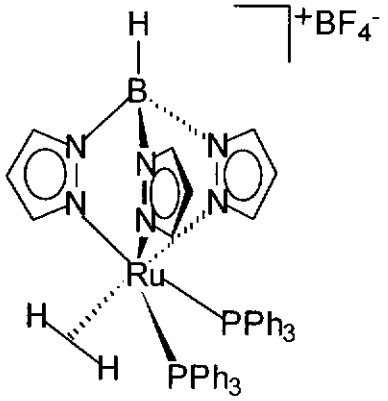
(15) : $TpRuH(CO)(PPh_3)$



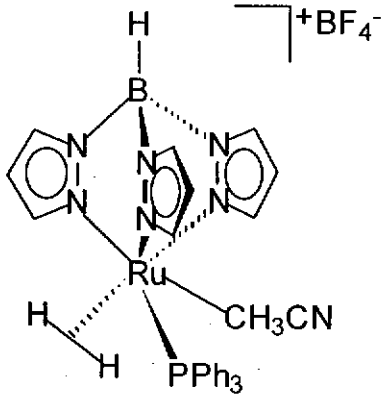
(16) : $TpRuH(H_2)(PPh_3)$



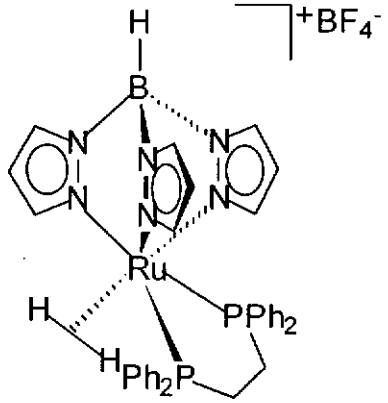
(17) : $[TpRu(H_2)(PPh_3)_2]BF_4$



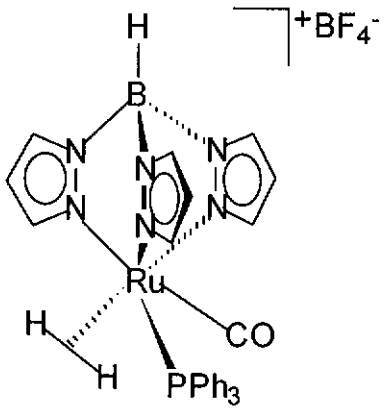
(18) : $[TpRu(H_2)(CH_3CN)(PPh_3)]BF_4$



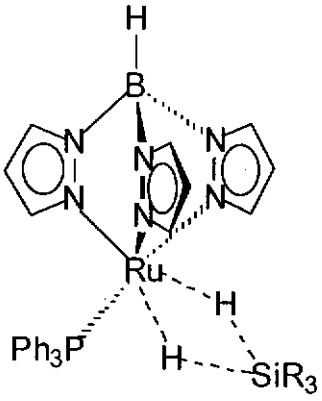
(19) : $[TpRu(H_2)(dppe)]BF_4$



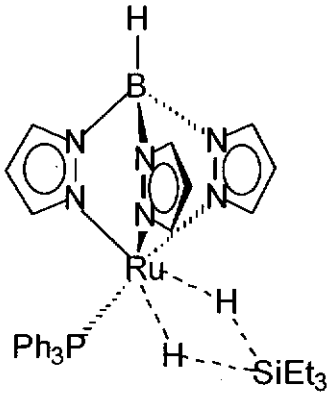
(20) : $[TpRu(H_2)(CO)(PPh_3)]BF_4$



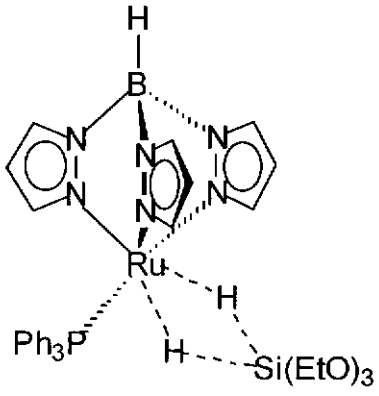
(21) : $TpRu(PPh_3)'H_2SiR_3'$



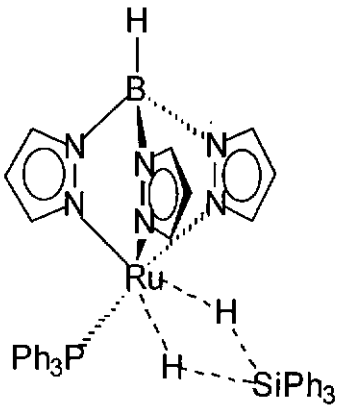
(21a) : $TpRuH(HSiEt_3)(PPh_3)$



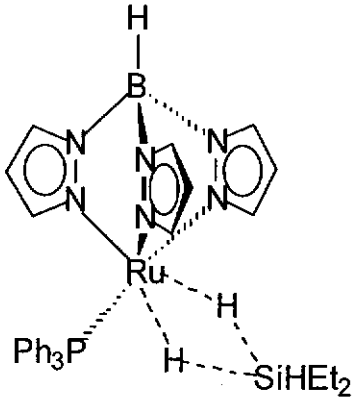
(21b) : $TpRuH(HSi(EtO)_3)(PPh_3)$



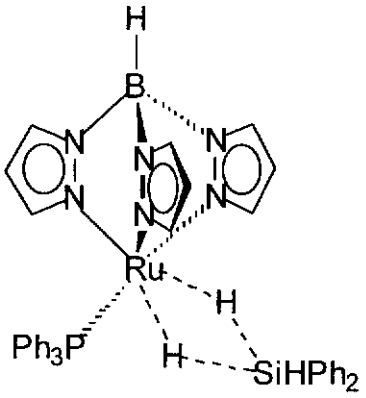
(21c) : $TpRuH(HSiPh_3)(PPh_3)$



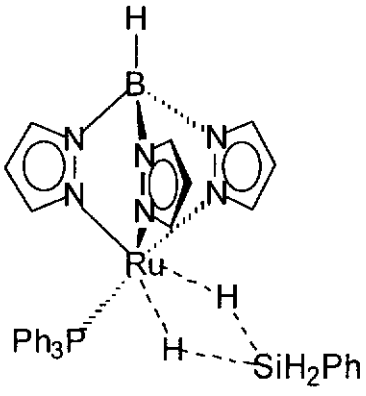
(21d) : $TpRuH(H_2SiEt_2)(PPh_3)$



(21e) : $TpRuH(H_2SiPh_2)(PPh_3)$



(21f) : $TpRuH(H_3SiPh)(PPh_3)$



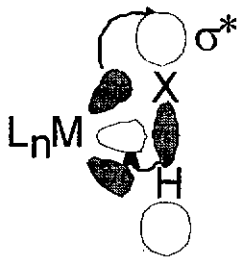
Chapter One

Introduction

Recent developments in coordination chemistry have demonstrated that certain σ bonds can coordinate to transition metals in an η^2-fashion without bond cleavage by the formation of three-centre two-electron bonds, giving rise to the so-called "σ complexes". The first σ complex $[Cp_2Ti(H_2BH_2)]$[1] was found in the 1960s, but it did not attract much attention at that time. The η^2-coordination of σ bonds not only is of fundamental importance from a structural point of view but also has significant implications for the activation of σ bonds in transition-metal-catalyzed transformation. Since we are beginning to recognize the key role of them in chemical reactions, there is an ever growing number of examples of nondestructive σ bond coordination to transition metals in the chemical literature.[2] Nowadays, a variety of well-characterized complexes are known to contain σ-coordinated ligands such as $(\eta^2\text{-}H_2)$,[3] and $(\eta^2\text{-}HSiR_3)$.[4] To date, the formal relationship of η^2-dihydrogen complexes with the intramolecular agostic C—H species is well established,[5] in the meantime, transition metal complexes can be obtained with a variety of σ-coordinated X—H fragments, and their mode of bonding can be understood by a common and quite general model.

The simplest ligand that forms exclusively σ complex with transition metals is the dihydrogen molecule. The bonding model for η^2-(σ- coordination) of H—X can be described in terms of two components: donation of electron density from the

σ-bonding orbital of the ligand into an empty d_σ orbital of the metal and back-donation of electron density from a filled d_π orbital of metal into the σ*- antibonding orbital of the ligand. The σ to M(d_σ) donation weakens but does not break the X—H bond because the resulting three-centre-two-electron (3c - 2e) orbital has bonding character over all three centres. On the other hand, the M(d_π) to (σ*) back-donation populates the σ*- antibonding orbital and thus can break the X—H bond if the back-donation is sufficiently strong.



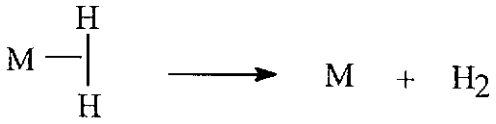
The relative stability of σ complex is controlled by the electronic and steric effect of the coordinated ligands. When varying the ancillary ligands and π-back-bonding capability of the metal-centre, the coordination of the complex will change from the non-classical η^2-(σ-complex) to the classical one. For example, increasing the basicity of the ancillary ligands should promote M(d_π) to (σ*) back-donation and thereby ultimately lead to the cleavage of the X—H bond.

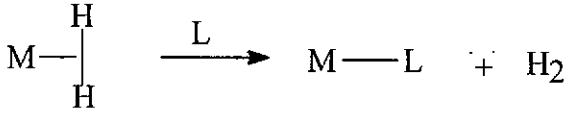
The first non-classical η^2-dihydrogen complex $[W(\eta^2\text{-}H_2)(CO)_3(PCy_3)_2]$ was reported by Kubas[6] and co-workers at 1984. Recent years have witnessed considerable interest in transition-metal η^2-dihydrogen complexes, their establishment has opened the possibility of activating dihydrogen without oxidative addition, and these complexes represent intermediates or transition states in a number of important catalytic processes such as hydrogenation, hydrogenolysis, and

hydroformylation. The η^2-dihydrogen coordination not only is of fundamental interest from a structural point of view but also has significance in metal-catalyzed transformations involving dihydrogen. In this respect, η^2-dihydrogen complexes have been found to be involved in the mechanistic pathway in homogeneous catalysis including hydrogenation of alkenes[7] and alkynes,[8] hydrogenation of ketones,[9] dehydrogenation of alcohols,[10] dimerization of alkynes,[11] and H/D isotopic exchange.[12]

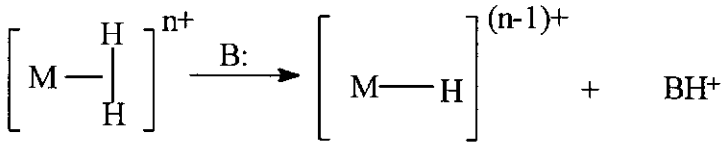
The followings are the features of η^2-dihydrogen metal complexes:[13]

(i) facile dissociation and substitution lability;

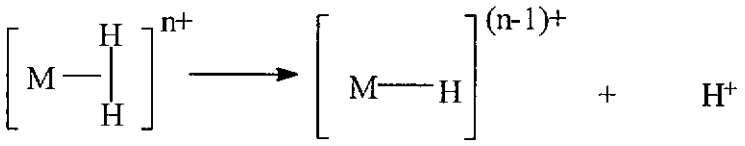




(ii) heterolytic cleavage by base (B =base);



(iii) high acidity,



These features render the η^2-dihydrogen complexes potentially valuable catalytic species. For example, coordinate unsaturation can be generated by dissociation of the labile dihydrogen ligand. Furthermore, heterolytic cleavage of acidic dihydrogen ligand by a base to give metal monohydride, which is one of the most interesting features of this class of compounds, opens the possibility of unique reactivity patterns of these complexes including catalysis and selective proton transfer to an ancillary ligand. Several enzymatic systems found in nature such as hydrogenases and nitrogenases are believed to involve the heterolytic activation of dihydrogen at a metal centre during sequential proton-electron transfer steps.[14]

In the past few years, there have been numerous efforts in defining the factors affecting the acidity properties of dihydrogen complexes, especially dihydrogen complexes of the type $[Cp'Ru(H_2)(PP)]^+$ (Cp' = Cp, Cp*; PP = diphosphines),[15,16] $[MH(H_2)(PP)]^+$ (M = Fe, Ru, Os; PP = diphosphines),[17,18] $[MCl(H_2)(PP)]^+$ (M= Fe, Ru, Os; PP = diphosphines),[18,19] and $[M(L)(H_2)(PP)_2]^{2+}$ (M = Fe, Ru, Os; PP = diphosphines; L = CO, CH_3CN).[18,20] Deprotonation of dihydrogen ligands with various bases have been reported for other complexes,[21] for example, $[IrH(H_2)(bq)(PPh_3)_2]^+$ (bq = 7,8-benzoquinolinate) by BuLi, $[Os(H_2)(NH_3)_5]^{5+}$ by NaOMe, and $[Os(H_2)(CO)(bpy)(PPh_3)_2]^{2+}$ by Et_2O. These studies showed that acidity of dihydrogen complexes can vary widely depending on the ligands and metals.

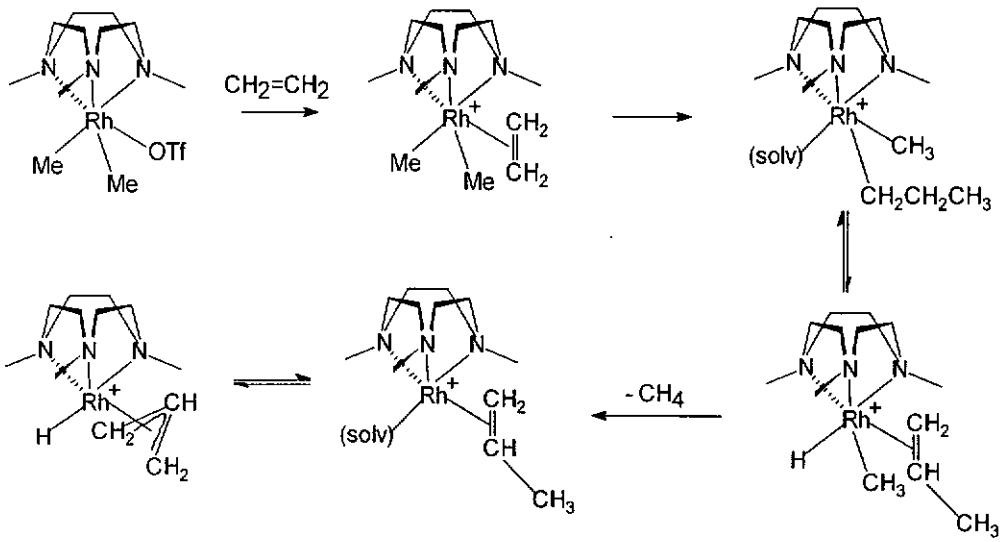
After the discovery of the first η^2-dihydrogen complex, a large number of isolable η^2-dihydrogen complexes have been prepared, the majority of which have been found to be singly charged cationic species. While the plethora of monocationic

complexes may be due to the common synthetic route of prontonating a neutral metal hydride, an underlying aspect may be that the positive charge confers additional stability on the dihydrogen complexes. In contrast, the numbers of well-characterized dicationic complexes are limited.

Recently, there have been several interesting reports on the synthesis and reactivity of dicationic dihydrogen complexes. The dicationic complexes $[Os(H_2)(NH_3)_5]^{2+}$ and $[Os(H_2)(en)_2(L)]^{2+}$ were first reported by Taube,[22] other noted examples included $[Os(H_2)(CH_3CN)_3(P^iPr_3)_2]^{2+}$,[23] $[Os(H_2)(CH_3CN)(dppe)_2]^{2+}$,[20] $[M(H_2)(CO)(dppp)_2]^{2+}$ (M = Ru, Os),[18] $[M(H_2)(CO)(bpy)(PR_3)_2]^{2+}$ (M = Ru, Os),[21k] and , most recently, $[Fe(H_2)(dppe)_2(L)]^{2+}$ (L = CO, CH_3CN).[18] In my research, monocationic hydrido ruthenium complexes containing neutral ^{R}Cn were prepared, and formation of the corresponding dicationic dihydrogen complexes was the result of the protonation of these hydrido complexes.

The macrocyclic 1,4,7-triazacyclononane derivatives ^{R}Cn,[24] (where ^{H}Cn = 1,4,7-triazacyclononane, ^{Me}Cn = 1,4,7-trimethyl-1,4,7-triazacyclononane) have been used extensively in inorganic and organic chemistry, they are 'hard', facial tri-amine chelating ligands. Some Werner-type coordination chemistry of these pure σ-donor ligands with rhodium (e.g.$^{Me}CnRhCl_3$) was originally reported by Wieghardt and co-workers.[25] More recently, Flood et al have extensively studied the aspects of organometallic chemistry in the coordination sphere of rhodium bounded with 1,4,7-trimethyl-1,4,7-triazacyclononane. The ^{Me}Cn-containing compounds that have been

examined are $^{Me}CnRhMe_{3-n}X_n$ (n = 0-3; X = H, Cl, Br and OTf). Flood has also revealed the key role of $^{Me}CnRhMe_2(OTf)$ in olefin metathesis.[26j]



In comparison with that of rhodium, the chemistry of ruthenium complexes of ^{R}Cn is still in its infancy. But recent studies by Che have witnessed the rich oxidation chemistry of high-valent ruthenium-oxo complexes of macrocyclic amines. Some of these ruthenium ^{R}Cn complexes show intriguing reactivities, for example, $[^{Me}CnRu^{VI}(O)_2(O_2CCF_3)]ClO_4$ and $[^{Me}CnRu^{VI}(O)(bpy)][ClO_4]_2$ are active oxidants for organic oxidation.[26g,h]

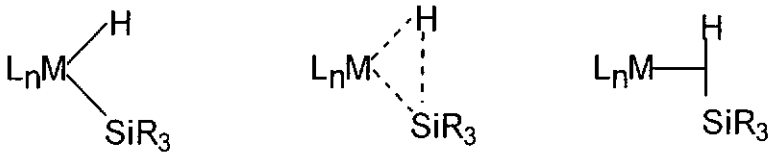
Cyclopentadienyls,[27] hydrotris(pyrazolyl)borates[28,29] and 1,4,7-triazacyclononane derivatives (^{R}Cn)[24,26] are very useful ligands in organometallic chemistry and homogeneous catalysis. The three ligands are similar in that they all coordinate to the metals in a facial geometry, and are formally 6e donors on ionic model. They are different in their π-accepting ability, with cyclopentadienyls being the strongest and 1,4,7-triazacyclononane derivatives the weakest. It is therefore expected that the three ligands should show differences in stabilizing dihydrogen

ligands and in affecting the acidity of the resulting dihydrogen and hydride complexes. However, such comparison has not been made yet. While numerous complexes of the type $[(C_5R_5)Ru(H_2)(L)(L')]^+$ have been reported,[15,16,30] only a few $[TpRu(H_2)(L)(L')]^+$ complexes are known,[29a,b,i] and the isostructural complexes $[^RCnRu(H_2)(L)(L')]^{2+}$ are virtually unknown. The pK_a values of complexes of the type $[(C_5R_5)Ru(H_2)(L)(L')]^+$ have been reported,[15,16] but that of the isostructural Tp and ^RCn complexes have not been well studied. In my research, dihydrogen complexes of ruthenium supported by 1,4,7-triazacyclononane and 1,4,7-trimethyl-1,4,7-triazacyclononane ligands have been synthesized and their chemical properties studied. Furthermore, the acidity measurements of $[^RCnRu(H_2)(L)(L')]^{2+}$ and $[TpRu(H_2)(L)(L')]^+$ have also been performed. These studies enable us to evaluate how the acidity of dihydrogen complexes change when they change from monocationic to dicationic.

Besides η^2-H_2, the chemistry of σ-bound silane ligands has also been intensively investigated. These silane ligands, which enable the investigation of a large range of σ-coordinated metal complex fragments, up to complete oxidative addition with cleavage of the Si—H bond and formation of silyl(hydrido) complexes, have thus widened our general understanding of the bonding of σ bound ligands.

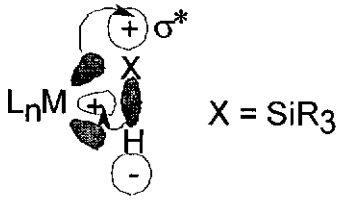
Transition metal silyl hydride complexes have been proposed as intermediates in many catalytic reactions, such as hydrosilylation of olefins[31] silane alcoholysis[32] and the polymerization of organosilanes.[33] The bonding in transition metal silyl hydride complexes has classically been described by either of two

structures, **A** (oxidative addition) or **C** (adducts formation). However, there are many complexes that cannot be accurately described by either **A** or **C** and are thus best represented by an intermediate structure such as **B.**



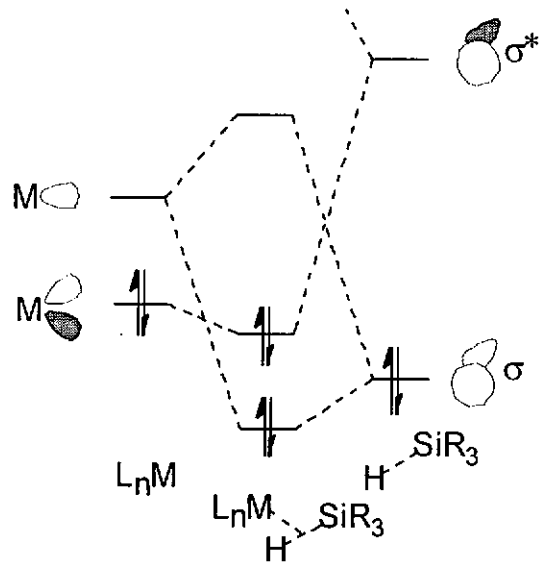
A **B** **C**

The metal centre fragment can react with a Si—H bond to give a σ complex, in which the Si—H bond acts as a $2e^-$ donor. The Si—H bond is coordinated side-on to the metal centre, this gives rise to a three-centre-two electron bond. In analogy to the σ/π bonding formalism for ethene bonding to a transition metal, in silane bonding to a transition metal, electron density is transferred from an occupied σ orbital of the Si—H bond into an unoccupied metal d_π orbital. By a synergistic interaction, electron density also transfers from an occupied metal d_π orbital to the σ* of the Si—H bond.



The M-(Si-H) can be strengthened by the backbonding of the d_π electrons on the metal into the Si—H bond σ* orbital. Modest backbonding accounts for the stability of many σ complexes, but strong backbonding can lead to Si—H bond

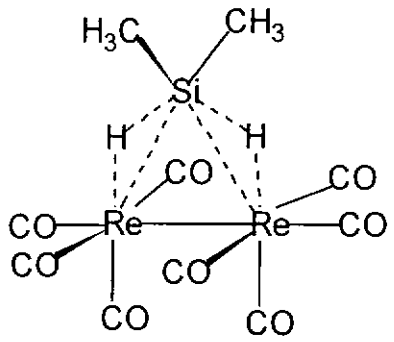
scission in the process known as oxidative addition to give compound of type Si-M-H as **A**.



The oxidative addition of a Si—H σ bond is one of the key steps in the mechanism of transition metal catalyzed hydrosilyation. There are numerous examples of the activation of Si—H σ bonds by $M(L_n)$ centres and of complex formation. These reveal that the bonding in silane complexes corresponds to a late step in the oxidative addition to the transition metal centre. The ^1J(SiH) coupling constants and the elongation of the Si—H interatomic distances (from X-ray and neutron scattering investigations) provide a measure of the extent of the oxidative addition in σ-coordinated M-H-SiR_3 complexes.

The first silane σ complex[34] was formed from $(CH_3)_2SiH_2$ and $[Re_2(CO)_{10}]$. The reduction of proton coupling constant of the CH_3 proton to Si—H from 4.2 Hz in the free silane to 1.5 Hz in silane-rhenium complex provides an evidence of a σ-silane complex. The first mononuclear σ-silane complex was mentioned at an ACS Meeting and reported in 1970 only as a news item in *C & E News*.[35] However, this

field did not develop significantly at that time, it may have been caused by the misconception that such relatively weak M-(SiH) interaction would not have usefully large effects on the reactivity of the Si—H bond.



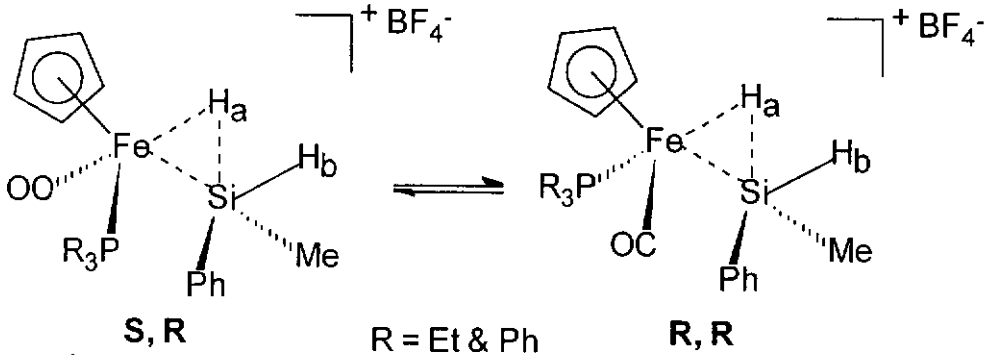
After the discovery of the distinctive properties of η^2-dihydrogen complexes[6] in the mid-80s, extensive studies on other σ complexes, such as the agostic species concerning C—H activation, have been carried out. During the same period, Schubert et al[36] have prepared a homologous series of manganese silane complexes which have the general formula Cp'Mn($HSiX_3$)(CO)(L) and some of their structures have been carefully characterized by neutron diffraction. They have described the changes in structure and bonding which result from systematic variations in the substituents on the silicon and the Cp ring, as well as variations of the ligand L. It was found that both steric and electronic factors play important roles in determining whether the silane be oxidatively added to the metal centre, and the extent of Si—H bond breaking in the η^2-silane complexes. Extended Huckel calculation by Rabaa and Sailard[37] of these type of complexes showed that the three centre Mn-(H-Si) interaction can be viewed as a σ Si—H bond coordination to the d^6 $CpMnL_2$ fragment. They also made generalization for other d^n L_nMHSiR_3 complexes in which, when the Si—H bond is fully broken, the addition is not oxidative, but the

bonding be better described as having a formally H^- and a formally SiR_3^+ ligand coordinated to a metal atom which has the same formal oxidation state as in the free ML_n fragment.

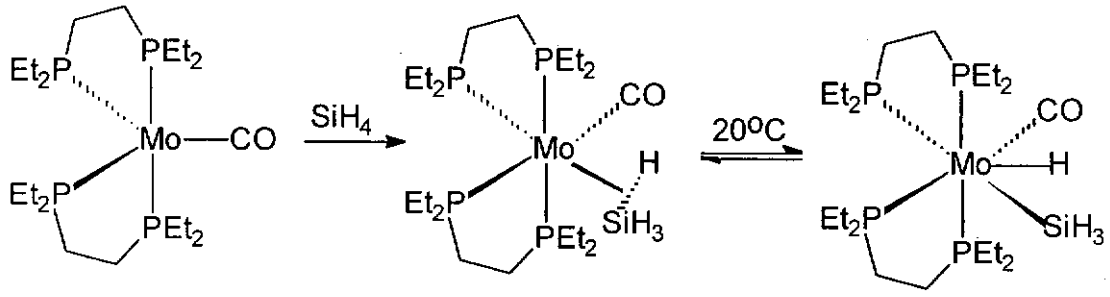
While there are numerous examples of neutral transition metal silane complexes, cationic complexes of this type are quite rare. During the investigations of silane alcoholysis catalyzed by a cationic Ir complex, Luo and Crabtree[32] suggested that cationic silane adducts and $[Ir(Et_2HSiSiHEt_2)(H)_2(PPh_3)_2]SbF_6$, detected spectroscopically at low temperature, were related to the intermediate species in the catalytic cycle. The extremely high activity of $([Ir(HSiEt_3)_2(H)_2(PPh_3)_2]SbF_6$ in silane alcoholysis could be accounted for by the Lewis acidity of the metal centre which renders the bound Si—H group more polarized and significantly increase the electrophilic character of the silicon, thus making it very susceptible to nucleophilic attack by an alcohol and hence increase the rate of the reaction.

Recently, Brookhart[38] introduced a general and convenient method for the generation of cationic iron η^2-silane complexes, $[CpFe(HSiR_3)(CO)(L)]^+$, which are stabilized through the use of the non-coordinating counterion BAr'_4^- (Ar' = $(CF_3)_2C_6H_3$). These species are easily formed by displacement of H_2 from the cationic η^2-H_2 complex by free silane. Diastereomeric iron silane complexes $[CpFe(H_2SiMePh)(CO)(PR_3)]BAr'_4$ (where, R = Et and Ph) have been generated,

these complexes exhibit dynamic behavior that results from interconversion of the diastereomers.[38]

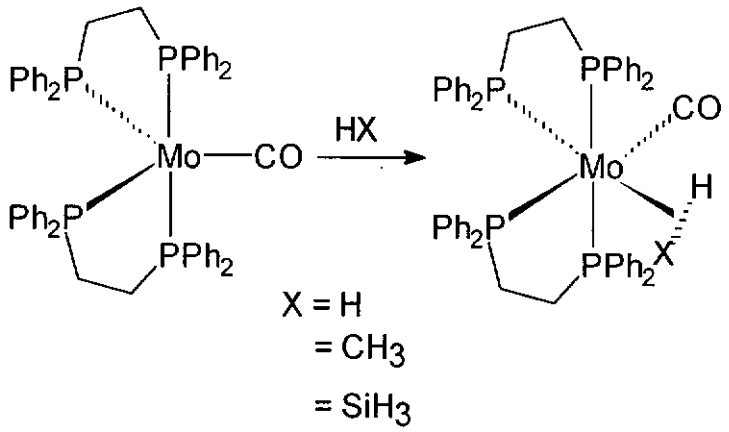


Moreover, Luo and Kubas[39] have succeeded in the synthesis, isolation, and structural characterization of a η^2-silane complex as formed by reaction of silane with the electronically and coordinatively unsaturated 16 e^- Mo^0 complexes of the type $Mo(CO)(R_2PC_2H_4PR_2)_2$. When the R group in the unsaturated Mo complex is an ethyl group, it reacts with silane and an equilibrium of two tautomers exists in solution at room temperature.



With the phenyl phosphine analogs, only side-on η^2-coordination is observed both in solution and in the solid state. Moreover, all Si—H, H—H and agostic C—H bonds are capable of binding to this metal centre $Mo(CO)(Ph_2PC_2H_4PPh_2)_2$ in an η^2-

fashion. This is the first example of a system which provides a unique opportunity to study the differences between the common features among the three prototypes of σ complexes[40].

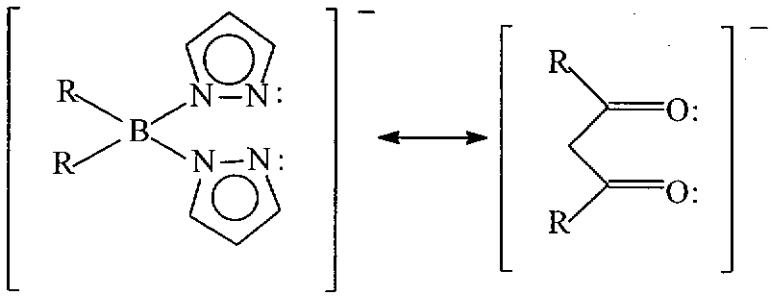


The work of Kubas on σ-complexes raises the possibility of having more than one σ-bonded groups attached to a metal centre. Complex of the general formula '$ML_n(H_2SiR_3)$', where 'H_2SiR_3' stands for $(SiR_3)(\eta^2\text{-}H_2)$ or $(H)(\eta^2\text{-}HSiR_3)$, is interesting because it can form one tautomer containing a $\eta^2\text{-}H_2$ or another one containing a $\eta^2\text{-}HSiR_3$ ligand. For example, the complex $OsCl(SiEt_3)(H_2)(CO)(P^iPr_3)_2$has been characterized as a dihydrogen complex by Oro et al,[41] it is formulated as $[ML_n(SiR_3)(\eta^2\text{-}H_2)]$. On the other hand, Crabtree[32] reported a $[ML_n(H)(\eta^2\text{-}HSiR_3)]$ structure for the complex$[Ir(\eta^2\text{-}HSiR_3)_2(H)_2(PPh_3)_2]^+$. Recently, ab Initio MO calculation on the model system of $[OsCl(CO)(PH_3)_2{'}H_2SiH_3{'}]$ has been performed by Lledos and co-workers,[42] the possible existence of two stable species, $[OsCl(SiH_3)(\eta^2\text{-}H_2)(CO)(PH_3)_2]$ and $[OsCl(H)(\eta^2\text{-}HSiH_3)(CO)(PH_3)_2]$, which are very close in energy has been postulated.

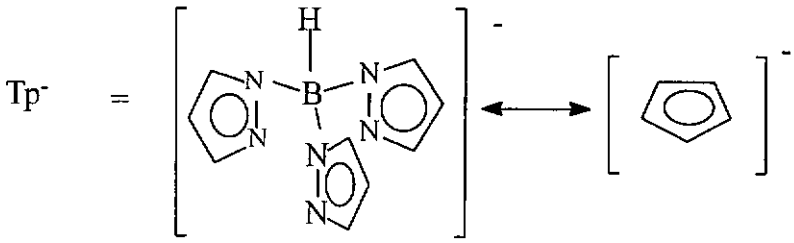
Coordination of η^2-silane ligands have been found on many transition metals and in different ligand environments. However, most of these known complexes contain cyclopentadienyl (Cp^-) and / or phosphine ligands,[36,38,43] but very few complexes supported by nitrogen donor ligands have been reported.[44] It is noted that nitrogen donors are among the various ligands that exert poor trans effect / influence and it can be easily labilized by common ligands like phosphine.

The poly(pyrazolyl)borate ($H_nB(pz)_{4-n}^-$) is one of the ligands containing nitrogen donors. This type of ligands have found wide application in coordination chemistry, and their complexes with most metals or metalloids in the periodic table have been prepared.[28a]

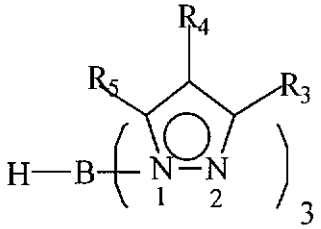
Throughout the years, poly(pyrazolyl)borates have been compared to β-diketonates of its bidentate form ($R_2Bpz_2^-$):



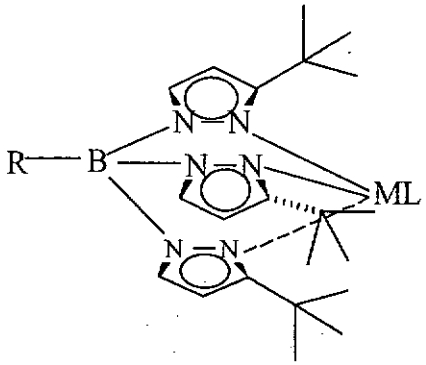
or to cyclopentadienyl ligands Cp / Cp* of its tridentate form Tp^-:



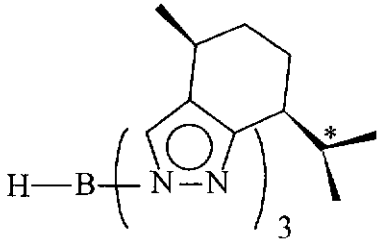
Both Cp^- and Tp^- are uni-negative charged, six-electron donating and facial tridentate ligand. Moreover, the pyrazolyl groups in Tp^- contains three C—H bonds which can be substituted by various substituents, such as alkyl, aryl, NR_2 and ArS:



Such substitution can produce a highly screened metal centre:



For instance, the cone angles of Tp^-, $^{3,5\text{-Me}}Tp^-$ and $^{3,5\text{-tBu}}Tp^-$ are 184°, 224°, and 244° respectively. Optically active poly(pyrazolyl)borate ligands can be generated by attachment of chiral substituents.[28a]



The ligand hydrotris(1-pyrazolyl)borate has been extensively used in this research. Its potassium salt can be easily synthesized by direct reaction of potassium borohydride with pyrazole. Due to the ready availability of hydrotris(1-pyrazolyl)borate ligand, considerable amount of work with this ligand has been reported.[29]

A number of η^2-dihydrogen complexes bearing hydrotris(1-pyrazolyl)borate ligand have been synthesized and characterized by our group.[29b] Some of these complexes such as $[TpRu(H_2)(PPh_3)_2]BF_4$ (**17**) and $[TpRu(H_2)(CH_3CN)(PPh_3)]BF_4$ (**18**) were shown to be involved in the catalytic hydrogenation of unsaturated hydrocarbon.[29b] In the light of the similarity in the bonding modes of the η^2-H_2 and the η^2-$HSiR_3$ ligands in η^2-dihydrogen complexes and the η^2-silane complexes, respectively, it is interesting to synthesize and to study the chemical properties of Tp ruthenium complexes containing η^2-silane ligands.These complexes are analogous to the Tp ruthenium η^2-dihydrogen complexes. The first attempt to synthesize the Tp ruthenium η^2-silane complexes was by reacting **17** with triethylsilane, it was expected that simple ligand substitution of η^2-H_2 with η^2-$HSiR_3$ would give the η^2-silane complexes $[TpRu(\eta^2\text{-}HSiR_3)(PPh_3)_2]BF_4$. But unfortunately, the expected η^2-silane complexes were not obtained, probably due to the instability of the η^2-$HSiR_3$ ligand in $[TpRu(\eta^2\text{-}HSiR_3)(PPh_3)_2]BF_4$ towards nucleophiles such as BF_4^- and adventitious H_2O in the solvent. It was later found that ruthenium hydrido solvento complex $[TpRuH(CH_3CN)(PPh_3)]$ (**13**) reacted with silane $HSiR_3$ (R_3 = Et_3, $(OEt)_3$, Ph_3, HEt_2, HPh_2, and H_2Ph) to yield the silane complexes [$TpRu(PPh_3)$"H_2SiR_3"]

(**21**) which, instead of equilibrating between the η^2-silane and η^2-H_2 tautomeric forms (eq. 1), interchanged the H atoms rapidly, and rendering them equivalent. (eq. 2) The silane complex **21** is analogous to the dihydrogen hydride complex [TpRuH(H_2)(PPh_3)] (**16**) that we have recently reported.[29a]

$$TpRu(PPh_3)(H)(HSiR_3) \rightleftharpoons TpRu(PPh_3)(H_2)(SiR_3) \quad (1)$$

$$TpRu(PPh_3)(H_a)(H_bSiR_3) \rightleftharpoons TpRu(PPh_3)(H_b)(H_aSiR_3) \quad (2)$$

Chapter Two

Syntheses, characterization and reactivity of ruthenium η^2-dihydrogen complexes

2.1 Introduction

Knowledge about the acidity of dihydrogen complexes may help to understand mechanisms of stoichiometric and/or catalytic reactions involving heterolytic cleavage of dihydrogen bond,[45] and to design new catalytic processes. The most interesting examples involving heterolytic cleavage of dihydrogen reported recently include intramolecular protonation of alkyl ligands by dihydrogen ligands in the hydrogenation reactions,[7,8] intramolecular protonation of vinylidene ligands by dihydrogen ligands to form carbyne complexes,[8] and transition metal catalyzed H/D exchange reactions.[12]

In this chapter, the preparation of some ruthenium hydrido and dihydrogen complexes containing Tp and ^{R}Cn are described. The acidity of these dihydrogen complexes have been measured, and differences in stability and acidity between the Cp, Tp and ^{R}Cn dihydrogen complexes are also discussed.

2.2 Experimental

2.2.1 Materials

All reactions were carried out under a dry N_2 atmosphere using Schlenk techniques. All solvents were distilled and degassed prior to use. Dichloromethane and acetonitrile were distilled from calcium hydride; tetrahydrofuran, diethyl ether and

hexane were distilled from sodium benzophenone ketyl. Deuterated dichloromethane was dried on P_2O_5 and vacuum transferred to a flask fitted with a rubber septum. Deuterated Tetrahydrofuran was dried on calcium hydride and vacuum transferred to a flask fitted with a rubber septum. 1,4,7-triazacyclononane, 1,4,7-trimethyl-1,4,7-triazacyclononane were prepared as reported.[25a] The complexes $RuHCl(PPh_3)_3$,[46] $^{Me}CnRuCl_3$,[47] $RuHCl(CO)(PPh_3)_3$,[48] $[^{Me}CnRuH(dppe)]CF_3SO_3$,[26d] $[^{Me}CnRuH(CO)(PPh_3)]PF_6$,[26d] $TpRuH(PPh_3)_2$,[29b] $[TpRu(H_2)(CH_3CN)(PPh_3)]BF_4$[29b] $[TpRu(H_2)(PPh_3)_2]BF_4$,[29b] $TpRuH(CH_3CN)(PPh_3)$,[29b] and $TpRuH(CO)(PPh_3)$[29a] were synthesized according to literature methods. $HBF_4.Et_2O$ (56%) and aqueous HBF_4 (50%) were purchased from Fluka, CF_3SO_3H was purchased from Aldrich and was used as received.

2.2.2 Instrumentation

Infrared spectra were obtained as KBr disc from a Nicolet Magna 750 FT IR spectrophotometer. ^1H NMR spectra were taken on a Bruker DPX 400 spectrometer. Chemical shifts were referenced to the residue peaks of the deuterated solvents($CDHCl_2$ δ 5.32 ppm, C_4D_7H δ 1.85 ppm, δ 3.70 ppm). $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker DPX 400 spectrometer at 161.70 MHz. ^{31}P chemical shifts were externally referenced to 85% H_3PO_4. T_1 relaxation measurements were carried out in CD_2Cl_2 at 400 MHz by the inversion-recovery method using a standard 180-τ-90 pulse sequence. Fast Atom Bombardment Mass Spectrometry was carried out with a Finnigan MAT 95S mass spectrometer using 3-nitrobenzyl alcohol as matrix. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona, U.S.A.

2.2.3 Syntheses

2.2.3.1 Hydrido complexes

[^{H}CnRuH(PPh$_3$)$_2$]BF$_4$ (1). A mixture of RuHCl(PPh$_3$)$_3$ (0.50 g, 0.54 mmol), 1,4,7-triazacyclononane (0.20 g, 1.55 mmol) and NaBF$_4$ (0.10 g, 0.91 mmol) in 100 mL of THF was stirred under nitrogen for 2 h. The mixture was filtered through celite, and the filtrate was concentrated to about 5 mL. Diethyl ether (10 mL) was added to precipitate out a yellow solid which was filtered out. The solid was washed with diethyl ether and vacuum dried at room temperature. Yield: 0.36 g (79%). Anal. Calcd for $C_{42}H_{46}BN_3F_4P_2Ru$: C, 59.86; H, 5.50; N, 4.99. Found: C, 59.10; H, 5.73; N, 5.03. IR (KBr, cm^{-1}): υ(Ru-H) 1958 (w). ^{1}H NMR (400 MHz, CD_2Cl_2): δ -15.98 (t, 1H, ^2J(HP) = 38.3 Hz, Ru-*H*), 2.29-3.44 (m, 2H, N-*H* and 12H, NC*H*$_2$), 5.24 (s, 1H, N-*H*), 7.19-7.43 (m, 30 H of PPh$_3$). ^{31}P{^{1}H} NMR (161.70 MHz, CD_2Cl_2): δ 67.4 (s). FAB MS (m/z): 756 [M-BF$_4$]$^+$, 494 [M-BF$_4$-PPh$_3$]$^+$.

[^{H}CnRuH(CO)(PPh$_3$)]BF$_4$ (2). A mixture of RuHCl(CO)(PPh$_3$)$_3$ (2.50 g, 2.69 mmol) and 1,4,7-triazacyclononane (0.50 g, 3.87 mmol) in 250 mL of 2-methoxyethanol was refluxed under nitrogen for 18 h. The mixture was filtered, and the filtrate was concentrated to about 40 mL. Sodium tetrafluoroborate (0.66 g, 6.00 mmol) was added, and the resulting mixture was filtered to afford the crude product which was washed with ethanol and diethyl ether. It was then extracted with 20 mL of dichloromethane, and the solvent of the extract was removed to yield a white solid. Yield: 0.44 g (27%). Anal. Calcd for $C_{25}H_{31}BN_3OF_4PRu$: C, 49.36; H, 5.14; N, 6.91. Found: C, 49.10; H, 5.23; N, 6.78. IR (KBr, cm^{-1}): υ(CO) 1920 (vs), υ(Ru-H) 1997 (w). ^{1}H NMR (400 MHz, CD_2Cl_2): δ -12.83 (d, 1H, ^2J(HP) = 28.8 Hz, Ru-*H*), 2.81 (s,

1H, N-*H*), 2.45-3.40 (m, 12H, NCH_2), 3.90 (s, 1H, N-*H*), 5.12 (s, 1H, N-*H*), 7.34-7.58 (m, 15H of PPh_3). $^{31}P\{^1H\}$ NMR (161.70 MHz, CD_2Cl_2): δ 68.1 (s). FAB MS (m/z): 522 $[M\text{-}BF_4]^+$.

TpRuH(dppe) (14). A 1,4-dioxane solution (100 mL) of $TpRuH(PPh_3)_2$ (0.50 g, 0.60 mmol) and dppe (0.30 g, 0.75 mmol) was stirred under nitrogen at 100 °C for 16 h. The solution was cooled and concentrated to about 5 mL. Diethyl ether (10 mL) was added to give a yellow solid which was filtered out. The solid was washed with diethyl ether and then dried under vacuum. Yield: 0.35 g (82%). Anal. Calcd for $C_{35}H_{35}BN_6P_2Ru$: C, 58.89; H, 4.94; N, 11.78. Found: C, 58.88; H, 5.10; N, 11.54. IR (KBr, cm^{-1}): υ(Ru-H) 1909 (w), υ(B-H) 2470 (br). ^1H NMR (400 MHz, CD_2Cl_2): δ -14.23 (t, 1H, ^2J(HP) = 28.0 Hz, Ru-*H*), 2.09-2.49 (m, 4H, CH_2CH_2), 5.34 [t, 1H, H(pz)], 5.58 (d, 1H, H(pz)], 5.90 [t, 2H, H(pz')], 7.03 [d, 2H, H(pz')], 7.47 [d, 1H, H(pz)], 7.61 [d, 2H, H(pz')] (pz = pyrazolyl group trans to hydride, pz' = pyrazolyl groups trans to dppe; all coupling constants for pyrazolyl proton resonances were about 2 Hz); 6.86, 6.98, 7.13, 7.35, 7.89 (m, 20 H of dppe phenyl groups). $^{31}P\{^1H\}$ NMR (161.70 MHz, CD_2Cl_2): δ 90.0 (s). FAB MS (m/z): 714 $[M]^+$.

2.2.3.2 Dihydrogen Complexes and Their Isotopomers.

The carbonyl dihydrogen complexes **6**, **8** and **20** are unstable with respect to loss of H_2 at room temperature. It is also difficult to obtain dihydrogen complexes **5**, **7** and **19** in pure form because they are usually contaminated by their corresponding aquo complexes. These dihydrogen complexes were therefore only characterized in situ.

The complexes [^{H}CnRu(H_2)(PPh_3)$_2$](BF_4)$_2$ (**5**), [^{Me}CnRu(H_2)(dppe)](CF_3SO_3)$_2$ (**7**) and [TpRu(H_2)(dppe)]BF_4 (**19**) were prepared as follows. In a typical experiment, a sample (10 mg) of a metal hydride was loaded into a 5 mm NMR tube, which was then capped with a rubber septum. The tube was evacuated and then filled with nitrogen for three cycles. Dichloromethane-d_2 (0.4 mL) was added to dissolve the sample, followed by addition of 5 μL of HBF_4·Et_2O or CF_3SO_3H. The solution was immediately analyzed by NMR spectroscopy.

[^{H}CnRu(H_2)(PPh_3)$_2$](BF_4)$_2$ (5). ^{1}H NMR (400 MHz, CD_2Cl_2): δ -9.04 [br, 2H, Ru-(H_2)], 2.35-4.29 (m, 2H, N-*H* and 12H, NCH_2), 5.84 (s, 1H, N-*H*), 7.26-7.44 (m, 30H of PPh_3). ^{31}P{^{1}H} NMR (161.70 MHz, CD_2Cl_2): δ 39.5 (s). T_1 (400 MHz, CD_2Cl_2), ms (temperature): 22 (273 K), 21 (263 K), 20 (253 K), 20 (243 K), 21 (233 K), 23 (223 K), 27 (213 K), 34 (203 K). A ln T_1 vs 1000/T plot gave a T_1(min) of 20 ms at 250 K.

[^{Me}CnRu(H_2)(dppe)](CF_3SO_3)$_2$ (7). ^{1}H NMR (400 MHz, CD_2Cl_2): δ -9.79 [br, 2H, Ru-(H_2)], 1.93 (m, 2H, NCH_2), 2.56-2.69 (m, 4H, PCH_2), 2.79-2.81 (m, 6H, NCH_2), 7.48-7.62 (m, 20H of PPh_3). ^{31}P{^{1}H} NMR (161.70 MHz, CD_2Cl_2): δ 57.4 (s). T_1 (400 MHz, CD_2Cl_2), ms (temperature): 29 (313 K), 27 (303 K), 26 (293 K), 25 (283 K), 25 (273 K), 24 (263 K), 25 (253 K), 26 (243 K), 28 (233 K), 31 (223 K), 37 (213 K), 47 (203 K). A ln T_1 vs 1000/T plot gave a T_1(min) of 24 ms at 266 K.

[TpRu(H_2)(dppe)]BF_4 (19). ^{1}H NMR (400 MHz, CD_2Cl_2): δ -9.28 [br, 2H, Ru-(H_2)], 2.82-2.96 (m, 4H, PCH_2), 5.25 [t, 1H, H(pz)], 5.52 [d, 1H, H(pz)], 6.09 [t,

2H, H(pz')], 6.82 [d, 2H, H(pz')], 7.51 [d, 1H, H(pz)], 7.79 [d, 2H, H(pz')] (pz = pyrazolyl group trans to H_2, pz' = pyrazolyl groups trans to dppe; all coupling constants for pyrazolyl proton resonances were about 2 Hz); 6.63, 7.06, 7.30, 7.53 (m, 20H of dppe phenyl groups). $^{31}P\{^1H\}$ NMR (161.70 MHz, CD_2Cl_2): δ 45.7 (s). T_1 (400 MHz, CD_2Cl_2), ms (temperature): 22 (293 K), 20 (283 K), 18 (273 K), 17 (263 K), 15 (253 K), 14 (243 K), 14 (233 K), 13 (228 K), 15 (218 K), 16 (213 K). A T_1 vs 1000/T plot gave a T_1(min) of 14 ms at 230 K.

The corresponding HD isotopomers were prepared analogously except that DBF_4, which was prepared by mixing $HBF_4{\cdot}Et_2O$ with D_2O in a volume ratio of 3:1, was used instead of $HBF_4{\cdot}Et_2O$ or CF_3SO_3H. The η^2-HD signals were observed after nulling the η^2-H_2 peaks by the inversion-recovery method.

$[^{H}CnRu(HD)(PPh_3)_2]^{2+}$. ^1H NMR (400 MHz, CD_2Cl_2): δ -.9.06 [tt, ^1J(HD) = 29.4 Hz, ^2J(HP) = 6.3 Hz, Ru-(*H*D)]

$[^{Me}CnRu(HD)(dppe)]^{2+}$. ^1H NMR (400 MHz, CD_2Cl_2): δ -9.85 [tt, ^1J(HD) = 29.4 Hz, ^2J(HP) = 8.0 Hz, Ru-(*H*D)].

$[TpRu(HD)(dppe)]^{+}$. ^1H NMR (400 MHz, CD_2Cl_2): δ -9.34 [t, ^1J(HD) = 32.5 Hz), Ru-(*H*D)].

The CO-containing dihydrogen complexes **6**, **8** and **20** were prepared as follows. In a typical experiment, a sample (10 mg) of the metal hydride was loaded into

a 5 mm NMR tube, which was then capped with a rubber septum. The tube was evacuated and filled with nitrogen for three cycles. Dichloromethane-d_2 (0.4 mL) was added to dissolve the sample. The solution was cooled to -78 °C, and 5 μL of HBF_4 was added through a microsyringe. The tube was loaded into the NMR probe precooled to -30 °C (**6** and **8**) or -80 °C (**20**), and the sample was immediately analyzed by NMR spectroscopy.

[^{H}CnRu(H$_2$)(CO)(PPh$_3$)](BF$_4$)$_2$ (6). ^{1}H NMR (400 MHz, CD_2Cl_2): δ -7.25 [br, 2H, Ru-(H_2)], 1.26-5.58 (m, 3H, N-*H* and 12H, NCH_2), 7.48-7.61 (m, 15H of PPh_3). $^{31}P\{^1H\}$ NMR (161.70 MHz, CD_2Cl_2): δ 45.7 (s). T_1 (400 MHz, CD_2Cl_2), ms (temperature): 15 (263 K), 13 (253 K), 14 (243 K), 18 (233 K), 19 (223 K), 20 (213 K). A ln T_1 vs 1000/T plot gave a T_1(min) of 14 ms at 248 K.

[^{Me}CnRu(H$_2$)(CO)(PPh$_3$)](PF$_6$)(CF$_3$SO$_3$) (8). ^{1}H NMR (400 MHz, CD_2Cl_2): δ -7.63 [br, 2H, Ru-(H_2)], 1.26-4.52 (m, 9H, NCH_3 and 12H, NCH_2), 7.41-7.66 (m, 15H of PPh_3). $^{31}P\{^1H\}$ NMR (161.70 MHz, CD_2Cl_2): δ 32.2 (s). T_1 (400 MHz, CD_2Cl_2), ms (temperature): 41 (258 K), 28 (253 K), 17 (248 K), 15 (243 K), 14 (238 K), 15 (223 K), 17 (215 K), 20 (203 K). A ln T_1 vs 1000/T plot gave a T_1(min) of 12 ms at 224 K.

[TpRu(H$_2$)(CO)(PPh$_3$)]BF$_4$ (20). ^{1}H NMR (400 MHz, CD_2Cl_2): δ -6.84 [br, 2H, Ru-(H_2)], 5.89 [br, 1H, H(pz)], 6.05 [br, 1H, H(pz)], 6.31 [br, 1H, H(pz)], 6.40 [br, 1H, H(pz)], 6.66 [br, 1H, H(pz)], 7.76 [br, 2H, H(pz)], 7.85 1H, H(pz)], 7.94 [br, 1H, H(pz)]. $^{31}P\{^1H\}$ NMR (161.70 MHz, CD_2Cl_2): δ 45.7 (s). T_1 (400 MHz, CD_2Cl_2), ms

(temperature): 13 (243 K), 12 (238 K), 11 (233 K), 11 (223 K), 12 (218 K), 13 (213 K), 14 (208), 47 (203 K). A ln T_1 vs 1000/T plot gave a T_1(min) of 12 ms at 224 K.

