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**Synthesis and Studies of a Molecular Hydrogen Complex of
Iron(II) Containing Bis(diphenylphosphino)methane (dppm)**

By

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**Submitted To the Department of Chemistry in Partial
Fulfillment of the Requirements for
the Degree of Master of Science**

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Author's Statement

It is necessary to note that during the writing of this thesis the English grammar has been extensively modified by my supervisors, Dr. A.N. Hughes and Dr. D.G. Holah.

Abstract

The complexes *trans*-[Fe(H)₂(η²-dppm)₂] **1** and *trans*-[FeH(η²-H₂)(η²-dppm)₂][BF₄] **2** were synthesized by improved methods involving anhydrous conditions and ¹H and ³¹P {¹H} NMR spectra of **1** have been recorded for the first time. Substitution reactions of complex **2** using different types of ligands were investigated. A series of derivatives was obtained and characterized, and these include *trans*-[FeH(CH₃CN)(η²-dppm)₂][BF₄] **3**, *trans*-[FeH(N₂)(η²-dppm)₂][BF₄] **9**, *trans*-[FeH(η¹-NCCH₂CH₂CN)(η²-dppm)₂][BF₄] **6**, *trans*-[FeH(CO)(η²-dppm)₂][BF₄] **8**, *trans*-[FeH(η²-CH₂=CH₂)(η²-dppm)₂][BF₄] **10** and *trans*-[FeH(pyridine)(η²-dppm)₂][BF₄] **7**. These derivatives, except **7**, were also obtained by the direct reactions of complex **1** with the corresponding substitution ligands in the presence of an excess of HBF₄•Et₂O (molar ratio Fe:HBF₄ 1:5).

At room temperature, the reaction of complex **1**, CH₃CN and an excess of HBF₄•Et₂O (molar ratio Fe:HBF₄ 1:5) was found to produce *trans*-[Fe(CH₃CN)₂(η²-dppm)₂][BF₄]₂•2CH₂Cl₂ which was characterized by NMR and X-ray diffraction studies. Convincing evidence indicates that the first reported bis-dihydrogen complex of iron, *trans*-[Fe(H₂)₂(η²-dppm)₂][BF₄]₂, is present in solution and is possibly a key intermediate in the formation of the bis-acetonitrile product. A stepwise protonation mechanism based upon the experimental evidence is suggested to explain these results.

Using spectroscopic data for the new complexes synthesized in this work as a basis, the electronic interactions between iron and different types of substituents, including H₂, were discussed.

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Contents

Abstract	i
Acknowledgement	ii
Contents	iii
List of Figures	vii
List of Tables	xiii
List of Spectra	xii
List of Schemes	ix
Abbreviations	x
Introduction	2
I. Molecular Hydrogen Complexes of Transition Metals	3
(I) Synthetic methods	3
(II) Electronic structure of dihydrogen complexes of transition metals	4
1. Bonding between H ₂ and the transition metal (M)	4
2. Bonding between M and the supporting ligand L	6
(III) Factors affecting the stability of the dihydrogen ligand.....	6
1. The effect of the phosphine ligand	6

2. The effect of transition metals M.....	8
3. The effect of ligands <i>trans</i> to H ₂	9
4. The effect of counter anions	10
(IV) Characteristics of dihydrogen complexes	11
1. The H-H distance	11
2. Spectroscopic properties	12
3. Equilibrium between dihydrogen and dihydride complexes.....	14
4. Intramolecular H atom exchange between dihydrogen and hydride ligands	15
5. The acidity of dihydrogen complexes	16
(V) The reactions of dihydrogen complexes	17
(VI) Bis-dihydrogen complexes of transition metals	18
II. The Current Situation Concerning Dihydrogen Complexes of Iron.....	20
(I) Characteristics of dihydrogen complexes of iron	20
1. The magnitudes of d_{H-H} , J_{H-D} and T_1	20
2. The acidity of dihydrogen complexes of iron	22
3. The intramolecular exchange of H atoms	23
4. The equilibrium between dihydrogen and dihydride complexes.....	25
5. The reactivity of the dihydrogen complexes toward replacement...26	
(II) Some substitution derivatives of iron dihydrogen complexes....	27
1. Substitution by N ₂	27

2. Substitution by CO	28
3. Substitution by organonitriles	29
4. Substitution by CH ₂ =CH ₂	30
III. Summary and Research Proposals	32
Experimental	34
Reagents and Solvents	34
Physical Measurements	34
Synthesis of the Compounds	35
Synthesis of <i>trans</i> -[Fe(H) ₂ (η ² -dppm) ₂], 1	35
Synthesis of <i>trans</i> -[Fe(H)(η ² -H ₂)(η ² -dppm) ₂][BF ₄], 2	36
Synthesis of <i>trans</i> -[Fe(H