The corresponding HD isotopomers were prepared analogously except that DBF_4 was used in place of $HBF_4 \cdot Et_2O$. The η^2-HD signals were observed after nulling the η^2-H_2 peaks by the inversion-recovery method.

$[^{H}CnRu(HD)(CO)(PPh_3)]^{2+}$. ^{1}H NMR (400 MHz, CD_2Cl_2): δ -.7.29 [t, ^1J(HD) = 31.8 Hz, Ru-(*H*D)].

$[^{Me}CnRu(HD)(CO)(PPh_3)]^{2+}$. ^{1}H NMR (400 MHz, CD_2Cl_2): δ -.7.65 [t, ^1J(HD) = 31.0 Hz, Ru-(*H*D)].

$[TpRu(HD)(CO)(PPh_3)]^{+}$. ^{1}H NMR (400 MHz, CD_2Cl_2): δ -6.87 [t, ^1J(HD) = 33.3 Hz, Ru-(*H*D)].

2.2.3.3 Solvento complex

$[^{H}CnRu(H_2O)(PPh_3)_2](BF_4)_2$ (9). A sample of **1** (0.20 g, 0.24 mmol) was added to a two-necked round bottom flask which was evacuated and flushed with nitrogen. Degassed THF (10 mL) was syringed into the flask, followed by addition of 5 equiv of aqueous tetrafluoroboric acid (50 μL, HBF_4, 8M). After the mixture was stirred at room temperature for 5 min, 0.5 mL of degassed water was added to the mixture, and the resulting solution was stirred for a further 30 min. Addition of degassed hexane (20 mL) led to the precipitation of a yellow solid, which was then

filtered out and washed with diethyl ether (2 X 5 mL). Finally, it was collected and dried under vacuum. Yield: 0.13 g (58%). Anal. Calcd for $C_{42}H_{47}B_2N_3F_8OP_2Ru$: C, 53.30; H, 5.01; N, 4.44. Found: C, 52.11; H, 4.92; N, 4.21. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.26 (s, 2H, H_2O), 2.43-4.03 (m, 3H, N-*H* and 12H, NCH_2), 7.19-7.75 (m, 30 H of PPh_3). $^{31}P\{^1H\}$ NMR (161.70 MHz, CD_2Cl_2): δ 38.7 (s).

2.2.4 Acidity Measurement.

pK_a values of **5**, **7**, and **17-20** were estimated by studying the equilibrium shown in eq. 5. All measurements were carried out at room temperature except that of **18** (-30 °C) and **20** (-80 °C). In a typical experiment, appropriate amounts of $[L_nRuH]^{(n-1)+}$ and L'_nRuH were dissolved in CD_2Cl_2 in an NMR tube, and then limited amount of $HBF_4{\cdot}Et_2O$ was added. ^{31}P and ^1H NMR spectra were taken. Relative molar concentrations of the equilibrated species were estimated from the ^1H NMR integrations of the hydride signals.

The pK_a values of the two ^{R}Cn carbonyl dihydrogen complexes **6** and **8** were estimated by use of the equilibrium depicted in eq. 6. In a typical experiment, appropriate amount of $HBF_4{\cdot}Et_2O$ was added to a CD_2Cl_2 solution of the metal hydride in an NMR tube. NMR spectra were recorded at -80 °C, and the relative molar concentrations of $HBF_4{\cdot}Et_2O$, Et_2O, the metal hydride and the dihydrogen complex were estimated based on the ^1H NMR integrations.

2.2.5 Crystallographic Analysis

$[^{H}CnRuH(PPh_3)_2]BF_4 \cdot 2CH_2Cl_2$ (1). Suitable crystals for X-ray diffraction study were obtained by layering of hexane on a dichloromethane solution of $[^{H}CnRuH(PPh_3)_2]BF_4$. A red block crystal of dimension 0.22x0.23x0.29 mm was mounted in a glass capillary and used for X-ray structure determination. All measurements were made on a Marresearch image plate scanner with graphite monochromated Mo Kα radiation. The crystal system is orthorhombic and the space group $P2_12_12_1$ (#19). The data were collected at 25 °C using the ω scan technique to a maximum 2θ value of 51.2°. A total of 4741 intensity measurements were made using the ω scan technique. The linear coefficient, μ, for Mo Kα radiation is 6.8 cm^{-1}. Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects. The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques using the TEXSAN program package. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. The final cycle of Full-matrix least square refinements was based on 3178 observed reflection ($I>3.00\sigma(I)$) and 328 variable parameters and converged with unweighted and weighted agreement factors R = 7.2%, R_w = 9.9% with GOF = 3.41. The data:parameter ratio was 9.69:1 and residual electron density/hole 0.63/-0.52 $eÅ^{-3}$. Further crystallographic details and selected bond distances and angles are given in Tables 1 and 2, respectively.

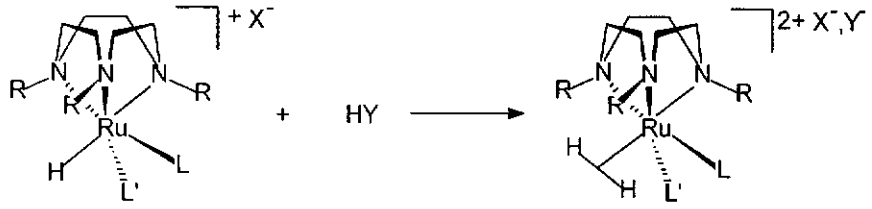
$[^{H}CnRu(H_2O)(PPh_3)_2](BF_4)_2$ (9). Suitable crystals for X-ray diffraction study were obtained by layering of hexane on a dichloromethane solution of $[^{H}CnRu(H_2O)(PPh_3)_2](BF_4)_2$ A red block crystal of dimension 0.12x0.16x0.26 mm was

mounted in a glass capillary and used for X-ray structure determination. All measurements were made on a Marresearch image plate scanner with graphite monochromated Mo Kα radiation. The crystal system is orthorhombic and the space group *P*1 (#2). The data were collected at 25 °C using the ω scan technique to a maximum 2 θ value of 50.6°. A total of 5388 intensity measurements were made using the ω scan technique. The linear coefficient, μ, for Mo Kα radiation is 4.7 cm^{-1}. Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects. The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques using the TEXSAN program package. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. The final cycle of Full-matrix least square refinements was based on 2725 observed reflection ($I>3.00\sigma(I)$) and 212 variable parameters and converged with unweighted and weighted agreement factors $R = 0.177$, $R_w = 0.242$ with GOF = 5.08. The data:parameter ratio was 12.85:1 and residual electron density/hole 1.77/-1.44 $eÅ^{-3}$. Further crystallographic details and selected bond distances and angles are given in Tables 3 and 4, respectively.

2.3 Results and Discussion

2.3.1 Synthesis and Characterization of $[^{R}Cn(H_2)(L)(L')]^{2+}$ Complexes.

The dihydrogen complexes $[^{R}CnRu(H_2)(L)(L')]^{2+}$ (**5-8**) were synthesized by protonation of the corresponding monohydride complexes **1-4** with $HBF_4.Et_2O$ or CF_3SO_3H (eq. 3).



(3)

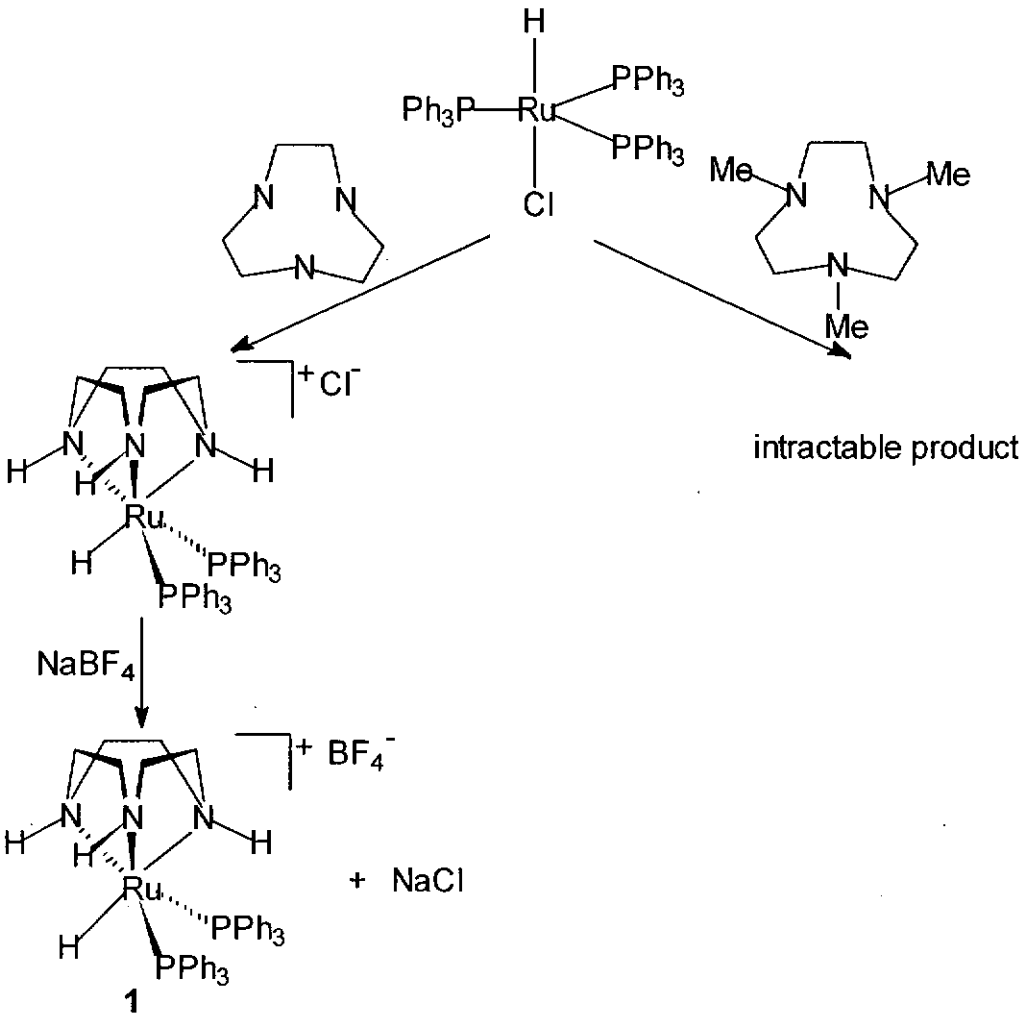
1, R = H, (L)(L') = $(PPh_3)_2$ — **5**, R = H, (L)L') = $(PPh_3)_2$ $X^- = Y^- = BF_4^-$

2, R = H, (L)(L') = $(CO)(PPh_3)$ — **6**, R = H, (L)L') = $(CO)(PPh_3)$ $X^- = Y^- = BF_4^-$

3, R = Me, (L)(L') = dppe — **7**, R = Me, (L)L') = dppe $X^- = Y^- = CF_3SO_3^-$

4, R = Me, (L)(L') = $(CO)(PPh_3)$ — **8**, R = Me, (L)L') = $(CO)(PPh_3)$ $X^- = PF_6^-$, $Y^- = CF_3SO_3^-$

The starting monohydride complexes $[^{Me}CnRuH(dppe)]CF_3SO_3$ (**3**)[26d] and $[^{Me}CnRuH(CO)(PPh_3)]PF_6$ (**4**)[26d] are known compounds. The monohydride complex $[^{H}CnRuH(PPh_3)_2]BF_4$ (**1**) was prepared by reacting ^{H}Cn with $RuHCl(PPh_3)_3$ in the presence of $NaBF_4$ (scheme 1). Preparation of the analogous complex $[^{Me}CnRuH(PPh_3)_2]BF_4$ was attempted by using ^{Me}Cn in place of ^{H}Cn. However, the preparation was not successful and some intractable materials were obtained. Failure of the reaction is probably due to large steric interaction between triphenylphosphine and the sterically more demanding ^{Me}Cn ligand. The complex $[^{H}CnRuH(CO)(PPh_3)]BF_4$ (**2**) was prepared by refluxing a mixture of ^{H}Cn and $RuHCl(CO)(PPh_3)_3$ in 2-methoxyethanol, followed by precipitation with $NaBF_4$. Similar procedure has been used previously for the preparation of $[^{Me}CnRuH(CO)(PPh_3)]PF_6$ (**4**).[26d]



Scheme 1

The new monohydride complexes can be readily characterized by their NMR, IR and elemental analysis. The structure of complex **1** has also been confirmed by X-ray diffraction. The molecular structure of the cation $[^{H}CnRuH(PPh_3)_2]^+$ is shown in Figure 2.1. Crystallographic details and selected bond distances and angles are given in Tables 1 and 2, respectively.

The structure **1** could be described as a distorted octahedron with the hydride trans to N(2). The distortion can be attributed to the coordination geometry of the ^{H}Cn ligand. The N-Ru-N angles and Ru-N bond distances in complex **1** are very similar to

those observed for related complexes such as $[^{Me}CnR(PMe_3)(P(OMe)_3(C{\equiv}CPh)]PF_6$,[26a] $[^{Me}CnRu(PMe_3)(\eta^3\text{-}PhC_3CHPh)]PF_6$,[26a], $[^{Me}CnRuH(\eta^4\text{-}COD)]PF_6$[26e] and $[^{Me}CnRu(\eta^5\text{-}C_8H_{11})]PF_6$.[26e] The bond Ru-N(2) (2.30(1) Å) is slightly longer than Ru-N(1) (2.20(1) Å) and Ru-N(3) (2.19(1) Å), presumably due to the trans influence of the hydride ligand. The P(1)-Ru-P(2) angle (96.4°) is smaller than that observed for $CpRuH(PPh_3)_2$ (101.4°)[49a] and comparable to that observed for $CpRuH(PMe_3)_2$.[49b,c]

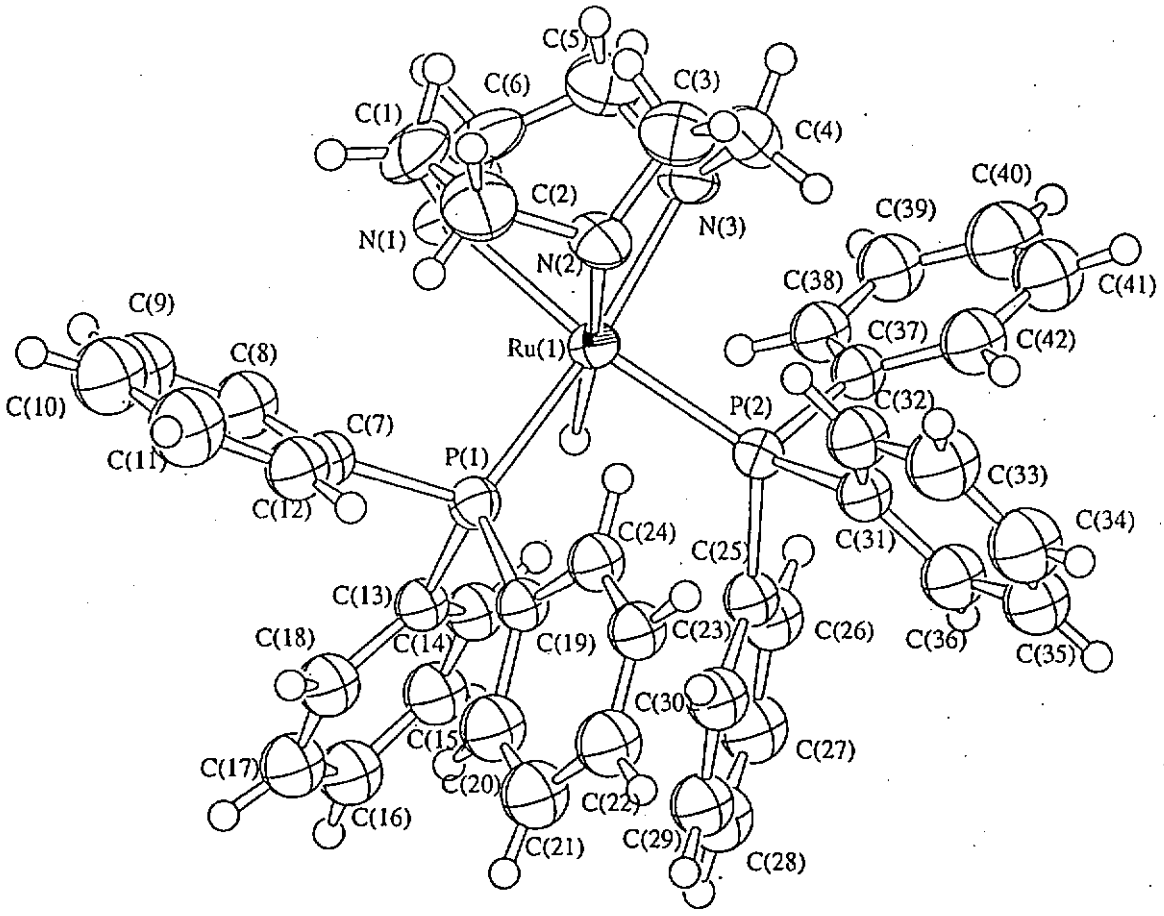


Figure 2.1. The molecular structure of $[^{H}CnRuH(PPh_3)_2]BF_4$ (**1**).

Table 1. Crystal Data and Refinement Details for $[^{H}CnRuH(PPh_3)_2]BF_4 \cdot 2CH_2Cl_2$

formula	$C_{44}H_{47}BCl_4F_4N_3P_2Ru$
fw	1009.51
color and habit	red block
crys dimens (mm)	0.22x0.23x0.29
crys sys	orthorhombic
space group	$P2_12_12_1$ (#19)
a, Å	10.598(1)
b, Å	20.046(1)
c, Å	21.973(1)
V, Å^3	4668.1(4)
Z	4
d_{calc}, g cm^{-3}	1.436
F(000)	2060.00
radiation	Mo Kα(λ = 0.71073 Å)
μ(MoKα), cm^{-1}	6.83
T, °C	25.0
diffractometer	Marresearch Image Plate Scanner
$2\theta_{max}$, deg	3.0 to 50.0
scan type	ω
explosure (min)	5
reflections collected	28766
unique reflections	4741
observed reflections	3178 ($F > 3.0\ \sigma(F)$)
absorption correction	inter-image scaling
no. of parameter refined	328
final R indices (obs. data)	R = 7.2%, Rw = 9.9%
goodness of fit	3.41
data to parameter ratio	9.69
largest difference peak	0.63 eÅ^{-3}
largest difference hole	-0.52 eÅ^{-3}

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[^{H}CnRuH(PPh_3)_2]BF_4 \cdot 2CH_2Cl_2$

Interatomic Distance (Å)					
Ru-P(1)	2.286(4)	Ru-P(2)	2.270(4)	Ru-N(1)	2.20(1)
Ru-N(2)	2.30(1)	Ru-N(3)	2.19(1)	Ru-H	1.8(2)

Intramolecular Angles (deg)					
P(1)-Ru-P(2)	96.4(1)	P(1)-Ru-N(1)	93.8(4)	P(1)-Ru-N(2)	102.2(4)
P(1)-Ru-N(3)	172.8(4)	P(1)-Ru-H	95(5)	P(2)-Ru-N(1)	164.5(4)
P(2)-Ru-N(2)	110.8(4)	P(2)-Ru-N(3)	90.6(3)	P(2)-Ru-H	85(6)
N(1)-Ru-N(2)	78.2(6)	N(1)-Ru-N(3)	79.0(5)	N(1)-Ru-H	82(6)
N(2)-Ru-N(3)	76.9(5)	N(2)-Ru-H	154(6)	N(3)-Ru-H	83(6)

Protonation of the monohydride complexes **1-4** with $HBF_4.Et_2O$ or CF_3SO_3H produced the dihydrogen complexes **5-8** (eq.3). The dihydrogen complex $[^{H}CnRu(H_2)(PPh_3)_2](BF_4)_2$ (**5**), isolated as yellow solid by addition of Et_2O to a CH_2Cl_2 solution of $[^{H}CnRuH(PPh_3)_2]BF_4$ acidified with slightly excess of $HBF_4.Et_2O$, was contaminated by a small amount of the aquo complex $[^{H}CnRu(H_2O)(PPh_3)_2](BF_4)_2$. Apparently, the aquo complex was formed by displacement of η^2-H_2 in **5** by adventitious water in the solvents. Similar contamination problem was encountered in the preparation of the dihydrogen complex $[^{Me}CnRu(H_2)(dppe)](CF_3SO_3)_2$ (**7**). But it will be seen (*vide infra*) that in the absence of acid, water acts as a base to deprotonate the η^2-H_2 in **5** or **7**. The dihydrogen complexes **5** and **7** are stable in the solid state at room temperature; but in solution, the η^2-H_2 ligand is displaced by strongly coordinating solvent such as acetonitrile. The very acidic CO-containing dihydrogen complexes **6** and **8** are unstable with respect to loss of H_2, both in solid state and in solution, at room temperature. These complexes were prepared by acidification at -30 °C with excess $HBF_4.Et_2O$, and were characterized in situ with NMR spectroscopy.

The existence of the η^2-H_2 moieties in complexes **5-8** was confirmed by variable-temperature T_1 measurements and the observation of large ^1J(HD) coupling constants for the corresponding isotopomers which were prepared by acidification of **1-4** with DBF_4 or CF_3SO_3D. In particular, the ^1J(HD) coupling constants for the isotopomers were observed in the range of 29.4 to 31.8 Hz and T_1(min) values in the range of 12 to 24 ms at 400 MHz. The changes in the ^1J(HD) and T_1(min) are rather small especially in view of the fact that the electronic properties of the ligands have been changed drastically. It is also interesting to note that the ^1J(HD) for

$[^{H}CnRu(HD)(CO)(PPh_3)]^{2+}$ (31.8 Hz) is slightly larger than that of $[^{Me}CnRu(HD)(CO)(PPh_3)]^{2+}$ (30.0 Hz), but the T_1(min) for $[^{H}CnRu(H_2)(CO)(PPh_3)]^{2+}$ (14 ms) is slightly longer than that of $[^{Me}CnRu(H_2)(CO)(PPh_3)]^{2+}$ (12 ms). The shorter T_1(min) for $[^{Me}CnRu(H_2)(CO)(PPh_3)]^{2+}$ is undoubtedly caused by the extra relaxation due to the methyl groups.[50]

Complexes **5-8** provide additional examples of *dicationic* dihydrogen complexes. In contrast to the abundance of isolable monocationic dihydrogen complexes, well characterized dicationic dihydrogen complexes are still very limited in numbers. Reported dicationic dihydrogen complexes were mainly those of the osmium complexes such as $[Os(H_2)(NH_3)_5]^{2+}$,[22a] $[Os(H_2)(en)_2(L)]^{2+}$,[22b] *trans*-$[Os(H_2)(dppe)_2(CH_3CN)]^{2+}$,[20] $[Os(H_2)(CO)(bpy)(PPh_3)_2]^{2+}$ (bpy = 2,2'-dipyridyl), $[Os(H_2)(CO)(bpy)_2]^{2+}$,[21k] and $[Os(H_2)(CO)(dppp)_2]^{2+}$.[18] Dicationic dihydrogen complexes of other metals are limited to *trans*-$[Fe(H_2)(L)(dppe)_2]^{2+}$ (L = CO, CNH)[51] and $[Ru(H_2)(CO)(dppp)_2]^{2+}$.[18] Very recently, Luther and Heinekey reported the synthesis, characterization and reactivity of the dicationic dihydrogen complexs $[Os(H_2)(CO)(bpy)(PMePh_2)_2]^{2+}$, $[Os(H_2)(CO)(phen)(PPh_3)_2]^{2+}$ and $[Ru(H_2)(CO)(bpy)(PPh_3)_2]^{2+}$.[52]

As stated before, during the preparation of the dihydrogen complex $[^{H}CnRu(H_2)(PPh_3)_2](BF_4)_2$ (**5**) via the protonation of $[^{H}CnRuH(PPh_3)_2]BF_4$ (**1**), the product was always contaminated by small amount of the aquo complex $[^{H}CnRu(H_2O)(PPh_3)_2](BF_4)_2$ (**9**). It was later found that addition of excess HBF_4 to **1** , followed by introduction of water, gave **9** as the sole product. This aquo complex can

be readily characterized by NMR, and elemental analysis. The structure of complex **9** has also been confirmed by X-ray diffraction. The molecular structure of the cation $[^{H}CnRu(H_2O)(PPh_3)_2]^{2+}$ is shown in Figure 2.2. Crystallographic details and selected bond distances and angles are given in Tables 3 and 4, respectively.

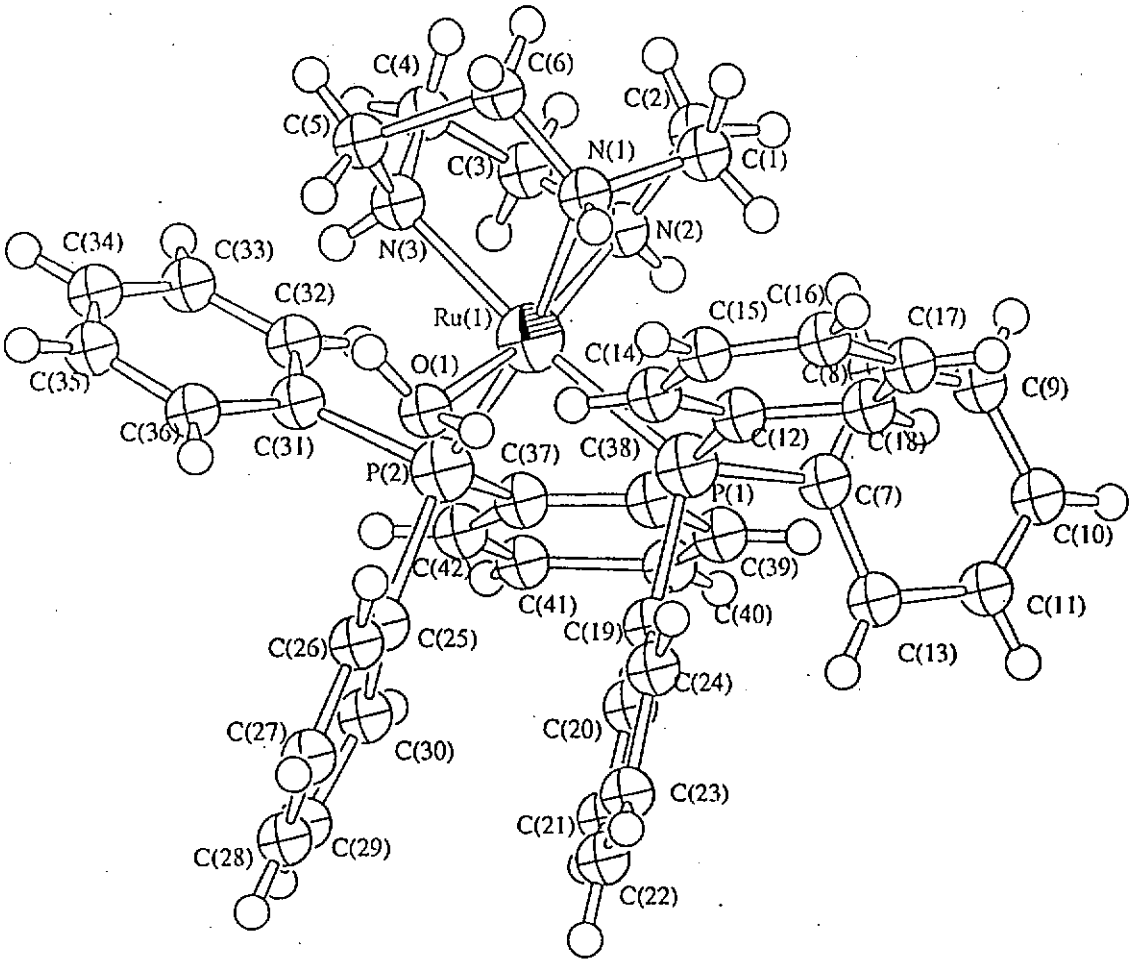


Figure 2.2. The molecular structure of $[^{H}CnRu(H_2O)(PPh_3)_2](BF_4)_2$ (**9**).

Table 3. Crystal Data and Refinement Details for $[^{H}CnRu(H_2O)(PPh_3)_2](BF_4)_2$

formula	$C_{42}H_{47}B_2F_8N_3P_2Ru$
fw	946.48
color and habit	red blcok
crys dimens (mm)	0.12x0.16x0.26
crys sys	triclinic
space group	*P*1(#2)
a, Å	11.199(1)
b, Å	11.938(1)
c, Å	18.163(1)
V, $Å^3$	2332.1(3)
Z	2
d_{cacl}, g cm^{-3}	1.348
F(000)	968.00
radiation	Mo Kα(λ = 0.716069 Å)
μ(MoKα), cm^{-1}	4.71
T, °C	25.0
diffractometer	Marresearch Image Plate Scanner
$2\theta_{max}$, deg	50.6
scan type	ω
explosure (min)	5
reflections collected	5388
observed reflections	2725 ($F > 3.0\ \sigma(F)$)
absorption correction	inter-image scaling
no. of parameter refined	212
final R indices (obs. data)	R = 17.7%, Rw = 24.2%
goodness of fit	5.08
data to parameter ratio	12.85
largest difference peak	1.77e$Å^{-3}$
largest difference hole	-1.44e$Å^{-3}$

Table 4. Selected Bond Distances (Å) and Angles (deg) for $[^{H}CnRu(H_2O)(PPh_3)_2](BF_4)_2$

Interatomic Distance (Å)

Ru-P(1)	2.385(9)	Ru-P(2)	2.375(10)	Ru-N(1)	2.20(3)
Ru-N(2)	2.10(3)	Ru-N(3)	2.17(3)	Ru-O	2.20(5)

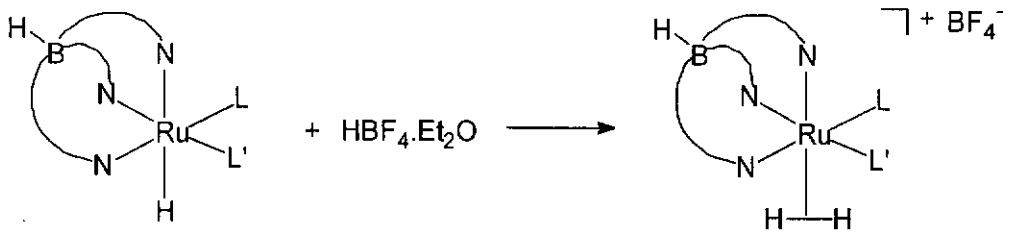
Intramolecular Angles (deg)

P(1)-Ru-P(2)	98.9(3)	P(1)-Ru-N(1)	90.9(8)	P(1)-Ru-N(2)	99.5(7)
P(1)-Ru-N(3)	171.1(9)	P(1)-Ru-O	87(1)	P(2)-Ru-N(1)	170.1(8)
P(2)-Ru-N(2)	97.3(7)	P(2)-Ru-N(3)	90.0(9)	P(2)-Ru-O	85(6)
N(1)-Ru-N(2)	82(1)	N(1)-Ru-N(3)	80(1)	N(1)-Ru-O	86(1)
N(2)-Ru-N(3)	79(1)	N(2)-Ru-O	166(1)	N(3)-Ru-O	91(1)

The structure of $[^{H}CnRu(H_2O)(PPh_3)_2](BF_4)_2$ (**9**) could be described as a distorted octahedron with the H_2O trans to N(2). The distortion can be attributed to the coordination geometry of the ^{H}Cn ligand. The N-Ru-N and P-Ru-P are very similar to those observed for complex **1.** The Ru-N(2) bond (2.10(1) Å) is slightly shorter than Ru-N(1) (2.20(1) Å) and Ru-N(3) (2.17(1) Å), presumably due to the smaller trans influence of the aquo ligand than that of the phosphines.

2.3.2 Synthesis and Characterization of $[TpRu(H_2)(L)(L')]^+$ *Complexes.*

The dihydrogen complexes $[TpRu(H_2)(PPh_3)_2]BF_4$ (**17**) and $[TpRu(H_2)(CH_3CN)(PPh_3)]BF_4$ (**18**) were recently synthesized by our group from protonation reactions of the corresponding monohydride complexes with HBF_4,Et_2O.[29b] With similar strategy, the new dihydrogen complexes $[TpRu(H_2)(dppe)]BF_4$ (**19**) and $[TpRu(H_2)(CO)(PPh_3)]BF_4$ (**20**) were prepared (eq. 4). Like **5** and **7**, the isolated **19** was contaminated by a small amount of the aquo complex $[TpRu(H_2O)(dppe)]BF_4$. It should be mentioned that the CO-containing dihydrogen complex **20** is unstable with respect to loss of H_2 at room temperature, therefore the acidification had to be carried out at -30 °C and **20** was not isolated, but was studied in situ.



(4)

12, (L)(L') = $(PPh_3)_2$
13, (L)(L') = $(CH_3CN)(PPh_3)$
14, (L)(L') = dppe
15, (L)(L') = $(CO)(PPh_3)$

17, (L)(L') = $(PPh_3)_2$
18, (L)(L') = $(CH_3CN)(PPh_3)$
19, (L)(L') = dppe
20, (L)(L') = $(CO)(PPh_3)$

The existence of the η^2-H_2 moiety in $[TpRu(H_2)(dppe)]BF_4$ **(19)** was confirmed by observation of a T_1(min) value of 14 ms for **19** and a large ^1J(HD) coupling constant of 32.5 Hz for the corresponding isotopomer $[TpRu(HD)(dppe)]BF_4$ which was prepared by acidification of **14** with DBF_4. Similarly, the existence of the η^2-H_2 moiety in **20** is evidenced by short T_1(min) of this complex and large ^1J(HD) coupling constant (33.3 Hz) of the corresponding isotopomer $[TpRu(HD)(CO)(PPh_3)]BF_4$.

2.3.3 Comparison of the Abilities of Cp, Tp, and ^{R}Cn in Stabilizing Dihydrogen Complexes.

Although Cp, Tp and ^{R}Cn are isoelectronic and all adopt facial geometry, their abilities to stabilize dihydrogen ligands are different. For example, while $[CpRuH_2(PPh_3)_2]^+$ is a classical dihydride complex, both $[TpRu(H_2)(PPh_3)_2]^+$ and $[^HCnRu(H_2)(PPh_3)_2]^{2+}$ are molecular dihydrogen complexes. Subtle differences in the Tp and ^{R}Cn complexes are also noted. Although the ^{R}Cn dihydrogen complexes **5-8** are dicationic and the Tp dihydrogen complexes **17-20** are monocationic, ^1J(HD) couplings of the isotopomers of the ^{R}Cn complexes are consistently smaller than those of the Tp counterparts. This is probably the result of ^{R}Cn being better σ-donors than Tp, and the

latter being able to act as a π-accepting ligand. In consonance with the trends in ^1J(HD) couplings, we have observed that the η^2-H_2 ligands in the Tp complexes **17-20** are much more readily displaced by water, in the absence of H_2 pressure, than those in **5-8**. Reactions of these complexes with water warrant further discussion later.

2.3.4 Acidity of the Dihydrogen Complexes.

Attempt has been made to rank the relative acidity of the dihydrogen complexes. A useful approach to do so is to measure the pseudo aqueous pK_a values.[6-10] In this approach, equilibrium constants for the reactions of L_nMH (precursors to dihydrogen complexes) and an acid with known aqueous pK_a value are determined in non-aqueous solutions. The pseudo aqueous pK_a of the dihydrogen complexes are then calculated in reference to the aqueous pK_a of the acid. The pseudo aqueous pK_a values of **5**, **7**, **17**, **18,** and **19** were estimated by studying the equilibrium shown in eq. 5 with ^{1}H NMR in CD_2Cl_2, using the hydride complexes $RuHCl(dppe)_2$, $CpRuH(PPh_3)_2$, and CpRuH(dppm) as the bases. The pseudo aqueous p*K*a values of $[RuCl(H_2)(dppe)_2]^+$,[9b] $[CpRuH_2(PPh_3)_2]^+$,[6b] and $[CpRu(H_2)(dppm)]^+$ [6b] have been determined previously in CD_2Cl_2 using similar method. The equilibrium mixture could be conveniently obtained by protonation with a limited amount of $HBF_4.Et_2O$ of a mixture of $[L_nRuH]^{(n-1)+}$ and L'_nMH.

$$[L_nRu(H_2)]^{n+} + L'_nMH \rightleftharpoons [L_nRuH]^{(n-1)+} + L'_nMH_2^+ \quad (5)$$

All the equilibria were obtained at room temperature, except in the case of $[TpRu(H_2)(CH_3CN)(PPh_3)]^+$, which was carried out at -30 °C. The relative concentrations of the dihydrogen complexes and the metal hydrides in equilibrium were estimated from integrations of the upfield hydride signals in the ^1H NMR spectra, and therefore the equilibrium constants can be estimated based on the known pK_a values of $L'_nMH_2^+$. The pseudo aqueous pK_a value of the Tp carbonyl dihydrogen complex $[TpRu(H_2)(CO)(PPh_3)]BF_4$ (**20**) was determined in a similar manner at -80°C, using $[^HCnRu(H)(CO)(PPh_3)]BF_4$ (**2**) as the base.

The pK_a values of the ^{R}Cn carbonyl dihydrogen complexes **6** and **8** could not be estimated by use of eq. 5 because they are much more acidic than the $L'_nMH_2^+$ complexes. The pK_a values of **6** and **8** were estimated by studying the protonation reactions of **2** and **4** with $HBF_4.Et_2O$ (eq. 6)

$$[^RCnRuH(CO)(PPh_3)]PF_6 + HBF_4.Et_2O \rightleftharpoons [^RCnRu(H_2)(CO)(PPh_3)](PF_6)(BF_4) + Et_2O \quad (6)$$

using ^1H NMR at -80 °C. The relative molar concentrations of $HBF_4{\cdot}Et_2O$, Et_2O, the ruthenium carbonyl hydrides, and the carbonyl dihydrogen complexes were estimated based on the ^1H NMR integrations. The pK_a values of **6** and **8** were estimated to be -1.3 and -2.6, respectively, taking the pK_a of $HBF_4.Et_2O$ as -2.4.[53] Details on the acidity measurements are summarized in Table 5.

Table 5. Acidity Measurements of Dihydrogen Complexes in CD_2Cl_2[a]

$M(H_2)$	B	Keq	$pK_a(M(H_2))$
$[^{H}CnRu(H_2)(PPh_3)_2](BF_4)_2$ (**5**)	$RuHCl(dppe)_2$	31.6	4.5
$[^{H}CnRu(H_2)(CO)(PPh_3)](BF_4)_2$ (**6**)	Et_2O	0.07[b]	-1.3
$[^{Me}CnRu(H_2)(dppe)_2](CF_3SO_3)_2$ (**7**)	$RuHCl(dppe)_2$	166	3.8
$[^{Me}CnRu(H_2)(CO)(PPh_3)](PF_6)(CF_3SO_3)$ (**8**)	Et_2O	1.56[b]	-2.6
$[TpRu(H_2)(PPh_3)_2]BF_4$ (**17**)	CpRuH(dppm)	0.303	7.6
$[TpRu(H_2)(CH_3CN)(PPh_3)]BF_4$ (**18**)	$CpRuH(PPh_3)_2$	0.277[c]	8.9
$[TpRu(H_2)(dppe)]BF_4$ (**19**)	CpRuH(dppm)	0.179	7.9
$[TpRu(H_2)(CO)(PPh_3)]BF_4$ (**20**)	$[^{H}CnRuH(CO)(PPh_3)]^+$	0.498[b]	-0.6

[a] pK_a values (on the pseudo aqueous scale) of the dihydrogen complexes are estimated by means of the equation: $pK_a(M(H_2)) = pKeq + pK_a(HB^+)$; Keq is the equilibrium constant of eq. 5 or the reciprocal of the equilibrium constant of eq. 6. [b] At -80 °C. [c] -30 °C.

2.3.5 Comments on the Acidity .

It should be stressed that the pseudo aqueous pK_a values of complexes **5-8** and **17-20** are obtained based on the assumption that the differences in the pK_a values of the dihydrogen complexes and the reference acids are the same in water and CD_2Cl_2. Since the assumption has not been confirmed yet, the pseudo aqueous pK_a values of the complexes may be different from the true aqueous pK_a values and should not be treated too seriously. However, the pseudo aqueous pK_a values can still provide valuable information in the trend of the acidity of the complexes. For comparison, the pseudo aqueous pK_a values of the new dihydrogen complexes and related $[(\eta^5\text{-}C_5R_5)RuH_2(L)(L')]^+$ complexes are listed in Table 6. In order to see the effect of H—H bonding on the acidity, the T_1(min) and r(HH) for the dihydrogen complexes, and ^1J(HD) for the HD isotopomers are also listed if available. The hydrogen-hydrogen separations r(HH) were calculated according to the empirical equation (eq 7)[19a]

$$r(HH) = 1.42 - 0.0167J(HD) \qquad (7)$$

which shows a linear relationship between J(HD) and r(HH) in a wide variety of η^2-H_2 complexes whose J(HD) values fall in the range 7 - 35 Hz. An essentially identical linear relationship is also predicted by quantum chemical calculation for complexes of the type $[Os(NH_3)_4L(H_2)]^{2+}$ for a wide range of *trans* ligands L.[54]

Table 6. Spectroscopic Properties and Acidities of Hydride Complexes

Complexes	T_1(min) ms[a] (temp)	^1J(HD) Hz	d(HH) Å[b]	pK_a[c]	reference
[^{H}CnRu(H_2)(PPh_3)$_2$](BF_4)$_2$ (**5**)	20 (250 K)	29.4	0.93	4.5	this work
[^{H}CnRu(H_2)(CO)(PPh_3)](BF_4)$_2$ (**6**)	14 (248 K)	31.8	0.89	-1.3[d]	this work
[^{Me}CnRu(H_2)(dppe)](CF_3SO_3)$_2$ (**7**)	24 (266 K)	29.4	0.93	3.8	this work
[^{Me}CnRu(H_2)(CO)(PPh_3)](PF_6)(CF_3SO_3) (**8**)	12 (224 K)	31.0	0.92	-2.6[d]	this work
[TpRu(H_2)(PPh_3)$_2$]BF_4 (**17**)	21 (240 K)	32.0	0.89	7.6	this work
[TpRu(H_2)(CH_3CN)(PPh_3)]BF_4 (**18**)	16 (231 K)	33.0	0.87	8.9[e]	this work
[TpRu(H_2)(dppe)]BF_4 (**19**)	14 (230 K)	32.5	0.88	7.9	this work
[TpRu(H_2)(CO)(PPh_3)]BF_4 (**20**)	12 (224 K)	33.3[d]	0.86	-0.6[d]	this work
[CpRuH_2(PPh_3)$_2$]$^+$			8.3	8.3	16b
[CpRu(H_2)(dppm)]$^+$		21.9	1.05	7.1	16b
[Cp*Ru(H_2)(dppm)]$^+$	18(220K)	20.9	1.07	9.2	16b
[CpRu(H_2)(dppe)]$^+$		24.9	1.00	7.0	16b

[a] At 400 MHz. [b] Calculated based on ^1J(HD) values as described in ref 19a. [c] pK_a values were determined in CD_2Cl_2, but reported on pseudo aqueous scale. [d] Determined at -80 °C. [e] Determined at -30 °C.

It can be seen from Table 6 that isostructural and monocationic Tp and Cp ruthenium dihydrogen complexes have similar acidity. The dicationic ^{R}Cn dihydrogen complexes **5** and **7** are significantly more acidic than their Tp and Cp analogues (by 3-4 pK_a units difference). The carbonyl-containing ^{R}Cn dihydrogen complexes $[^{Me}CnRu(H_2)(CO)(PPh_3)]^{2+}$ (pK_a = -2.6) and $[^{H}CnRu(H_2)(CO)(PPh_3)]^{2+}$ (pK_a = -1.3) are also more acidic than the analogous monocationic Tp complex $[TpRu(H_2)(CO)(PPh_3)]^{+}$ (pK_a = -0.6), but to a smaller extent. Several highly acidic dicationic dihydrogen complexes have been reported, for example, the dicationic dihydrogen complex *trans*-$[Os(H_2)(dppe)_2(CH_3CN)]^{2+}$ has a pseudo aqueous pK_a value close to -2.[20] The complex $[Os(H_2)(CO)(bpy)(PPh_3)_2]^{2+}$ can be deprotonated by diethyl ether.[21k] The dicationic dihydrogen complexes $[M(H_2)(CO)(dppp)_2]^{2+}$ (M = Ru; Os) were reported to have pK_a values close to -6.[18] It should be mentioned that dicationic dihydrogen complexes are not necessarily stronger acids than monocationic complexes, for example, $[Os(H_2)(NH_3)_5]^{2+}$ was reported to be a weak acid and is stable to moderately strong base such as NaOMe. The high pK_a value of this complex is probably due to the strong electron donating effect of the NH_3 ligands.[22a]

Within the ^{H}Cn, ^{Me}Cn and the Tp dihydrogen complex series, substitution of phosphine group for CO leads to a 5-8 unit decrease in the pK_a value. The observation is very similar to that observed for $[RuCl(H_2)(L)(PMP)]^{+}$ (L = CO, PPh_3).[55] The same trend has also been observed for classical hydride complexes. For example, $MnH(CO)_5$ has a pK_a(CH_3CN) of 15.1[56] vs 20.4 for $MnH(CO)(PPh_3)$;[57] $CpCrH(CO)_3$ has a pK_a(CH_3CN) of 13.3[58] vs 21.8 for $CpCrH(CO)_2(PPh_3)$,[59] and $HCo(CO)_4$ has a pK_a of 8.3[56] vs 15.4 for $HCo(CO)_3(PPh_3)$.[56] These observations may indicate that the inductive

effect of the ligands is very important in determining the acidity of the dihydrogen complexes.

It is well established that the acidity of hydride complexes are strongly influenced by the metals as well as the auxillary ligands.[60,61] With a few exceptions, the acidity of isostructural classic hydride complexes decreases as ligands become more electron-donating, and as the metal is replaced successively by heavier metals in the same group. The relative acidity of most of the complexes studied in this work are consistent with the trend. However, exception is observed for complexes **6** and **8**. It might be expected that complex **8** should be less acidic than complex **6** because ^{Me}Cn is more electron-donating than ^{H}Cn, as reflected from the ^{1}J(HD) coupling constants of the corresponding isotopomers of complexes **6** and **8**. In fact, complex **8** was found to be more acidic than complex **6** based on the equilibrium study as described before. The more acidic nature of complex **8** compared to complex **6** is further supported by the fact that the complex $[^{H}CnRuH(CO)(PPh_3)]^+$ is preferentially protonated when a mixture of $[^{H}CnRuH(CO)(PPh_3)]^+$ and $[^{Me}CnRuH(CO)(PPh_3)]^+$ was treated with a limited amount of $HBF_4{\cdot}OEt_2$.(Fig 2.3)

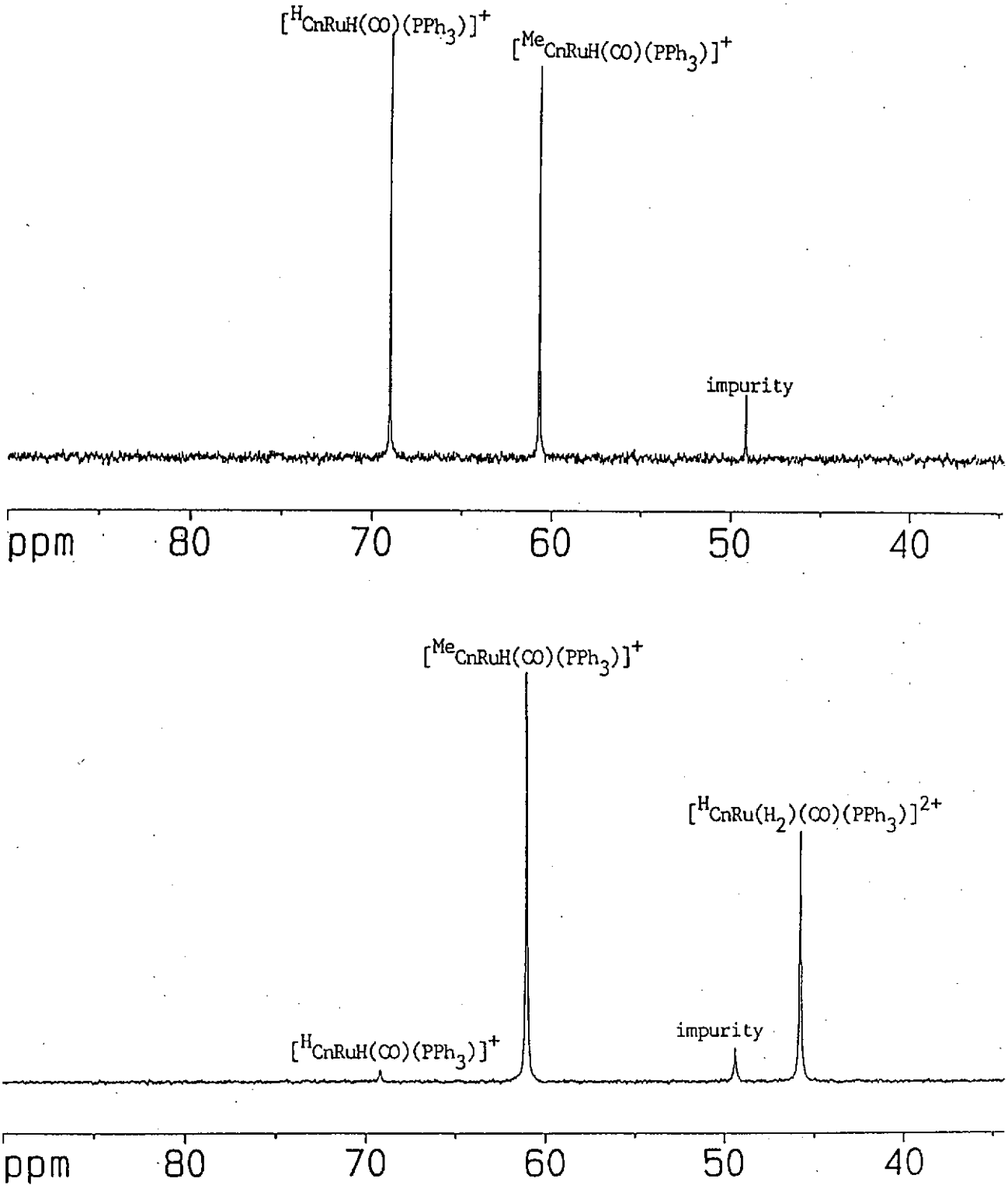


Figure 2.3. The ^{31}P NMR spectra of (a) $[^{Me}CnRuH(CO)(PPh_3)]^+$ and $[^{H}CnRuH(CO)(PPh_3)]^+$ in CD_2Cl_2 at -35 °C and (b) ($[^{Me}CnRuH(CO)(PPh_3)]^+$ and $[^{H}CnRuH(CO)(PPh_3)]^+$) + $HBF_4.Et_2O$ in CD_2Cl_2 at -80 °C

It is not apparent why the ^{Me}Cn complex **8** is more acidic than the ^{H}Cn complex **6**. It is possible that the H-H bond strength in **6** and **8** may play some role in determining the relative acidity. The more electron donating ^{Me}Cn ligand in **8** renders the H-H interacton weaker than that in complex **6** which contains the less donating ^{H}Cn ligand, and the weaker H-H interaction may make a dihydrogen complex more acidic than may be suggested by the general trend in the acidity of classic hydride complexes. Morris *et al.* has recently proposed that dramatic reduction of pK_a value of *trans*-$[RuCl(H_2)(dppe)_2]^+$ vs that of *trans*-$[RuH(H_2)(dppe)_2]^+$ could be attributed to a lower H-H bond strength in the former. The high acidity of the trihydride complex $[RuH_3(dppf)_2]^+$ (dppf = 1,1'-bis(diphenylphosphino)ferrocene) compared to that of $[RuH(H_2)(dppe)_2]^+$ is also in accord with this idea.[19b]

2.3.6 Reactions of Dihydrogen Complexes with Water.

The roles of the dihydrogen complexes $[TpRu(H_2)(PPh_3)_2]^+$ (**17**) and $[TpRu(H_2)(CH_3CN)(PPh_3)]^+$ (**18**) in olefin hydrogenation reactions have been discussed in a recent publication of our group.[29b] It was noted that their catalytic activities are greatly enhanced when the reactions were performed in THF/H_2O mixed solvents instead of anhydrous THF. The enhancement effect is attributed to deprotonation of η^2-H_2 by H_2O to generate the active metal hydride species. The deprotonation reaction with water has been demonstrated with NMR study with complex **17**. It is somewhat surprising to find out in the present study that the pseudo aqueous pK_a of complexes **17** (7.6) and **18** (8.9) are significantly higher than that of H_3O^+ (-1.74).[62] As H_2O is a very weak base, it is not expected that H_2O should be basic enough to deprotonate these dihydrogen complexes.

In order to see if deprotonation by water would also occur on other dihydrogen complexes with pseudo aqueous pK_a values significantly higher than that of H_3O^+, the reactivities of complexes $[TpRu(H_2)(dppe)]BF_4$ (**19**, pK_a = 7.9), $[^{H}CnRu(H_2)(PPh_3)_2](BF_4)_2$ (**5**, pK_a = 4.5) and $[^{Me}CnRu(H_2)(dppe)](CF_3SO_3)_2$ (**7**, pK_a = 3.8) toward water have been tested.(eq. 8)

$$[LRu(H_2)L'_2]^{n+} + H_2O \rightleftharpoons [LRu(H)L'_2]^{(n-1)+} \qquad (8)$$

5, L = ^{H}Cn, n = 2
7, L = ^{Me}Cn, n = 2
19, L = Tp, n = 1

In the absence of H_2 pressure, like complex **17**, H_2O displaced the η^2-H_2 ligand in **19** to give $[TpRu(H_2O)(dppe)]$ BF_4, The reaction took a different route under H_2 pressure in CD_2Cl_2/H_2O biphasic medium. When 50-100 μL of H_2O was added to a 0.4 mL CD_2Cl_2 solution of **19** in a Wilmad pressure valved NMR tube, phase separation occurred. The ^{1}H NMR spectrum of the CD_2Cl_2 phase showed that some of the η^2-H_2 was displaced by H_2O via simple ligand substitution reaction. But after pressurizing the tube with 15 atm of H_2, most of the dihydrogen complex was reformed, partial deprotonation of η^2-H_2 by H_2O took place, as evidenced by the appearance of the ruthenium hydride signal in the ^{1}H NMR spectrum.

The dihydrogen complexes **5** and **7** are more stable with respect to loss of H_2 at room temperature, thus deprotonation studies with H_2O can be carried out in the absence of H_2 atmosphere in CD_2Cl_2. It was shown that the dihydrogen complexes

were deprotonated completely to form the monohydride complexes. The observation is probably not surprising, as complexes **5** and **7** are more acidic than their Tp analogues.

Deprotonation of η^2-H_2 in complexes **5**, **7**, **17** and **19**, which have pseudo aqueous pK_a values above 3, in biphasic conditions, is probably due to the strong solvation of H^+ by H_2O. It is also likely that the difference in the pK_a values of the dihydrogen complexes in aqueous solution may not be as large as the pseudo aqueous pK_a values may imply.

Chapter Three

Syntheses, characterization and reactivity of ruthenium η^2-*silane complexes*

3.1 Introduction

In recent years, the chemistry of metal-σ-silane complexes has been extensively studied.[4] However, there is no report on ruthenium-σ-silane complexes containing hydrotris(1-pyrazolyl)borate ligand (Tp). This chapter describes the preparation of some ruthenium-σ-silane complexes supported by Tp ligand.

There are several common methods for the preparation of metal-silane complex:

(i) reaction between an unsaturated transition metal centre and free silane,

e.g. $Mo(CO)(R_2PC_2H_4PR_2)_2 + HSiR_3 \longrightarrow Mo(HSiR_3)(CO)(R_2PC_2H_4PR_2)_2$ [39,40]

(ii) photochemical reaction of a carbonyl-containing complex with free silane;

e.g. $CpMn(CO)_2L + HSiR_3 \xrightarrow{h\nu} CO + CpMn(HSiR_3)(CO)L$ [36]

(iii) protonation of transition metal silyl complex;

e.g. $CpFeSiR_3(CO)L + H^+ \longrightarrow [CpFe(HSiR_3)(CO)L]^+$ [38]

(iv) displacement of the labile ligands (e.g. solvento and η^2-dihydrogen ligands) by free silane.

e.g. $[Ir(H)_2(THF)_2L_2]^+ + 2HSiR_3 \longrightarrow 2THF + [Ir(H)_2(HSiR_3)_2L_2]^+$ [32]

The last preparative method was employed for the preparation of Tp σ-silane complexes in this research. The reactions between free silanes and the η^2-dihydrogen complexes **(17, 18 & 20)** bearing hydrotris(1-pyrazolyl)borato ligand were first attempted, but the expected η^2-silane complex $[TpRu(\eta^2\text{-}HSiR_3)(PPh_3)_2]BF_4$ was not obtained. The solvento hydrido complex $TpRuH(CH_3CN)(PPh_3)_2$ **(13)** was then used in place of the dihydrogen complexes, it was found to react with a variety of silanes, leading to the formation of the corresponding hydrido σ-silane complexes $TpRu(PPh_3)'H_2SiR_3'$ **(21a-21f)**.

3.2 Experimental

3.2.1 Materials

All reactions were carried out under a dry N_2 atmosphere using standard Schlenk techniques. All solvents were distilled and degassed prior to use. Dichloromethane and acetonitrile were distilled from calcium hydride; tetrahydrofuran, diethyl ether and hexane were distilled from sodium benzophenone ketyl. Deuterated dichloromethane was dried on P_2O_5 and vacuum transferred to a flask fitted with a rubber septum for storage. Deuterated tetrahydrofuran was dried on calcium hydride and vacuum transferred to a flask fitted with a rubber septum for storage. The complexes $[TpRu(H_2)(PPh_3)_2]BF_4$,[29b] $TpRuH(CH_3CN)(PPh_3)$,[29b] $TpRuH(PPh_3)_2$,[29b] $TpRuH(H_2)(PPh_3)$,[29b] $TpRuCl(CH_3CN)(PPh_3)$,[29b] $[TpRu(H_2)(CH_3CN)(PPh_3)]BF_4$[29b], $TpRu(CH_3)(CO)(PPh_3)$[29a] and $TpRuH(CO)(PPh_3)$,[29a] were synthesized according to literature methods. Triethylsilane, triethoxysilane, triphenylsilane, diethylsilane,

diphenylsilane, phenylsilane, and $HBF_4.Et_2O$ were purchased from Fluka and were used as received.

3.2.2 Instrumentation

Infrared spectra were obtained from a Nicolet Magna 750 FT IR spectrophotometer. ^1H NMR spectra were taken from a Bruker DPX 400 spectrometer; chemical shift were referenced to the proton residue of the deuterated solvents ($CDHCl_2$ δ 5.32 ppm; C_4D_7H δ 1.85 ppm, δ 3.70 ppm). $^{31}P\{^1H\}$ NMR spectra were taken on a Bruker DPX-400 spectrometer at 161.98 MHz. ^{31}P Chemical shifts were externally referenced to 85% H_3PO_4 in D_2O (δ 0.00 ppm). $^{29}Si\{^1H\}$ NMR spectra were taken on a Bruker DPX-400 spectrometer at 79.50 MHz. ^{29}Si Chemical shifts were externally referenced to TMS in $CDCl_3$ (δ 0.00 ppm). Relaxation time T_1 measurements were carried out in THF-d_8 at 400 MHz by inversion-recovery method using standard 180°-τ-90° pulse sequence. High-pressure NMR studies were performed using a Wilmad pressure-valved NMR tube, the maximum pressure used was 15 atm (room temperature). FAB MS was carried out with a Finnigan MAT 95S mass spectrometer using 3-nitrobenzyl alcohol as matrix.

3.3.3 Syntheses

TpRuH(HSiEt$_3$)(PPh$_3$) (21a). A THF solution (10 mL) of $TpRuH(CH_3CN)(PPh_3)$ (**13**) (0.2 g, 0.32 mmol) and $HSiEt_3$ (0.3 mL, 4 mmol) was stirred under nitrogen at 80 °C for 4 h. The solution was cooled and the solvent was removed by vacuum. Hexane (10 mL) was added to the system and it was then cooled to -30 °C to give an orange solid which was filtered out. The solid was further washed with precooled hexane (5 mL)and then dried under vacuum. Yield: 0.09g (41%). IR

(KBr, cm^{-1}): υ(Ru-H) 2044 (w), υ(B-H) 2461 (br). ^1H NMR (400 MHz, THF-d_8, 20 °C): δ -11.62 (d, 2H, ^2J(HP) = 22.8 Hz, ^{29}Si satellite, ^1J(HSi) = 23.3 Hz, Ru-*H*, T_1 = 593 ms), 0.79 (q, 6H, ^3J(HH) = 7.8 Hz, CH_2CH_3), 1.14 (t, 9H, ^3J(HH) = 7.8 Hz, CH_2CH_3), 5.88 [t, 2H, H(pz)], 6.12 (t, 1H, H(pz')], 7.37 [d, 2H, H(pz)], 7.64 [d, 1H, H(pz')], 7.73 [d, 2H, H(pz)], 8.00 [d, 1H, H(pz')] (pz = pyrazolyl groups trans to hydrides, pz' = pyrazolyl group trans to PPh_3; all coupling constants for pyrazolyl proton resonances were about 2 Hz); 7.11 - 7.84 (m, 15H of PPh_3 phenyl groups). $^{31}P\{^1H\}$ NMR (161.70 MHz, THF-d_8, 20 °C): δ 67.9 (s) $^{29}Si\{^1H\}$ NMR (79.50 MHz, THF-d_8, 20 °C): δ 24.7 (s) FAB MS (m/z): 576 $[M\text{-}HSiEt_3]^+$.

TpRuH(HSi(EtO)$_3$)(PPh$_3$) (21b). This complex was prepared by using the same procedure as for the preparation of **21a**, except that $HSi(EtO)_3$ was used. The yield of the orange solid obtained was 0.11 g (46%). IR (KBr, cm^{-1}): υ(Ru-H) 2057 (w), υ(B-H) 2472 (br). ^1H NMR (400 MHz, THF-d_8, 20 °C): δ -11.41 (d, 2H, ^2J(HP) = 22.4 Hz, ^{29}Si satellite, ^1J(HSi) = 52.8 Hz, Ru-*H*, T_1 = 688 ms), 1.06 (t, 9H, ^3J(HH) = 7.8 Hz, OCH_2CH_3), 3.97 (q, 6H, ^3J(HH) = 7.8 Hz, OCH_2CH_3), 5.90 [t, 2H, H(pz)], 6.07 (t, 1H, H(pz')], 7.07 [d, 2H, H(pz)], 7.61 [d, 1H, H(pz')], 7.76 [d, 2H, H(pz)], 8.51 [d, 1H, H(pz')] (pz = pyrazolyl groups trans to hydrides, pz' = pyrazolyl group trans to PPh_3; all coupling constants for pyrazolyl proton resonances were about 2 Hz); 6.06 - 7.87 (m, 15H of PPh_3 phenyl groups). $^{31}P\{^1H\}$ NMR (161.70 MHz, THF-d_8, 20 °C): δ 66.4 (s) $^{29}Si\{^1H\}$ NMR (79.50 MHz, THF-d_8, 20 °C): δ -0.72 (s) FAB MS (m/z): 576 $[M\text{-}HSi(EtO)_3]^+$.

TpRuH(HSiPh$_3$)(PPh$_3$) (21c).This complex was prepared by using the same procedure as for the preparation of **21a**, except that HSiPh$_3$ was used. The yield of the orange solid obtained was 0.13 g (49%). IR (KBr, cm^{-1}): υ(Ru-H) 2040 (w), υ(B-H) 2468 (br). ^{1}H NMR (400 MHz, THF-d_8, 20 °C): δ -10.11 (d, 2H, ^2J(HP) = 23.2 Hz, , ^{29}Si satellite, ^1J(HSi) = 28.4 Hz, Ru-*H* , T_1 = 436 ms), δ 5.53 [t, 1H, H(pz)], δ 5.98 (t, 2H, H(pz')], δ 7.45 [d, 1H, H(pz')], δ 7.51 [d, 2H, H(pz)], δ 7.67 [d, 1H, H(pz')], δ 7.82 [d, 2H, H(pz)] (pz = pyrazolyl groups trans to hydrides, pz' = pyrazolyl group trans to PPh$_3$; all coupling constants for pyrazolyl proton resonances were about 2 Hz); δ 5.89 - 7.69 (m, 30H of phenyl groups). ^{31}P{^{1}H} NMR (161.70 MHz, THF-d_8, 20 °C): δ 65.0 (s) ^{29}Si{^{1}H} NMR (79.50 MHz, THF-d_8, 20 °C): δ 26.9 (s) FAB MS (m/z): 576 [M-Ph$_3$SiH]$^+$.

TpRuH(H$_2$SiEt$_2$)(PPh$_3$) (21d). This complex was prepared by using the same procedure as for the preparation of **21a**, except that H$_2$SiEt$_2$ was used. The yield of the orange solid obtainsed was 0.13 g (61%). IR (KBr, cm^{-1}): υ(Ru-H) 2062 (w), υ(B-H) 2469 (br). ^{1}H NMR (400 MHz, THF-d_8, 20 °C): δ -10.93 (dd, 2H, ^2J(HP) = 22.0 Hz, ^2J(HH) = 2.8 Hz, , ^{29}Si satellite, ^1J(HSi) = 23.5 Hz, Ru-*H* , T_1 = 690 ms), 1.08 (m, 6H, CH$_2$*CH$_3$*), 1.21 (m, 4H, *CH$_2$*CH$_3$), 4.60 (m, 1H, Si-*H*) 5.92 [t, 2H, H(pz)], 6.14 [t, 1H, H(pz')], 7.08 [d, 2H, H(pz)], 7.68 [d, 1H, H(pz')], 7.78 [d, 2H, H(pz)], 7.87 [d, 1H, H(pz')] (pz = pyrazolyl groups trans to hydrides, pz' = pyrazolyl groups trans to PPh$_3$; all coupling constants for pyrazolyl proton resonances were about 2 Hz); 7.22 - 7.56 (m, 15H of PPh$_3$ phenyl groups). ^{31}P{^{1}H} NMR (161.70 MHz, THF-d_8, 20 °C): δ 68.5 (s) ^{29}Si{^{1}H} NMR (79.50 MHz, THF-d_8, 20 °C): δ 16.9 (s) FAB MS (m/z): 576 [M-H$_2$SiEt$_2$]$^+$.

TpRuH(H_2SiPh_2)(PPh_3) (21e). This complex was prepared by using the same procedure as for the preparation of **21a**, except that H_2SiPh_2 was used. The yield of the orange solid obtained was 0.14 g (58%). IR (KBr, cm^{-1}): υ(Ru-H) 2082 (w), υ(B-H) 2470 (br). ^1H NMR (400 MHz, THF-d_8, 20 °C): δ -9.71 (dd, 2H, ^2J(HP) = 20.8 Hz, ^2J(HH) = 3.0 Hz, , ^{29}Si satellite, ^1J(HSi) = 23.5 Hz, Ru-*H* , T_1 = 545 ms), 5.72 (dt, 1H, ^2J(HH) = 3.0 Hz, *J*(HH) = 10.6 Hz, Si-*H*) 5.80 [t, 1H, H(pz')], 5.97 [t, 2H, H(pz)], 7.13 [d, 2H, H(pz)], 7.35 [d, 1H, H(pz')], 7.60 [d, 1H, H(pz')], 7.84 [d, 2H, H(pz)] (pz = pyrazolyl groups trans to hydrides, pz' = pyrazolyl group trans to PPh_3; all coupling constants for pyrazolyl proton resonances were about 2 Hz); 6.18 - 7.77 (m, 25H of phenyl groups). $^{31}P\{^1H\}$ NMR (161.70 MHz, THF-d_8, 20 °C): δ 65.6 (s) $^{29}Si\{^1H\}$ NMR (79.50 MHz, THF-d_8, 20 °C): 9.0 (s) FAB MS (m/z): 576 $[M- H_2SiPh_2]^+$.

TpRuH(H_3SiPh)(PPh_3) (21f). This complex was prepared by using the same procedure as for the preparation of **21a**, except that H_3SiPh was used. The yield of the orange solid obtained was 0.12 g (55%). IR (KBr, cm^{-1}): υ(Ru-H) 2029 (w), υ(B-H) 2471 (br). ^1H NMR (400 MHz, THF-d_8, 20 °C): δ -10.32 (d, 2H, ^2J(HP) = 21.2 Hz, , ^{29}Si satellite, ^1J(HSi) = 27.4 Hz, Ru-*H* , T_1 = 615 ms), 5.22 (d, 2H, *J*(HP) = 3.3 Hz, Hz Si-*H*) 5.98 [t, 1H, H(pz')], 5.99 [t, 2H, H(pz)], 7.08 [d, 1H, H(pz')], 7.37 [d, 2H, H(pz)], 7.67 [d, 1H, H(pz')], 7.84 [d, 2H, H(pz)] (pz = pyrazolyl groups trans to hydrides, pz' = pyrazolyl group trans to PPh_3; all coupling constants for pyrazolyl proton resonances were about 2 Hz); 6.32 - 7.83 (m, 20H of phenyl groups). $^{31}P\{^1H\}$ NMR (161.70 MHz, THF-d_8, 20 °C): δ 67.2 (s) $^{29}Si\{^1H\}$ NMR (79.50 MHz, THF-d_8, 20 °C): δ -17.2 (s) FAB MS (m/z): 576 $[M- H_3SiPh]^+$.

3.2.4 NMR studies of reactions of the ruthenium complexes

$[TpRu(PPh_3)_2(H_2)]BF_4$ (17)(generated in situ by protonation of $TpRuH(PPh_3)_2$ with $HBF_4.Et_2O$) with triethylsilane. A sample of 10 mg of $TpRuH(PPh_3)_2$ (**12**) was loaded into a 5 mm NMR tube which was then capped with a rubber septum. The tube was evacuated and then filled with nitrogen for three cycles. Dichloromethane-d_2 (0.4 mL) was added to the tube to dissolve the sample, followed by the addition of 5 μL of tetrafluoroboric acid in etheral solution ($HBF_4.Et_2O$ 56%). Then 10 μL of triethylsilane was added and the tube was allowed to heat at 40 °C for ten hours. The solution was analyzed by NMR spectroscopy.

$[TpRu(H_2)(CH_3CN)(PPh_3)]BF_4$ (18) (generated in situ by protonation of $TpRuH(CH_3CN)(PPh_3)$ with $HBF_4.Et_2O$) with triethylsilane. A sample of 10 mg of $TpRuH(CH_3CN)(PPh_3)$ (**13**) was loaded into a 5 mm NMR tube which was then capped with a rubber septum. The tube was evacuated and then filled with nitrogen for three cycles. Dichloromethane-d_2 (0.4 mL) was added to the tube to dissolve the sample. The solution was cooled to -78 °C, 5 μL of tetrafluoroboric acid and then 10 μL of triethylsilane were added through microsyringes. The tube was loaded into an NMR probe precooled to -60 °C and the sample was analyzed as it slowly warmed up to room temperature.

[TpRu(H_2)(CO)(PPh_3)]BF_4 (20) (generated in situ by protonation of TpRuH(CO)(PPh_3) with $HBF_4.Et_2O$) with triethylsilane. The procedure for **18** was followed exactly, subitituting [TpRu(H_2)(CO)(PPh_3)]BF_4 **(20)** for **18**.

[TpRu"CH_4"(CO)(PPh_3)]BF_4 (generated in situ by protonation of TpRu(CH_3)(CO)(PPh_3) with $HBF_4.Et_2O$) with triethylsilane. A sample of 10 mg of TpRu(CH_3)(CO)(PPh_3) was loaded into a 5mm NMR tube which was then capped with a rubber septum. The tube was evacuated and then filled with nitrogen for three cycles. Dichloromethane-d_2 (0.4 mL) was added to the tube to dissolve the sample. The solution was cooled to -78 °C, 5 µl of tetrafluoroboric acid and then 10 µL of triethylsilane were added through microsyringes. The tube was loaded into an NMR probe precooled to -60 °C and the sample was analyzed as it slowly warmed up to room temperature.

TpRuCl(CH_3CN)(PPh_3) (11) with diphenylsilane. A sample of 10 mg of TpRuCl(CH_3CN)(PPh_3) **(11)** was loaded into a 5mm NMR tube which was then capped with a rubber septum. The tube was evacuated and then filled with nitrogen for three cycles. Tetrahydrofuran-d_8 (0.4 mL) was added to the tube to dissolve the sample, followed by the addition of 20 µL of diphenylsilane. The tube was heated at 60 °C for ten hours, after which the sample was analyzed by NMR spectroscopy. ^{1}H NMR indicated that TpRuH(H_2SiPh_2)(PPh_3) **(21d)** was formed.

TpRuH($HSiR_3$)(PPh_3) (21) with acetonitrile. A sample of 10 mg of TpRuH($HSiR_3$)(PPh_3) (**21**) was loaded into a 5mm NMR tube which was then capped with a rubber septum. The tube was evacuated and then filled with nitrogen for three cycles. Tetrahydrofuran-d_8 (0.4 mL) was added to the tube to dissolve the sample followed by the addition of 20 μL of. acetonitrile. The tube was allowed to heat at 60 °C for ten hours, after which the sample was analyzed by NMR spectroscopy. ^{1}H NMR indicated that **21** was converted to TpRuH(CH_3CN)(PPh_3) **(13)**.

TpRuH($HSiR_3$)(PPh_3) (21) with hydrogen. A sample of 10 mg of TpRuH($HSiR_3$)(PPh_3) (**21**) was loaded into a 5mm Wilmad pressure NMR tube. The tube was evacuated and then filled with nitrogen for three cycles. Tetrahydrofuran-d_8 (0.3 mL) was added to the tube to dissolve the sample. The tube was then pressurised with 15 atm of H_2 and allowed to heat at 80 °C for ten hours, after which the sample was analyzed by NMR spectroscopy. ^{1}H NMR indicated the presence of TpRuH(H_2)(PPh_3) **(16)**, and small amount of unreacted **21**.

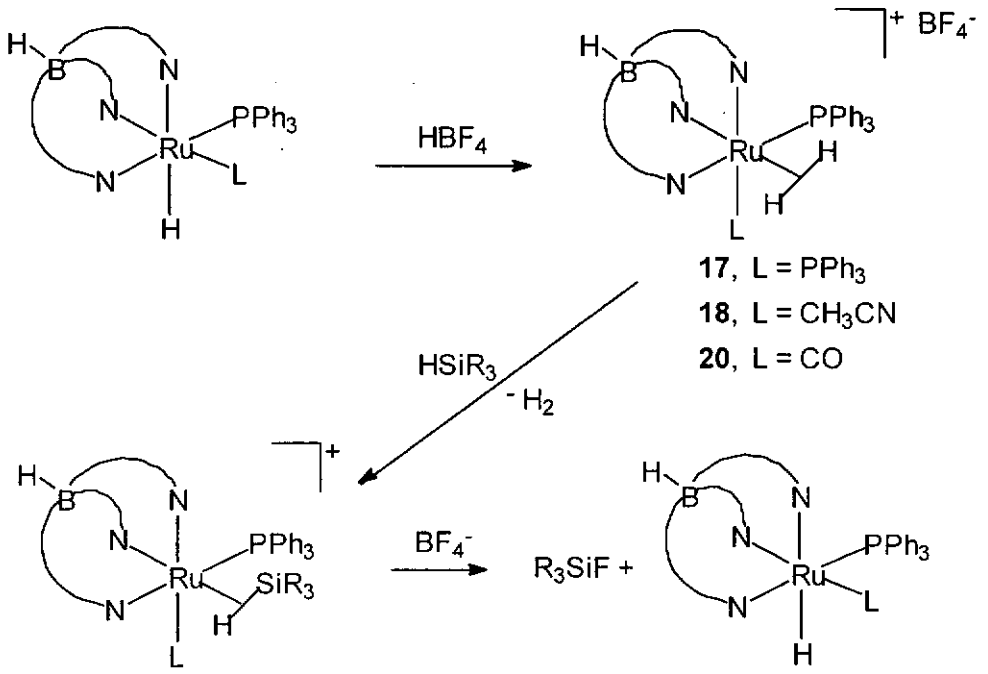
3.3 Results and Discussion

3.3.1 Reactions of Tp dihydrogen complexes with silane

It is well documented that labile ligands in transition metal complexes can be displaced by free silanes to form the η^2-silane complexes.[32,38] While there are numerous examples of neutral transition metal η^2-silane complexes, cationic complexes of this type are rare. Crabtree spectroscopically observed the cationic σ-silane complex $[(IrH_2(\eta^2\text{-}HSiEt_3)_2(PPh_3)_2]SbF_6$ during his investigations of silane alcoholysis catalysed by $[(IrH_2S_2(PPh_3)_2]SbF_6$.[32] A cationic ruthenium trichlorosilane complex $[CpRu(\eta^2\text{-}HSiCl_3)(PMe_3)]BAr'_4$ (BAr'_4 = $B(3,5\text{-}(CF_3)_2C_6H_3)_4$) has been prepared by protonation of $CpRu(SiCl_3)(PMe_3)_2$ with $[H(Et_2O)_2][BAr'_4]$ in CH_2Cl_2[63] Brookhart has recently developed a general method for the generation of cationic η^2-silane complexes $[CpFe(\eta^2\text{-}HSiR_3)(CO)L]^+$ (L = PEt_3, PPh_3; R_3 = HPh_2, HMePh, HEt_2, H_2Ph) which are stabilized through the use of the non-nucleophilic counterion BAr'_4^-. These species are easily formed by displacement of the η^2-H_2 ligand from the cationic η^2-dihydrogen complex $[CpFe(H_2)(CO)L]^+$ by the free silane.[38] In view of the rarity of cationic η^2-silane complexes and the fact that the hydrotris(pyrazolyl)borato (Tp) ligand has a high tendency of forming octahedral η^2-dihydrogen complex,[29g,f] the reactions of some of the Tp ruthenium η^2-dihydrogen complexes recently reported by our group[29a,b] with free silane were studied, in hope of obtaining stable cationic Tp-supported ruthenium η^2-silane complexes for further reactivity investigations.

However, in our work of reacting the η^2-dihydrogen complexes $[TpRu(H_2)(PPh_3)_2]BF_4$ (**17**), $[TpRu(H_2)(CH_3CN)(PPh_3)]BF_4$ (**18**), and

$[TpRu(H_2)(CO)(PPh_3)]BF_4$ (**20**) with R_3SiH (R_3 = Et_3, $(EtO)_3$, Ph_3, HEt_2, HPh_2 and H_2Ph), it was found that the hydride complexes, $TpRuH(PPh_3)_2$, $TpRuH(CH_3CN)(PPh_3)$ and $TpRuH(CO)(PPh_3)$ were produced, respectively; no silane complexes were formed. The formation of the hydride complexes can be accounted for by the reaction sequence depicted in Scheme 2. Substitution of the η^2-H_2 ligand in the η^2-dihydrogen complex for the silane molecule generates the σ-silane complex intermediate, which, due to the very high electrophilicity of the silicon centre of the η^2-$HSiR_3$ ligand, is readily attacked by the nucleophile BF_4^- to form the hydride complex $TpRuH(L)(PPh_3)$. It has been proposed that the extreme sensitivity of the electrophilic silicon centre of $[CpFe(\eta^2\text{-}HSiEt_3)(CO)(PEt_3)]BF_4$ to nucleophile, even the traditionally non-nucleophilic counterion BF_4^-, is responsible for the generation of the hydride complex $CpRuH(CO)(PEt_3)$, which in acidic medium, is protonated to give the η^2-dihydrogen complex $[CpFe(H_2)(CO)(PEt_3)]BF_4$.[38]



Scheme 2

Reaction of the transient 'CH_4' complex [TpRu"CH_4"(CO)(PPh_3)]BF_4, generated via protonation of TpRu(CH_3)(CO)(PPh_3) with $HBF_4.Et_2O$, with free silanes again led to the formation of the hydrido complex TpRuH(CO)(PPh_3), no σ-silane complexes were detected.

The reactions of the η^2-dihydrogen complexes **17**, **18**, and **20**, as well as the transient 'CH_4' complex with free silanes seem to form unstable cationic η^2-silane complexes, which, like [CpFe(η^2-$HSiEt_3$)](CO)(PEt_3)]BF_4, deteriorated to the metal hydride species due to nucleophilic attack of the η^2-silane ligand by the counterion BF_4^-. Since nucleoplilic attack of the highly electrophilic silicon centre of η^2-silane ligand is now a well-established reaction, it is believed that further research on the reactivities of Tp ruthenium η^2-dihydrogen complexes toward free silanes is not likely to produce results of great interest, therefore this work is not further investigated.

The recent work of Kubas on coordination of Si—H, H—H, and agostic C—H σ-bonds to the same [Mo($R_2PC_2H_4PR_2$)(CO)] fragment is exciting since it is the first system by which comparison between the coordination features of different σ-bonds to the same metal centre can be made. An alternative approach to this kind of comparison is the study of system that can tautermerize between different σ-complexes. A complex of the general formula L_nM'H_2SiR_3', where 'H_2SiR_3' stands for (SiR_3)(η^2-H_2)or (H)(η^2-$HSiR_3$), is a good example of such a system.

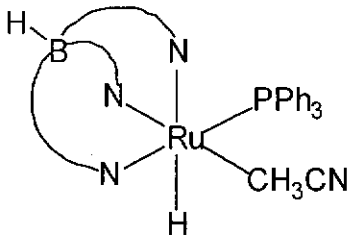
As has been mentioned above, Crabtree reported a $L_nM(H)(\eta^2\text{-}HSiR_3)$ structure for the $[(IrH_2(\eta^2\text{-}HSiEt_3)_2(PPh_3)_2]SbF_6$ complex, which was an intermediate during the $[(IrH_2S_2(PPh_3)_2]SbF_6$ (S = THF. CH_3OH, H_2O, Me_2CO) catalysed silane alcoholysis reaction. $[(IrH_2(\eta^2\text{-}HSiEt_3)_2(PPh_3)_2]SbF_6$ was stable only at low temperature and extremely sensitive to nucleophiles. Attempted isolation under a variety of conditions led to decomposition to the known $[Ir_2(\mu\text{-}H)_3H_2(PPh_3)_4]SbF_6$. On the other hand, reaction of $OsHCl(CO)(P^iPr_3)_2$ with Et_3SiH was reported to give the η^2-dihydrogen silyl complex $OsCl(SiEt_3)(H_2)(CO)(P^iPr_3)_2$ which was an intermediate in the hydrosilylation of phenylacetylene catalysed by $OsHCl(CO)(P^iPr_3)_2$.[41] Chaudret reported the preparation of a highly reactive σ-silane complex $RuH_2(\eta^2\text{-}HSiPh_3)(H_2)(PCy_3)_2$ by substitution reaction of the bis-dihydrogen complex $RuH_2(H_2)_2(PCy_3)_2$ with $HSiPh_3$. $RuH_2(\eta^2\text{-}HSiPh_3)(H_2)(PCy_3)_2$ reacts instantaneously with H_2 or N_2 to give $RuH_2(H_2)_2(PCy_3)_2$ or $RuH_2(N_2)_2(PCy_3)_2$ together with free Ph_3SiH.[64] Recently, ab initio MO calculation at the MP2 and MP4 levels on the $[OsCl(CO)(PH_3)'H_2SiH_3']$ model system predicts the existence of two stable octahedral species of very close energy: a dihydrogen complex $[OsCl(SiH_3)(H_2)\ (CO)(PH_3)]$ and a σ-silane complex $[OsClH(\eta^2\text{-}HSiH_3)(CO)(PH_3)]$.[42]

We have recently reported the synthesis of $TpRuH(H_2)(PPh_3)$ (**16**) by heating a THF solution of $TpRuH(CH_3CN)(PPh_3)$ under 40 atm of H_2. ^{1}H-NMR study revealed rapid fluxionality between the hydride and η^2-H_2 ligands downs to -110 °C.[29a] In view of the analogy between η^2-dihydrogen complexes and σ-silane complexes and the delicate balance between the $L_nM(H)(\eta^2\text{-}HSiR_3)$ and

$L_nM(SiR_3)(H_2)$ structures, it is interesting to study the reactions of $TpRuH(CH_3CN)(PPh_3)$ with free silanes.

3.3.2 Synthesis of $TpRu(PPh_3)'H_2SiR_3'$ **(21)**

Reactions of $TpRuH(CH_3CN)(PPh_3)$ (**13**) with free silanes $HSiR_3$ in THF produce $TpRu(PPh_3)'H_2SiR_3'$(R_3 = Et_3 (**21a**), $(EtO)_3$ (**21b**), Ph_3 (**21c**), HEt_2 (**21d**), HPh_2 (**21e**), H_2Ph (**21f**)) (eq. 9) for which NMR and IR data are collected in Table 7.



$\xrightarrow[-CH_3CN]{HSiR_3}$ $TpRu(PPh_3)"H_2SiR_3"$ (9)

21a R = Et_3
21b R = $(EtO)_3$
21c R = Ph_3
21d R = HEt_2
21e R = HPh_2
21f R = H_2Ph

The complexes $TpRu(PPh_3)'H_2SiR_3'$ are excellent model compounds for comparing the coordinating features of the two structures: $L_nM(H)(\eta^2\text{-}HSiR_3)$ and $L_nM(SiR_3)(H_2)$. The facial coordination of Tp (*vide infra*) in $TpRu(PPh_3)'H_2SiR_3'$ guarantee cis-dispositions of the hydride and η^2-silane ligands in one of the possible structures and of the silyl and η^2-H_2 ligands in the other.

Table 7. NMR and IR Spectroscopic Data for $TpRu(PPh_3)'H_2SiR_3'$ 21a-f

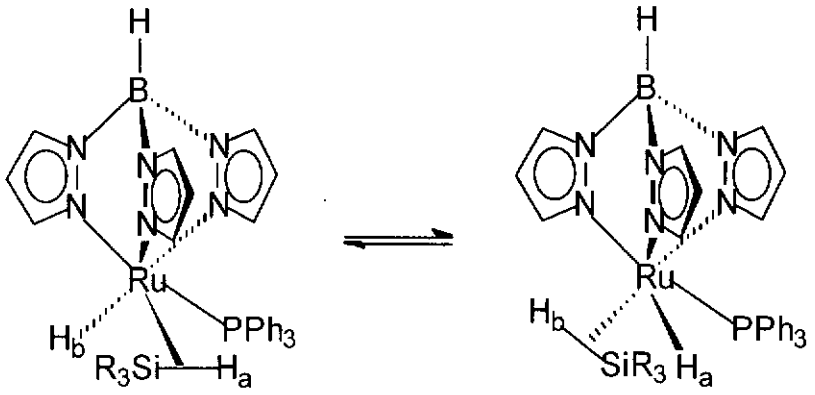
	$\delta(^1H)$ (ppm)[a]	$^1J(SiH)$[b] (Hz)	$\delta(^{31}P\{^1H\})$ (ppm)[a]	$\delta(^{29}Si\{^1H\})$ (ppm)[a]	υ(Ru-H) (KBr,cm^{-1})	υ(B-H) (KBr,cm^{-1})
(21a) $R_3=Et_3$	-11.62 (d, 2H, ^2J(HP) = 22.8 Hz, Ru-*H*, T_1 = 593 ms), 0.79 (q, 6H, CH_2CH_3), 1.14 (t, 9H, CH_2CH_3), 9H of Tp,[c] 5.88 (t, 2H), 6.12 (t, 1H), 7.37 (d, 2H), 7.64 (d, 1H), 7.73 (d, 2H), 8.00 (d, 1H), 7.11 - 7.84 (m, 15H of PPh_3)	23.3	67.9 (s)	24.7	2044(w).	2461(br)
(21b) $R_3=EtO_3$	-11.41 (d, 2H, ^2J(HP) = 22.4 Hz, Ru-*H*, T_1 = 688 ms), 1.06 (t, 9H, OCH_2CH_3), 3.97 (q, 6H, OCH_2CH_3), 9H of Tp,[c] 5.90 (t, 2H), 6.07 (t, 1H), 7.07 (d, 2H), 7.61 (d, 1H), 7.76 (d, 2H), 8.51 (d, 1H),; 6.06 - 7.87 (m, 15H of PPh_3)	52.8	66.4 (s)	-0.72	2057(w)	2472(br)
(21c) $R_3=Ph_3$	-10.11 (d, 2H, ^2J(HP) = 23.2 Hz, Ru-*H* , T_1 = 436 ms), 9H of Tp,[c] 5.53 (t, 1H), 5.98 (t, 2H), 7.45 (d, 1H), 7.51 (d, 2H), 7.67 (d, 1H), 7.82 (d, 2H); 5.89 - 7.69 (m, 30H of Ph)	28.4	65.0 (s)	26.9	2040(w)	2468(br)
(21d) $R_3=HEt_2$	-10.93 (dd, 2H, ^2J(HP) = 22.0 Hz, ^2J(HH) = 2.8 Hz, Ru-*H*, T_1 = 690 ms), 1.08 (m, 6H, CH_2CH_3), 1.21 (m, 4H, CH_2CH_3), 4.60 (m, 1H, Si-*H*) 9H of Tp,[c] 5.92 (t, 2H), 6.14 (t, 1H), 7.08 (d, 2H), 7.68 (d, 1H), 7.78 (d, 2H), 7.87 (d, 1H); 7.22 - 7.56 (m, 15H of PPh_3)	23.5	68.5 (s)	16.9	2062(w)	2469(br)

(21e) R_3=HPh_2	-9.71 (dd, 2H, ^2J(HP) = 20.8 Hz, ^2J(HH) = 3.0 Hz, Ru-*H* , T_1 = 545 ms), 5.72 (dt, 1H, ^2J(HH) = 3.0 Hz, J(HH) = 10.6 Hz Si-*H*) 9H of Tp,[c] 5.80 (t, 1H), 5.97 (t, 2H), 7.13 (d, 2H), 7.35 (d, 1H, H), 7.60 (d, 1H), 7.84 (d, 2H); 6.18 - 7.77 (m, 25H of Ph)	23.5	65.6 (s)	9.0	2082(w)	2470(br)
(21f) R_3=H_2Ph	-10.32 (d, 2H, ^2J(HP) = 21.2 Hz, Ru-*H* , T_1 = 615 ms), 5.22 (d, 2H, J(HP) = 3.3 Hz, Hz Si-*H*) 9H of Tp,[c] 5.98 (t, 1H), 5.99 (t, 2H), 7.08 (d, 1H,), 7.37 (d, 2H), 7.67 (d, 1H), 7.84 (d, 2H); 6.32 - 7.83 (m, 20H of Ph)	27.4	67.2 (s)	-17.2	2029(w)	2471(br)

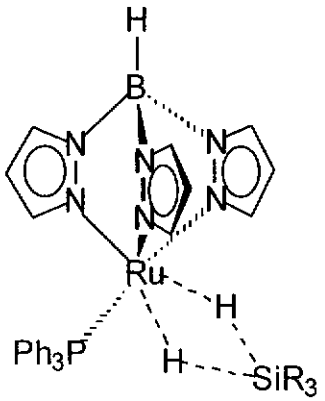
[a] in THF-d_8. [b] obtaining from the ^{29}Si satellites of the hydride singal in ^{1}H NMR. [c] All coupling constants for pyrazolyl proton resonances were about 2 Hz.

3.3.3 Characterization and Structure of $TpRu(PPh_3)$ 'H_2SiR_3'

The ^{1}H NMR spectrum of each of the complexes $TpRu(PPh_3)$'H_2SiR_3' (**21a-f**) shows a hydride signal, which integrates to two hydrogens, in the upfield region; it is coupled to the triphenylphosphine, with a coupling constant falling in the range of 20.8 - 23.2 Hz, which is typical for a cis-disposed phosphine ligand. For the secondary silane complexes **21d** and **21e**, the hydride signals show additional coupling to the normal Si-H hydrogens. It is important to note that all the hydride signals of **21a-f** are flanked by ^{29}Si satellites. All the ^1J(Si-H) values, except that of **21b**, lie at the lower end of the range of values (20 - 70 Hz) found for the known η^2-silane complexes in which the silicon bears one or more substituents other than the hydrogen.[40] The Si-H coupling constants of our complexes, although low, unequivocally indicate the presence of the η^2-silane ligands. Therefore it seems adequate to assign the η^2-silane hydride structure $TpRuH(\eta^2\text{-}HSiR_3)(PPh_3)$, rather than the η^2-H_2 silyl structure $TpRu(SiR_3)(\eta^2\text{-}H_2)(PPh_3)$ to $TpRu(PPh_3)$'H_2SiR_3'.The rejection of the η^2-H_2 structure is further supported by the relaxation time measurements which show that the room temperature T_1 values of **21a-f** (436 - 690 ms) are well outside the range of T_1 values for non-classical η^2-dihydrogen complexes.[65] The fact that only one hydride signal was observed even down to -110 °C can be explained in terms of rapid fluxionality between H_a and H_b, (eq. 10) or more appropriately by having $TpRu(PPh_3)$'H_2SiR_3' to adopt the structure **C**. This bonding mode of silane is reminiscent of the η^2-BH_4 ligand.[66]

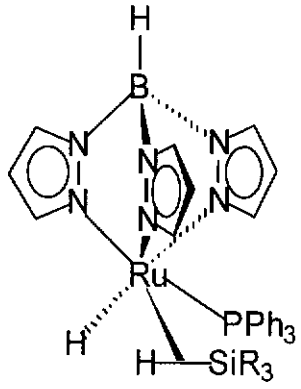


A B (10)



C

The existence of a rapid equilibrium between structure **A** and **B,** or the adoption of structure **C** for $TpRu(PPh_3)'H_2SiR_3'$ is in accord with the observation of two groups of resonances (3 peaks in each group) for the pyrazole protons of the Tp ligand in the range 5.80 - 8.00 ppm in the ^1H NMR spectrum. Each peak in one of the groups integrates to 2H, while every one in the other group corresponds to 1H. This 6 peak pattern for Tp protons is consistent with two of the pyrazole rings being trans to two identical ligands. Should all three pyrazole rings of the Tp ligand in $TpRu(PPh_3)'H_2SiR_3'$ be trans to three different ligands as in the non-dynamic structure **D,** a 9 peak pattern would have been observed for the Tp protons.



D

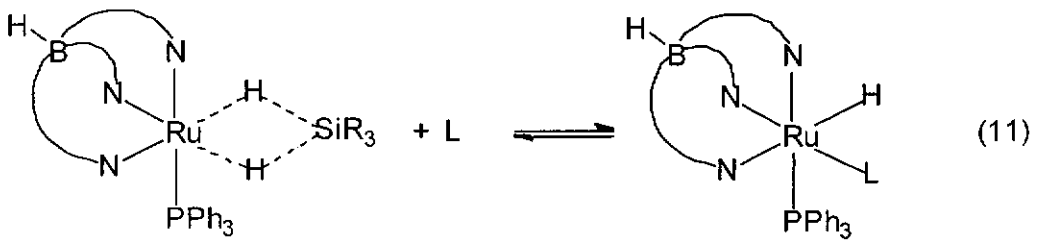
The $^{29}Si\{^1H\}$ NMR spectra of **21a-f**, which show singlets and are therefore devoid of silicon-phosphorous couplings, are also supportive of the presence of η^2-silane ligands in $TpRu(PPh_3)'H_2SiR_3'$. It is generally true that metal-silyl complexes containing phosphine ligands show silicon-phosphorous coupling,[67] which , in phosphine- containing η^2-silane complexes, are rarely observable.[40, 43]

Finally, it is worth commenting on the denticity of the Tp ligands in **21a-f**. Although it is well known that the tendency for hydrotris(pyrazolyl)borate to adopt a facial tridentate coordination mode is very strong, and reduced denticity is usually only observed in cases where it is disfavoured by the electronic nature of the metal, e.g., d^8-ML_4 square-planar geometry,[68] bidentate coordinations of hydrotris(pyrazolyl)borate ligand to d^6 Ru(II) and Os(II) centres has recently been reported.[69] The κ^2-Tp Ru(II) and Os(II) complexes were prepared by displacement of a phosphine and a halo ligands from the precursor complex with hydrotris(pyrazolyl)borate at room temperature. Thermolysis of these κ^2-Tp complexes via loss of a phosphine ligand gives the conventional tridentate Tp complexes. A common spectroscopic feature of the κ^2-Tp Ru(II) and Os(II)

complexes is that the υ(B-H) are shifted to lower frequencies (~ 2440 cm^{-1}) compared to those of the κ^3-Tp complexes which are usually above 2460 cm^{-1}. Perusal of Table 7 reveals that the υ(B-H) of **21a - 21f** are all above 2460 cm^{-1}, these complexes were prepared by thermo displacement of CH_3CN from $TpRuH(CH_3CN)(PPh_3)$ (**13**) which already contained a tridentate hydrotris(pyrazolyl)borate ligand, therefore it is very unlikely that the denticity of hydrotris(pyrazolyl)borate would decrease from 3 to 2 during the reactions, these facts are taken together, it is probably true that tridentate coordination Tp in **21a - 21f** is maintained.

3.3.4 Reactivity of $TpRu(PPh_3)$ 'H_2SiR_3'

The η^2-silane complexes **21a-f** react reversibly with triphenylphosphine, acetonitrile, and pressurized H_2, to give $TpRuH(PPh_3)_2$ (**12**), $TpRuH(CH_3CN)(PPh_3)$ (**13**), and $TpRuH(H_2)(PPh_3)$ (**16**), respectively. (eq. 11) While the dihydrogen complex **16** can be used in place of **13** for preparation of the η^2-silane complexes **21a-f**, it was found that reaction of **12** with excess free silanes only led to partial formation of **21a-f**, probably due to the stronger coordination of the phosphine ligand.



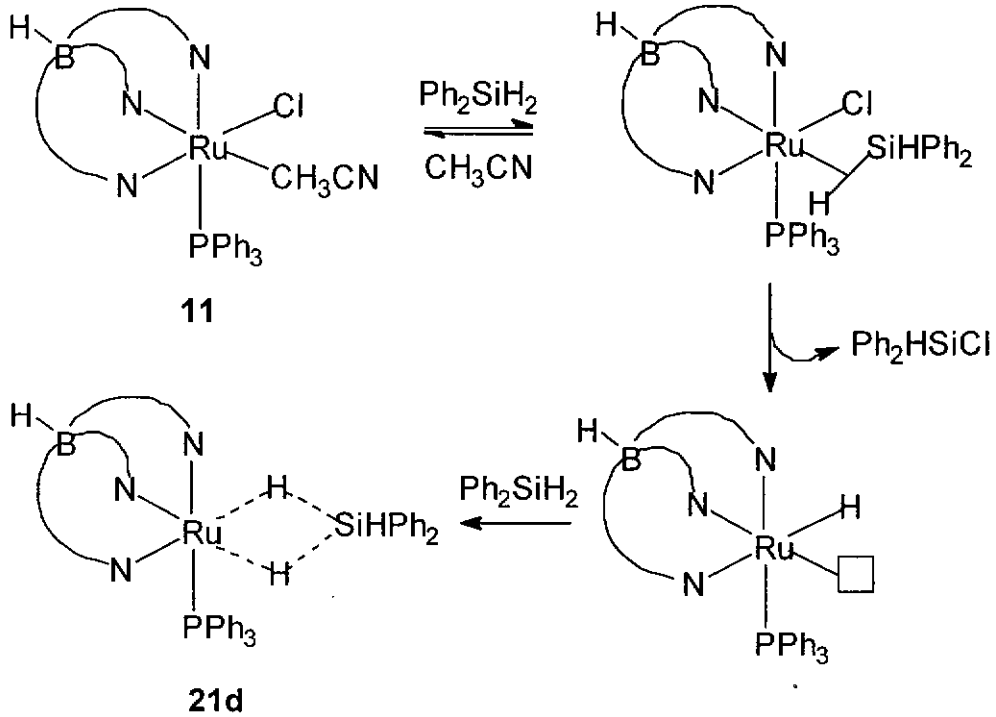
21a-f

12, L = PPh_3
13, L = CH_3CN
16, L = H_2

(11)

3.3.5 Reaction of $TpRuCl(CH_3CN)(PPh_3)$ with diphenylsilane.

Surprisingly, it was found that reaction of $TpRuCl(CH_3CN)(PPh_3)$ (**11**) with the diphenylsilane did not give the chloro η^2-silane complexes $TpRuCl(\eta^2\text{-}H_2SiPh_3)(PPh_3)$, but rather **21d** was formed. The formation of **21d** from **11** can best be explained by the mechanism depicted in Scheme3. The main feature of the scheme is the SiH/RuCl redistribution process that leads to the severance of the Ru—Cl bond and the formation of the Ru—H bond. It has been suggested that the Si—Cl bond energy is high enough to allow SiH/IrCl redistribution which causes the iridium complex $IrCl(CO)(PPh_3)_2$ to react with triorganosilanes to give the hydrido complex and the chlorotriorganosilanes.[70] Yamamoto has recently reported facile transfer of a chloro ligand bonded to the Rh centre onto the Si atom bonded to the same metal centre, even in the rigid octahedral coordination.[71]



Scheme 3

Chapter Four

Conclusion

Like Cp and Tp, the macrocyclic facially chelating ligand ^{R}Cn (where ^{H}Cn = 1,4,7-triazacyclononane, ^{Me}Cn = 1,4,7-trimethyl-1,4,7-triazacyclononane), are shown tobe a good ligands for the preparation of ruthenium η^2-dihydrogen complexes.

Some ruthenium hydrido complexes containing ^{R}Cn were prepared in this work, these hydrido complexes were prepared by reacting the hydrido precursors ($RuHCl(PPh_3)_3$ and $RuHCl(CO)(PPh_3)_3$) with free ^{R}Cn. Protonation of these hydrido complexes produced the first dihydrogen complexes supported by triazacyclononane ligands. These complexes are also new members of the still very small family of dicationic dihydrogen complexes. Triazacyclononane ligands seem to have similar properties as the hydrotris(pyrazolyl)borates in stabilizing dihydrogen ligands.

The acidity of Tp and ^{R}Cn dihydrogen complexes have been measured and it was found that the dicationic ^{R}Cn dihydrogen complexes are more, and in some cases significantly more acidic than their hydrotris(pyrazolyl)borato and cyclopentadienyl analogues, which are monocationic. Water can deprotonate ^{R}Cn and Tp dihydrogen complexes with pseudo aqueous pK_a values significantly larger than that of H_3O^+, probably due to strong solvation of H^+ by H_2O.

The second part of this work concerns the chemistry of η^2-silane complexes. The reactions between free silanes and the η^2-dihydrogen complexes (**17, 18** and **20**)

bearing hydrotris(1-pyrazolyl)borato ligand were first attempted, but the expected η^2-silane complex $[TpRu(\eta^2\text{-}HSiR_3)(PPh_3)_2]BF_4$ was not obtained, probably due to nucleophilic attack of the η^2-silane ligand by the counterion BF_4^- to give the metal hydride.

The η^2-silane complexes $TpRu(PPh_3)'H_2SiR_3'$ (**21a-f**) have been synthesized via reaction of $TpRuH(CH_3CN)(PPh_3)$ (**13**) with free silanes. The NMR spectroscopic data indicate that the "H_2SiR_3" moiety in **21a-f** is $(H)(\eta^2\text{-}HSiR_3)$ rather than $(SiR_3)(\eta^2\text{-}H_2)$. The chemical equivalence of the two hydrogen atoms is attributed to rapid fluxionality between the two, i.e., $TpRu(PPh_3)(H_a)(\eta^2\text{-}H_bSiR_3) \leftrightarrow TpRu(PPh_3)(H_b)(\eta^2\text{-}H_aSiR_3)$ or better to the adoption of a η^2-BH_4-type bonding mode by the "H_2SiR_3" moiety to the metal centre. **21a-f** react reversibly with PPh_3, CH_3CN, and pressurized H_2 to give $TpRuH(PPh_3)_2$, $TpRuH(PPh_3)(CH_3CN)$, and $TpRuH(H_2)(PPh_3)$, respectively. Reaction of the chloro complex $TpRuCl(PPh_3)(CH_3CN)$ with H_2SiPh_2 did not give the chloro η^2-silane complexes $TpRuCl(PPh_3)(\eta^2\text{-}H_2SiPh_2)$, but rather **21d** was formed. The formation of **21d** is best explained by a reaction sequence which include a SiH/RuCl redistribution step.

Reference

1. Noth, R.; Hartwimmer, R. *Chem. Ber.* **1960**, *93*, 2238.
2. Crabtree, R. H. *Angew. Chem. Int. Ed. Eng.* **1993**, *32*, 789.
3. (a) Kubas, G. J. *Comments Inorg. Chem.* **1988**, *7*, 17. (b) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (c) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95. (d) Banister, J. A.; Lee, P. D.; Poliakoff, M. *Organometallics* **1995**, *14*, 3876.
4. (a) Graham, W. A. G. *J. Organomet. Chem.* **1986**, *300*, 81. (b) Schubert, U. *Adv. Organomet.Chem.* **1990**, *30*, 151.
5. (a) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal complexes*, D. Reidel Publishing: Dordcht, **1984**. (b) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (c) Jones, W. D.; Feher, F. *J. Acc. Chem. Res.* **1989**, *22*, 91.
6. Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 541.
7. Esteruelas, M. A.; Oro, L. A.; Valreo, C. *Organometallics* **1992**, *11*, 3362.
8. Marinelli, G.; Rachidi, I. E.-I.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1989**, *111*, 2346.
9. Harman, W. D.; Halpern, H. J. *J. Am. Chem. Soc.* **1990**, *10*, 462.
10. Morton, D.; Cole-Hamilton, D. J. *J. Chem. Soc, Chem. Commun.* **1988**, 1154.
11. Bianchini, C.; Peruzzini, M.; Zanobini, F.; Frediani, P.; Albinat, A. *J. Am. Chem. Soc.* **1991**, *113*, 5453.
12. Albeniz, A. C.; D. Heinekey, M.; Crabtree, R. H. *Inorg. Chem.* **1991**, *30*, 3632.
13. Heinekey, D. M.; Oldman Jr, W. J. *Chem. Rev.* **1993**, *93*, 913.

14. Volbeda, A.;Charon, M. H.; Piras, C.; Hatchikan, E.C.; Frey, M.; Fontecilla-Camps, J. C. *Nature* **1995**. *373*. 580.

15. (a) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166. (b) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865.

16. (a) Jia, G.; Lough, A. J.; Morris, R. H. *Organometallics* **1992**, *11*, 161. (b) Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875. (c) Jia, G.; Morris, R. H.; Schweitzer, C. T. *Inorg. Chem.* **1991**, *31*, 593. (d) Jia, G.; Morris, R. H. *Inorg. Chem.* **1990**, *29*, 581.

17. Cappellani, E. P.; Drouin, S. D.; Jia, G.; Maltby, P. A. Morris, R. H.; Schweitzer, C. T. *J. Am. Chem. Soc.* **1994**, *116*, 3375.

18. Rocchini, E.; Mezzetti, A.; Rüegger, H.; Burckhardt, U.; Gramlich, V.; Del Zotto, A.; Martinuzzi, P.; Rigo, P. *Inorg. Chem.* **1997**, *36*, 711.

19. (a) Maltby, P. A.; Schlaf, M.; Steinbeck, M.; Lough, A. J.; Morris, R. H.; Klooster, W. T.; Koetzle, T. F.; Srivastava, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 5396. (b) Chin, B.; Lough, A. J.; Morris, R. H.; Schweitzer, C. T.; D'Agostino, C. *Inorg. Chem.* **1994**, *33*, 6278.

20. Schlaf, M.; Lough, A. J.; Maltby, P. A.; Morris, R. H. *Organometallics* **1996**, *15*, 2270.

21. See for examples: (a) Lough, A. J.; Park, S.; Ramchandran, R.; Morris, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 8356. (b) Schlaf, M.; Lough, A. J.; Morris, R. H. *Organometallics* **1993**, *12*, 3808. (c) Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Common.* **1985**, 794. (d) Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032. (e) Baker, M. V.; Field, L. D.; Young, D. J. *J. Chem. Soc., Chem. Commun.* **1988**, 546. (f) Van Der Sluys, L. S.; Miller, M. M.; Kubas,

G. J.; Caulton, K. G. *J. Am. Chem. Soc.* **1991**, *113*, 2513. (g) Bicnchini, C.; Perez, P. J.; Peruzzini, M.; Zanobini, F.; Vacca, A. *Inorg. Chem.* **1991**, *30*, 279. (h) Sellman, D.; Käppler, J.; Moll, M. *J. Am. Chem. Soc.* **1993**, *115*, 1830. (i) Mudalige, D. C.; Rettig, S. J.; James, B. R.; Cullen, W. R. *J. Chem. Soc., Chem. Commun.* **1993**, 830. (j) Bianchini, C.; Linn, K.; Masi, D.; Peruzzini, M.; Polo, A.; Vacca, A.; Zanobini, F. *Inorg. Chem.* **1993**, *32*, 2366. (k) Heinekey, D.M.; Luther, T. A. *Inorg. Chem.* **1996**, *35*, 4396. (l) Heinekey, D. M.; Voges, M. H.; Barnhart, D. M. *J. Am. Chem. Soc.* **1996**, *118*, 10792.

22. (a) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1990**, *112*, 2261. (b) Li, Z. W.; Taube, H. *J. Am. Chem. Soc.* **1991**, *113*, 8946.
23. Smith, K.-T.; Tilset, M.; Kuhlmnn, R; Caulton, K. G. *J. Am. Chem. Soc.* **1995**, *117*, 9473.
24. Flood's notation is adopted with slight modification. ^{H}Cn = 1,4,7-triazacyclononane, ^{Me}Cn = 1,4,7-trimethyl-1,4,7-triazacyclononane.
25. (a) Wieghardt, K.; Chaudhuri, P.; Nuber, B.; Weiss, J.; *Inorg. Chem.* **1982**, *21*, 3086. b) Chaudhuri, P.; Wieghardt, K. *Prog. Inorg. Chem.* **1987**, *35*, 329.
26. For recent work on ^{R}Cn complexes, see for examples: (a) Yang, S. M.; Chen, M. C. W.; Cheung, K. K.; Che, C. M.; Peng, S. M. *Organometallics* **1997**, *16*, 2819. (b) Wang, L.; Sowa, J. R., Jr.; Wang, C.; Lu, R. S.; Gassman, P. G.; Flood, T. C. *Organometallics* **1996**, *15*, 4240. (c) Wang, L.; Wang, C.; Bau, R.; Flood, T. C. *Organometallics* **1996**, *15*, 491. (d) Yang, S. M.;Cheng, W. C.; Peng, S. M.; Cheung, K. K.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1995**, 2955. (e) Yang, S. M.; Cheng, W. C.; Cheung, K. K.; Che, C. M.; Peng, S. M. *J. Chem. Soc., Dalton Trans.* **1995**, 227. (f) Wang, C.; Ziler, J. W.; Flood, T. C. *J. Am. Chem. Soc.* **1995**,

117, 1647. (g) Cheng, W. C.; Yu, W. Y.; Cheung, K. K.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1994**, 57. (h) Cheng, W. C.; Yu, W. Y.; Cheung, K. K.; Che, C. M. *J. Chem. Soc., Chem. Commun.* **1994**, 1063. (i) Wang, L.; Lu, R. S.; Bau, R.; Flood, T. C. *J. Am. Chem. Soc.* **1993**, *115*, 6999. (j) Wang, C.; Flood, T. C. *J. Am. Chem. Soc.* **1992**, *114*, 3169. (k) Sun, N. Y.; Simpson, S. J. *J. Organomet. Chem.* **1992**, *434*, 341.

27. Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 2nd Ed, John Wiley & Sons: New York, 1994.

28. Reviews on Tp complexes: (a) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943. (b) Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *34*, 115. (c) Trofimenko, S. *Chem. Rev.* **1972**, *72*, 497. (d) Trofimenko, S. *Acc. Chem. Res.* **1971**, *4*, 17.

29. For recent work on tris(pyrazolyl)borato dihydrogen complexes, see for examples: (a) Chen, Y. Z.; Chan, W. C.; Lau, C. P.; Chu, H. S.; Lee, H. L.; Jia, G. *Organometallics* **1997**, *16*, 1241. (b) Chan, W. C.; Lau, C. P.; Chen, Y. Z.; Fang, Y. Q.; Ng, S. M.; Jia, G. *Organometallics* **1997**, *16*, 34. (c) Bohanna, C.; Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Martínez, M.-P. *Organometallics* **1997**, *16*, 4464. (d) Eckert, J.; Albinati, A.; Bucher, U. E.; Venanzi, L. M. *Inorg. Chem.* **1996**, *35*, 1292. (e) Vicente, C.; Shul'pin, G. G.; Moreno, B.; Sabo-Etienne, S.; Chaudret, B. *J. Mol. Catal. A: Chem.* **1995**, *98*, L5. (f) Moreno, B.; Sabo-Etienne, S.; Chaudret, B.; Rodriguez, A.; Jalon, F.; Trofimenko, S. *J. Am. Chem. Soc.* **1995**, *117*, 7441. (g) Moreno, B.; Sabo-Etienne, S.; Chaudret, B. *J. Am. Chem. Soc.* **1994**, *116*, 2635. (h) Heinekey, D. M.; Oldham, W. J., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 3137. (i) Halcrow, M. A.; Chaudret, B.; Trofimenko, S. *J. Chem. Soc.,*

Chem. Commun. **1993**, 465. (j) Bucher, U. E.; Lengweiler, T.; Nanz, D.; von Philipsborn, W.; Vernanzi, L. M. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 548.

30. (a) de los Ríos, I.; Tenorio, M. J.; Padilla, J.; Puerta, M. C.; Valerga, P. *Organometallics* **1996**, *15*, 4565. (b) Lemke, F. R.; Brammer, L. *Organometallics* **1995**, *14*, 3980. (c) Conroy-Lewis, F. M.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1986**, 506. (d) Conroy-Lewis, F. M.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1675. (e) Wilczewski, T. *J. Organomet. Chem.* **1989**, *361*, 219. (f) Chinn, M. S.; Heinekey, D. M.; Payne, N. G.; Sofield, C. D. *Organometallics* **1989**, *8*, 1824. (g) Klooster, W. T.; Koetzle, T. F.; Jia, G.; Fong, T. P.; Morris, R. H.; Albinati, A. *J. Am. Chem. Soc.* **1994**, *116*, 7677.
31. (a) Brookhart, M; Grant, B. E. *J Am Chem Soc.* **1993**, *115*, 2151. (b) Takahashi, T.; Hasegowa, M.; Suznki, N.; Sabari, M.; Rousset, C. J.; Fanwuick, P. E. ;Negishi, E. *J Am Chem. Soc.* **1991**, *113*, 8564
32. Lxo, X-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 2527
33. (a) Aitken, C.T.; Harrrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059. (b) Harrod, J. K.; Yun, S. S. *Organometallics* **1987**, *6,* 1381.
34. Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1969**, *91*, 45
35. Graham, W. A. G; Bennett, M. *J. Chem Eng. New.* **1970**, 48 (*24*) 75.
36. a) Schubert; U.; Ackermann. K.; Worle, B. *J. Am. Chem. Soc.* **1982**, *104*, 7378. b) Schubert, U.;Bahr, K.; Muller, J. *J. Organomet. Chem.* **1987**, *327*, 357.
37. Rabaa, H.; Saillard, J-Y.; Schubert, U. *J. Organomet. Chem.* **1987**, *330*, 397
38. Scharrer, E.; Chang, S. Brookhart, M. *Organometallics* **1995**, *14*, 5686.
39. Luo, X-L.; Kubas, G. J.; Burns, C. J.; Bryan, J. C.; Unkefer, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 1159.

40. Luo, X-L.; Kubas, G. J.; Burns, C. J.; Bryan, J. C.; Unkefer, C. J. *Organometallics* **1991**, *10*, 462.

41. Esteruelas, M. A.; Oro, L. A.; Valreo, C., *Organometallics* **1991**, *10*, 462.

42. Maseras, F.; Lledos, A. *Organometallics* **1996**, *15*, 1218.

43. Spaltenstein, E.; Palma, P.; Kreutzer, K. A.; Willoughby, C. A.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**. *116*, 10308.

44. Procopio, L. J.; Carroll, P. J.; Berry, D. H. *J. Am. Chem. Soc.* **1994**, *116*, 177.

45. Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155.

46. Kono, H. *J. Organomet. Chem.* **1977**, *132*, 53.

47. Wieghardt, K.; Chaudhuri, P.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1989**, *28*, 459.

48. Ahmad. N, Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 48.

49. (a) Smith, K. T.; Rømming, C.; Tilset, M. *J. Am. Chem. Soc.* **1993**, *115*, 8681. (b) Lemke, F. R.; Brammer, L. *Organometallics* **1995**, *14*, 3980. (c) Brammer, L.; Klooster, W. T.; Lemke, F. R. *Organometallics* **1996**, *15*, 1721.

50. Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173.

51. Forde, C. E.; Landau, S. E.; Morris, R. H. *J. Chem. Soc., Dalton Trans.* **1997**, 1663.

52. Luther, T-A.; Heinekey, D.M. *Inorg. Chem.* **1998**, *37*, 127.

53. Perdoncin, G.; Seorrano, G. *J. Am. Chem. Soc.* **1977**, *99*, 6983.

54. Hush, N. S. *J. Am. Chem. Soc.* **1997**, *119*, 1717.

55. Jia, G.; Lee, H. M.; Williams, I. D.; Lau, C. P.; Chen, Y. Z. *Organometallics* **1997**, *16*, 3941.

56. Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257.

57. Kristjánsdóttir, S. S.; Moody, A. E.; Weberg, R. T.; Norton, J. R. *Organometallics* **1988**, *7*, 1983.

58. Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255.

59. Parker, V. D.; Handoo, K. L.; Roness, F.; Tilset, M. *J. Am. Chem. Soc.* **1991**, *113*, 7493.

60. Kristjándóttir, S. S.; Norton, J. R. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: Weinheim, FRG, 1992.

61. (a) Angelici, R. J. *Acc. Chem. Res.* **1995**, *28*, 51. (b) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41.

62. Ritchie, C. D. *Physical Organic Chemistry, The Fundamental Concept*, Marcel Dekker, Inc.: New York 1990, p.238.

63. Lemke, F. R. *J. Am. Chem. Soc.* **1994**, *116*, 11183.

64. Sabo-etienne, S.; Hernandez, M.; Chung, G.; Chaudret, B. *New. J. Chem.* **1994**, *18*, 175.

65. Crabtree, R. H.; Lavin, M.; Bonnneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032.

66. (a) Oishi, Y.; Albright, T. A.; *Polyhedron*, **1995**, *14*, 2603. (b) Hartwig, F.; De Gala, S. R.; *J. Am. Chem. Soc.* **1994**, *116*, 3661.

67. (a) Johnson, T. J.; Coan, P. S.; Caulton, K. G. *Inorg. Chem.* **1993**, *32*, 4594. (b) Sun, J.; Lu, R. S.; Bau, R.; Yang, G. K. *Organometallics*. **1994**, *13*, 1317.

68. (a) Albinati, A.; Bovens, M.; Ruegger, H.; Venanzi, L. M. *Inorg. Chem.* **1997**, *36*, 5991. (b) Akita, M.; Ohta, K.; Takahashi, Y.; Hikichi, S.; Moro-oka, Y. *Organometallics* **1997**, *16*, 4121.

69. (a) Burns, I. D.; Hill, A. F.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T. *Organometallics* **1998**, *17,* 1552.(b) Bohanna, C.; Esteruelas, M. A.; Gomez, A. V.; Lopez, A. M.; Martinez, M-P. *Organometallics* **1997**, *16,* 4464.

70. (a) Chalk, A. J. *J. Chem. Soc., Chem. Commun.* **1969**, 1207. (b) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16.

71. Osakada, K.; Sarai, S.; Koizumi, T.; Yamamoto, T. *Organometallics* **1997**, *16,* 3980.

Appendix

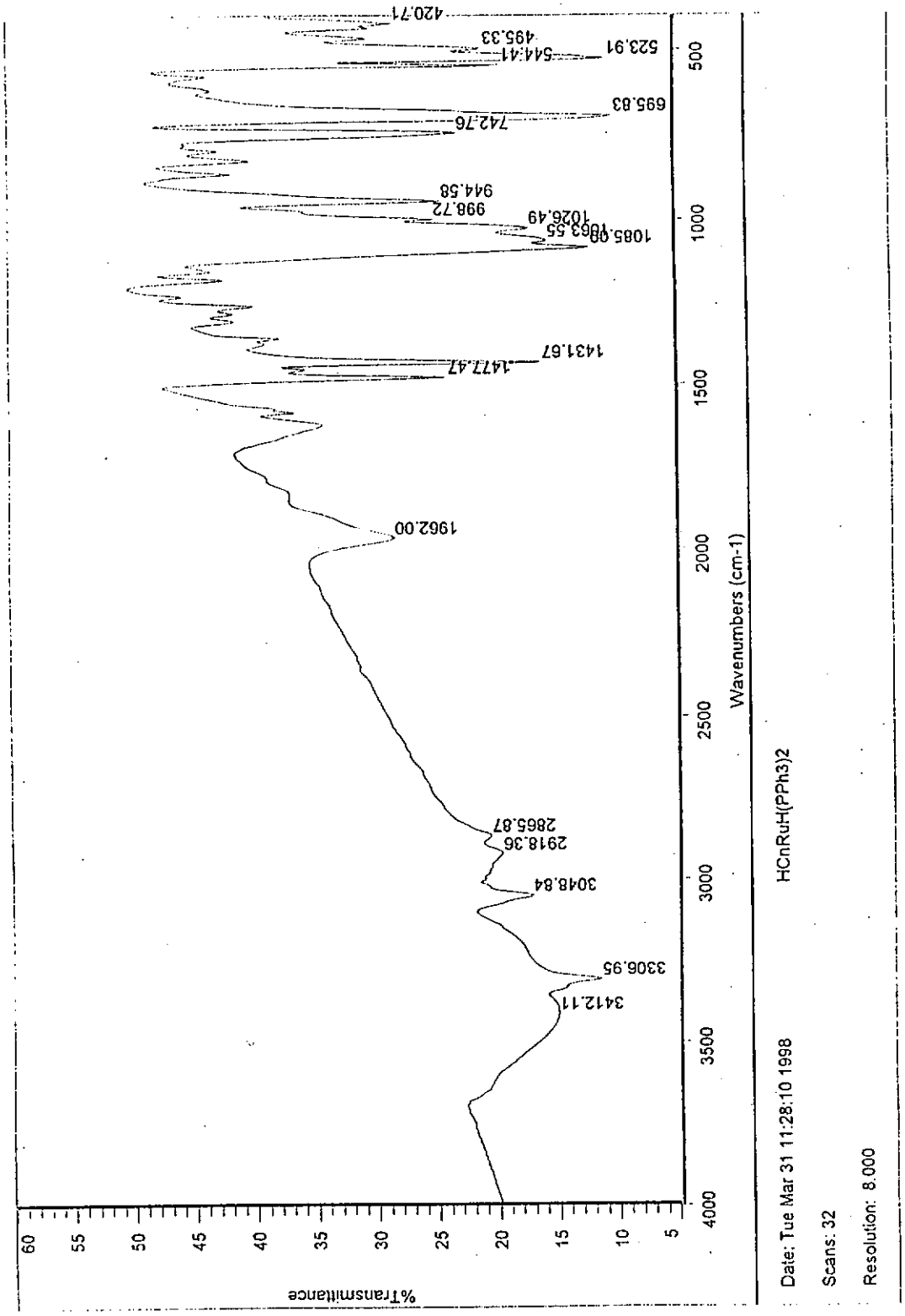


Figure 2.4 Infra-red spectrum of $[^{H}CnRuH(PPh_3)_2]BF_4$ (**1**) in KBr disc

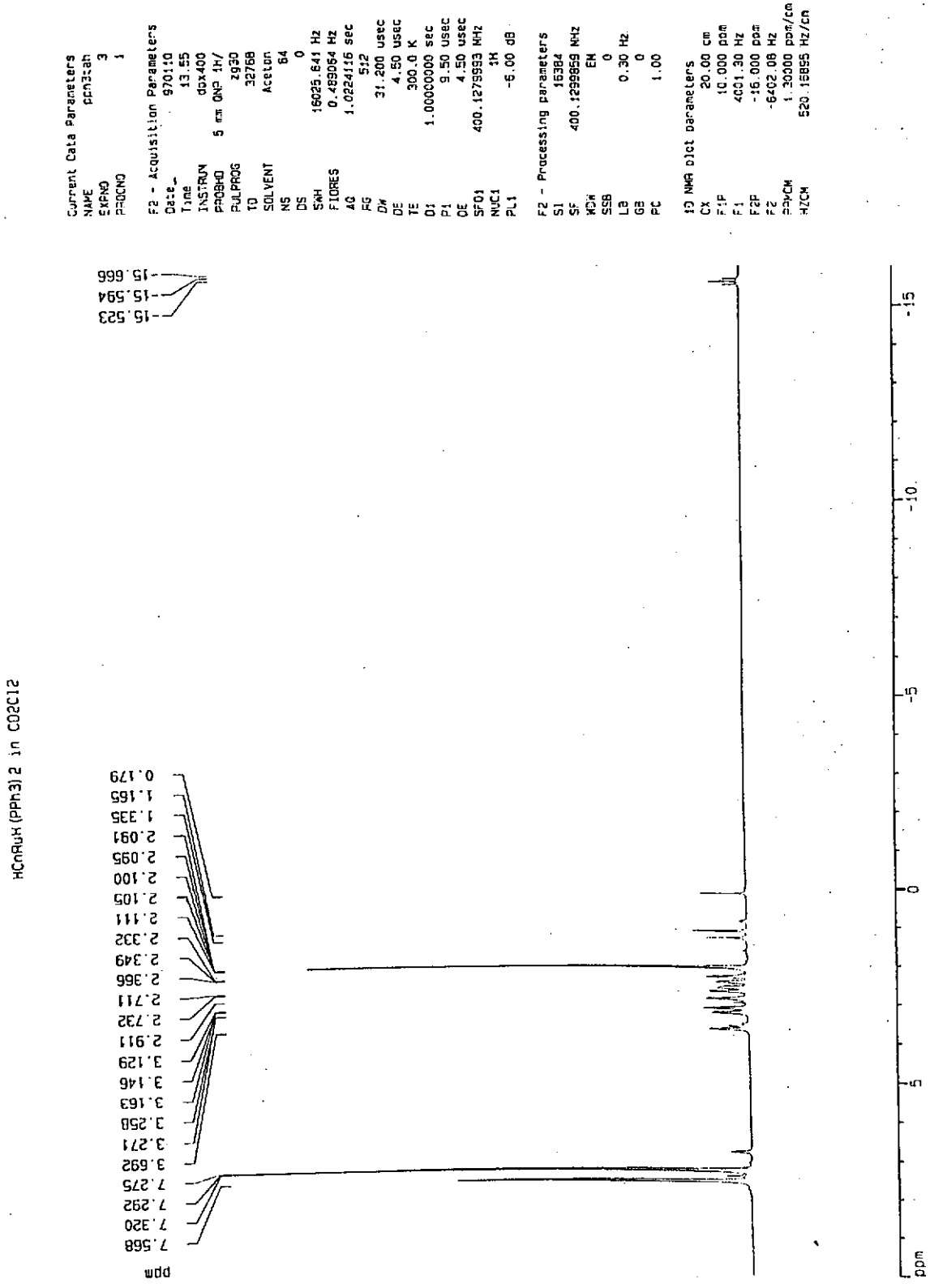


Figure 2.5. 400 MHz ^{1}H-NMR spectrum of [^{H}CnRuH(PPh$_3$)$_2$]BF$_4$ (1).

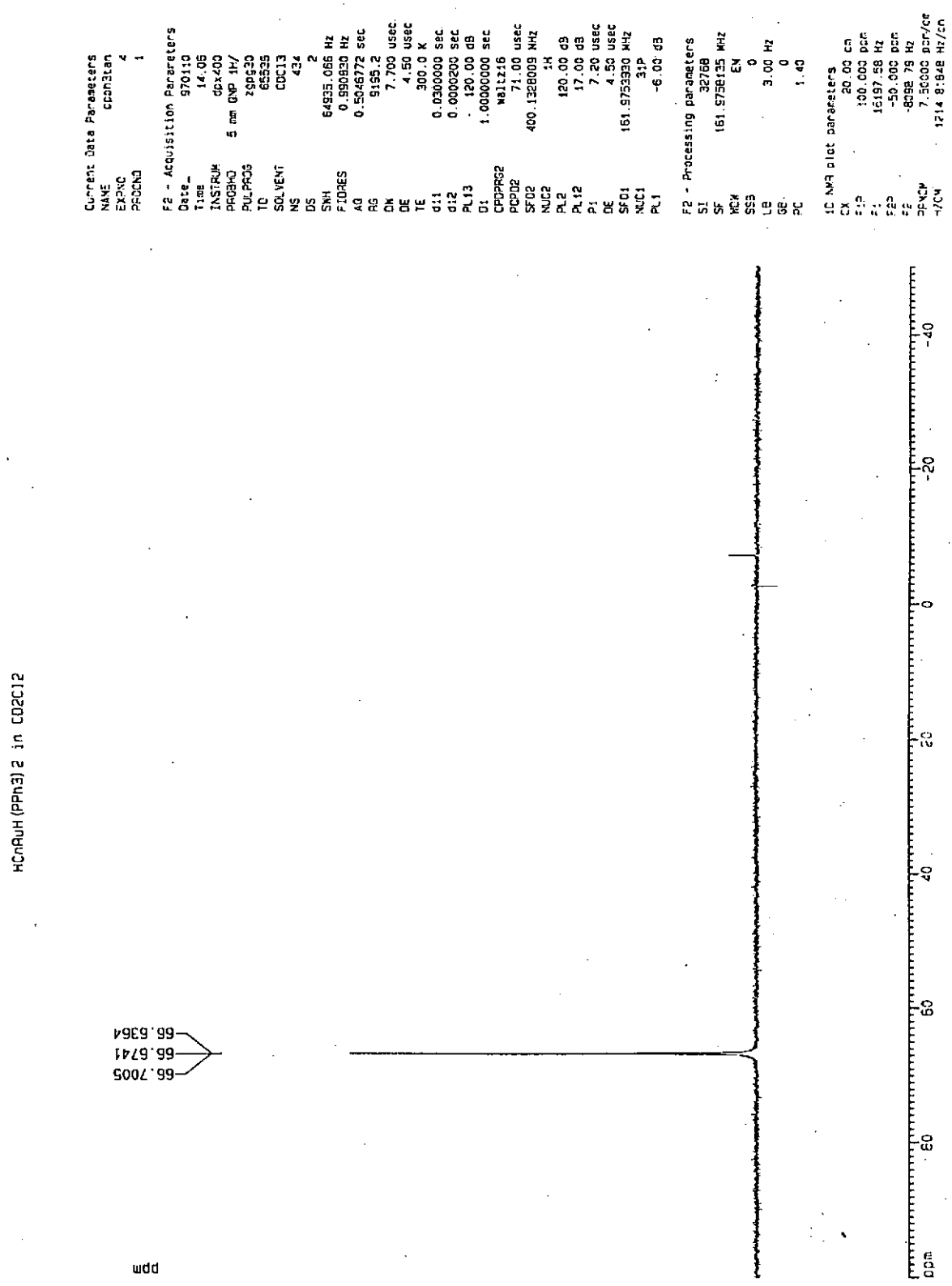


Figure 2.6 161 MHz $^{31}P\{^{1}H\}$-NMR spectrum of $[^{H}CnRuH(PPh_3)_2]BF_4$ (1).

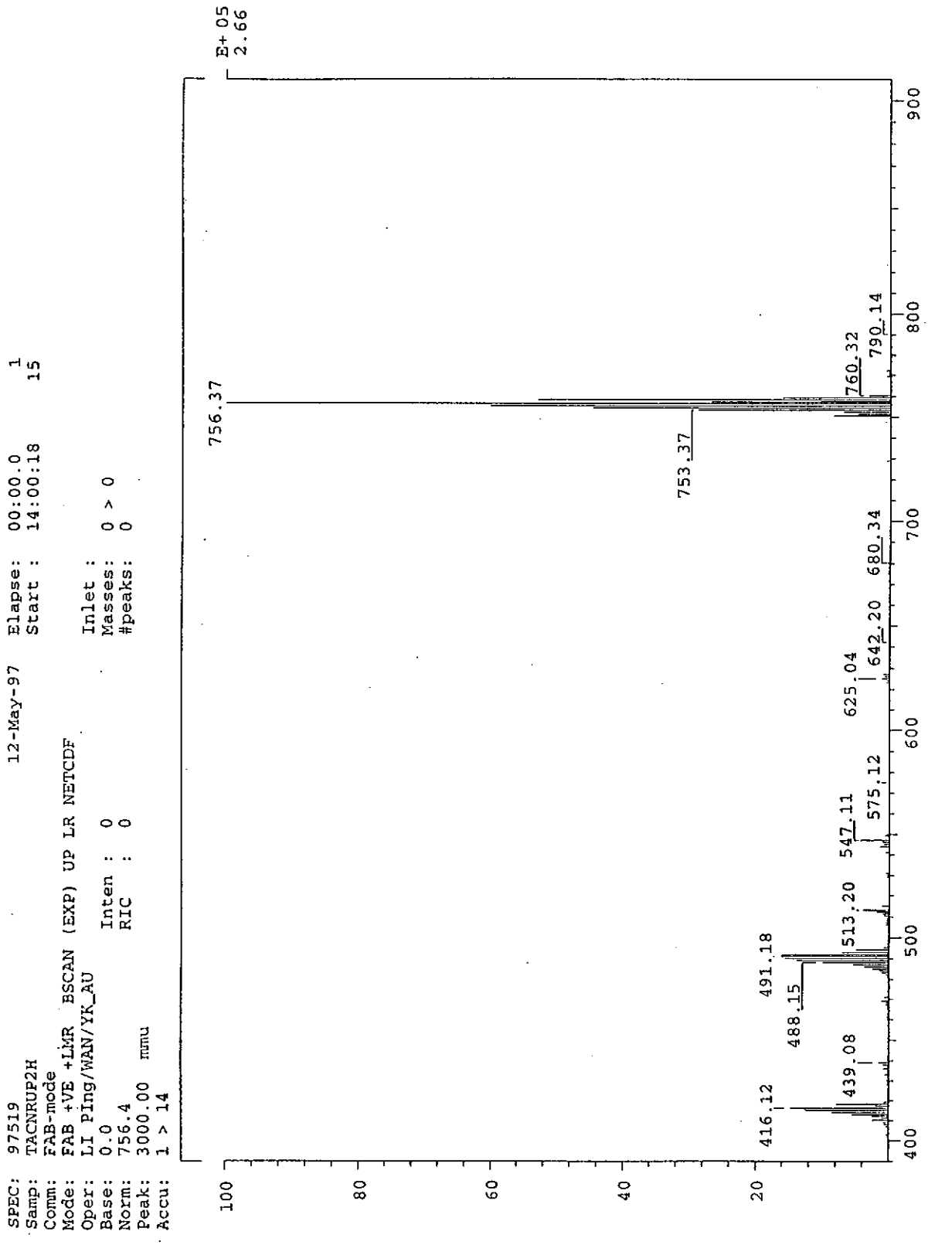


Figure 2.7 FAB mass spectrum of $[^{H}CnRuH(PPh_3)_2]BF_4$ (**1**).

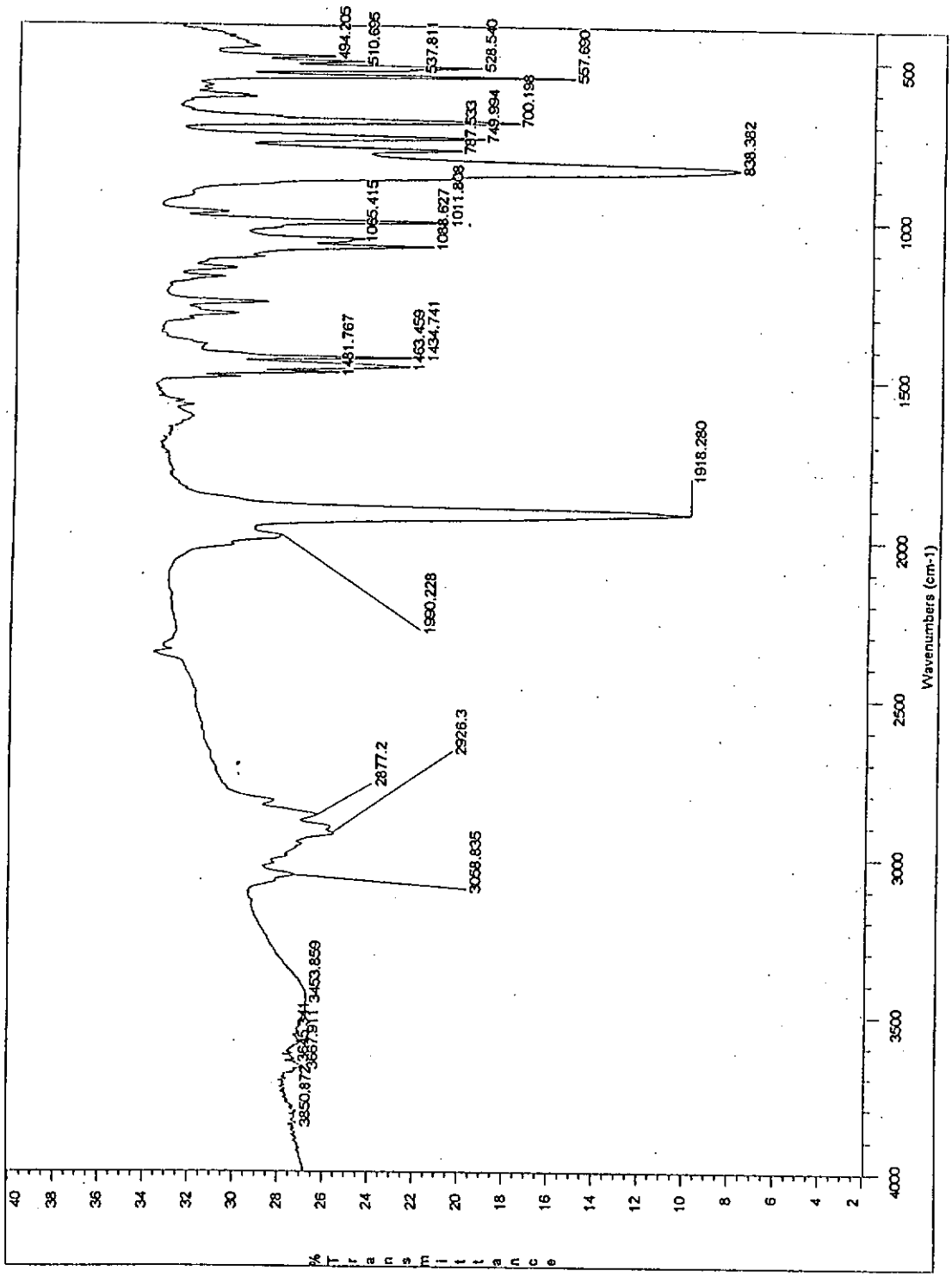


Figure 2.8 Infra-red spectrum of $[^{H}CnRuH(CO)(PPh_3)]BF_4$ (**2**) in KBr disc

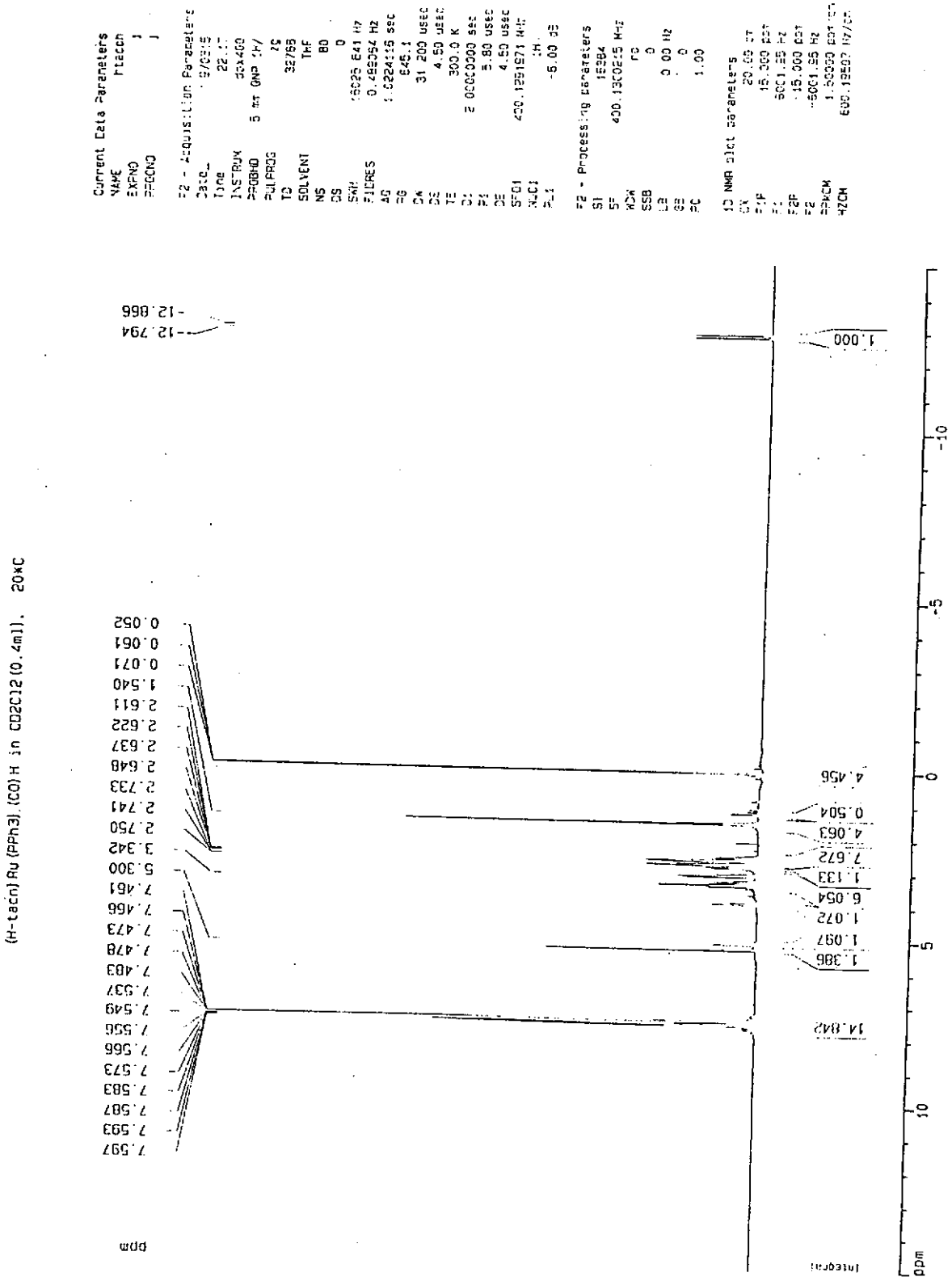


Figure 2.9. 400 MHz ^{1}H-NMR spectrum of [^{H}CnRuH(CO)(PPh_3)]BF_4 (**2**).

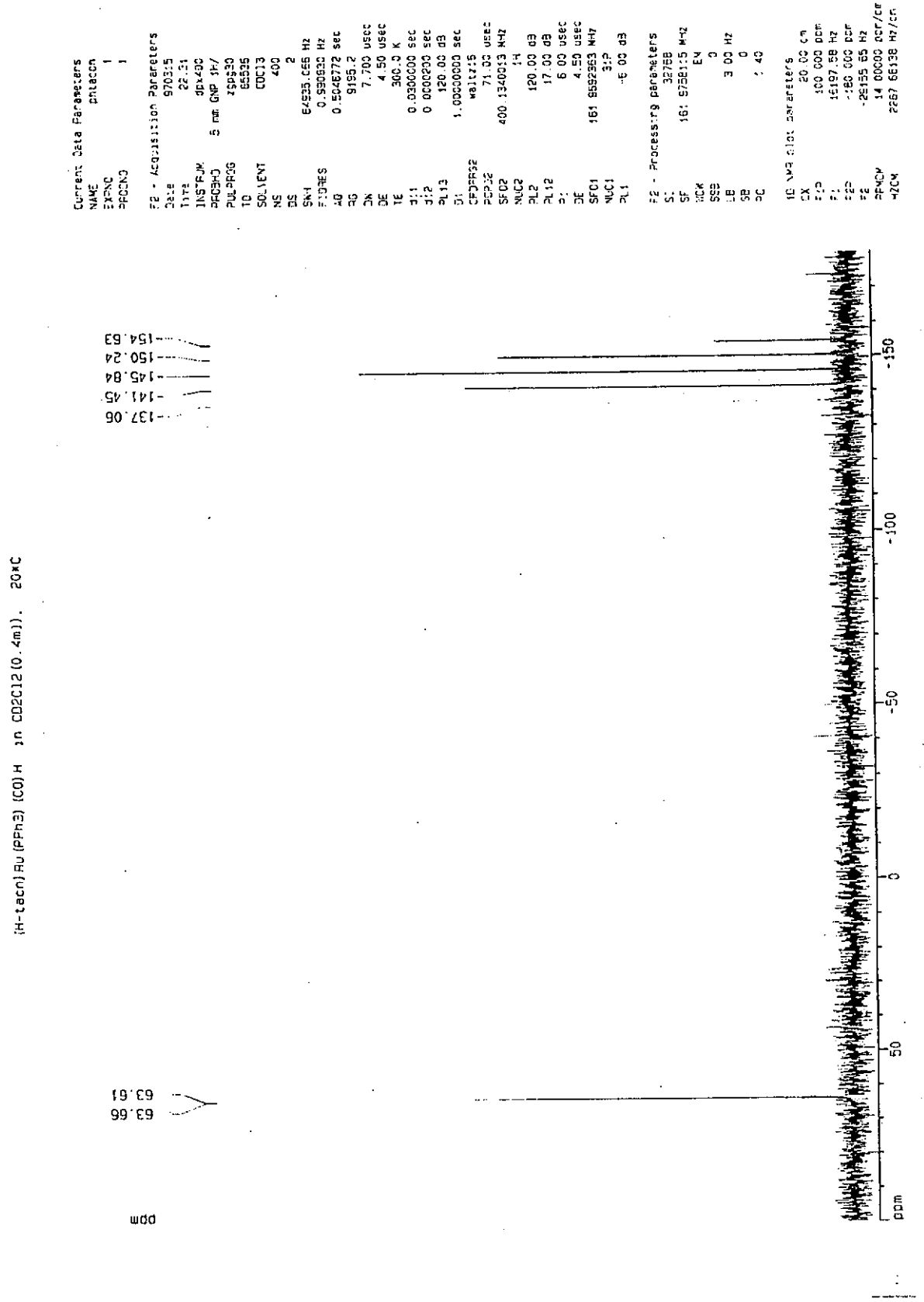


Figure 2.10. 161 MHz $^{31}P\{^{1}H\}$-NMR spectrum of $[^{H}CnRuH(CO)(PPh_3)]BF_4$ (2).

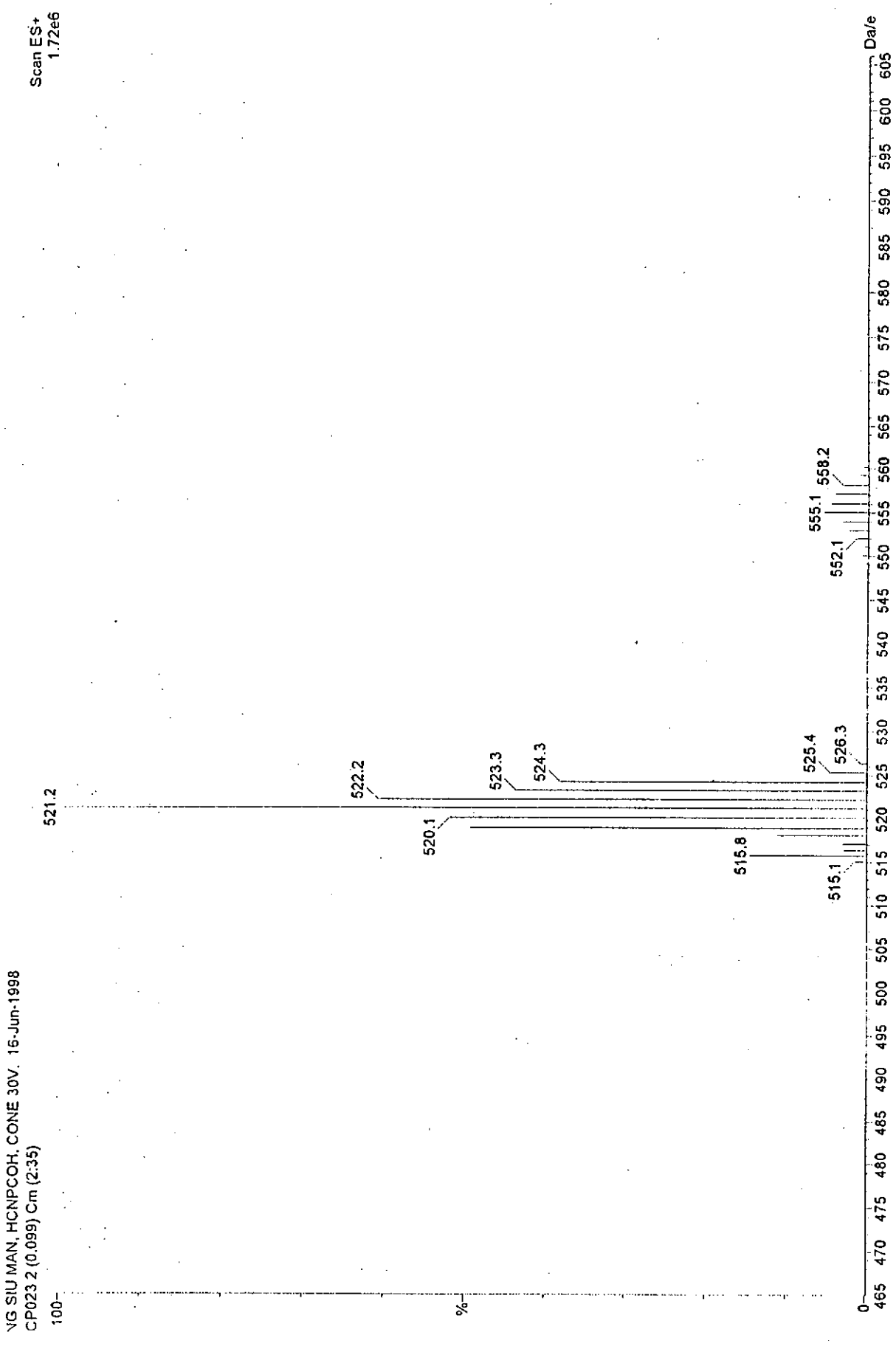


Figure 2.11 FAB mass spectrum of [^{H}CnRuH(CO)(PPh_3)]BF_4 (**2**).

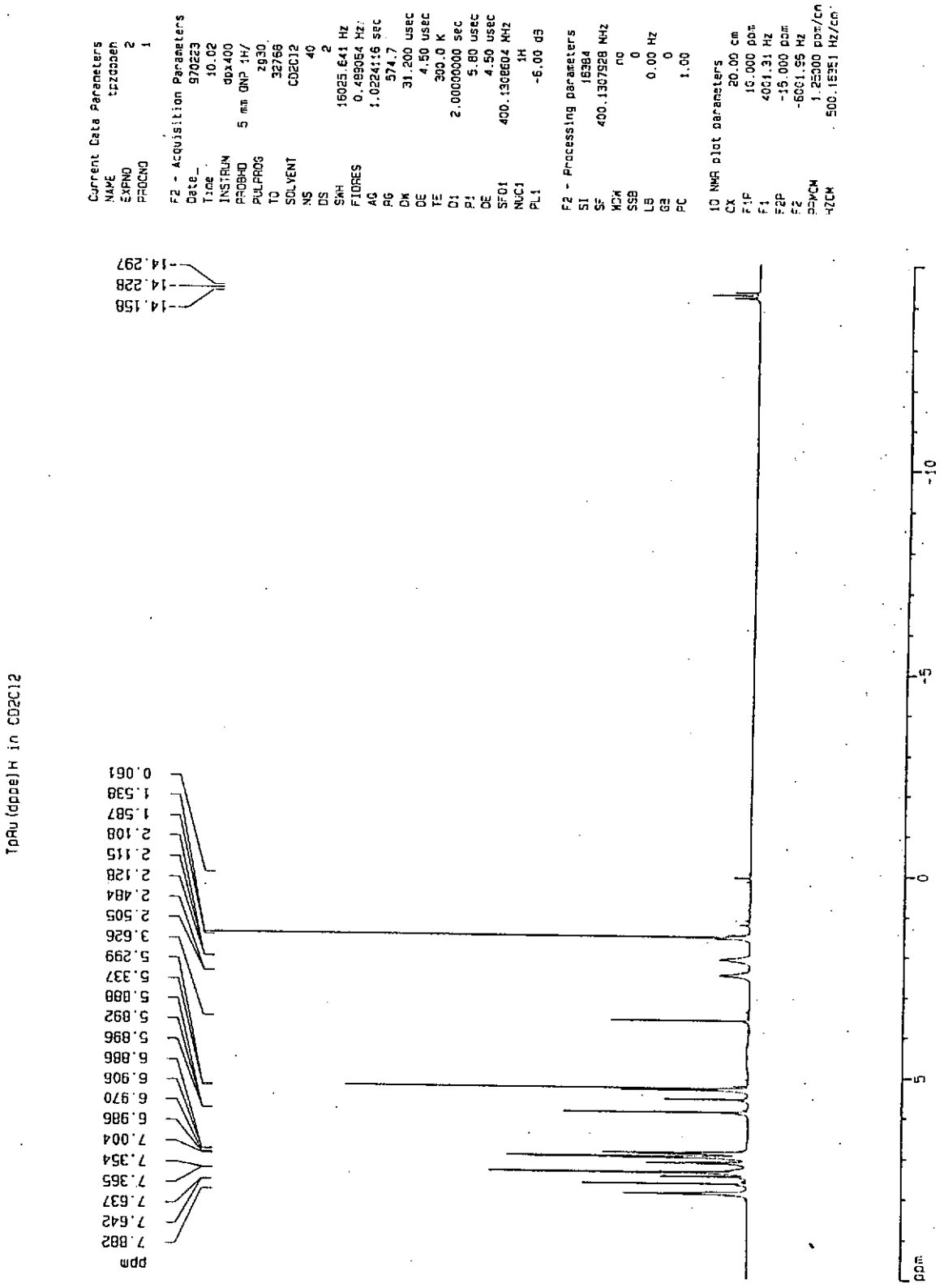


Figure 2.13. 400 MHz ^{1}H-NMR spectrum of TpRuH(dppe) (**14**).

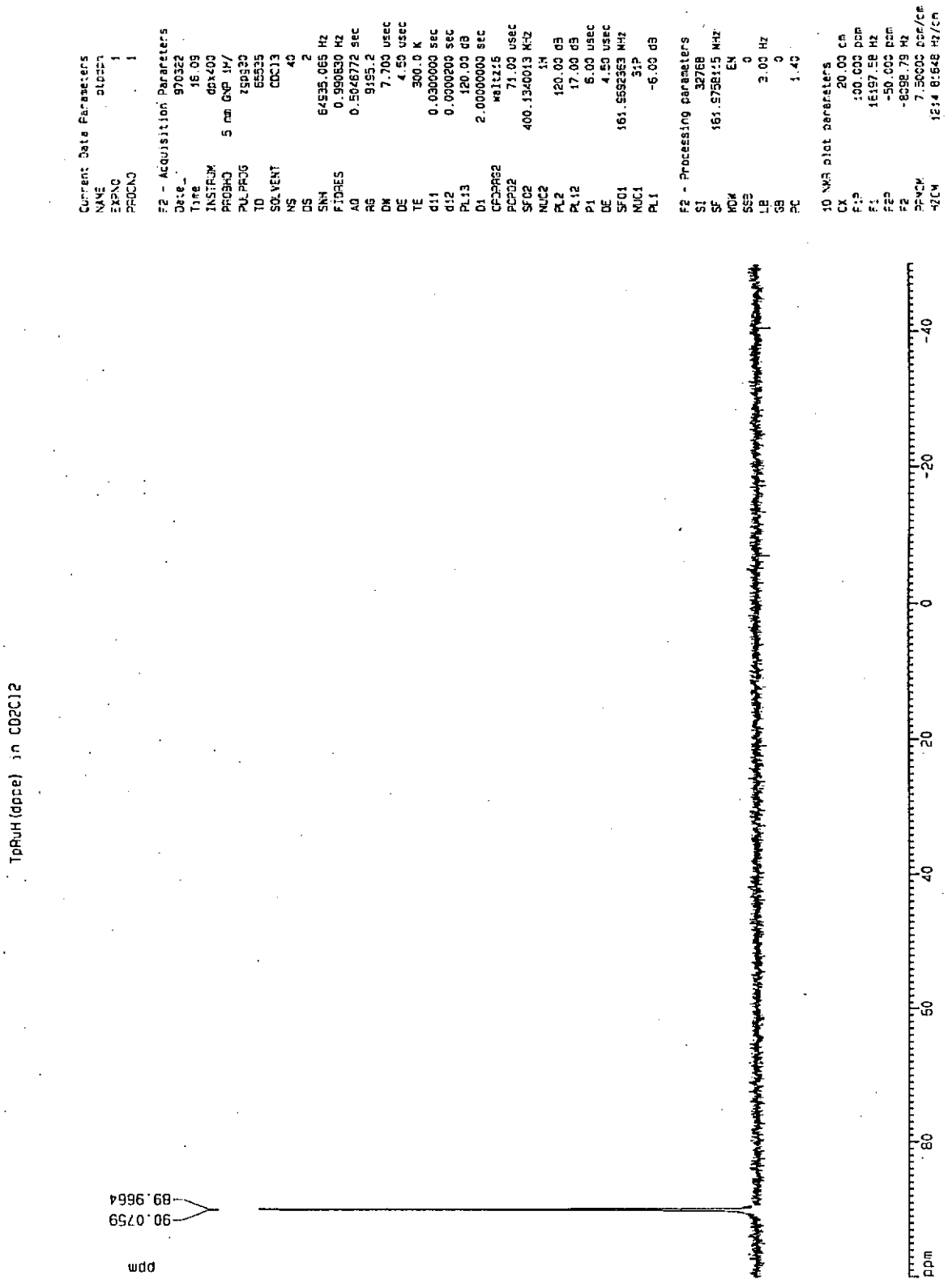


Figure 2.14. 161 MHz $^{31}P\{^{1}H\}$-NMR spectrum of TpRuH(dppe) (14).

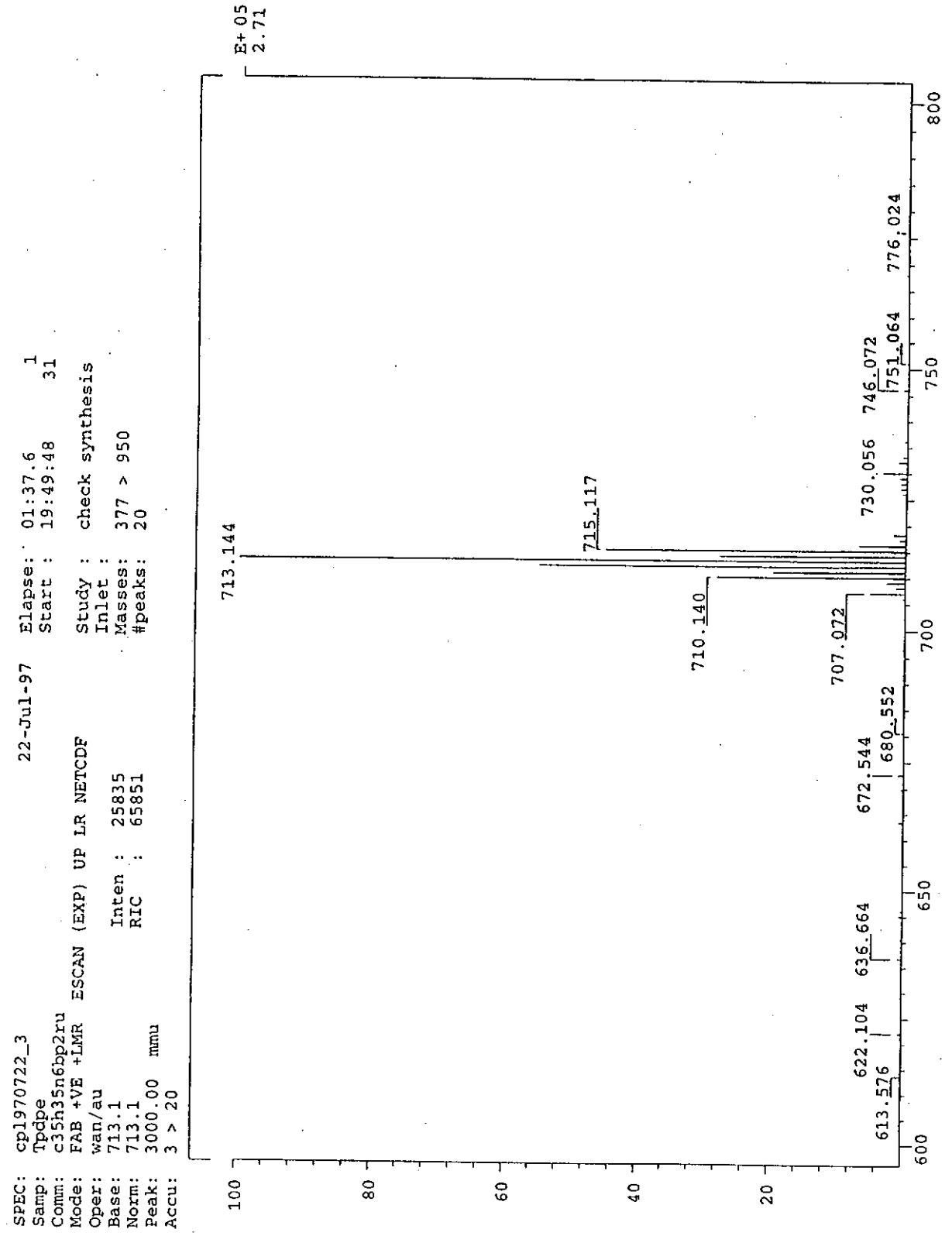


Figure 2.15 FAB mass spectrum of TpRuH(dppe) (**14**).

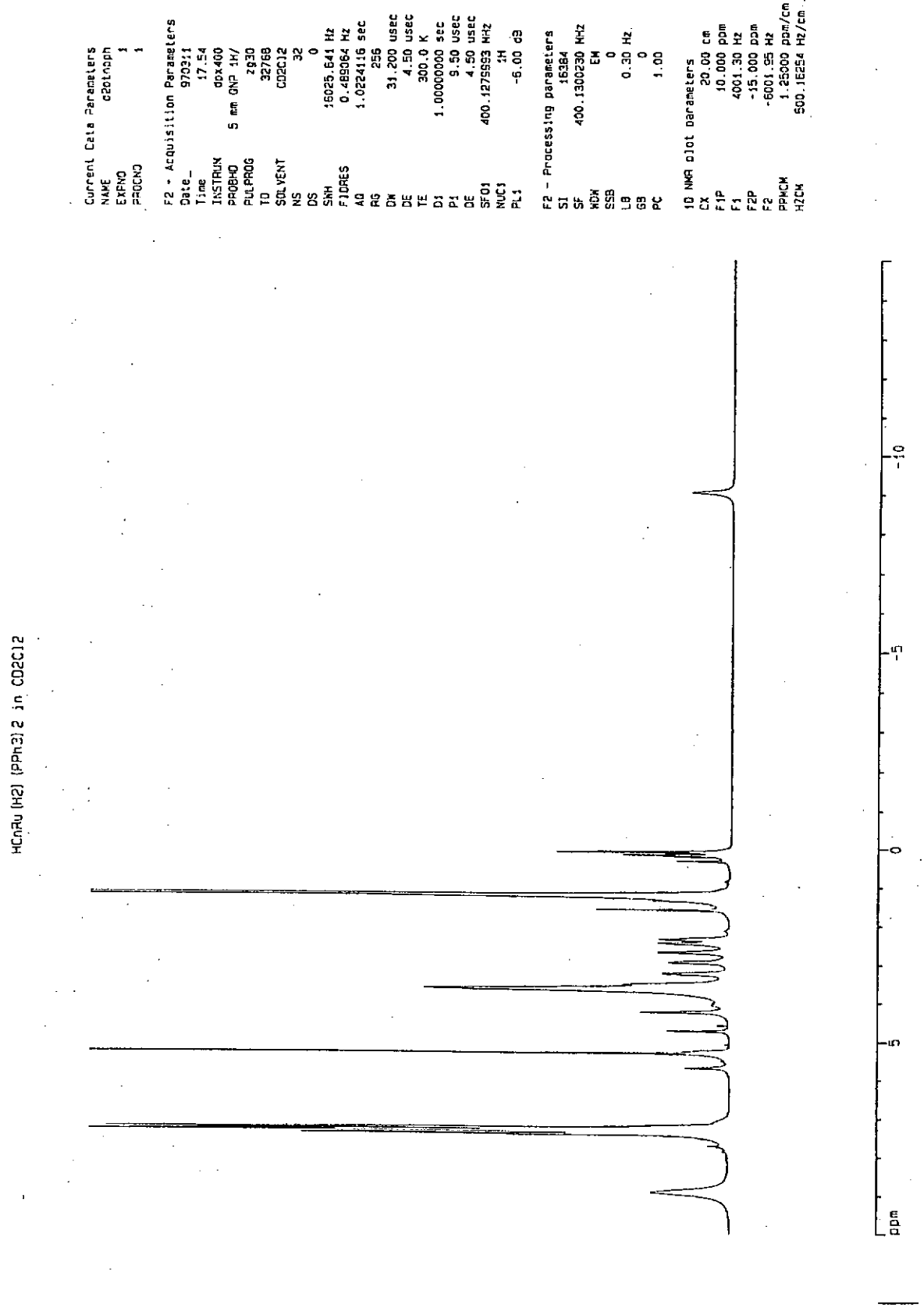


Figure 2.16. 400 MHz ^{1}H-NMR spectrum of [^{H}CnRu(H_2)(PPh_3)$_2$](BF_4)$_2$(**5**)

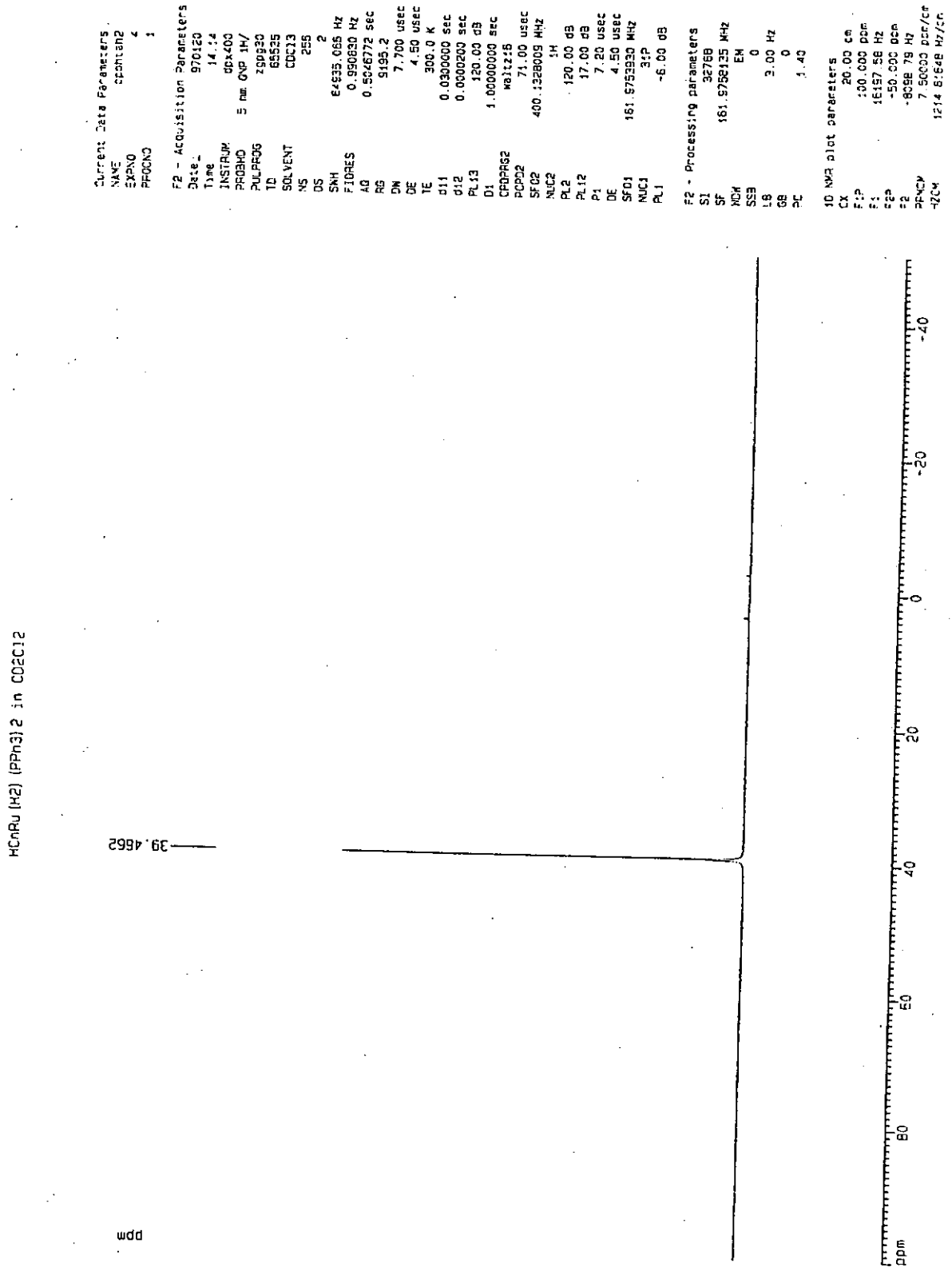


Figure 2.17. 161 MHz $^{31}P\{^{1}H\}$-NMR spectrum of $[^{H}CnRu(H_2)(PPh_3)_2](BF_4)_2$(**5**)

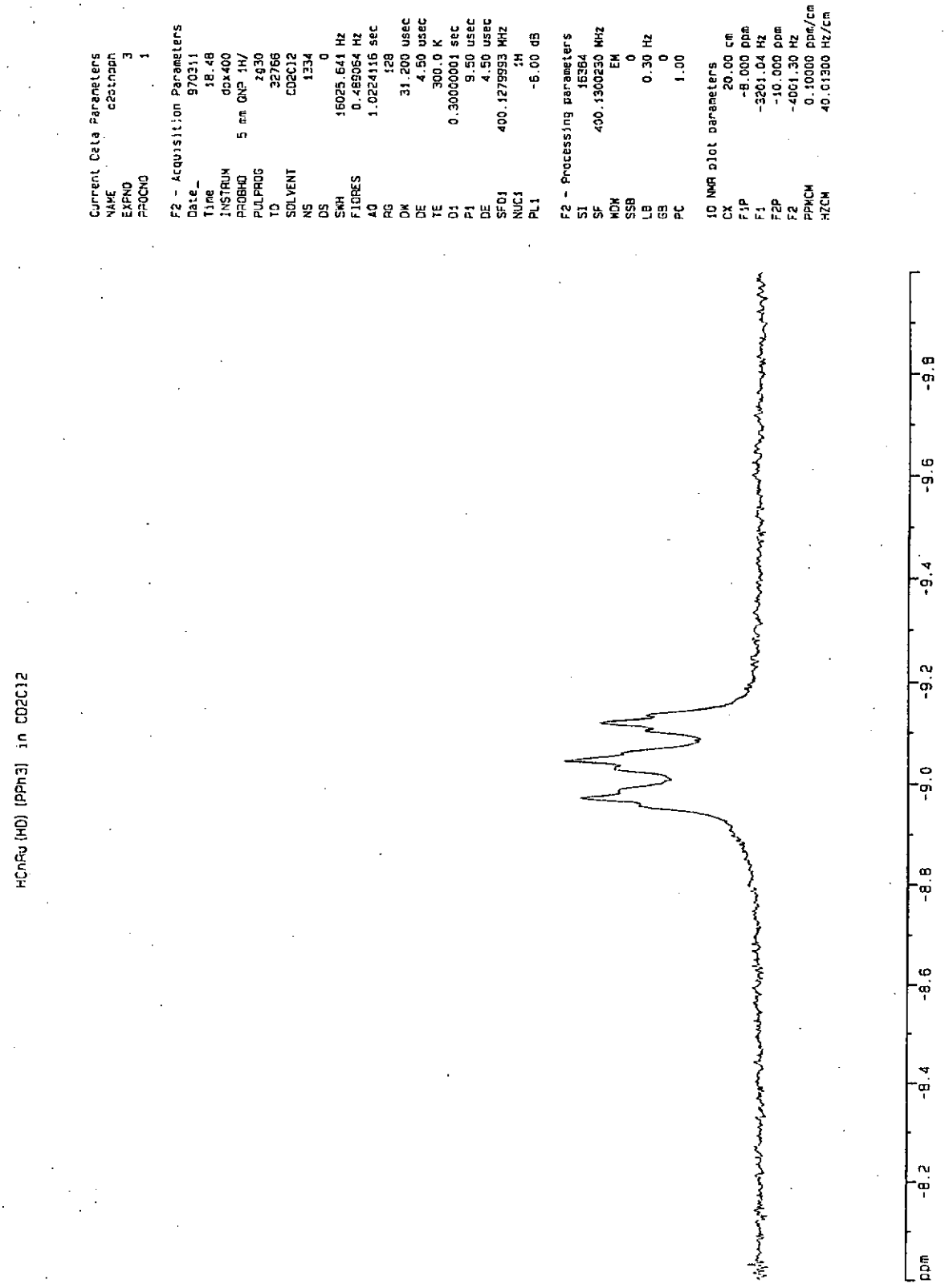


Figure 2.18. 400 MHz ^{1}H-NMR spectrum of [^{H}CnRu(HD)(PPh_3)$_2$] (BF_4)$_2$ (**5-d_1**)

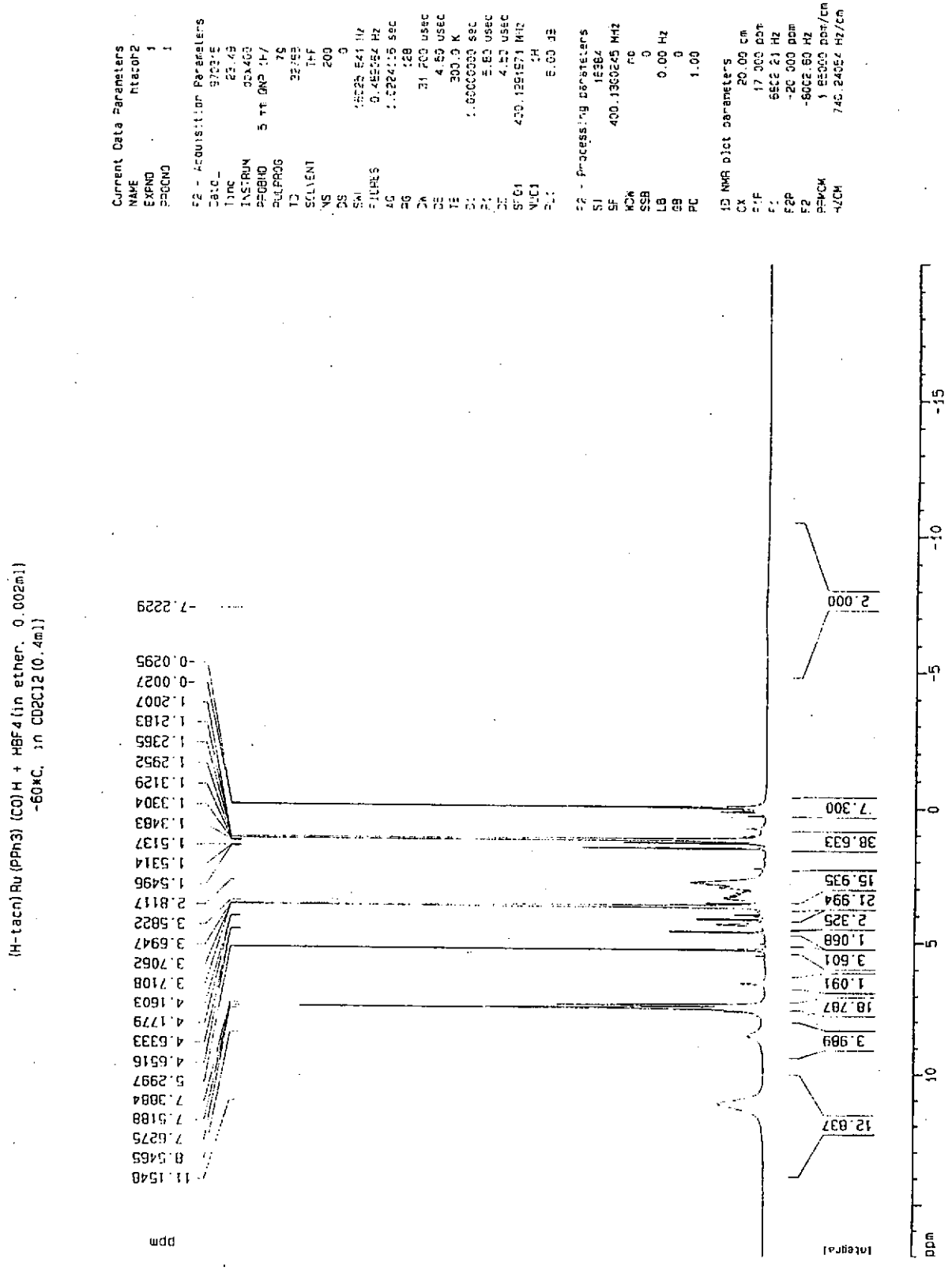


Figure 2.19. 400 MHz ^{1}H-NMR spectrum of [^{H}CnRu(H$_2$)(CO)(PPh$_3$)](BF$_4$)$_2$(**6**)

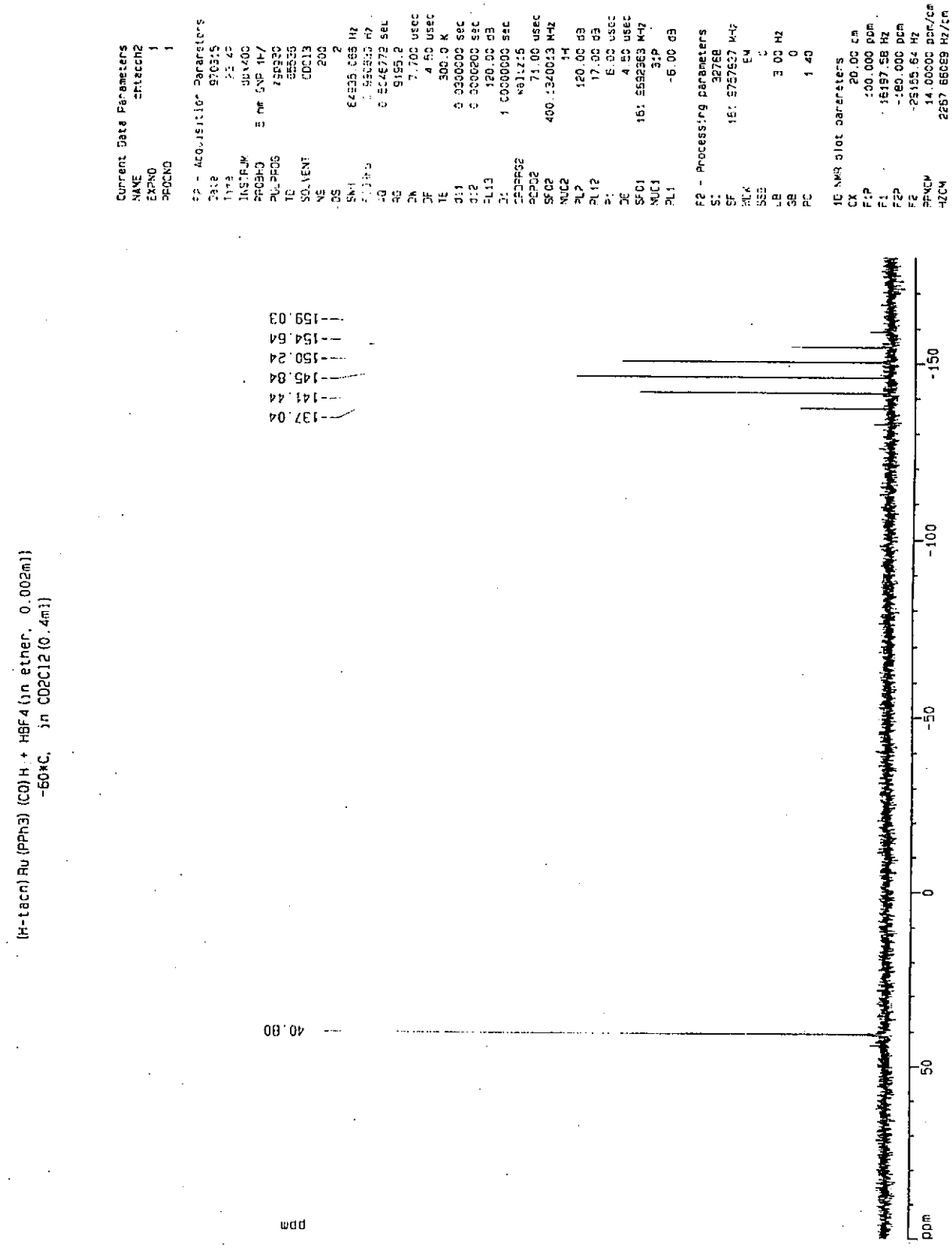


Figure 2.20. 161 MHz $^{31}P\{^{1}H\}$-NMR spectrum of $[^{H}CnRu(H_2)(CO)(PPh_3)](BF_4)_2$(6)

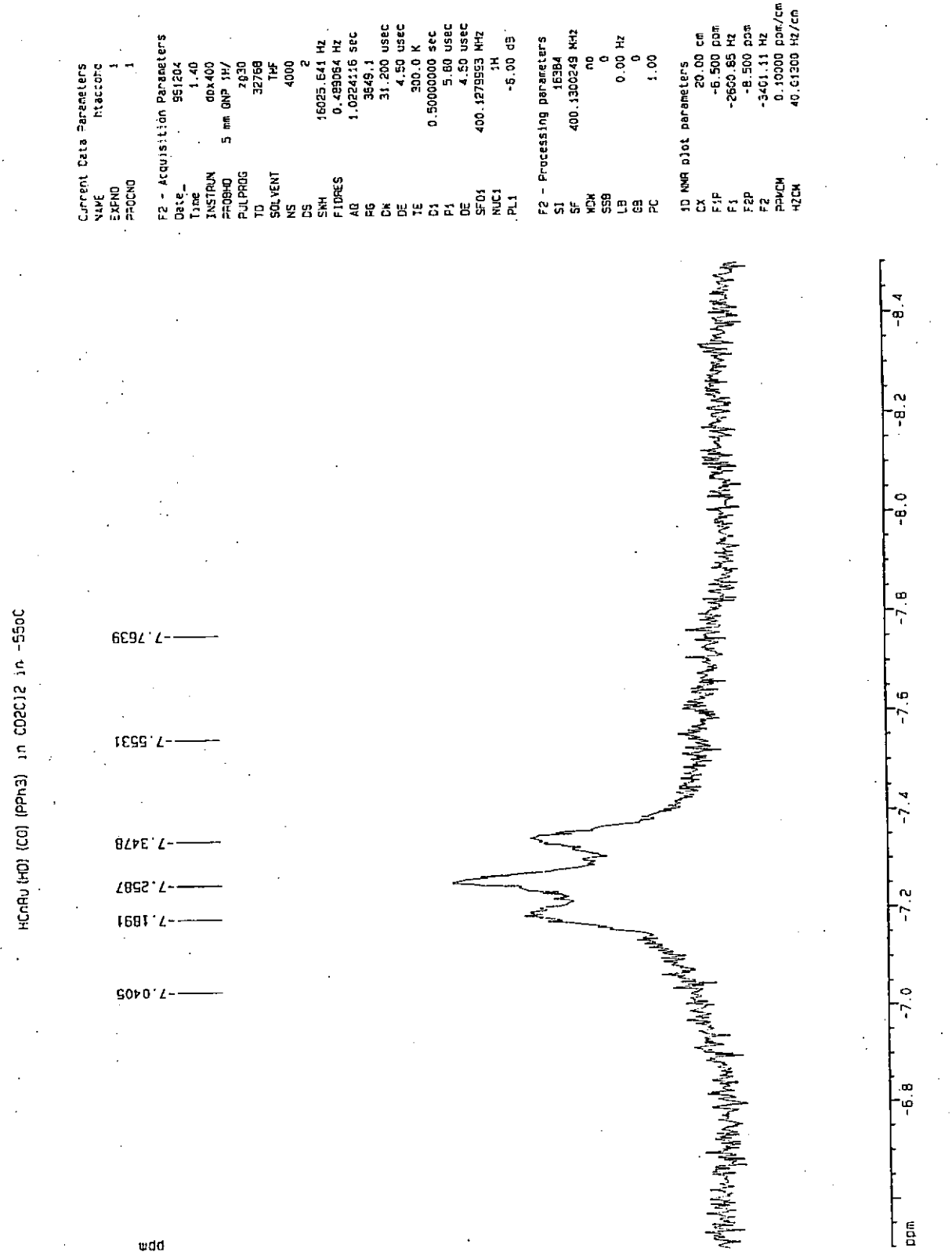


Figure 2.21. 400 MHz ^{1}H-NMR spectrum of [^{H}CnRu(HD)(CO)(PPh_3)] $(BF_4)_2$ (**6-*d*$_1$**)

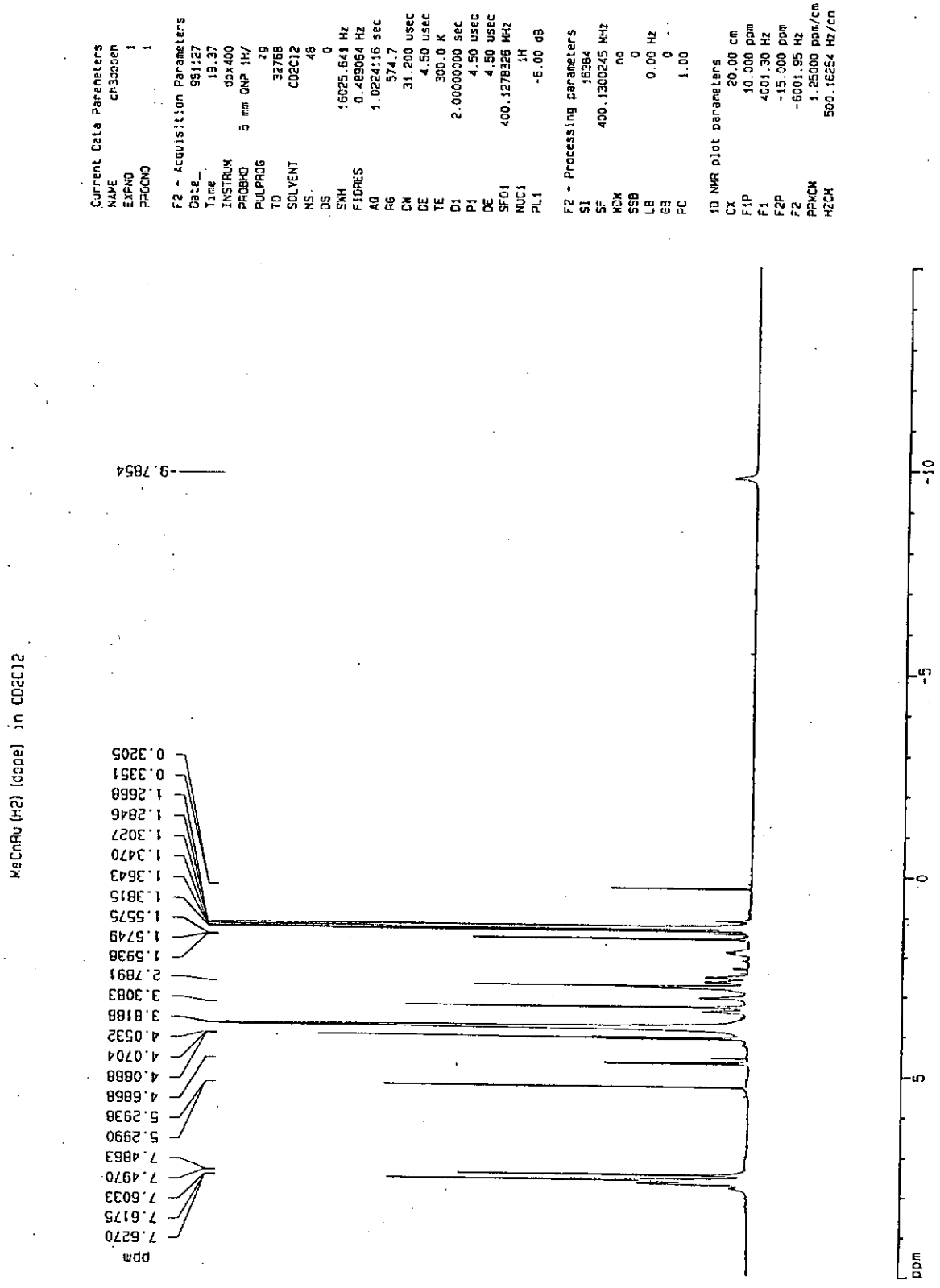


Figure 2.22. 400 MHz ^{1}H-NMR spectrum of [^{Me}CnRu(H_2)(dppe)](CF_3SO_3)$_2$(7)

Figure 2.23. 161 MHz $^{31}P\{^{1}H\}$-NMR spectrum of $[^{Me}CnRu(H_2)(dppe)](CF_3SO_3)_2$(7)

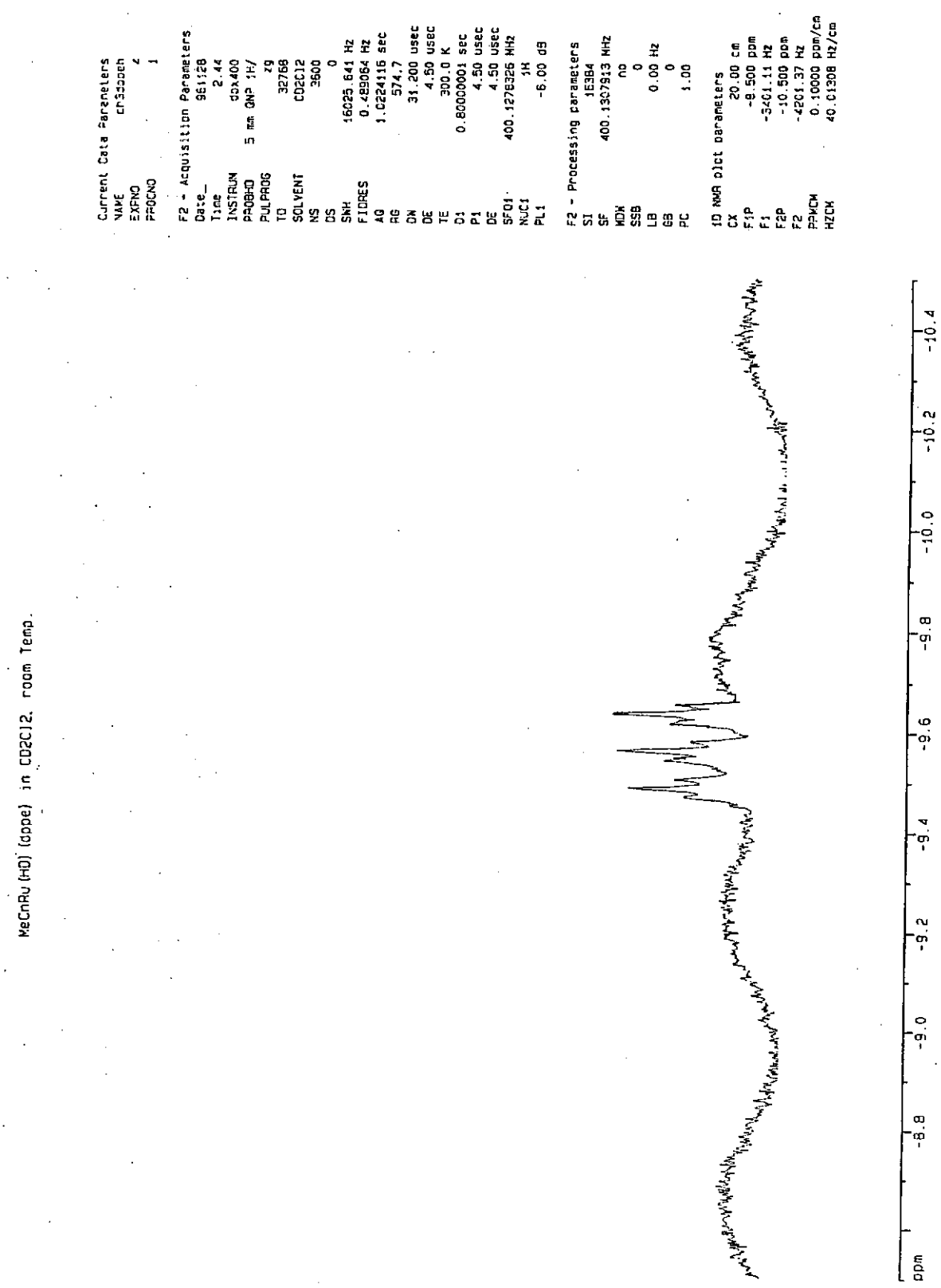


Figure 2.24. 400 MHz ^{1}H-NMR spectrum of [^{Me}CnRu(HD)(dppe)]$(CF_3SO_3)_2$(7-d_1)

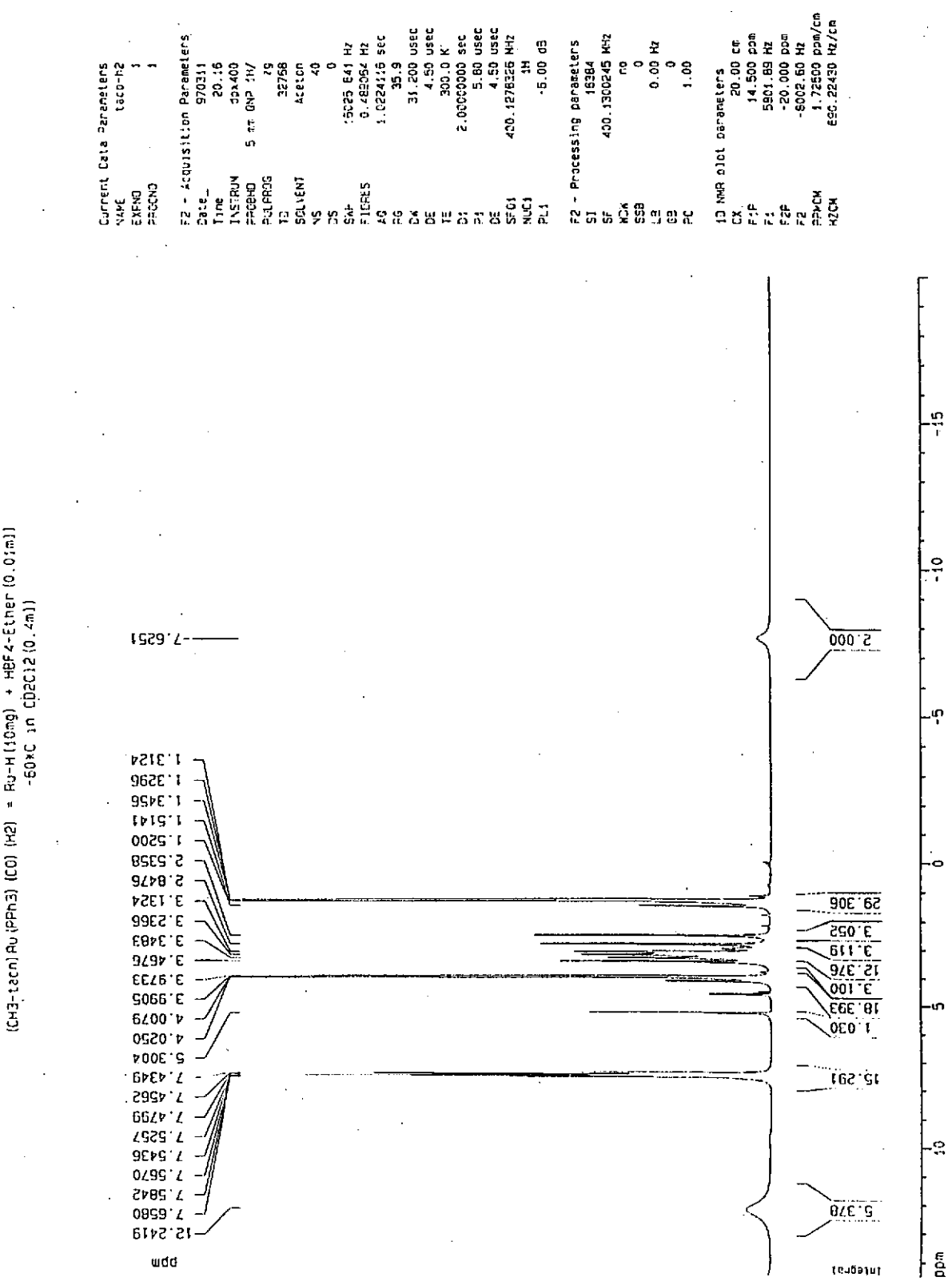


Figure 2.25. 400 MHz ^{1}H-NMR spectrum of [^{Me}CnRu(H$_2$)(CO)(PPh$_3$)](PF$_6$)(CF$_3$SO$_3$) (**8**)

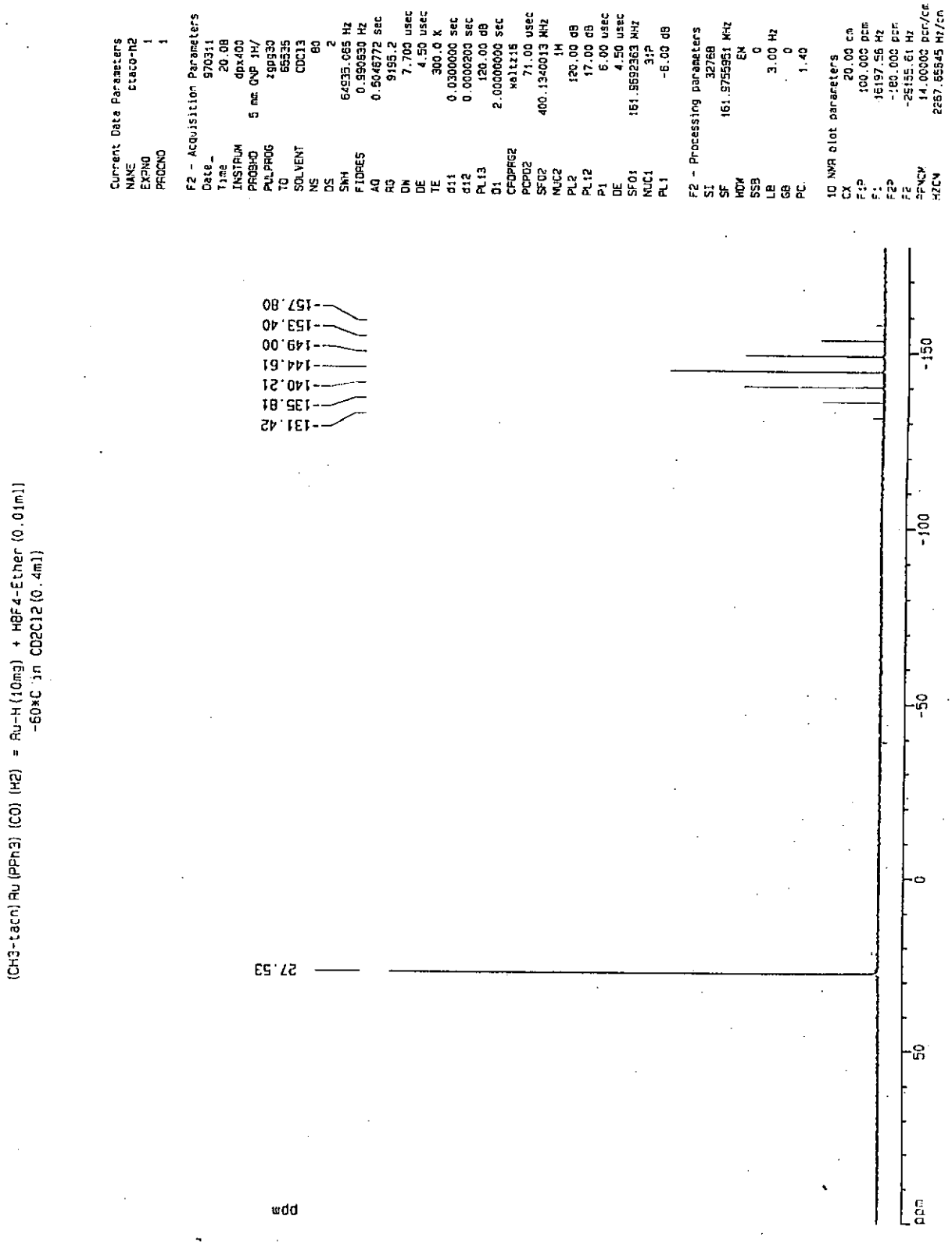


Figure 2.26. 161 MHz $^{31}P\{^{1}H\}$-NMR spectrum of $[^{Me}CnRu(H_2)(CO)(PPh_3)](PF_6)(CF_3SO_3)$ (**8**)

Figure 2.27. 400 MHz ^{1}H-NMR spectrum of
$[^{Me}CnRu(HD)(CO)(PPh_3)](PF_6)(CF_3SO_3)$ (**8-d_1**)

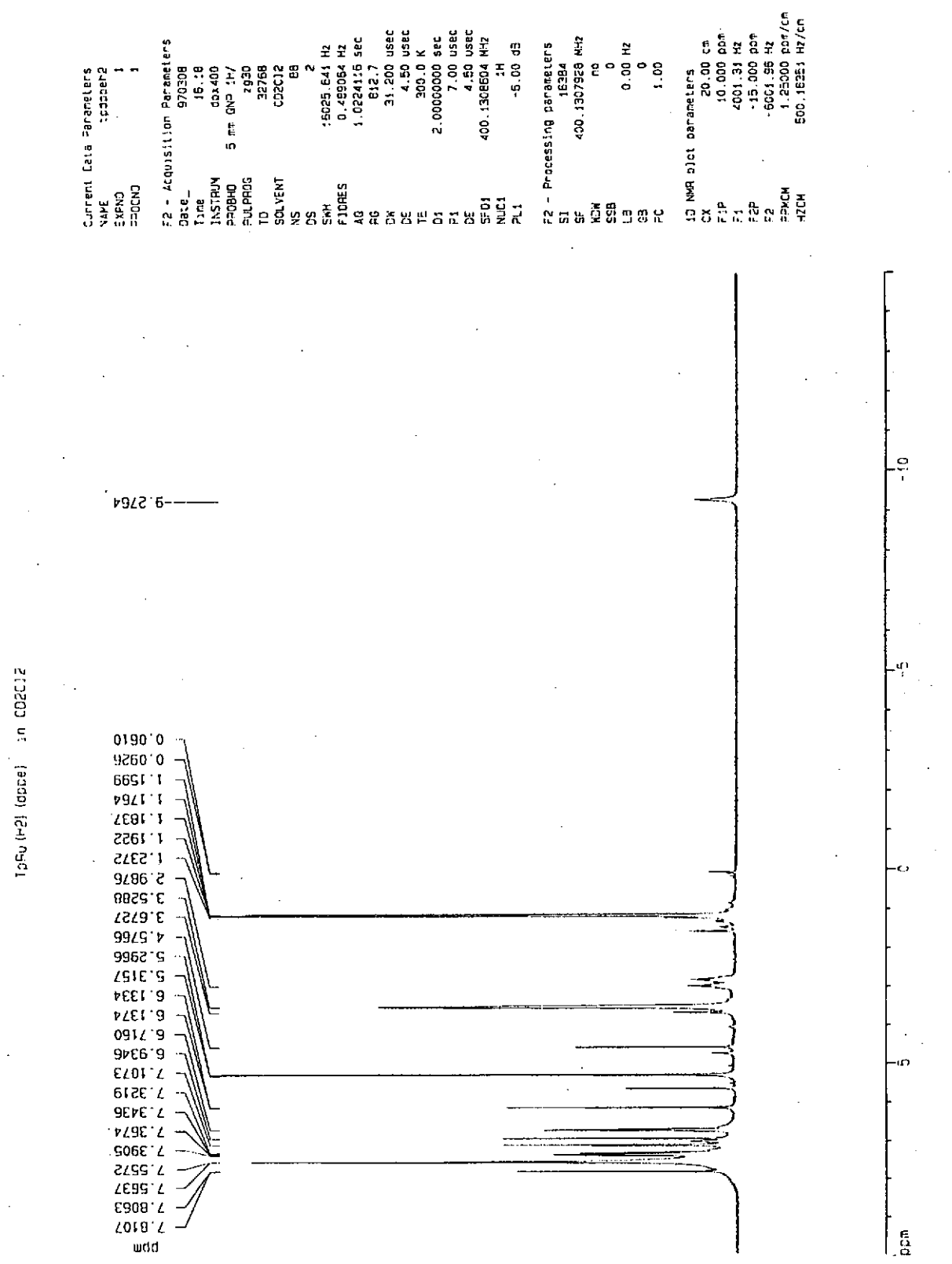


Figure 2.28. 400 MHz ^{1}H-NMR spectrum of [TpRu(H_2)(dppe)]BF_4 (**19**)

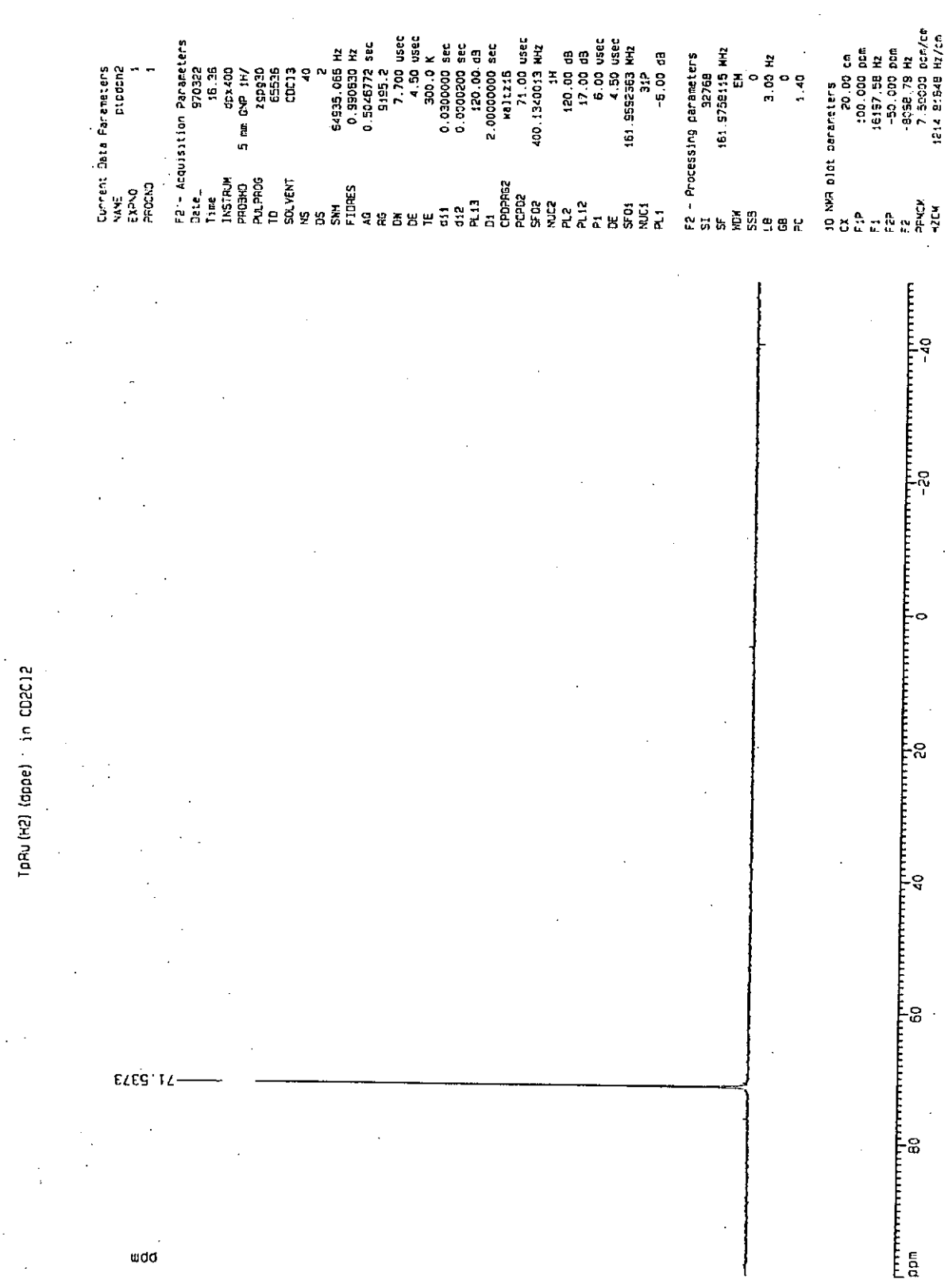


Figure 2.29. 161 MHz $^{31}P\{^{1}H\}$-NMR spectrum of $[TpRu(H_2)(dppe)]BF_4$ (**19**)

Figure 2.30. 400 MHz ^{1}H-NMR spectrum of [TpRu(HD)(dppe)]BF_4 (**19-d_1**)

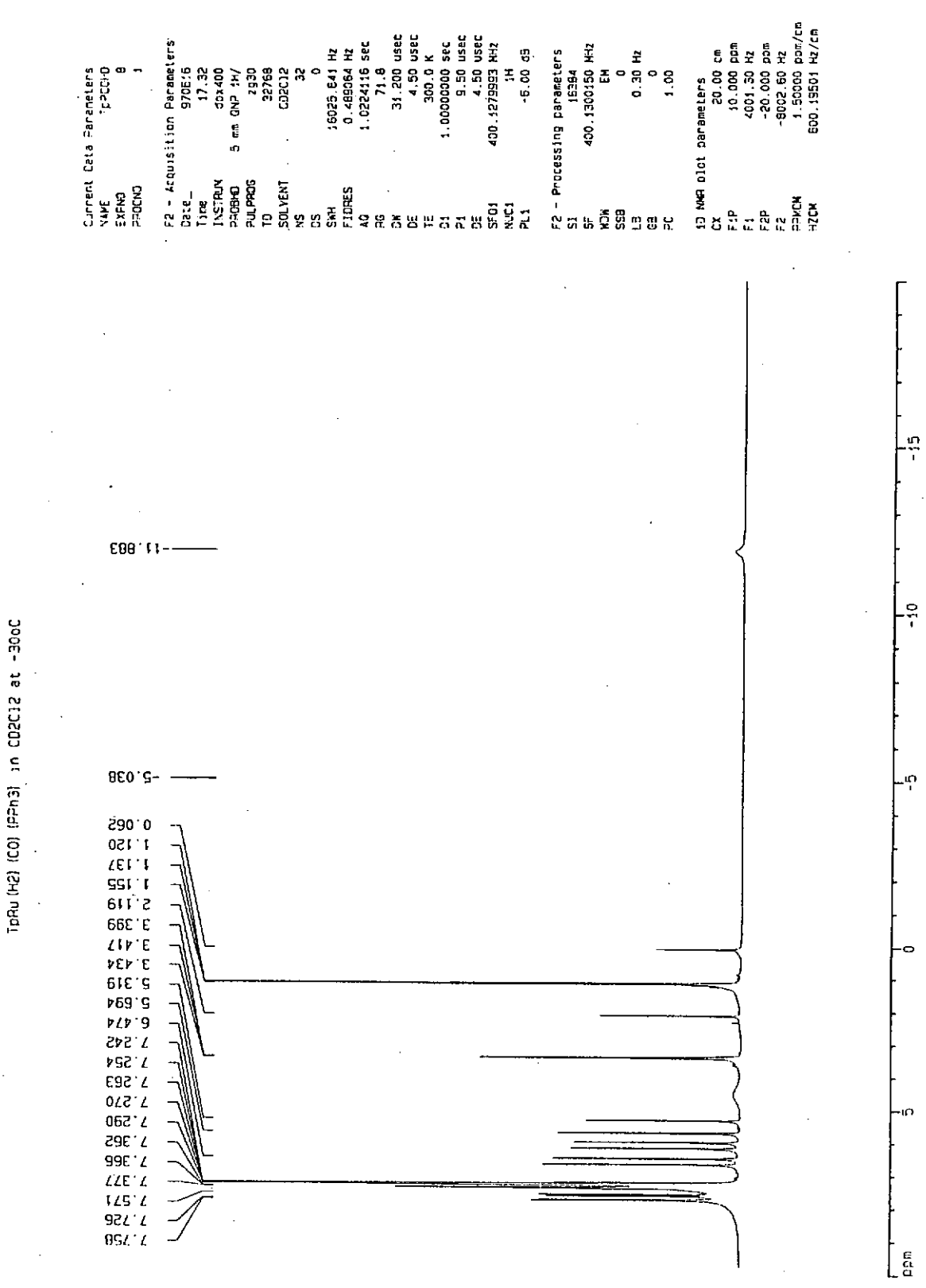


Figure 2.31. 400 MHz ^{1}H-NMR spectrum of $[TpRu(H_2)(CO)(PPh_3)]BF_4$ (**20**)

Figure 2.32. 161 MHz $^{31}P\{^{1}H\}$-NMR spectrum of $[[TpRu(H_2)(CO)(PPh_3)]BF_4$ (**20**)

Figure 2.33. 400 MHz ^{1}H-NMR spectrum of [TpRu(HD)(CO)(PPh$_3$)]BF$_4$ (**20-d_1**)

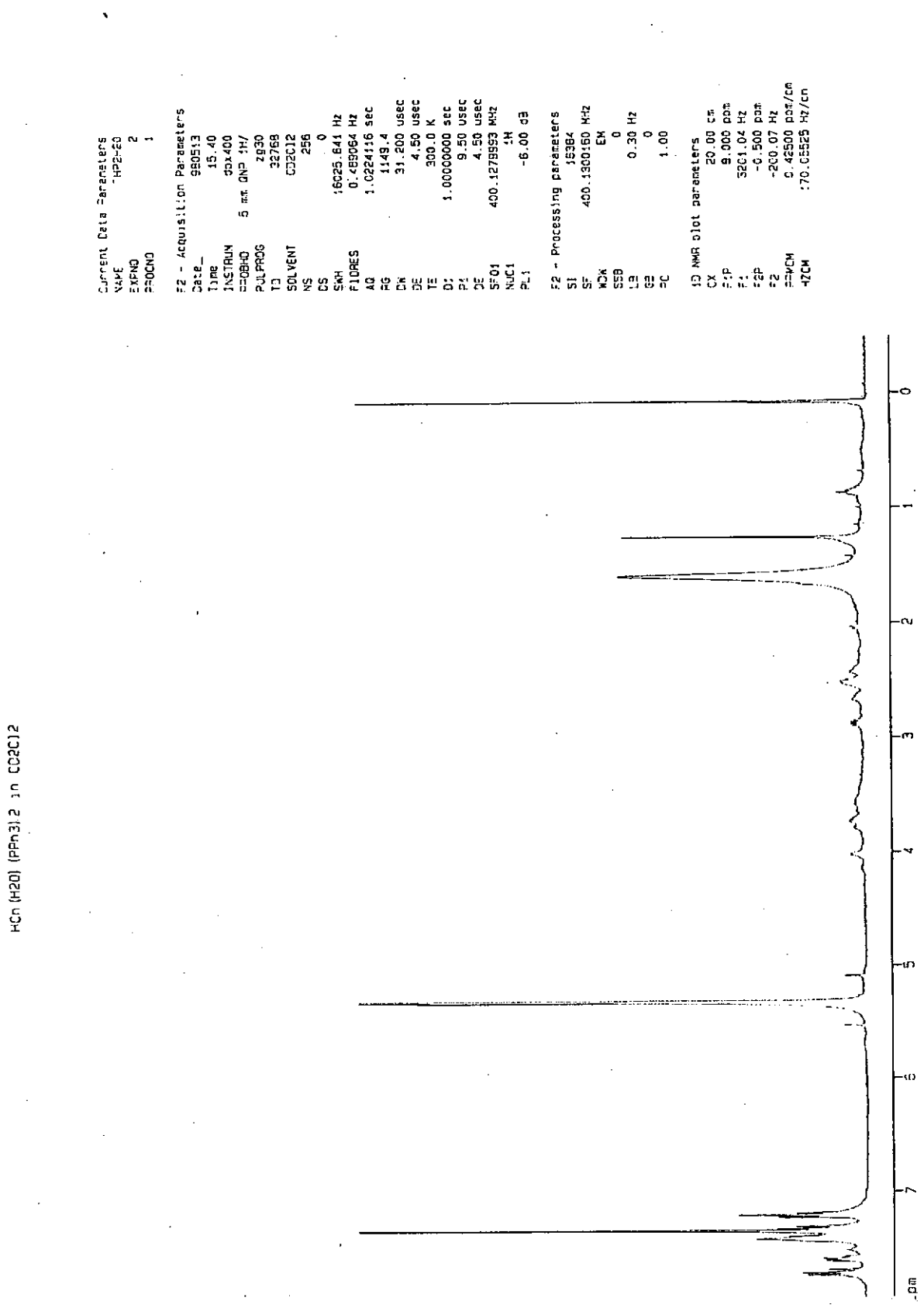


Figure 2.34. 400 MHz ^{1}H-NMR spectrum of [^{H}CnRu(H$_2$O)(PPh$_3$)$_2$](BF$_4$)$_2$ (**9**)

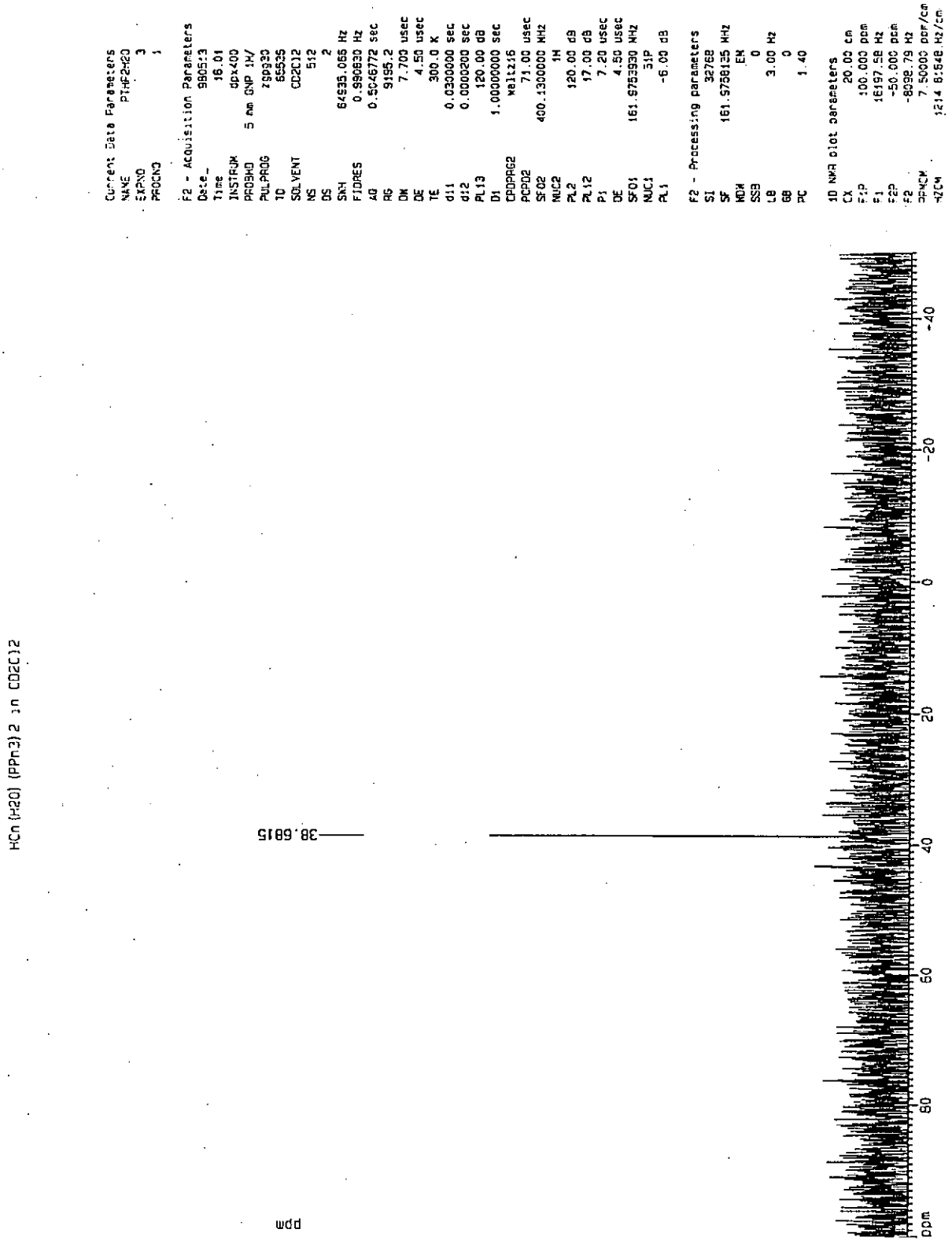


Figure 2.35. 161 MHz $^{31}P\{^{1}H\}$-NMR spectrum of $[^{H}CnRu(H_2O)(PPh_3)_2](BF_4)_2$ (**9**)

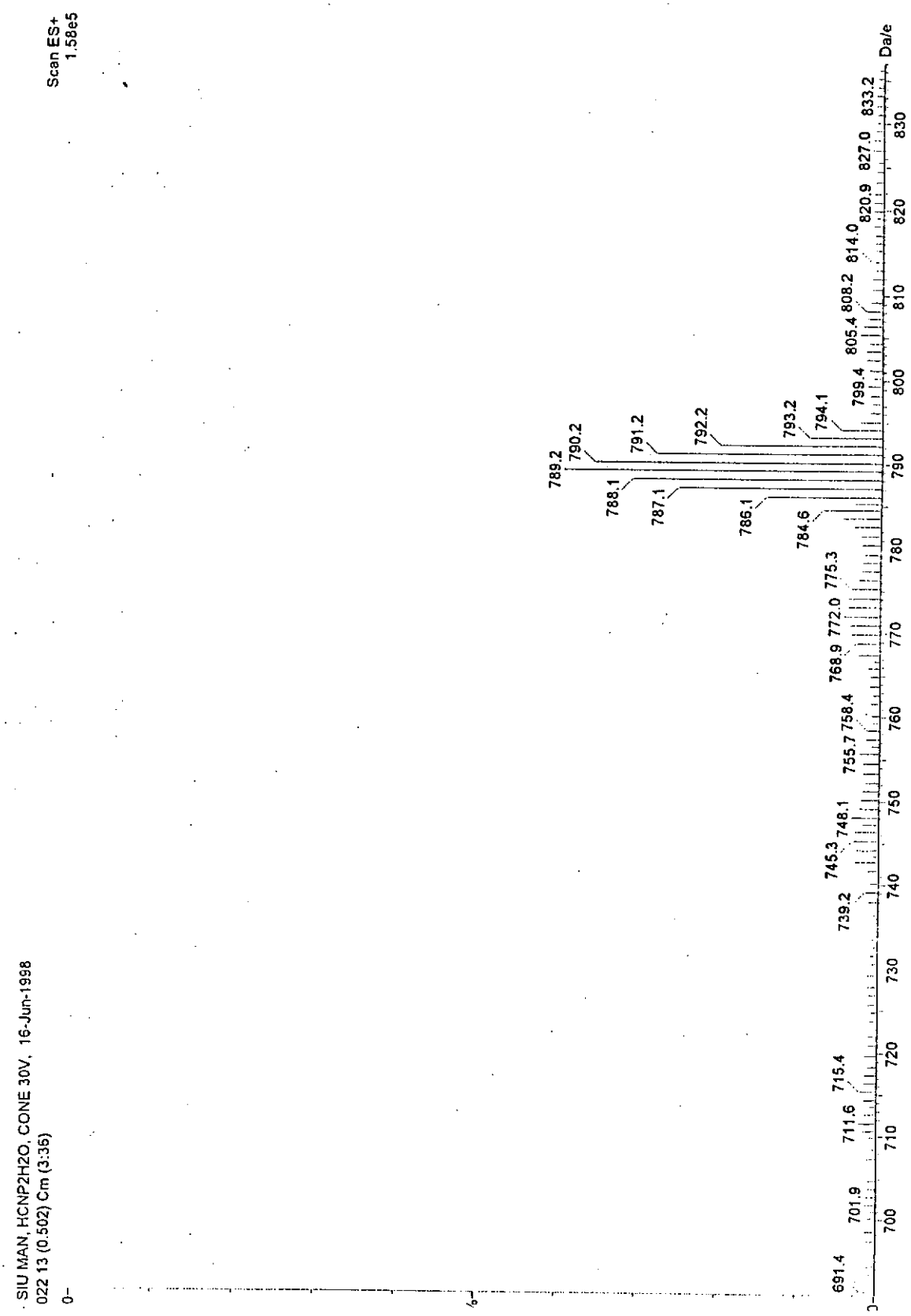


Figure 2.36. FAB mass spectrum of $[^{H}CnRu(H_2O)(PPh_3)_2](BF_4)_2$ (**9**)

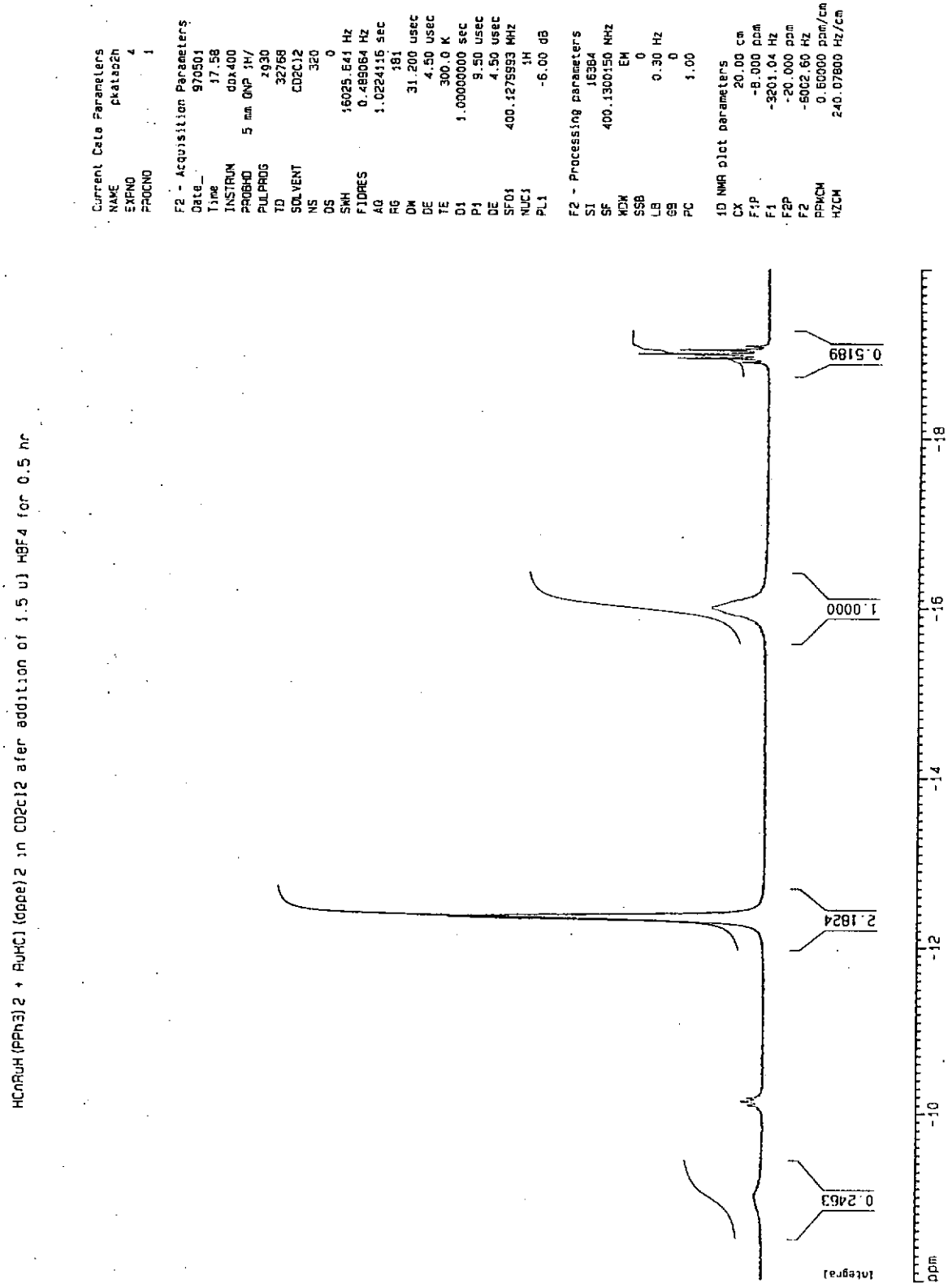


Figure 2.37. The ^{1}H-NMR spectra of [^{H}CnRuH(PPh$_3$)$_2$]BF$_4$ (1) and RuHCl(dppe)$_2$ + HBF$_4$.Et$_2$O in CD$_2$Cl$_2$

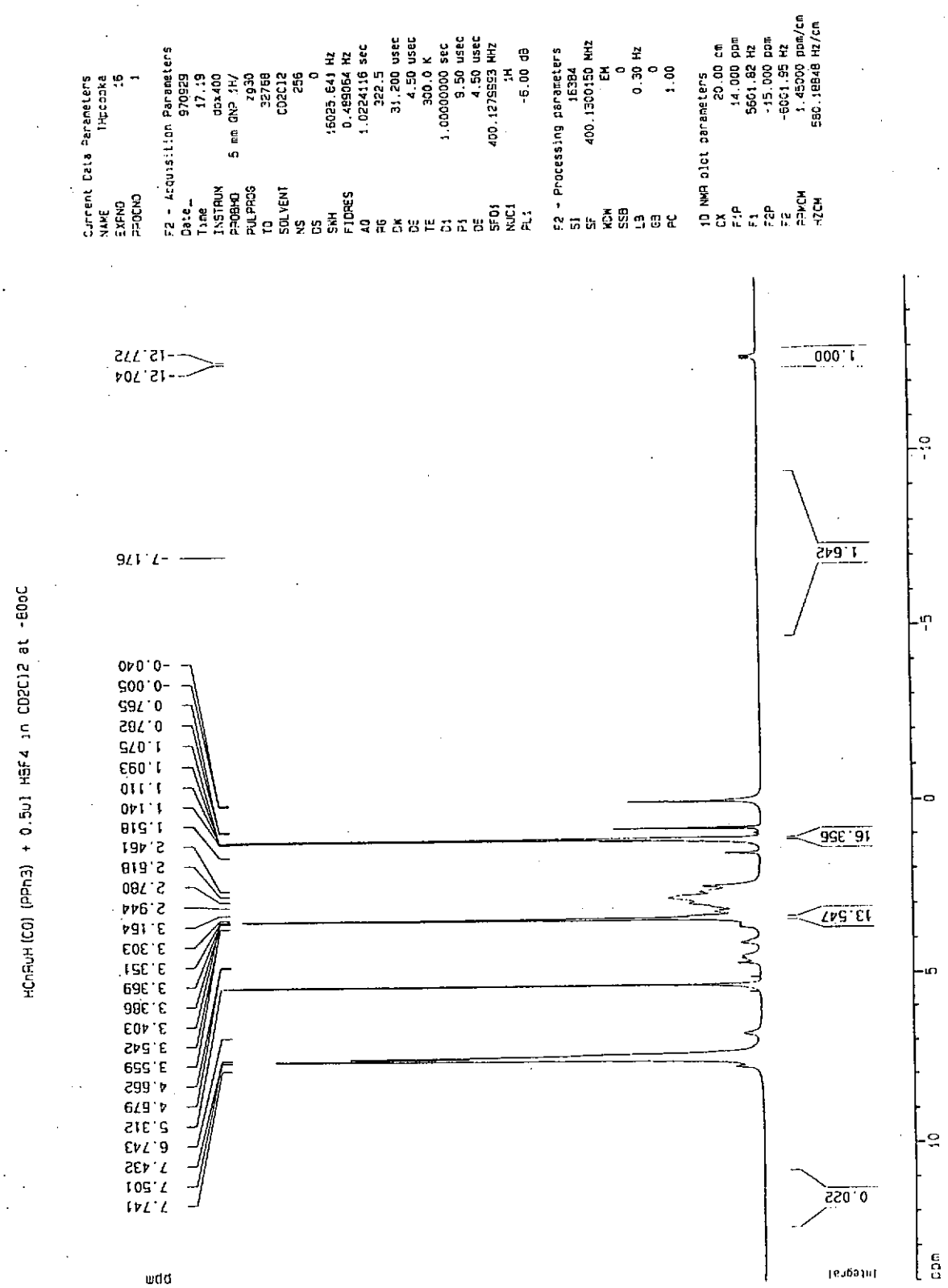


Figure 2.38. The ^{1}H-NMR spectra of [^{H}CnRuH(CO)(PPh_3)$_2$]BF_4 (2) and $HBF_4.Et_2O$ in CD_2Cl_2 -80 °C

Figure 2.39. The ^{1}H-NMR spectra of [^{Me}CnRuH(dppe)](CF_3SO_3) (**3**) and $RuHCl(dppe)_2$ + $HBF_4.Et_2O$ in CD_2Cl_2

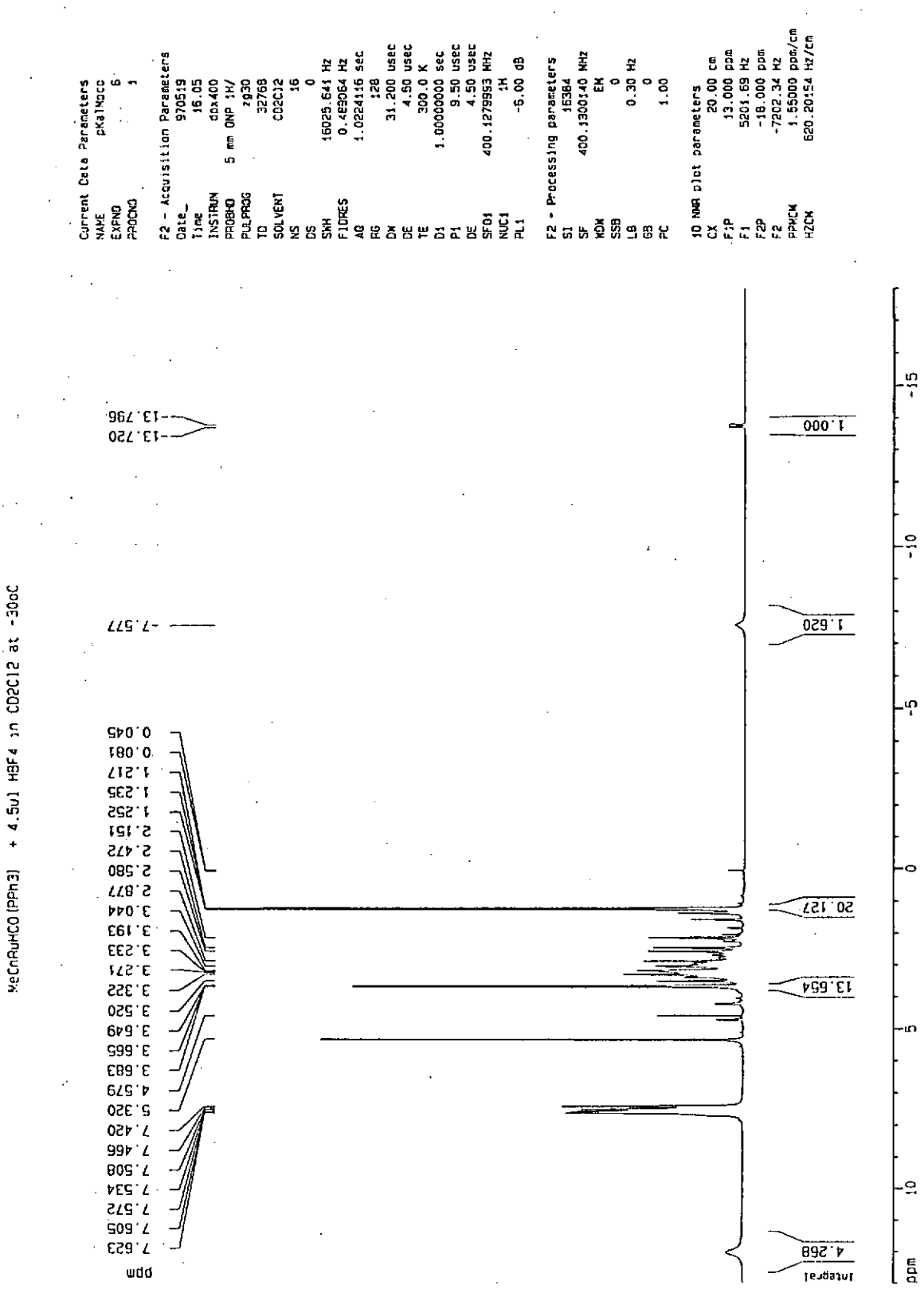


Figure 2.40. The ^{1}H-NMR spectra of $[^{H}CnRuH(CO)(PPh_3)_2]PF_6$ (**4**) and $HBF_4.Et_2O$ in CD_2Cl_2 -30 °C

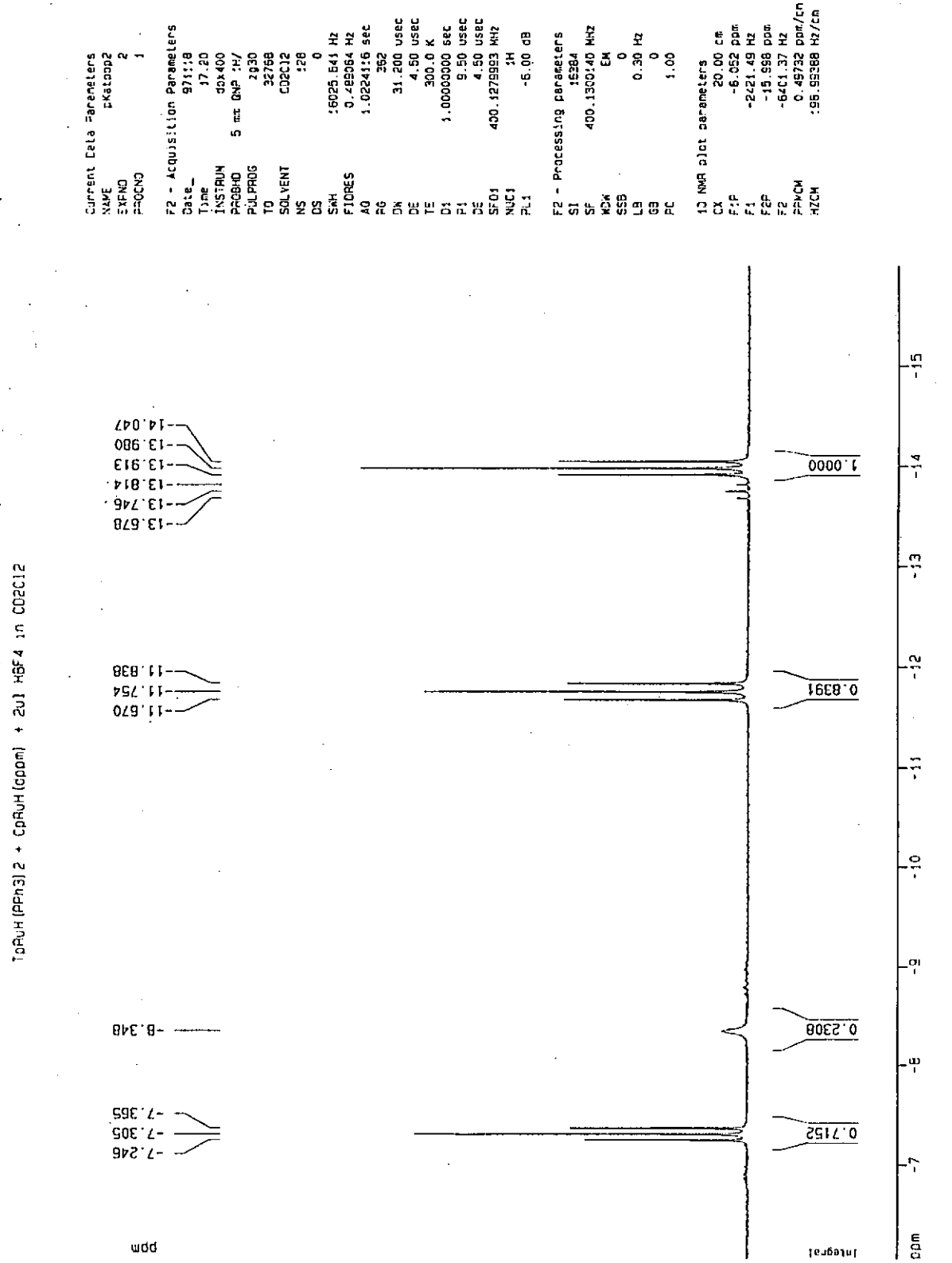


Figure 2.41. The ^{1}H-NMR spectra of $TpRuH(PPh_3)_2$ (**12**) and CpRuH(dppm) + $HBF_4.Et_2O$ in CD_2Cl_2

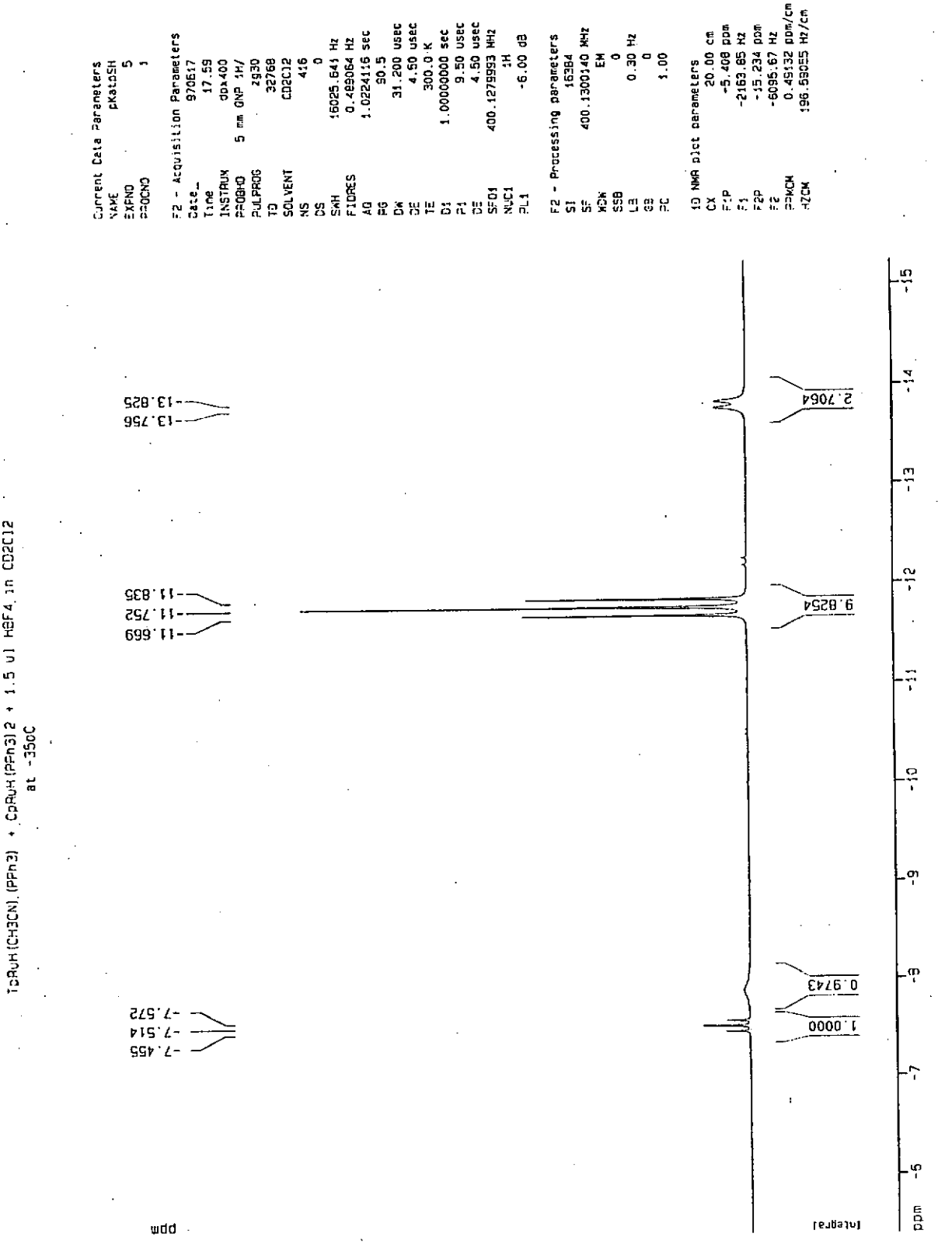


Figure 2.42. The ^{1}H-NMR spectra of TpRuH(CH_3CN)(PPh_3) (**13**) and CpRuH(PPh_3)$_2$ + $HBF_4.Et_2O$ in CD_2Cl_2 -35 °C

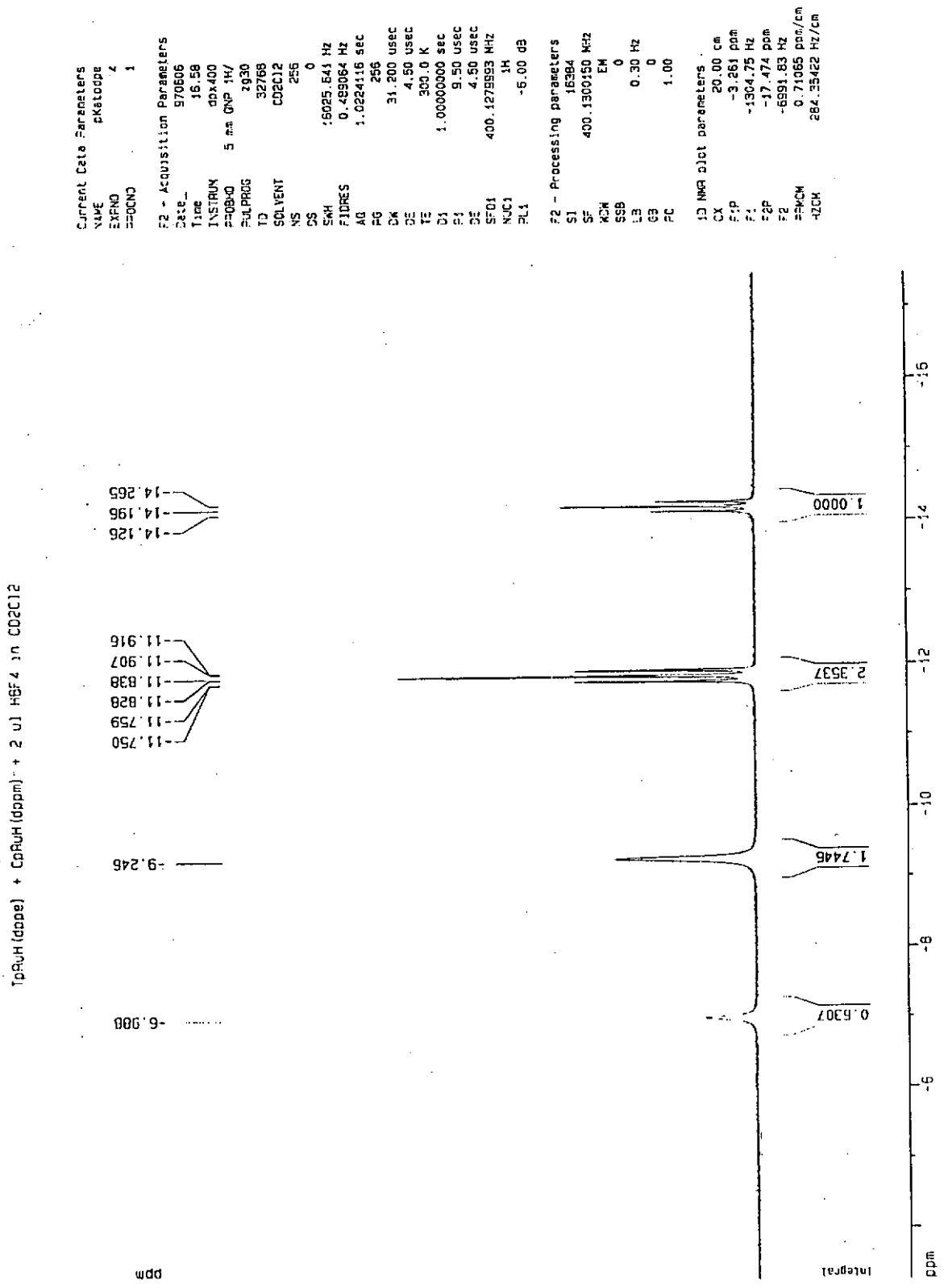


Figure 2.43. The ^{1}H-NMR spectra of TpRuH(dppe) (**14**) and CpRuH(dppm) + $HBF_4.Et_2O$ in CD_2Cl_2

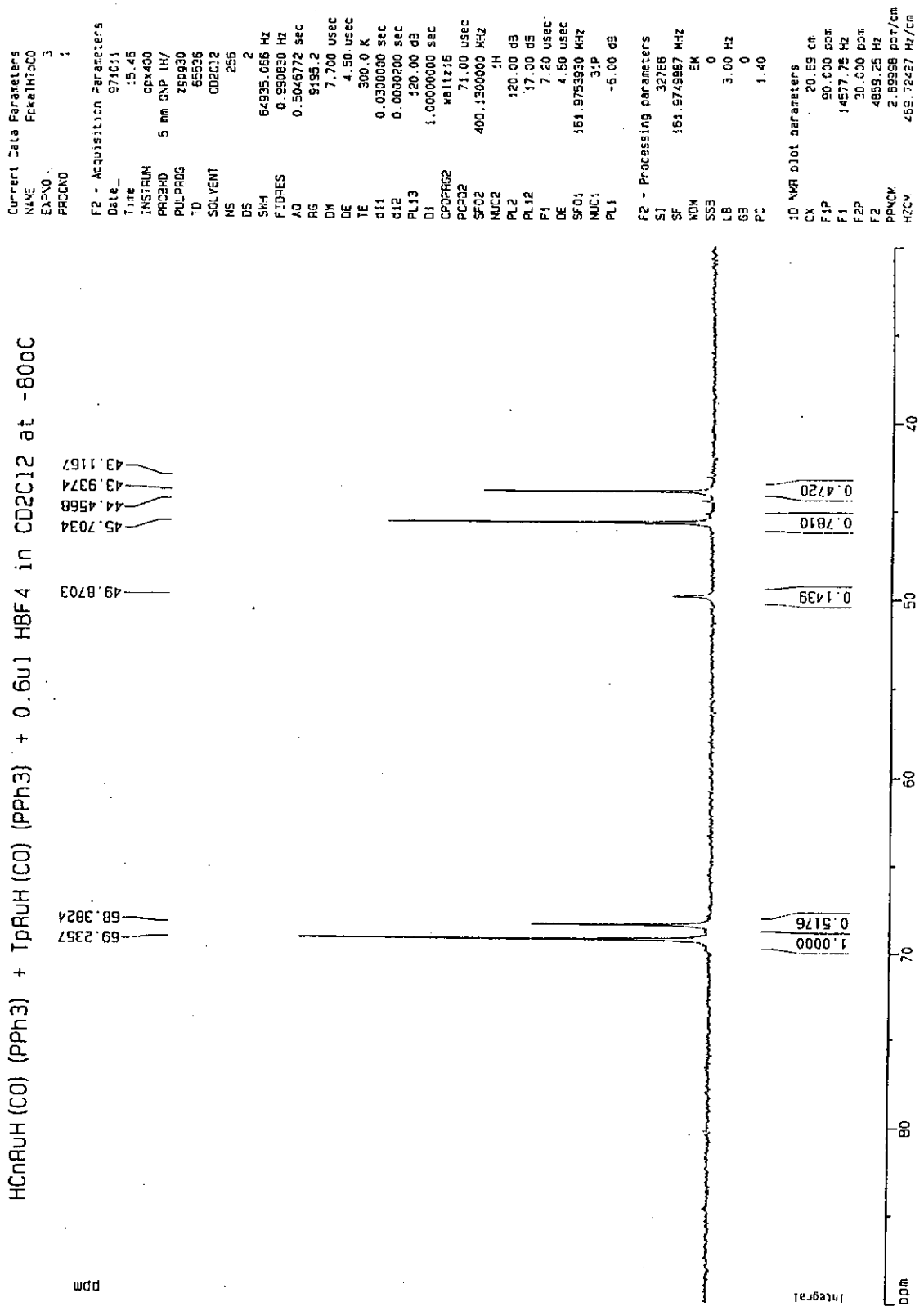


Figure 2.44. The $^{31}P\{^{1}H\}$-NMR spectra of $TpRuH(CO)(PPh_3)$ (**15**) and $[^{H}CnRuH(CO)(PPh_3)_2]PF_6$ (**4**) + $HBF_4.Et_2O$ in CD_2Cl_2

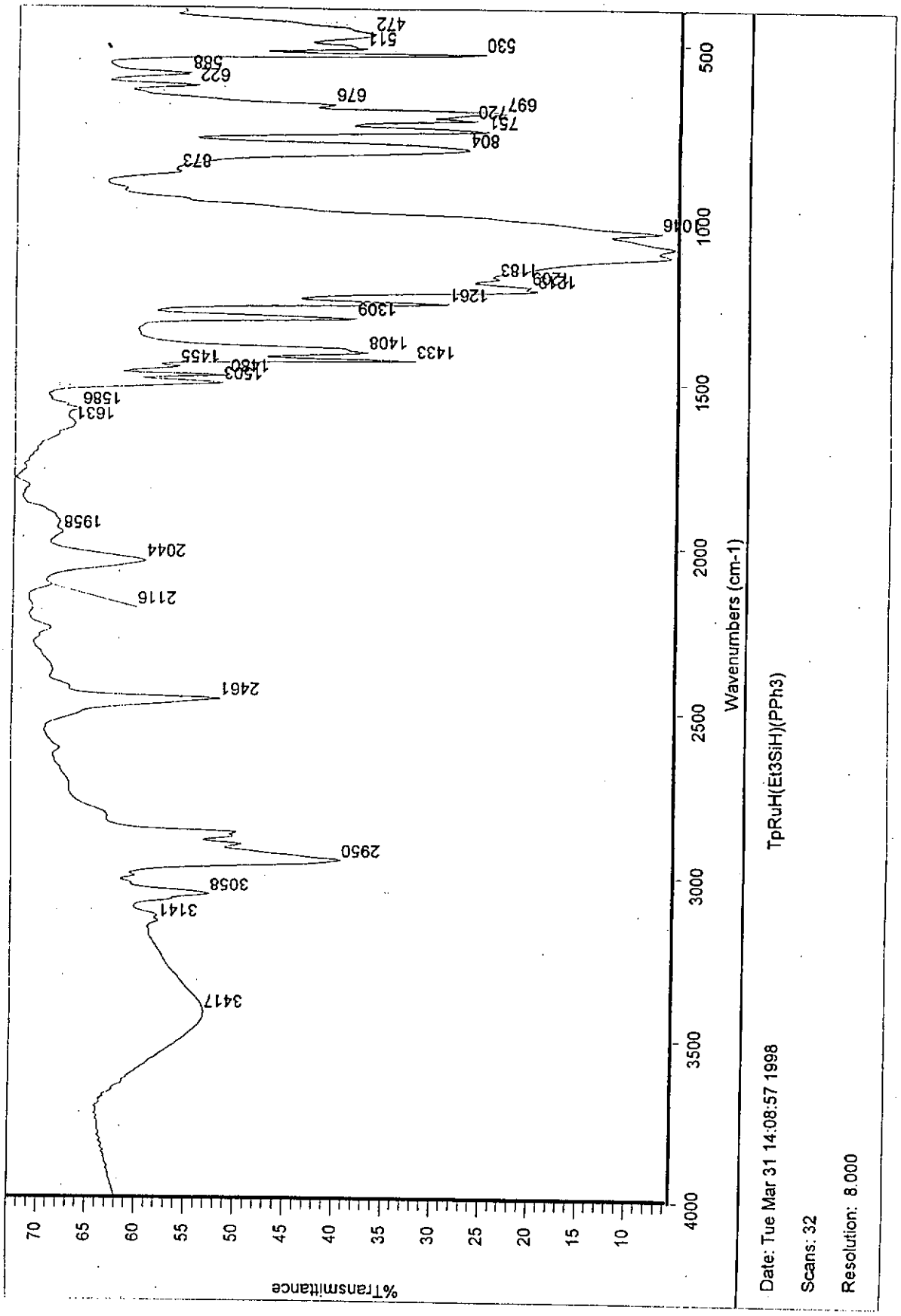


Figure 3.1. Infra-red spectrum of $TpRuH(HSiEt_3)(PPh_3)$ (**21a**) in KBr disc

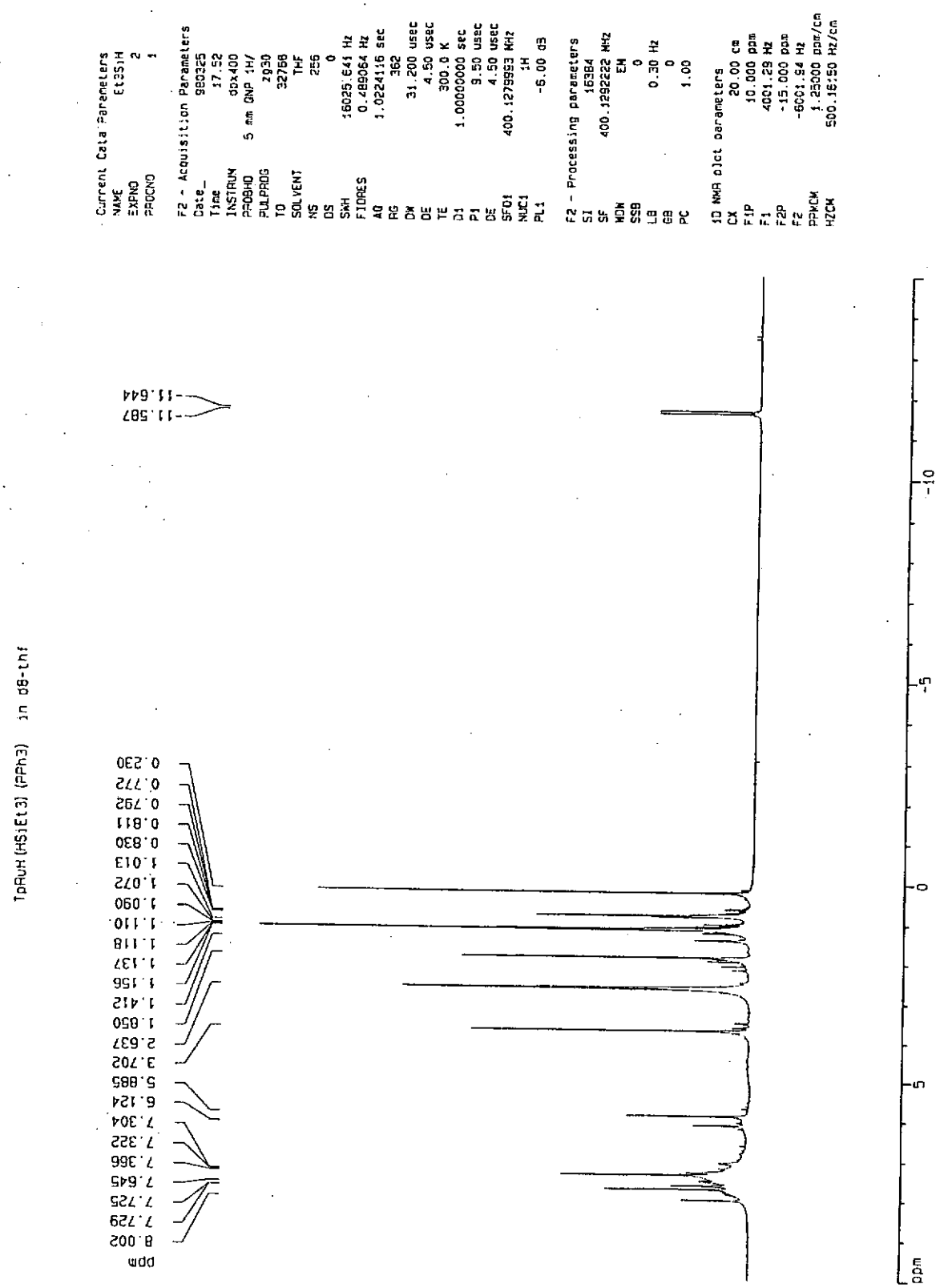


Figure 3.2(a). 400 MHz ^{1}H-NMR spectrum of TpRuH(HSiEt$_3$)(PPh$_3$) (**21a**)

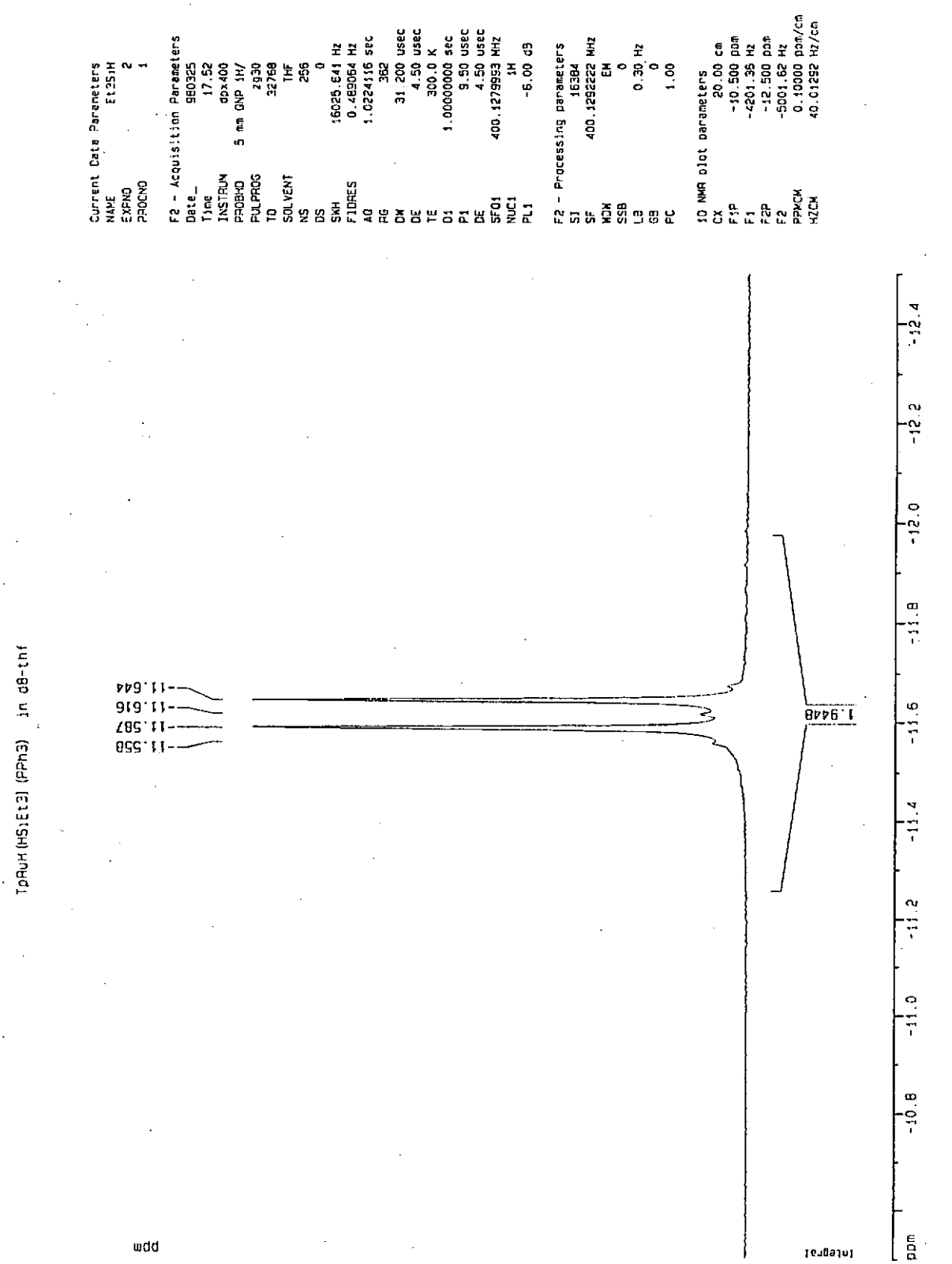


Figure 3.2(b). Expanded upfield region of Figure 3.2(a)

Figure 3.3. 161 MHz $^{31}P\{^{1}H\}$-NMR spectrum of $TpRuH(HSiEt_3)(PPh_3)$ (**21a**)

Figure 3.4. 79 MHz $^{29}Si\{^{1}H\}$-NMR spectrum of $TpRuH(HSiEt_3)(PPh_3)$ (**21a**)

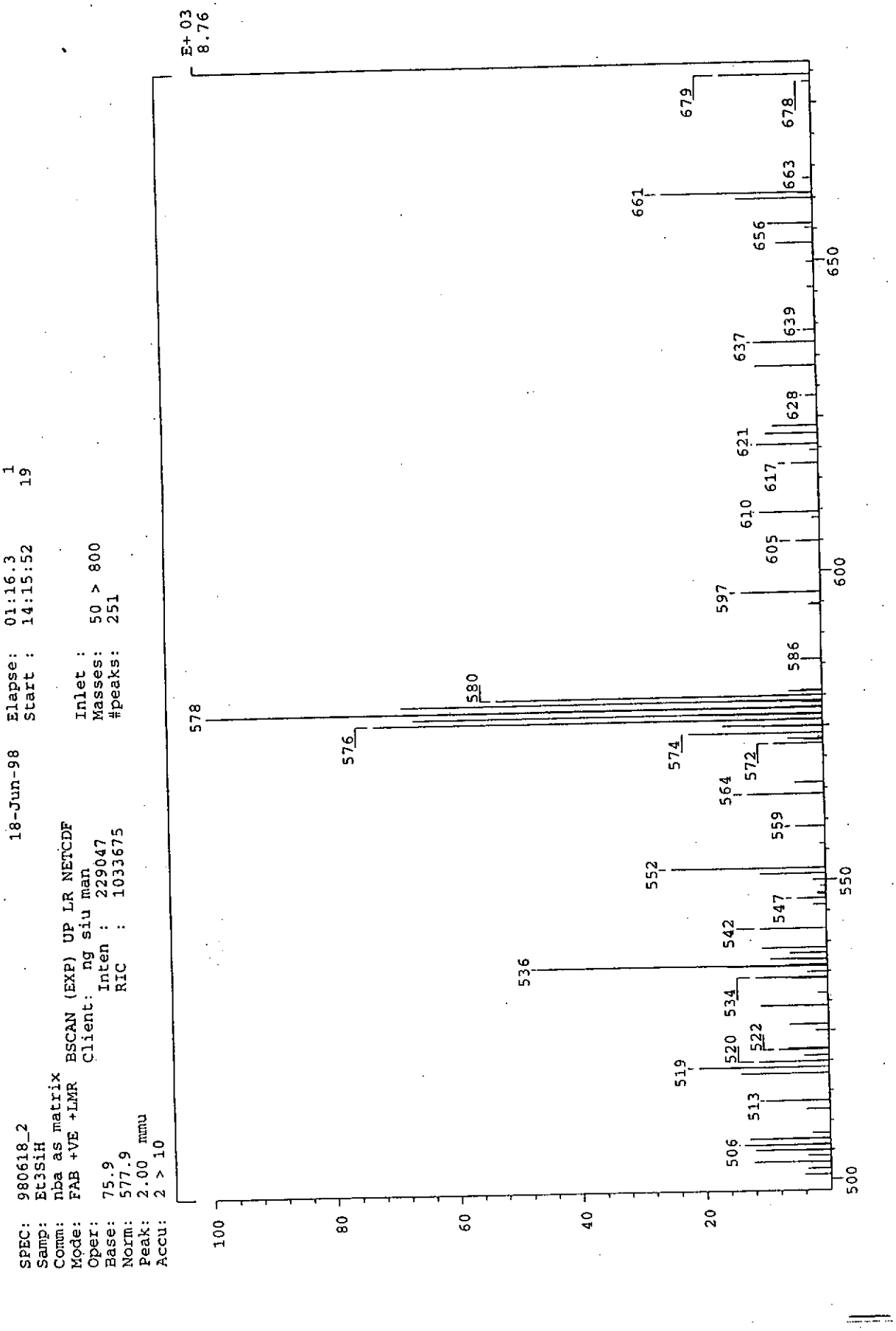


Figure 3.5. FAB mass spectrum of $TpRuH(HSiEt_3)(PPh_3)$ (**21a**)

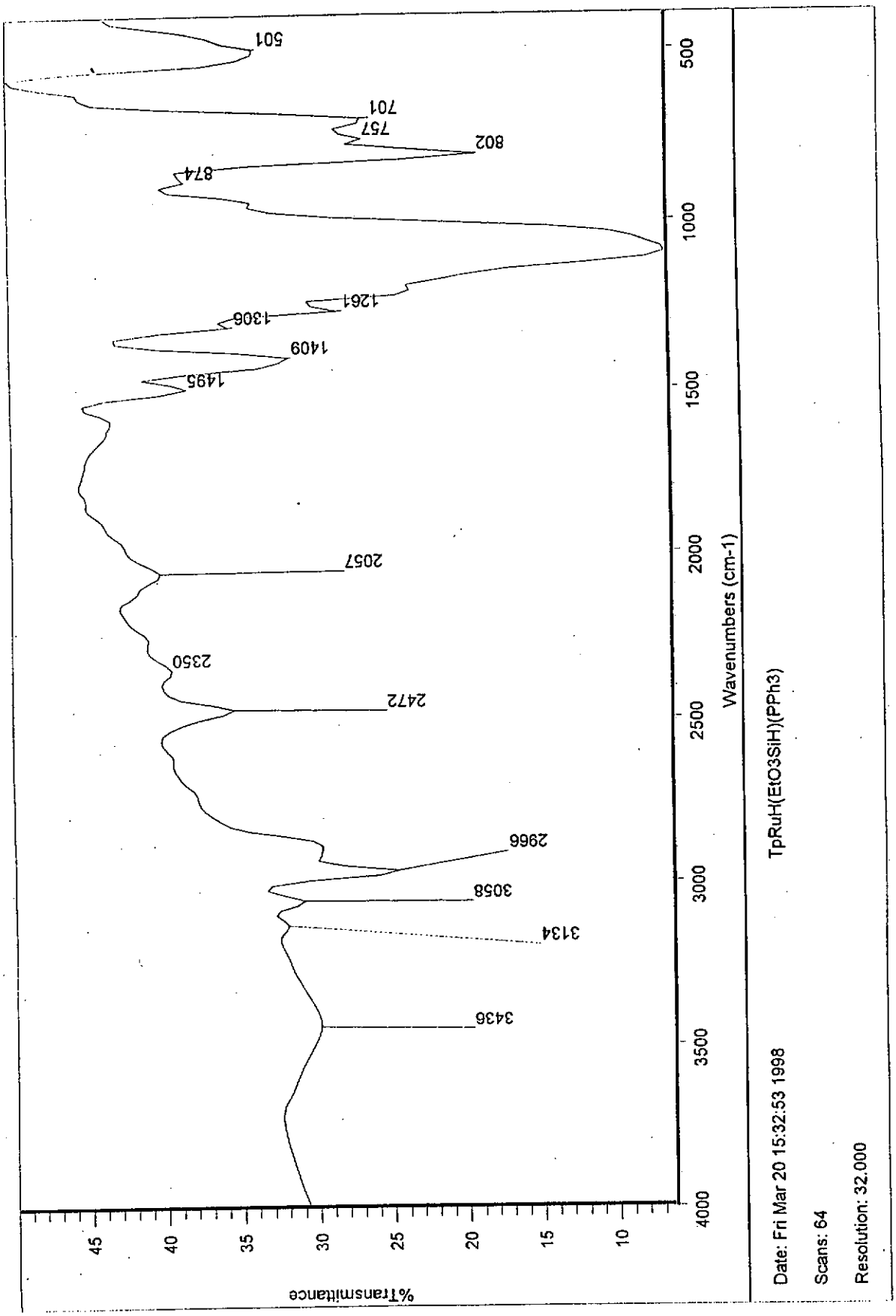


Figure 3.6. Infra-red spectrum of $TpRuH(HSi(EtO)_3)(PPh_3)$ (**21b**) in KBr disc

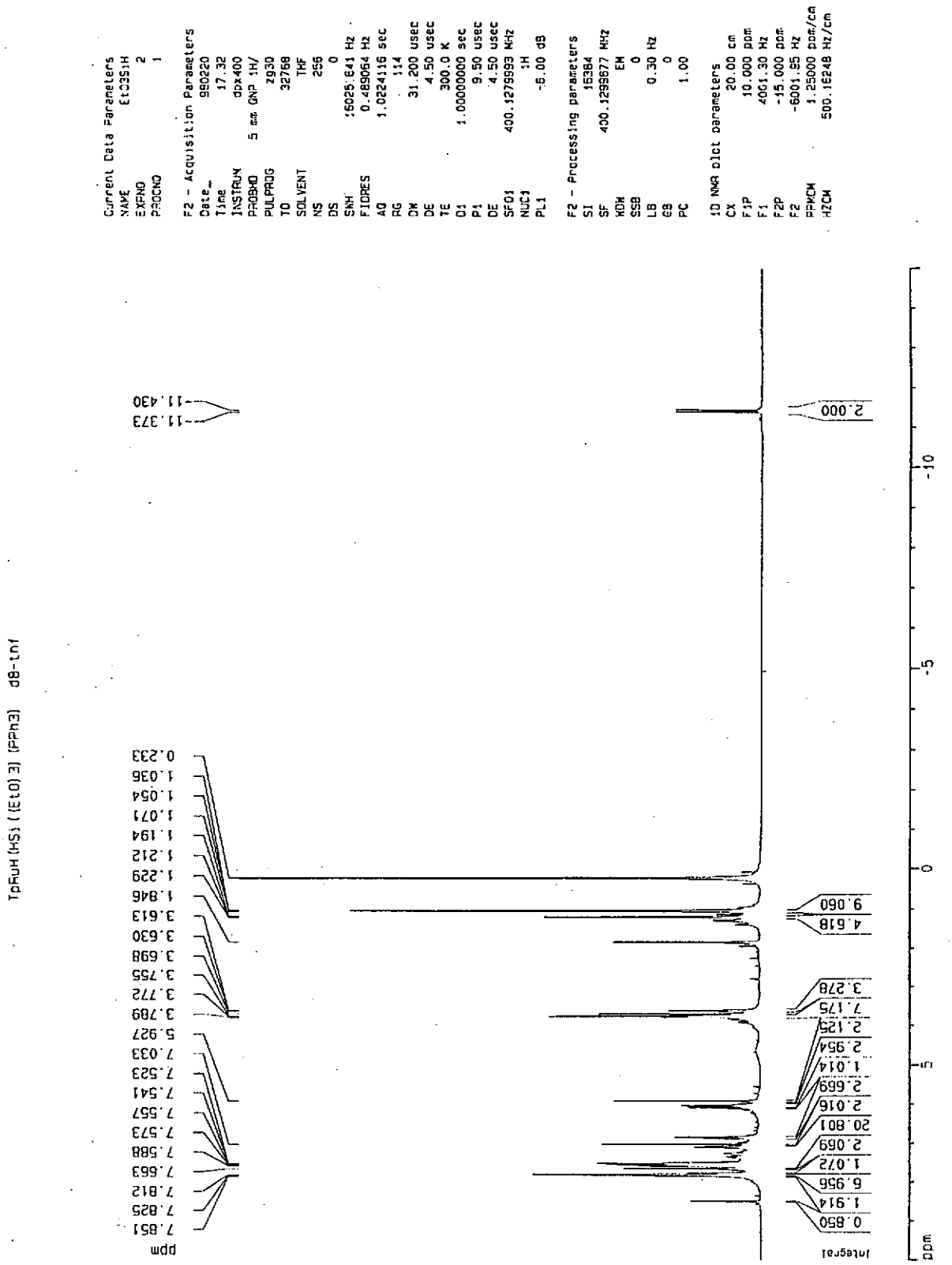


Figure 3.7(a). 400 MHz ^{1}H-NMR spectrum of TpRuH(HSi(EtO)$_3$)(PPh$_3$) (**21b**)

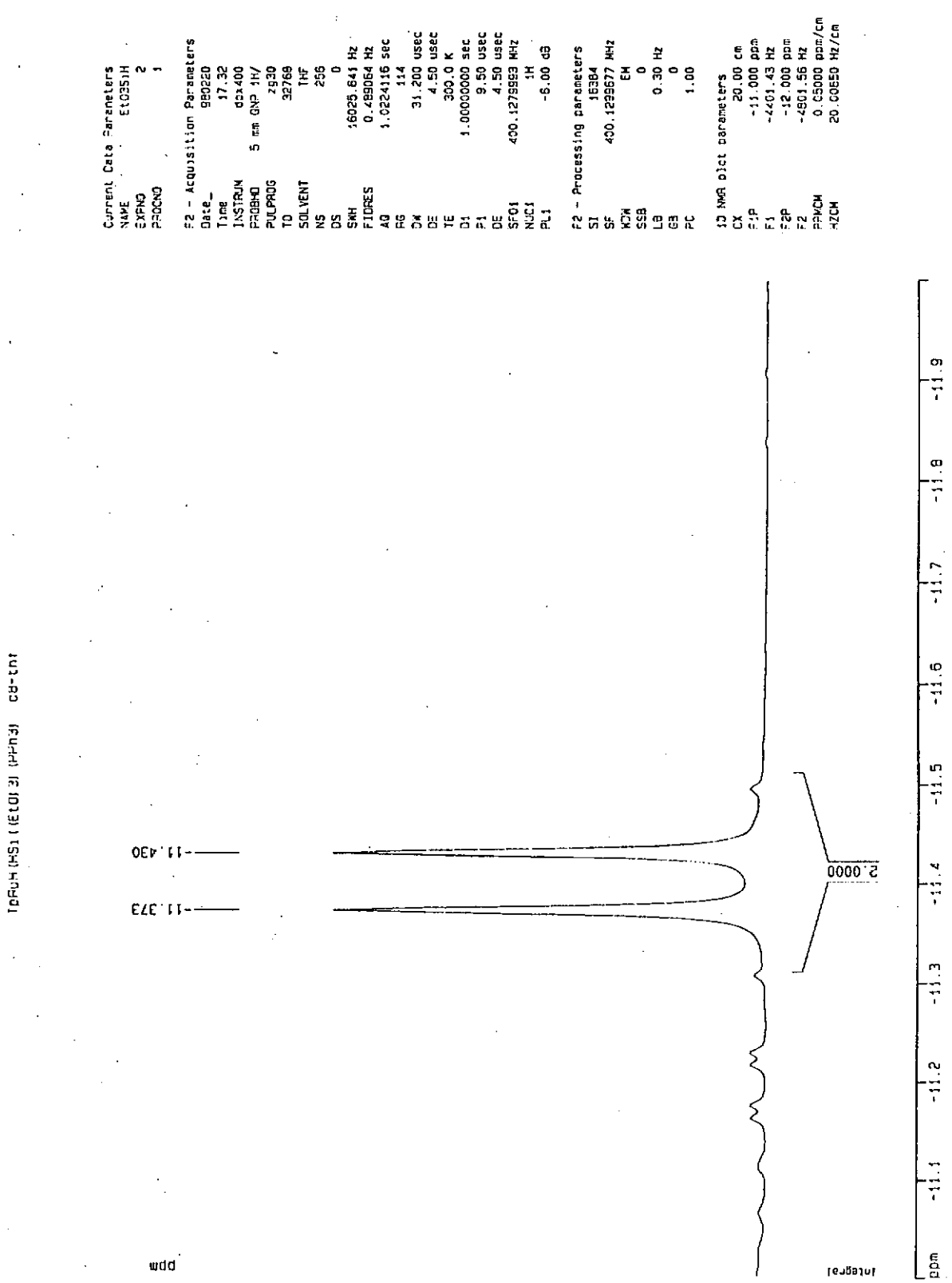


Figure 3.7(b). Expanded upfield region of Figure 3.7(a)

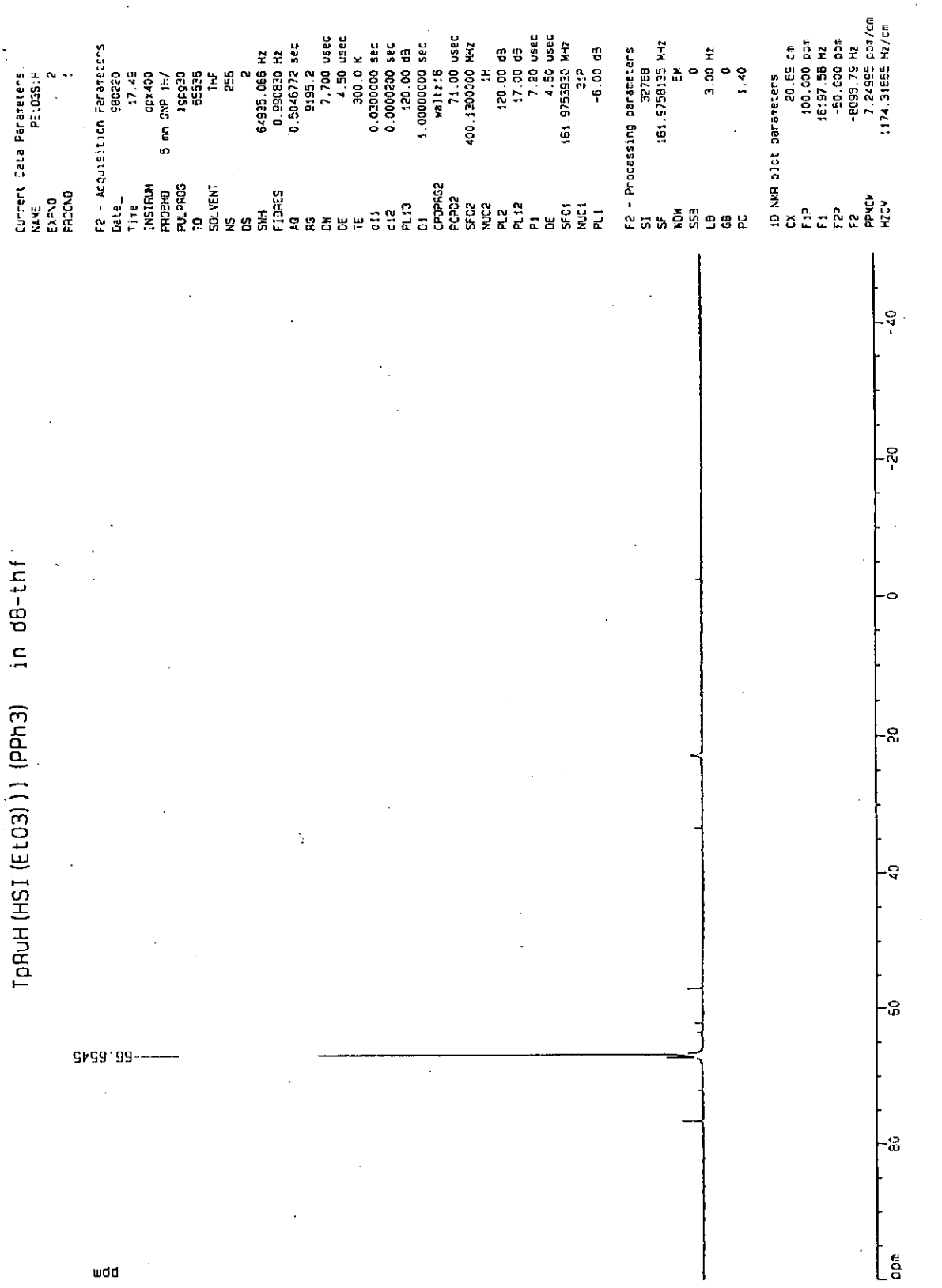


Figure 3.8. 161 MHz $^{31}P\{^{1}H\}$-NMR spectrum of $TpRuH(HSi(EtO)_3)(PPh_3)$ (**21b**)

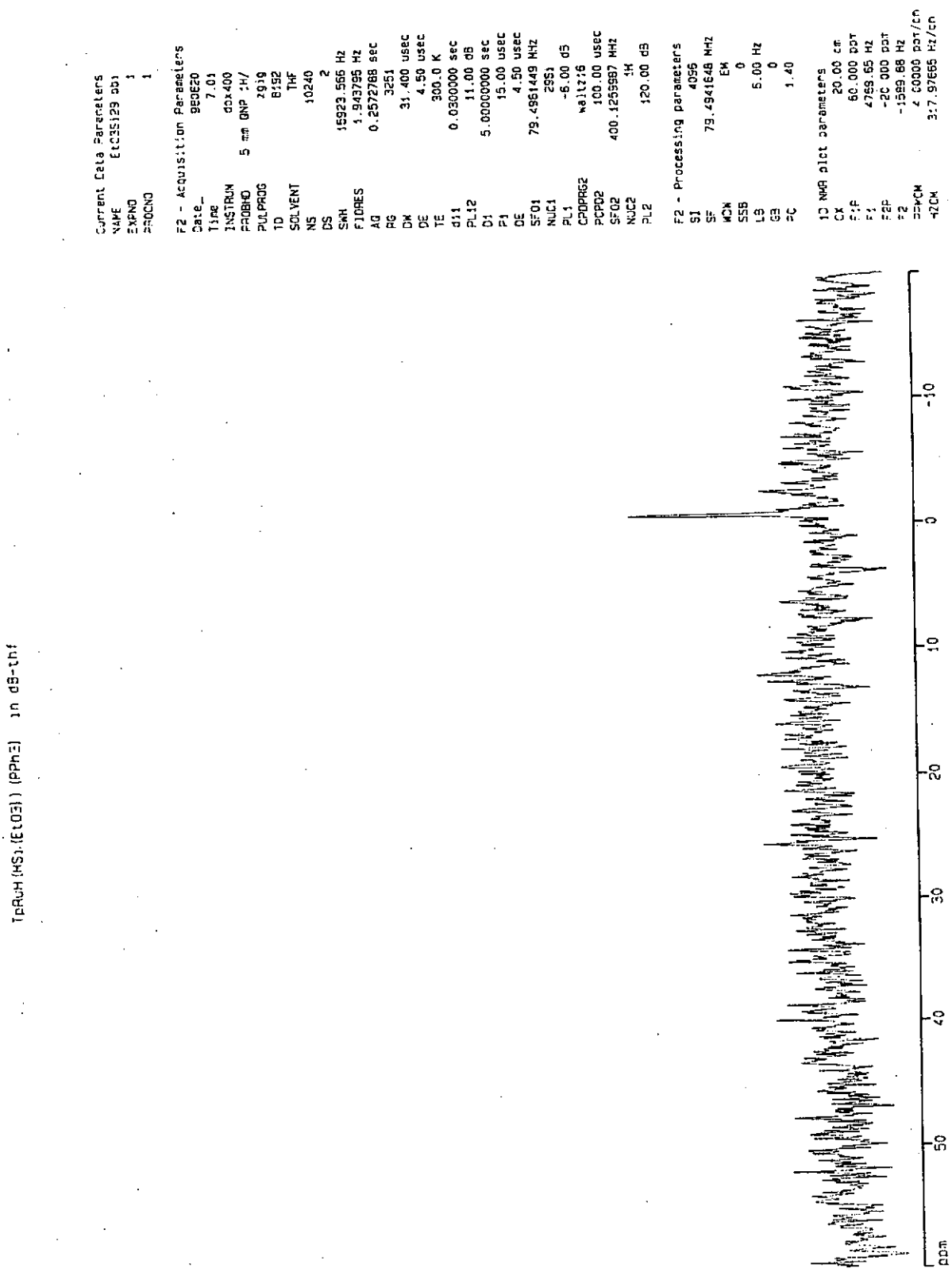


Figure 3.9. 79 MHz $^{29}Si\{^{1}H\}$-NMR spectrum of $TpRuH(HSi(EtO)_3)(PPh_3)$ (**21b**)

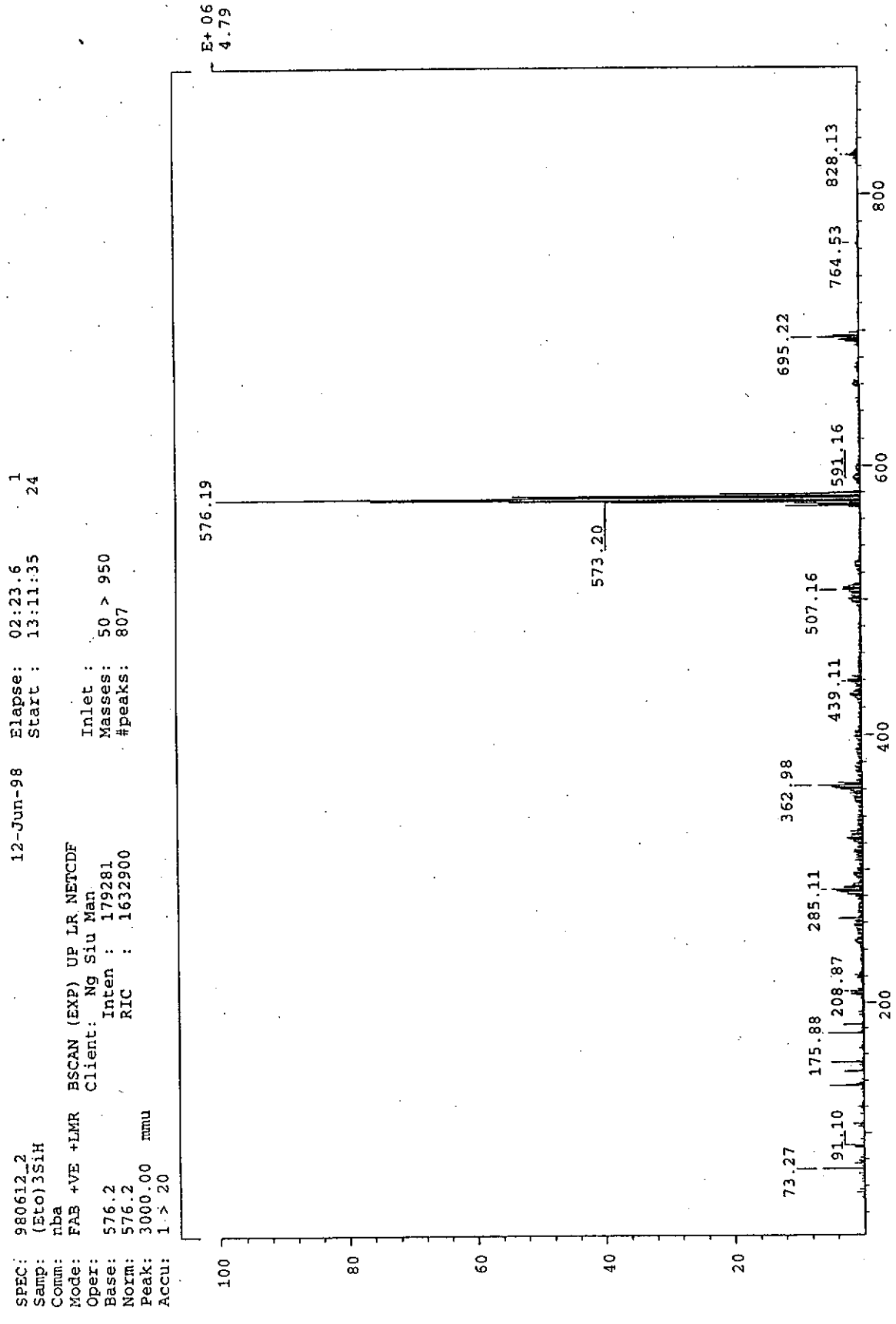


Figure 3.10. FAB mass spectrum of $TpRuH(HSi(EtO)_3)(PPh_3)$ (**21b**)

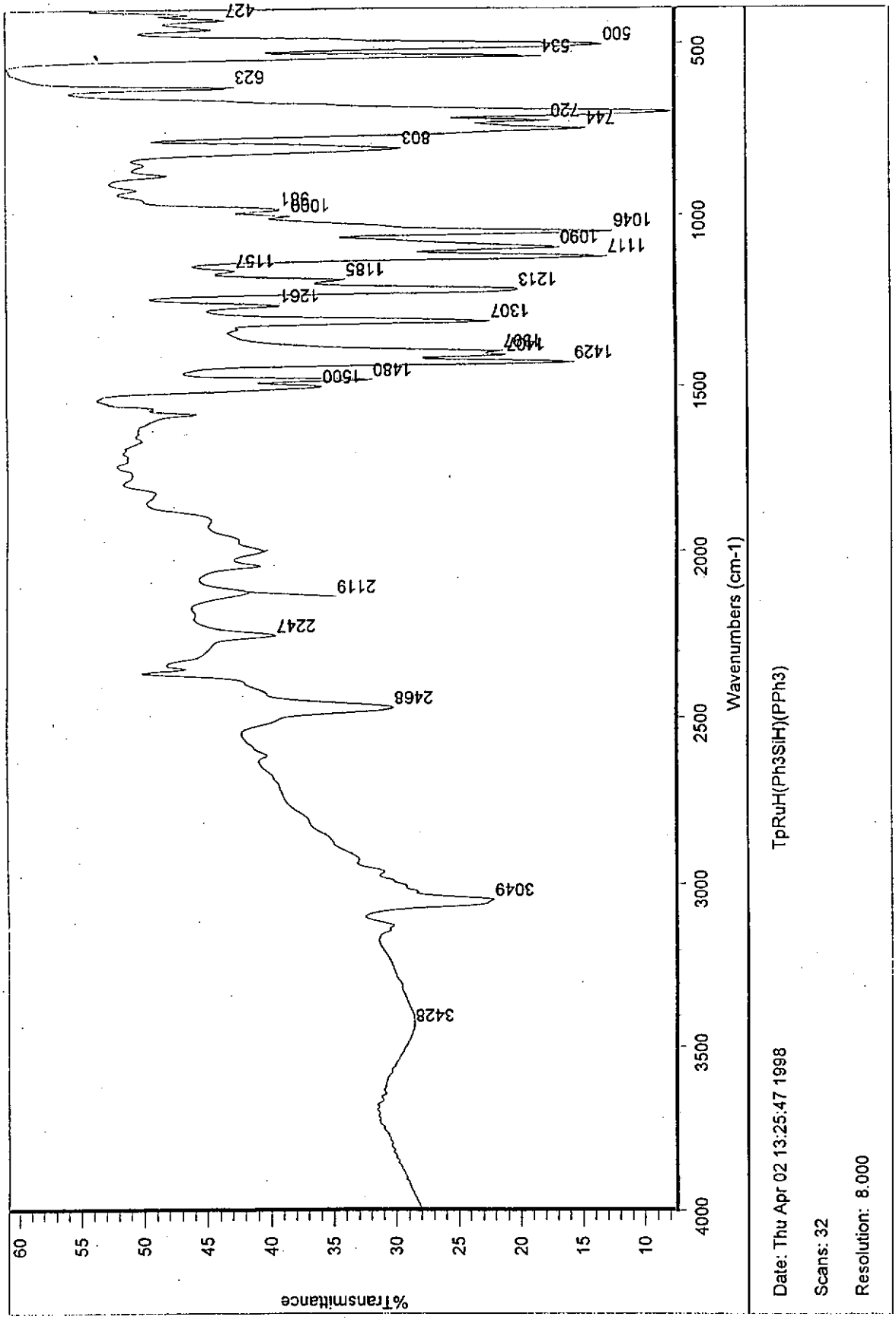


Figure 3.11. Infra-red spectrum of $TpRuH(HSiPh_3)(PPh_3)$ (**21c**) in KBr disc

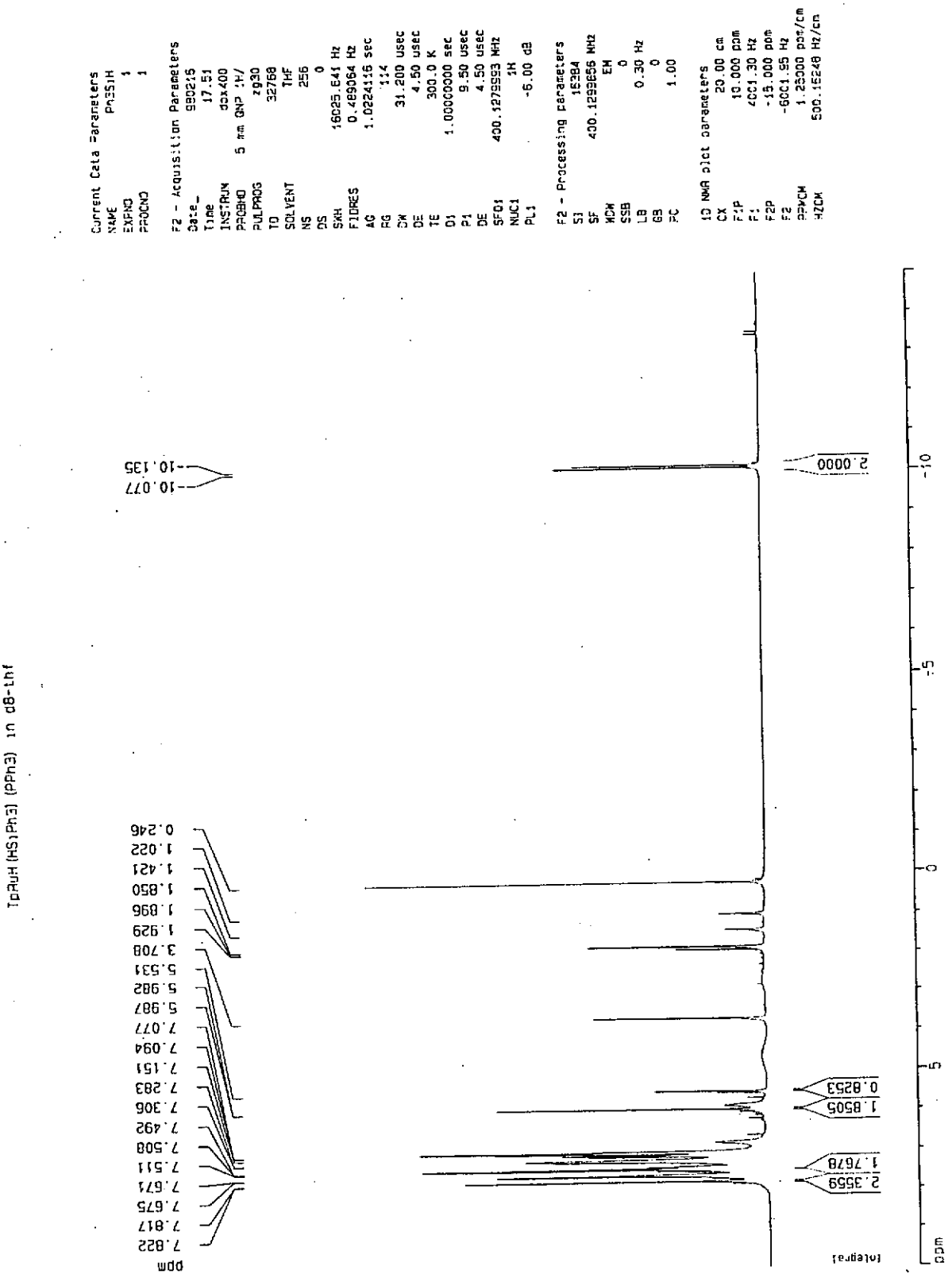


Figure 3.12(a). 400 MHz ^{1}H-NMR spectrum of TpRuH(HSiPh$_3$)(PPh$_3$) (**21c**)

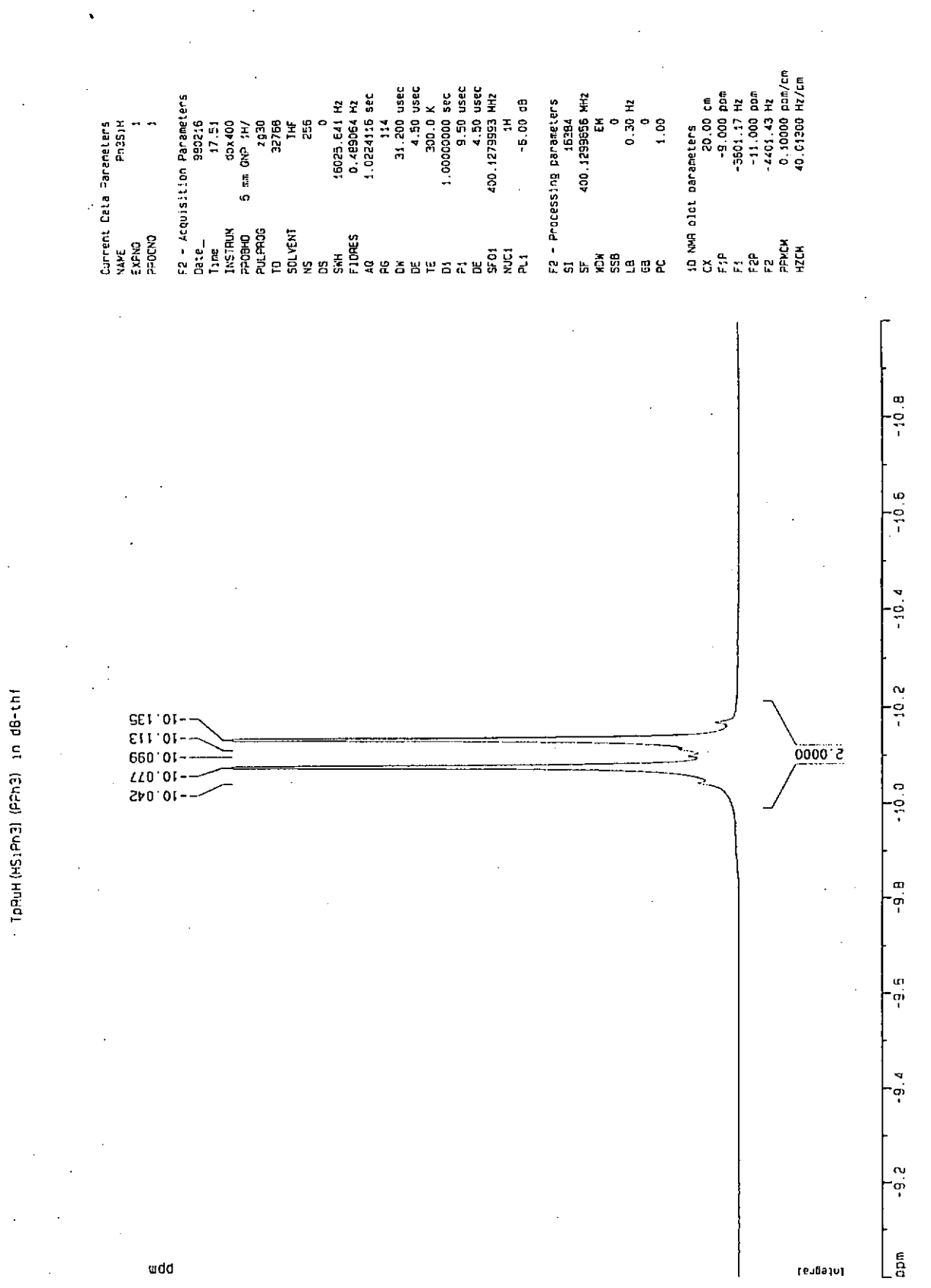


Figure 3.12(b). Expanded upfield region of Figure 3.12(a)

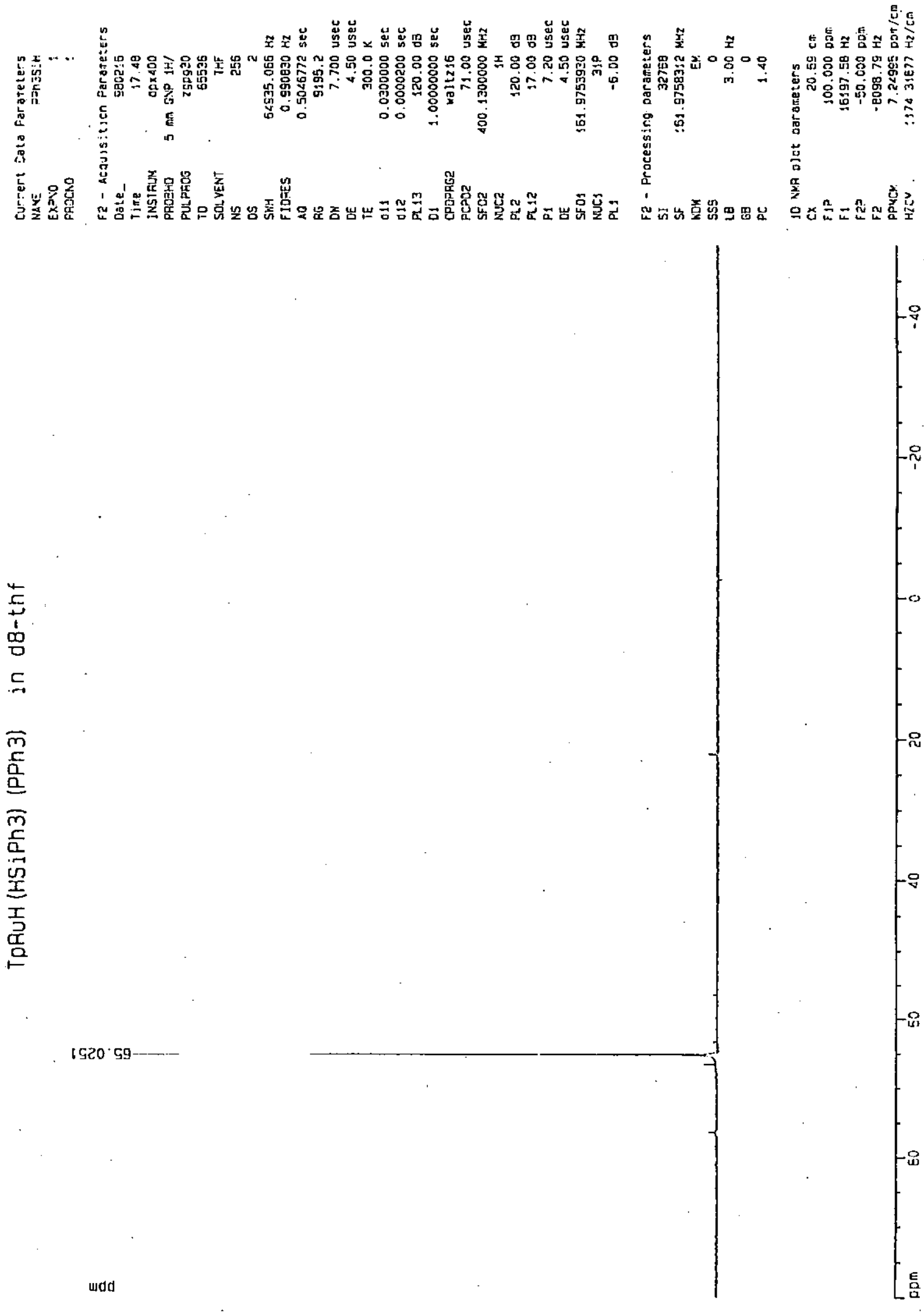


Figure 3.13. 161 MHz $^{31}P\{^{1}H\}$-NMR spectrum of $TpRuH(HSiPh_3)(PPh_3)$ (**21c**)

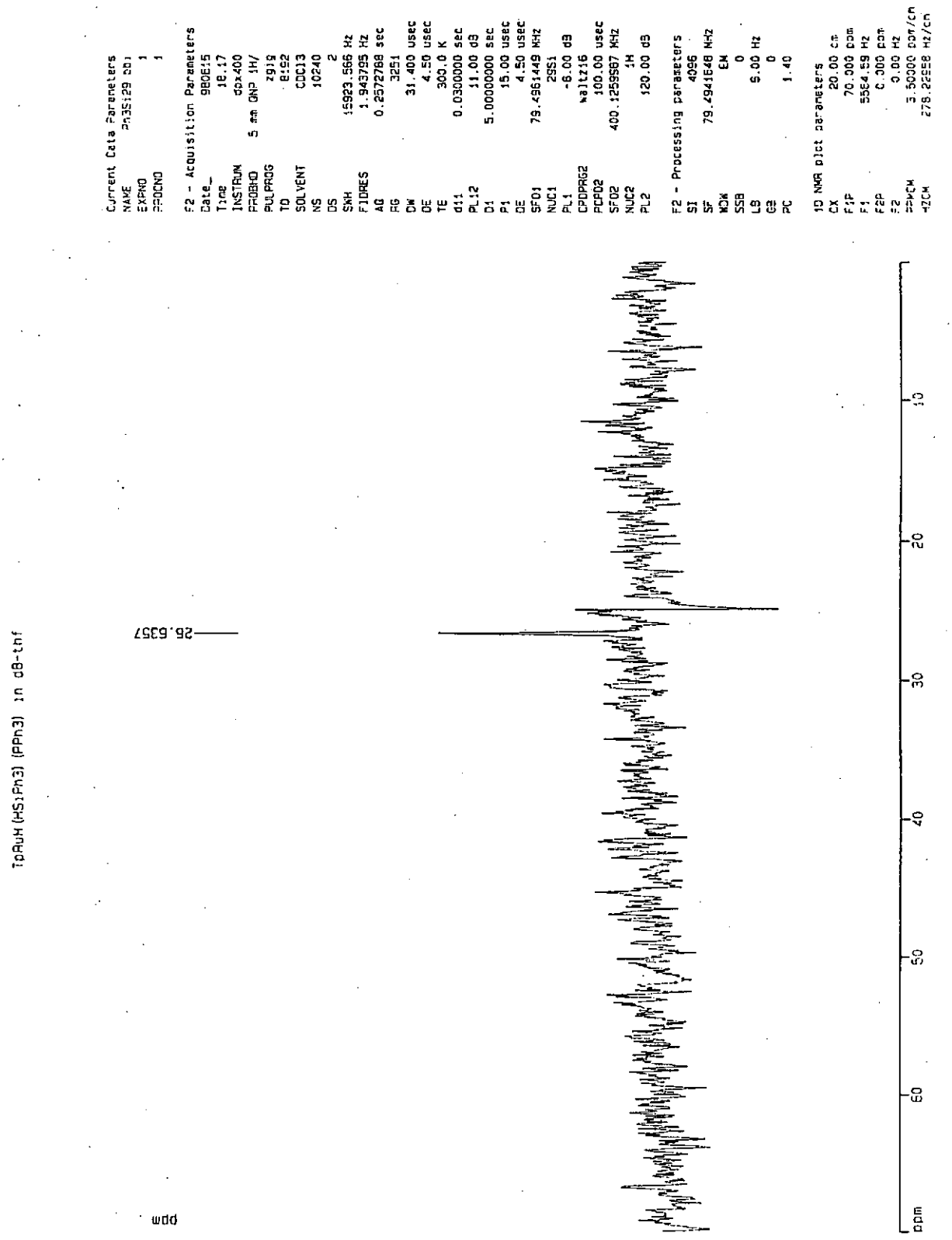


Figure 3.14. 79 MHz $^{29}Si\{^{1}H\}$-NMR spectrum of $TpRuH(HSiPh_3)(PPh_3)$ (**21c**)

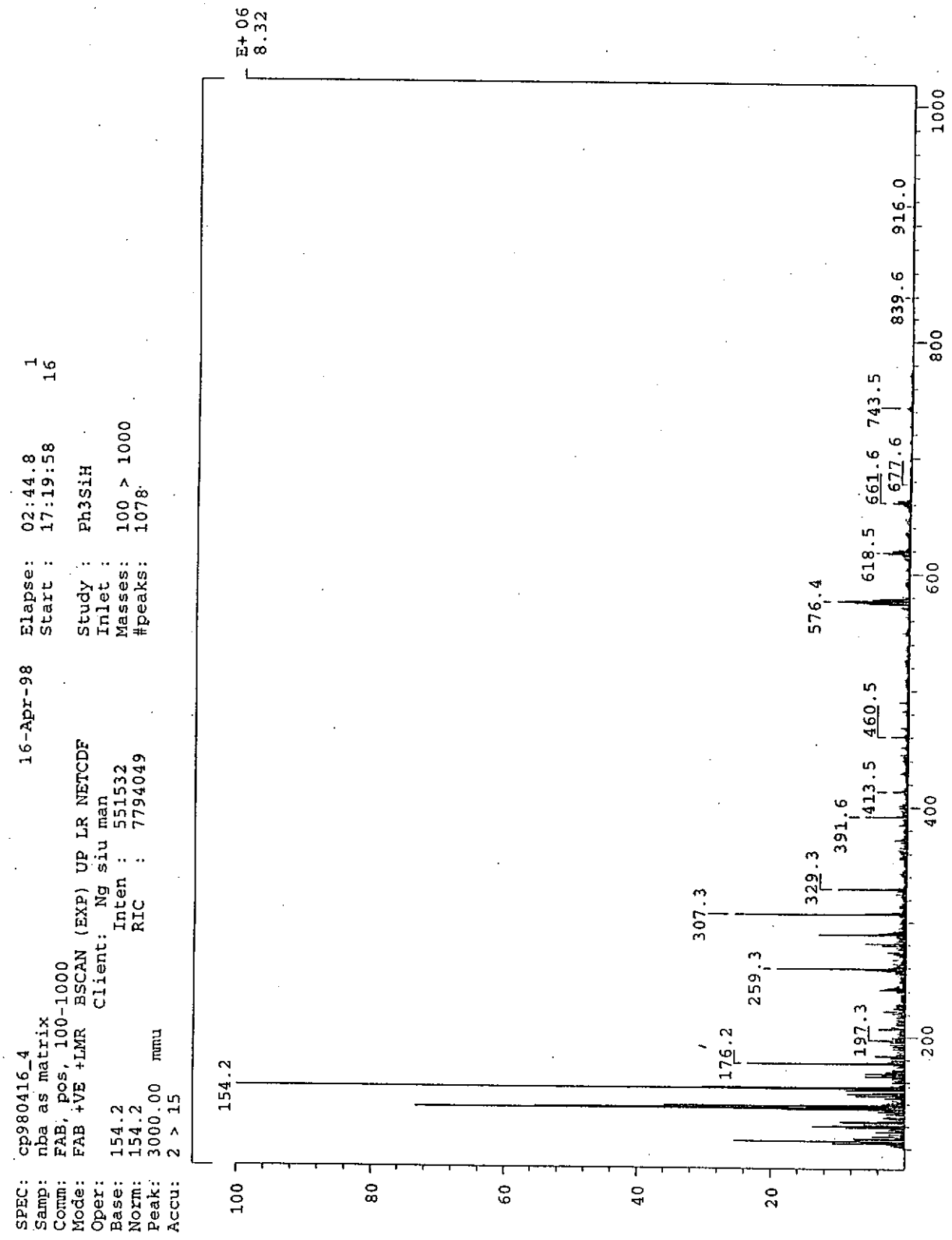


Figure 3.15. FAB mass spectrum of $TpRuH(HSiPh_3)(PPh_3)$ (**21c**)

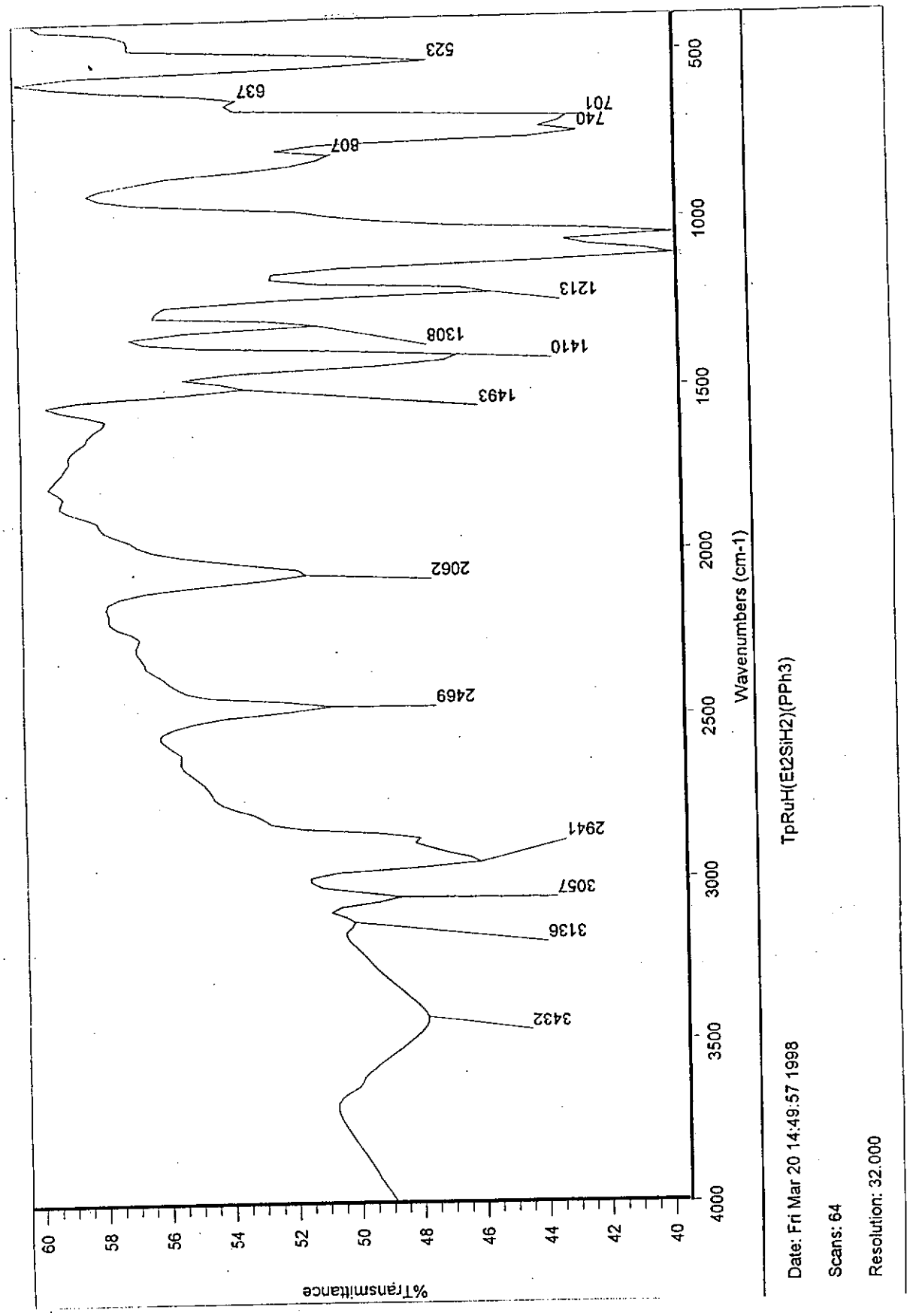


Figure 3.16. Infra-red spectrum of $TpRuH(H_2SiEt_2)(PPh_3)$ (**21d**) in KBr disc

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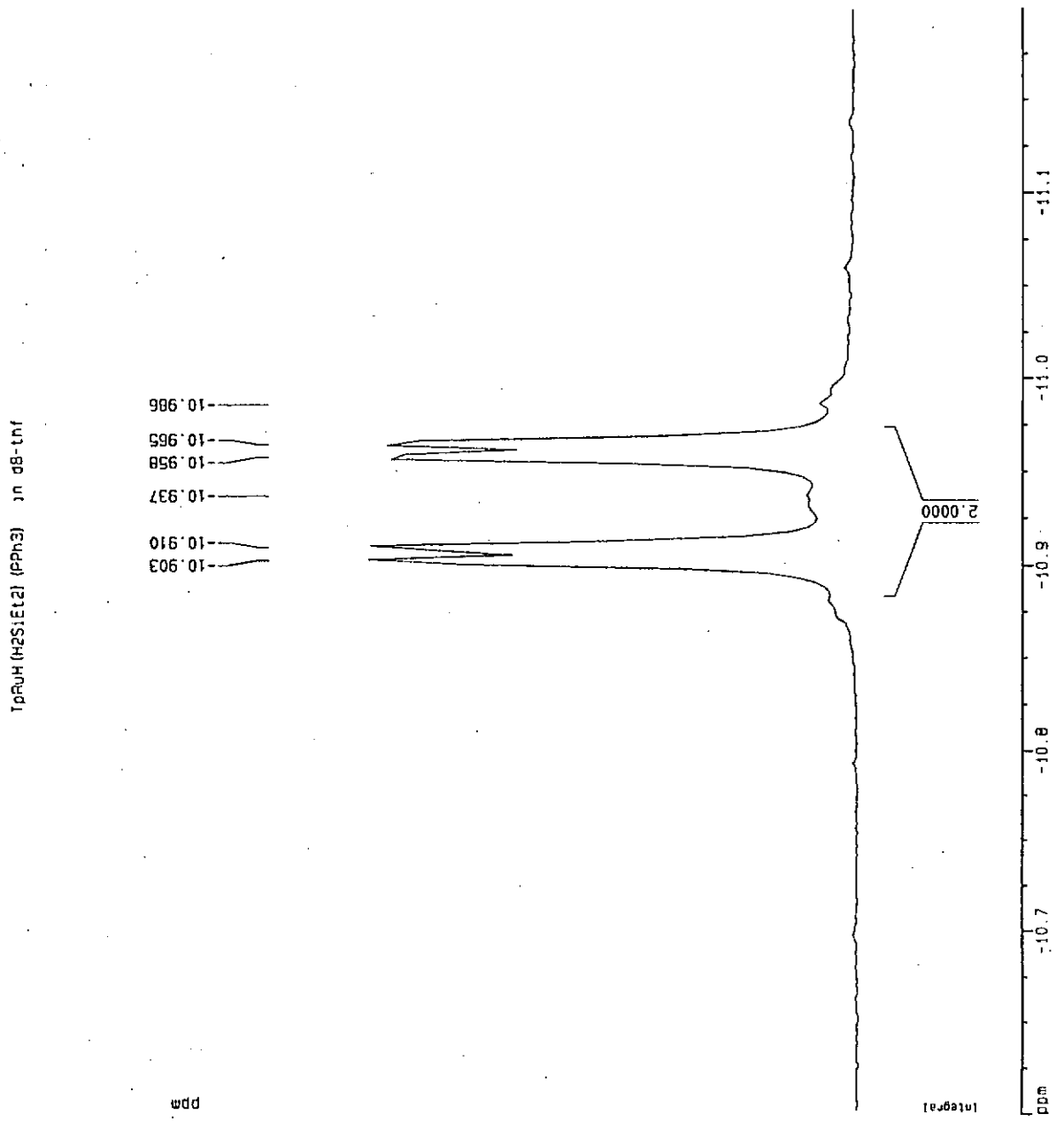

Figure 3.17(b). Expanded upfield region of Figure 3.17(a)

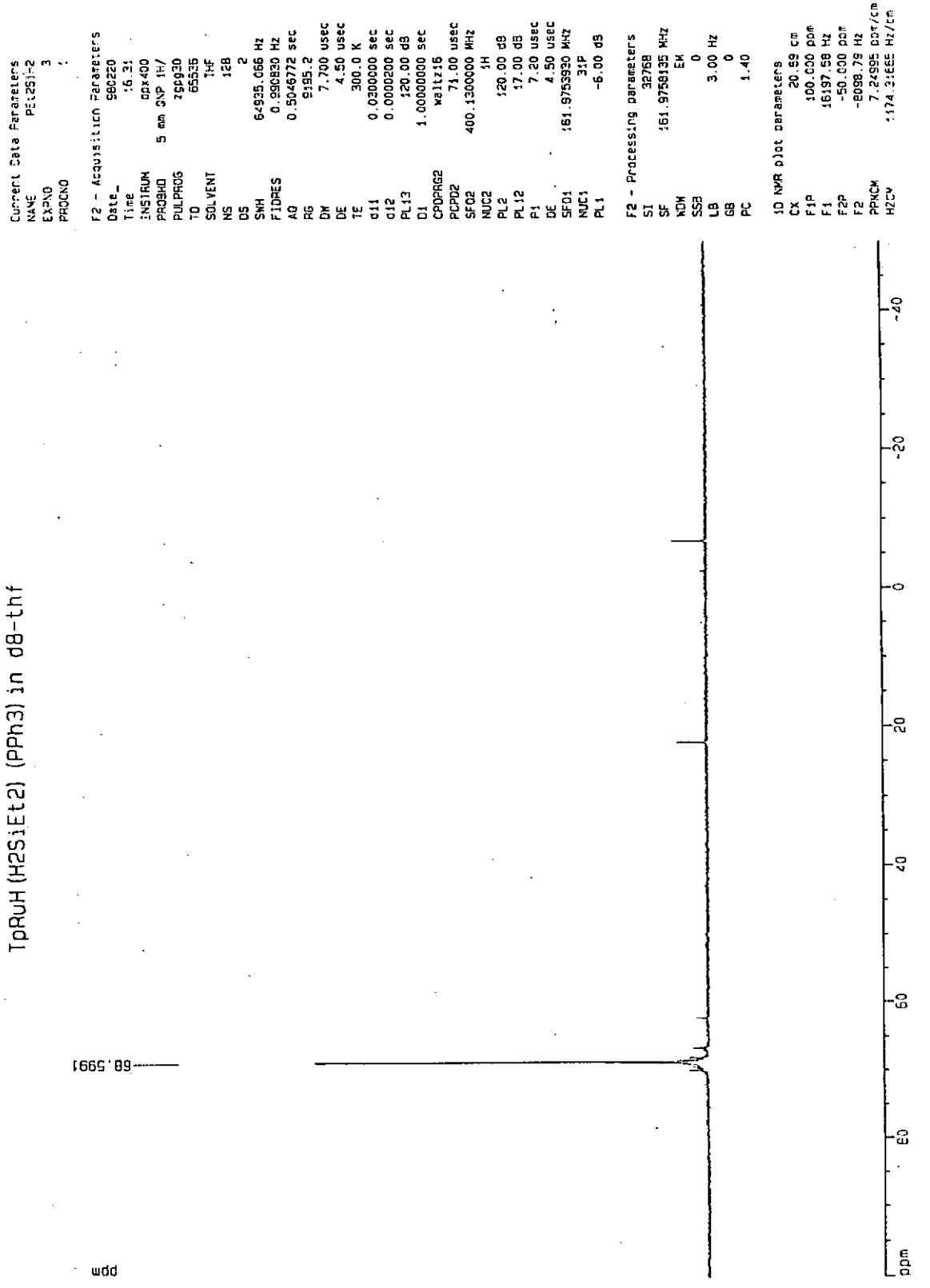

Figure 3.18. 161 MHz $^{31}P\{^{1}H\}$-NMR spectrum of $TpRuH(H_2SiEt_2)(PPh_3)$ (**21d**)

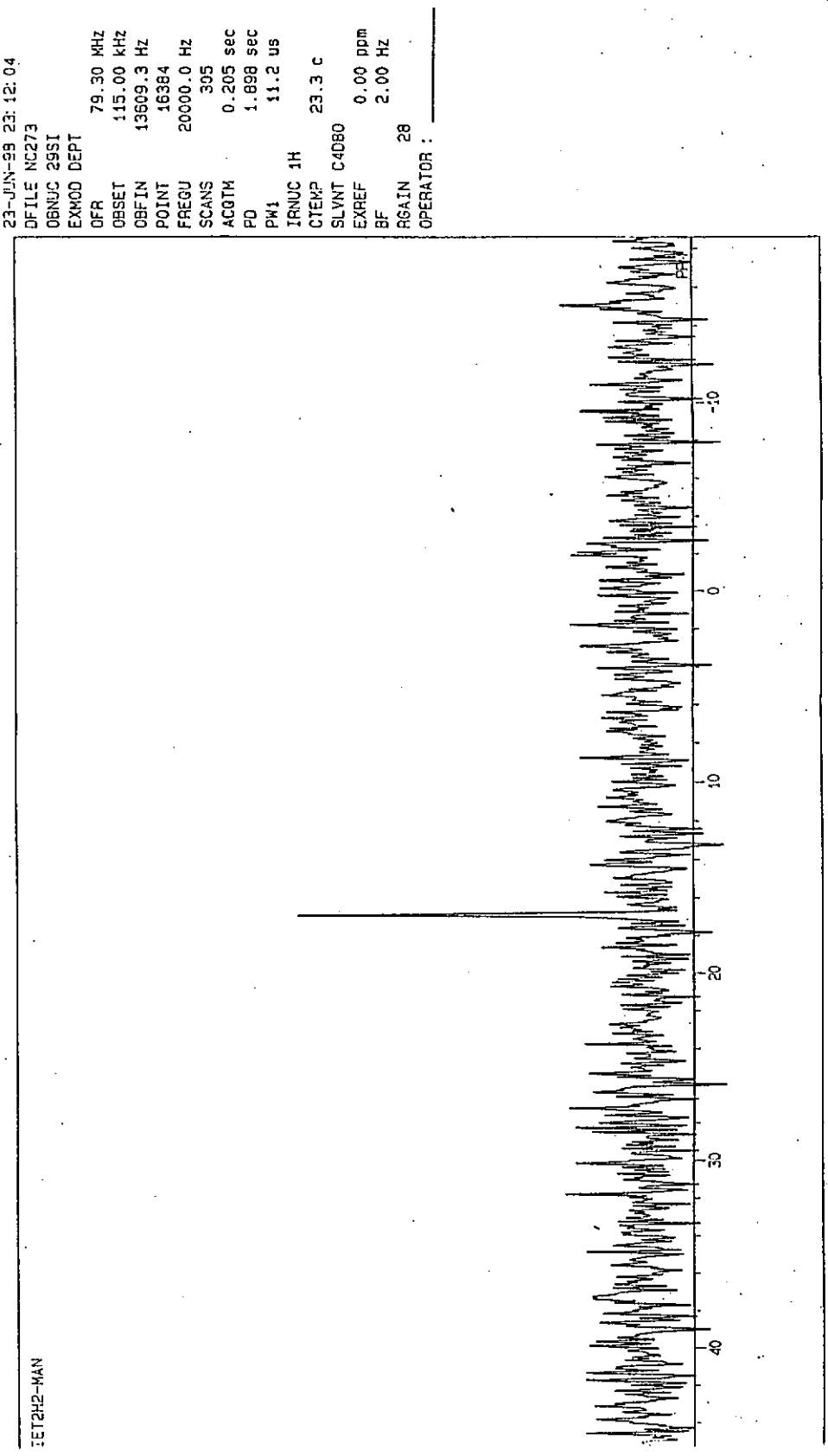

Figure 3.19. 79 MHz $^{29}Si\{^{1}H\}$-NMR spectrum of $TpRuH(H_2SiEt_2)(PPh_3)$ (**21d**)

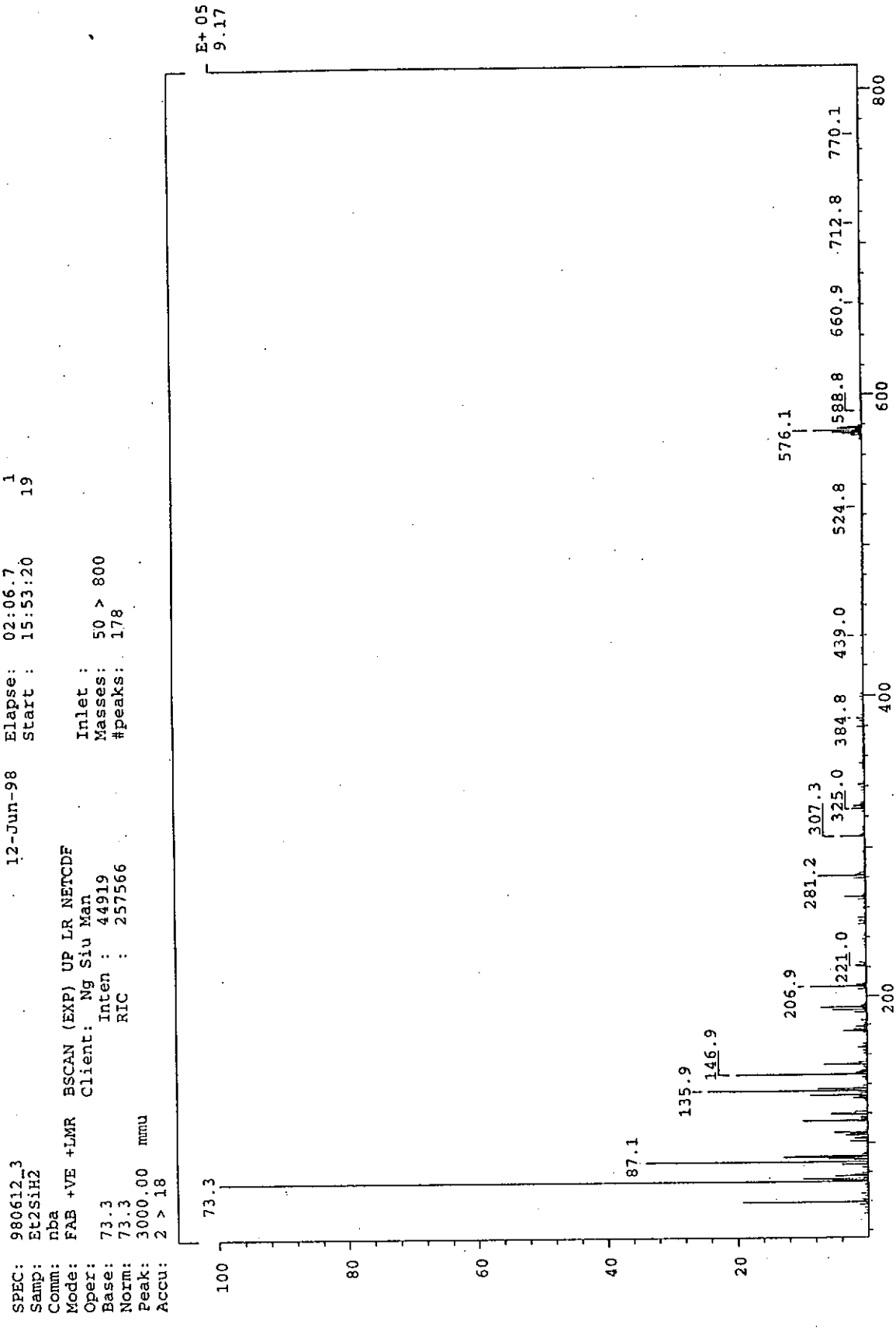

Figure 3.20. FAB mass spectrum of $TpRuH(H_2SiEt_2)(PPh_3)$ (**21d**)

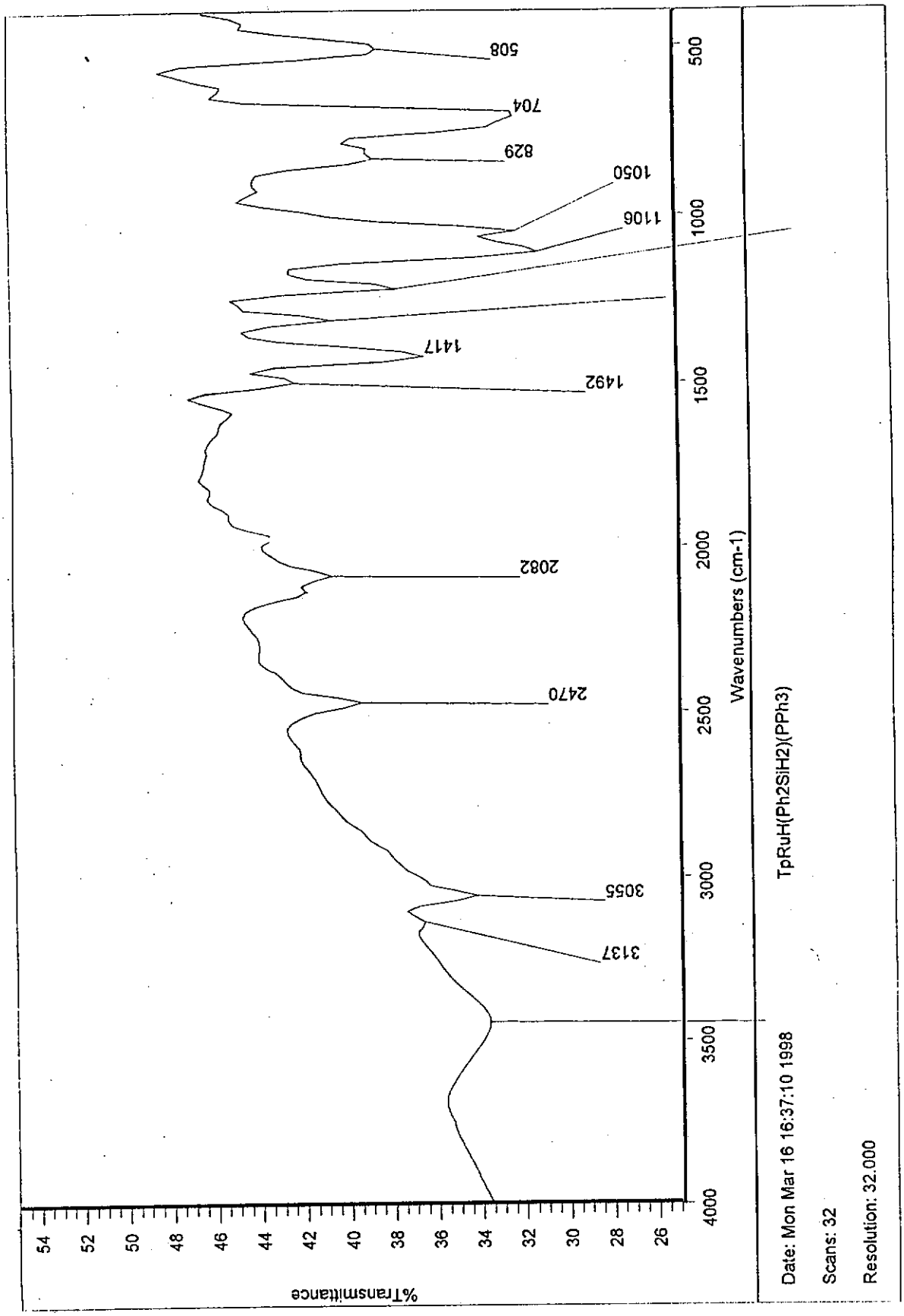

Figure 3.21. Infra-red spectrum of $TpRuH(H_2SiPh_2)(PPh_3)$ (**21e**) in KBr disc

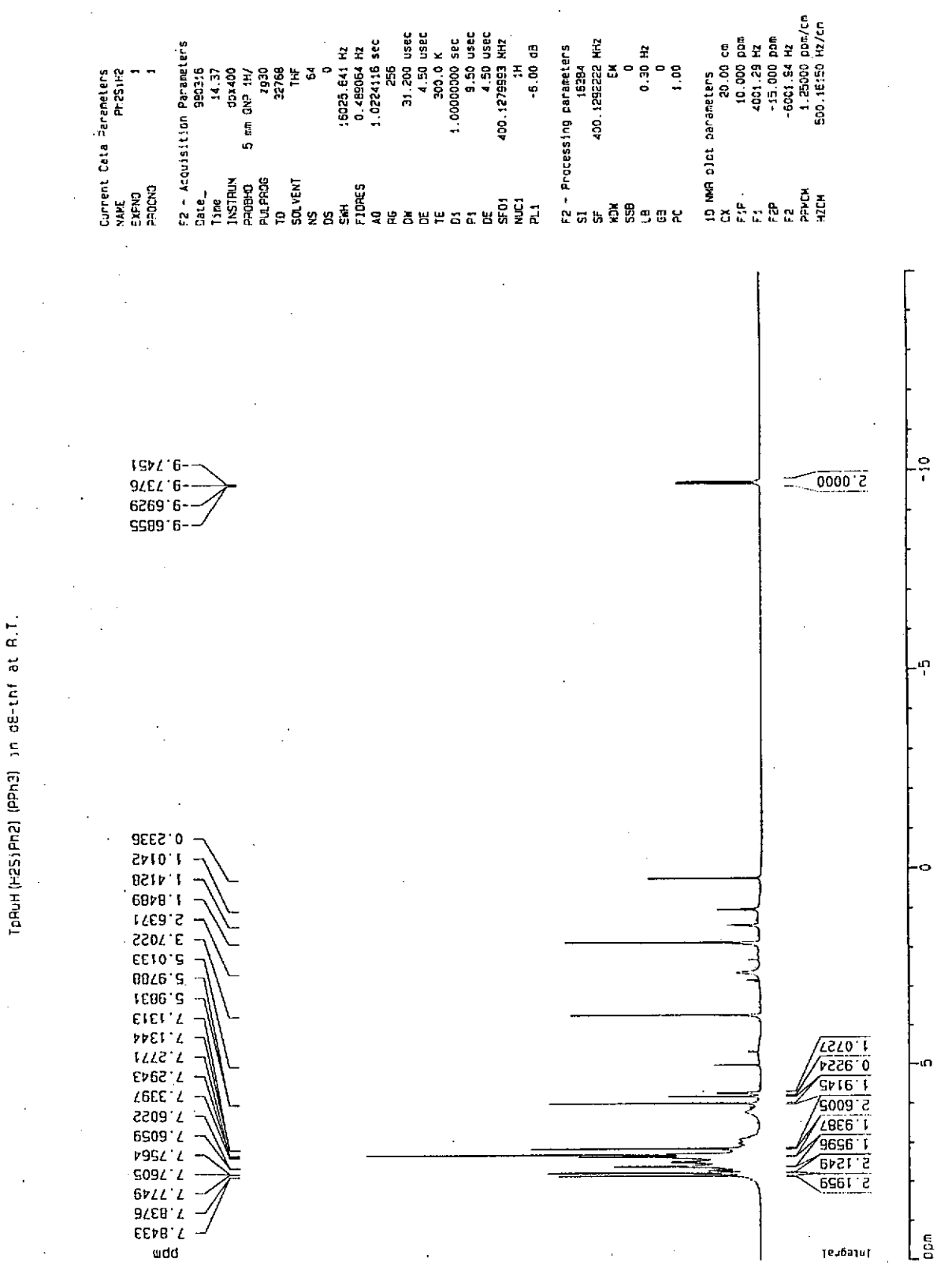

Figure 3.22(a). 400 MHz ^{1}H-NMR spectrum of TpRuH(H_2SiPh_2)(PPh_3) (**21e**)

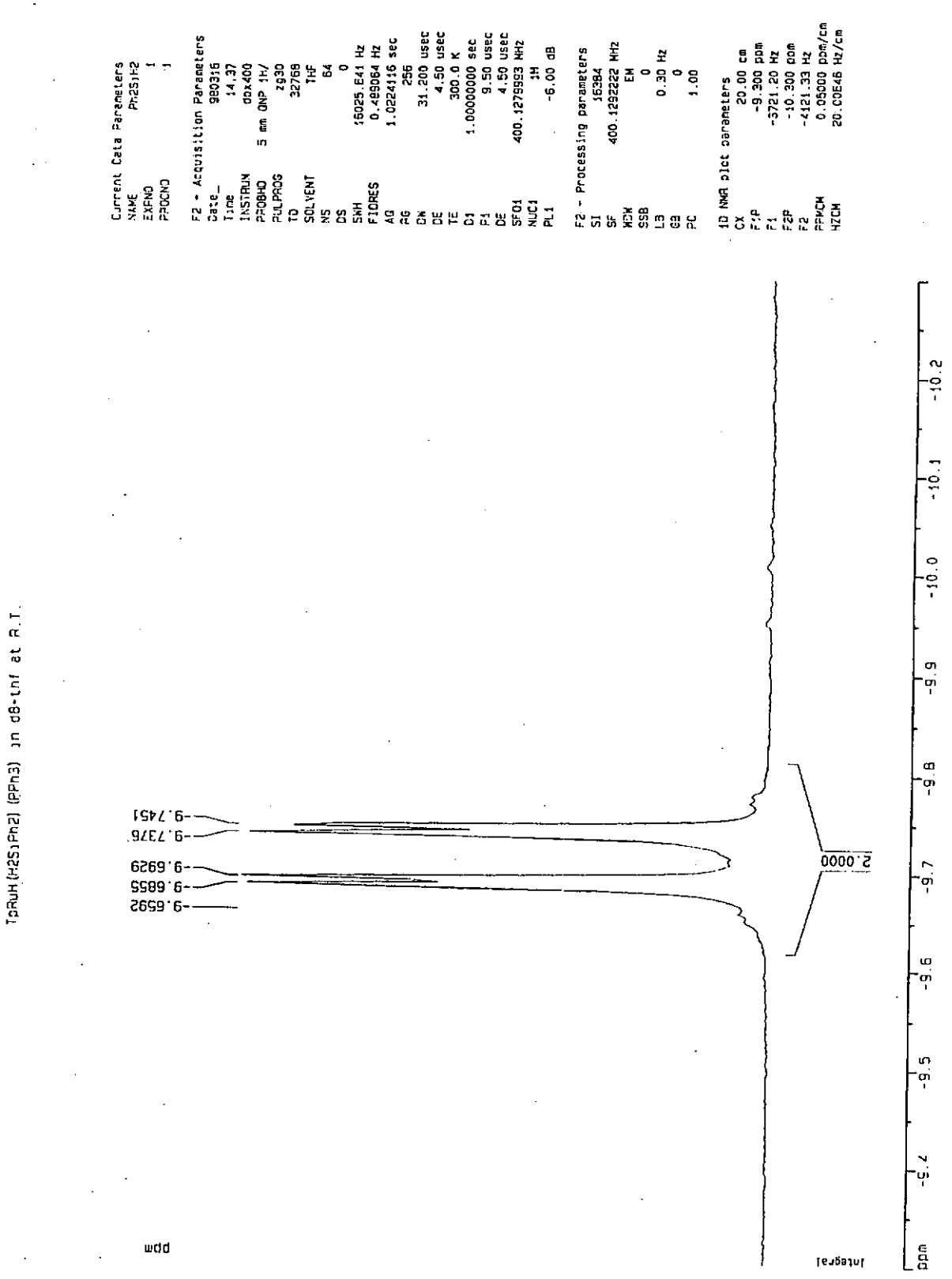

Figure 3.22(b). Expanded upfield region of Figure 3.22(a)

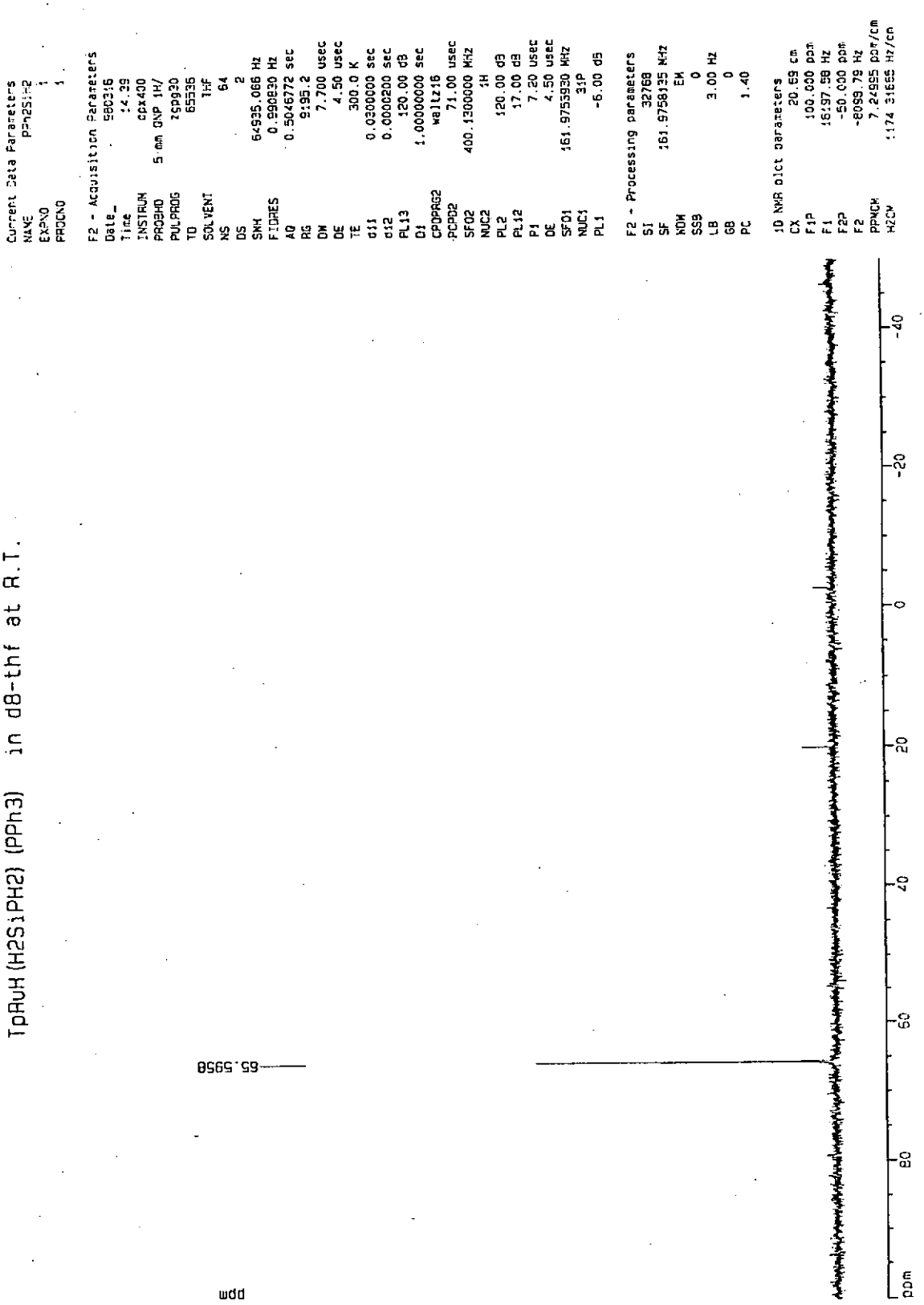

Figure 3.23. 161 MHz $^{31}P\{^{1}H\}$-NMR spectrum of $TpRuH(H_2SiPh_2)(PPh_3)$ (**21e**)

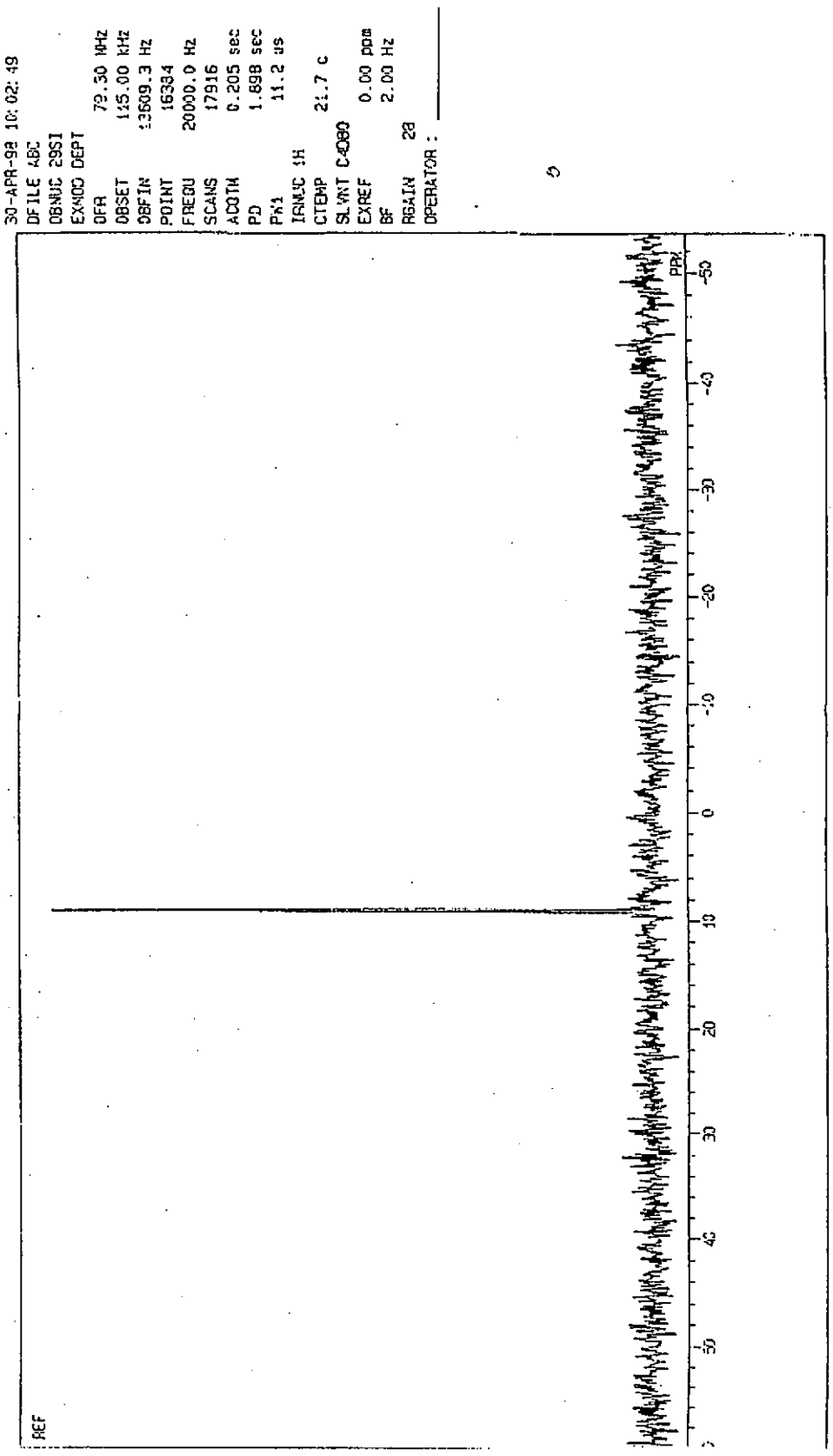

Figure 3.24. 79 MHz $^{29}Si\{^{1}H\}$-NMR spectrum of $TpRuH(H_2SiPh_2)(PPh_3)$ (**21e**)

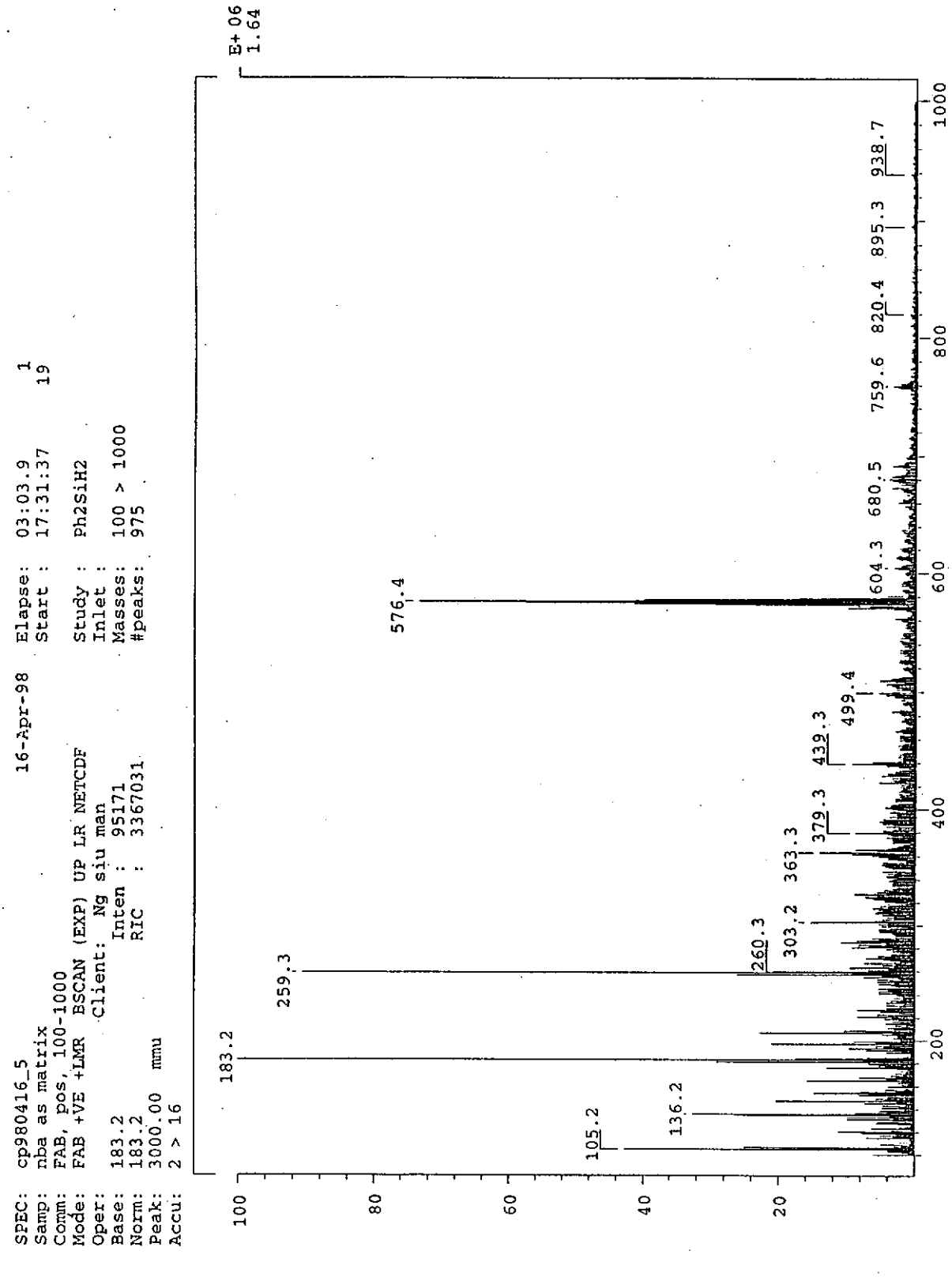

Figure 3.25. FAB mass spectrum of $TpRuH(H_2SiPh_2)(PPh_3)$ (**21e**)

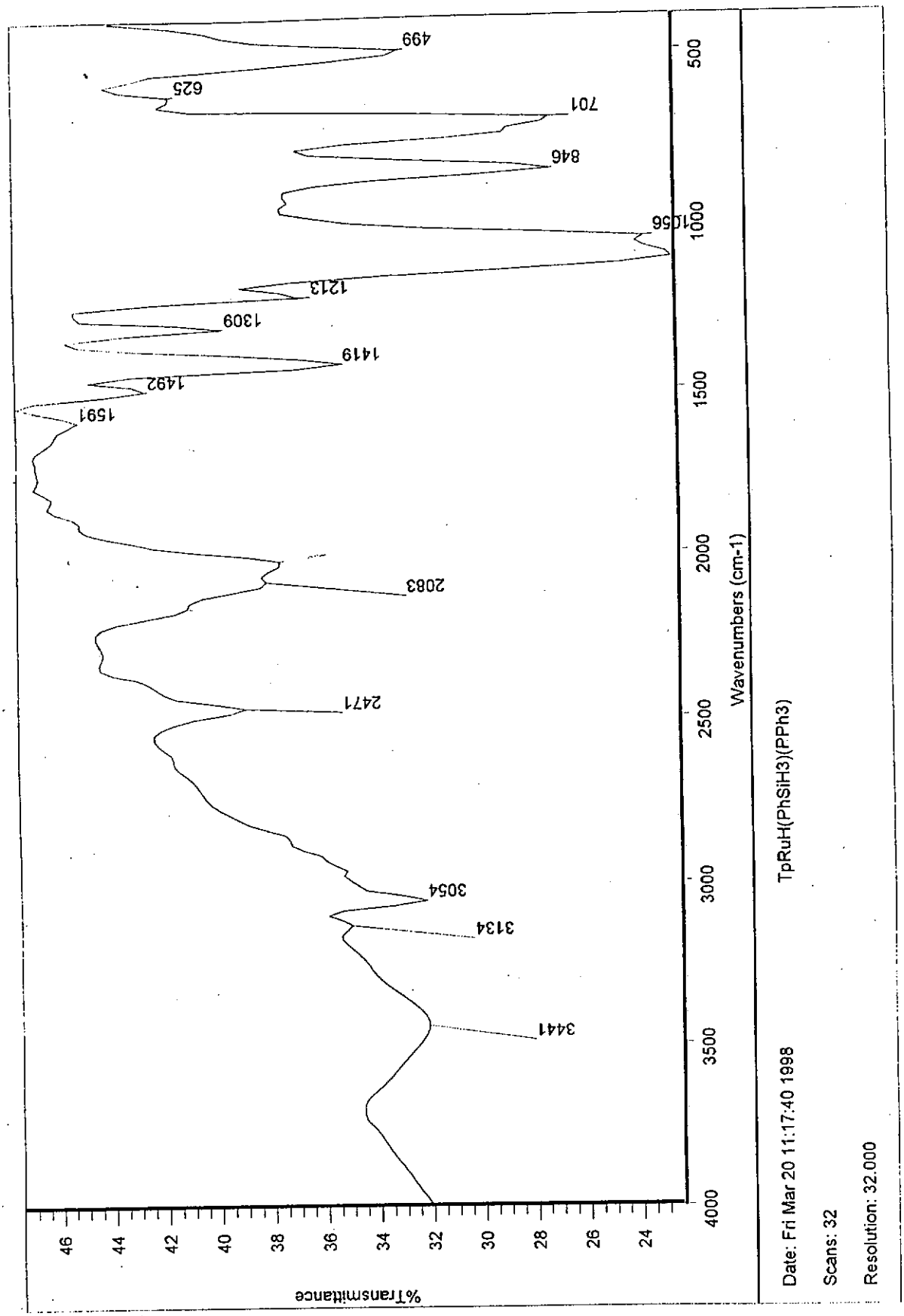

Figure 3.26. Infra-red spectrum of $TpRuH(H_3SiPh)(PPh_3)$ (**21f**) in KBr disc

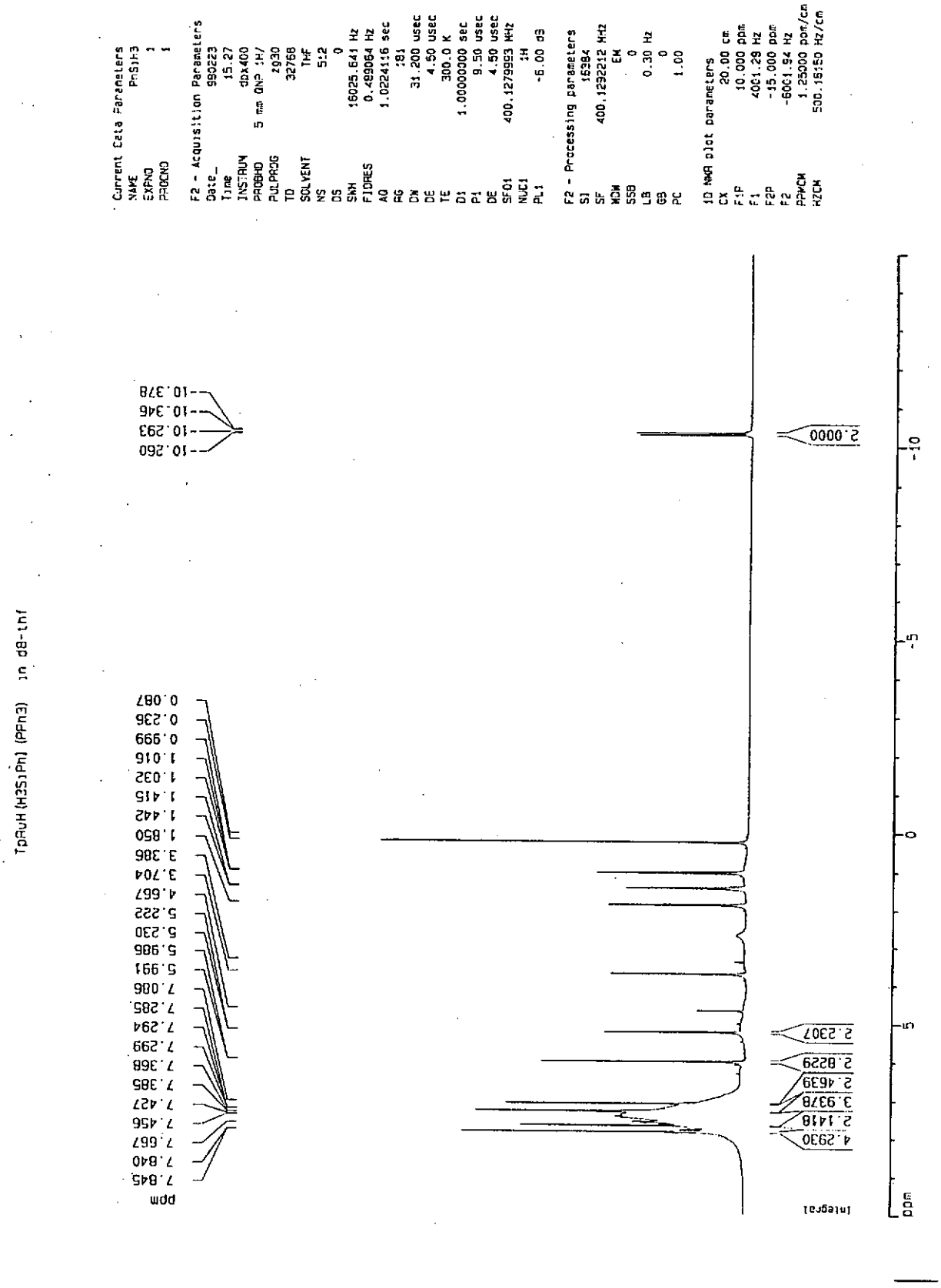

Figure 3.27(a). 400 MHz ^{1}H-NMR spectrum of TpRuH(H_3SiPh)(PPh_3) (**21f**)

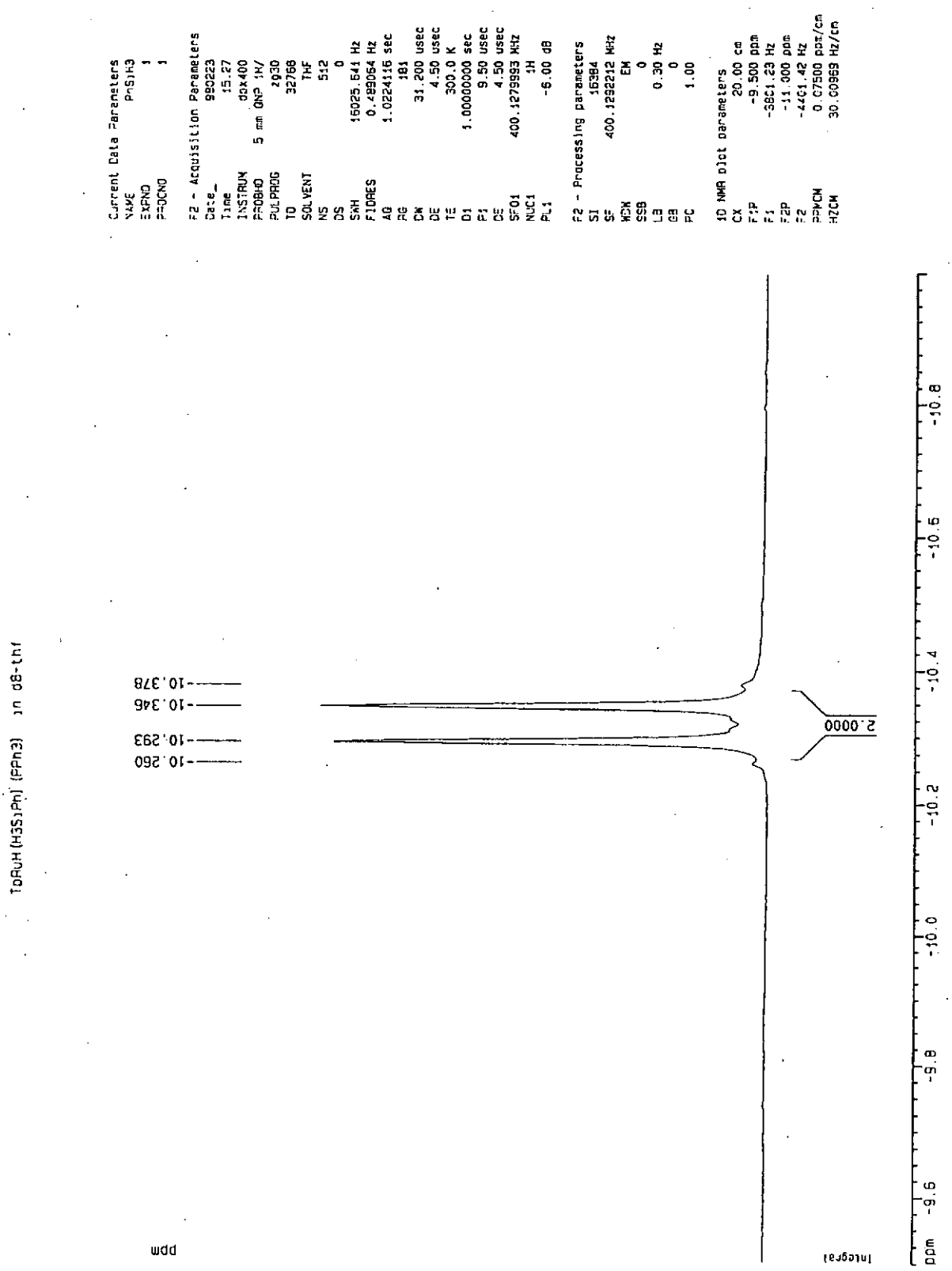

Figure 3.27(b). Expanded upfield region of Figure 3.27(a)

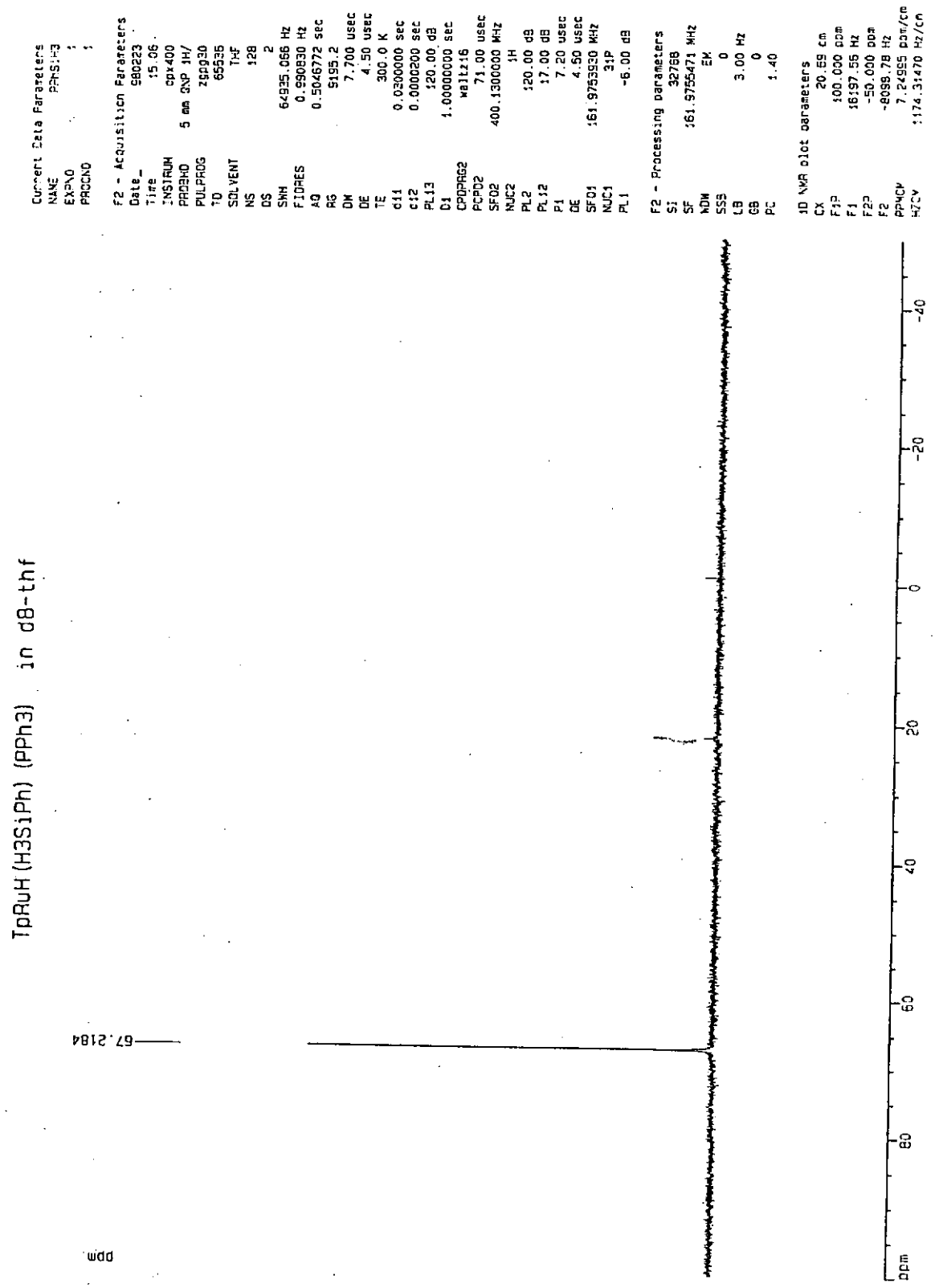

Figure 3.28. 161 MHz $^{31}P\{^{1}H\}$-NMR spectrum of $TpRuH(H_3SiPh)(PPh_3)$ (**21f**)

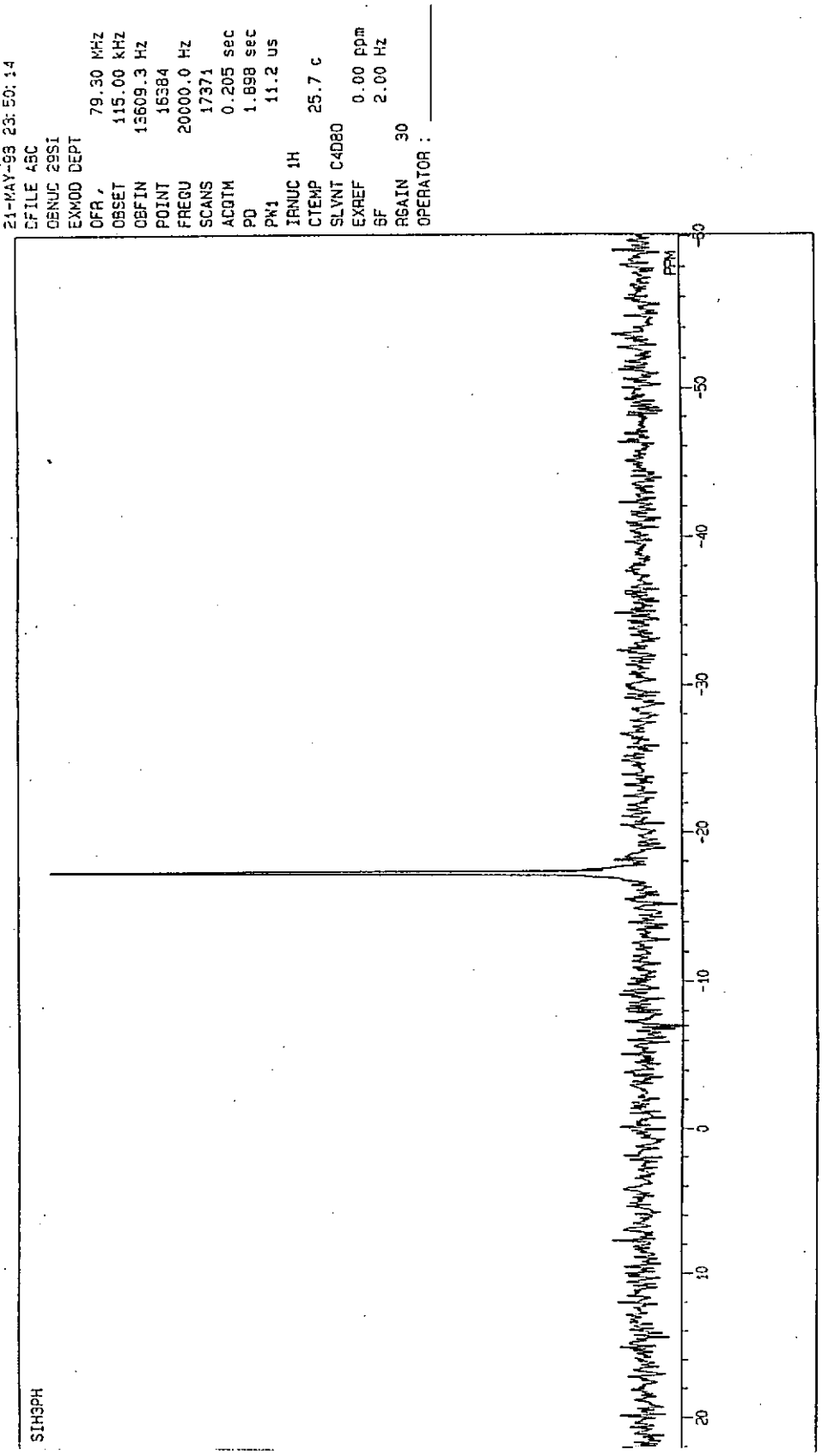

Figure 3.29. 79 MHz $^{29}Si\{^{1}H\}$-NMR spectrum of $TpRuH(H_3SiPh)(PPh_3)$ (**21f**)

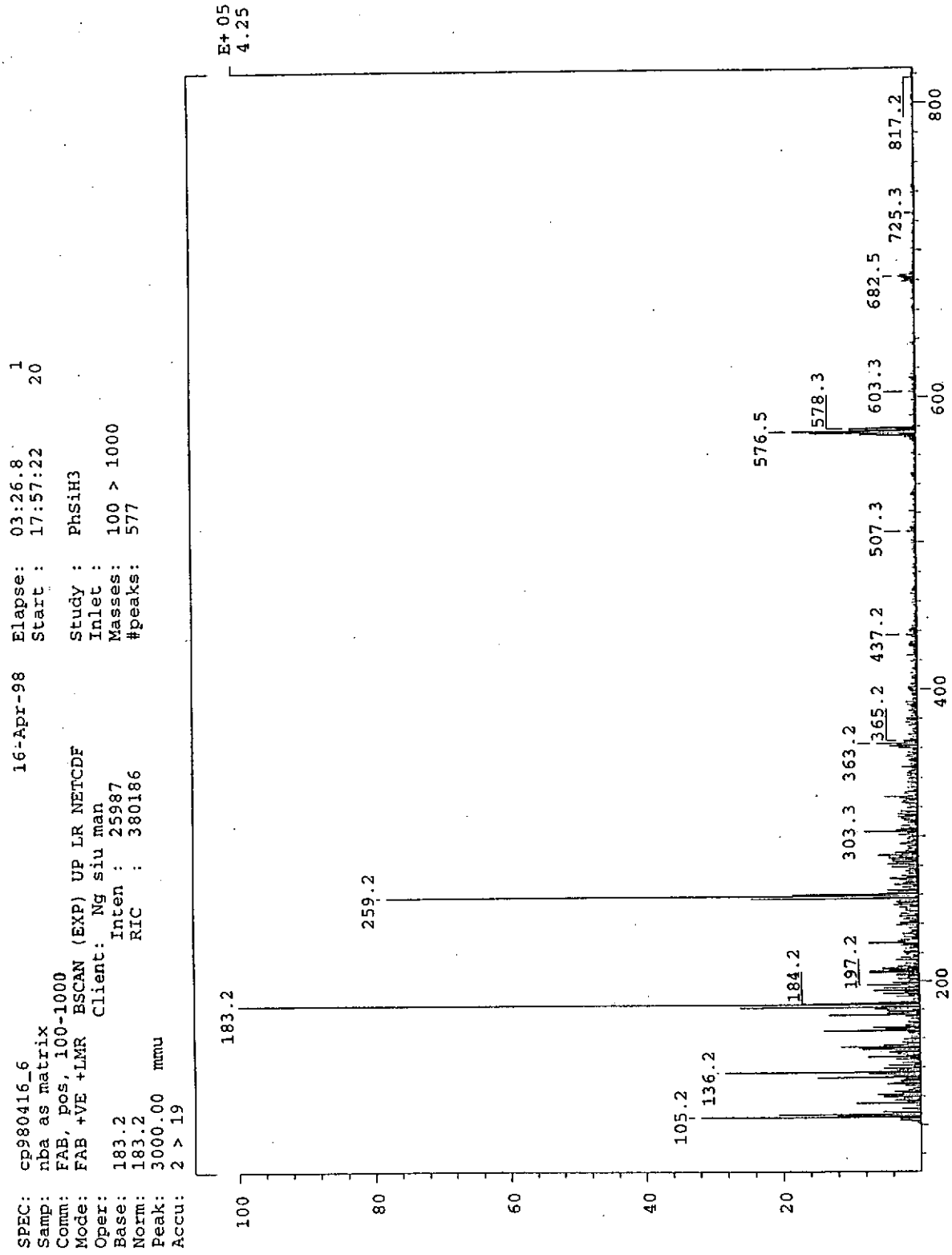

Figure 3.30. FAB mass spectrum of $TpRuH(H_3SiPh)(PPh_3)$ (**21f**)

Publication

1. Ng, S. M.; Fang, Y. Q.; Lau, C. P.; Wong, W. T.; Jia, G. 'Synthesis, Characterization, and Acidity of Ruthenium Dihydrogen Complexes with 1,4,7-Triazacyclononane, 1,4,7-Trimethyl-1,4,7-Triazacyclononane, and Hydrotris(pyrazolyl)borato Ligand' *Organometallics* **1998**, *17*, 2052-2059.

2. Chan, W. C; Lau, C. P.; Chen, Y. Z.; Fang, Y. Q.; Ng, S. M.; Jia, G. 'Synthesis and Characterization of Hydrotris(1-pyrazolyl)borate of Dihydrogen Complexes of Ruthenium and Their Roles in Catalytic Hydrogenation Reactions' *Organometallics* **1997**, *16*, 34-44.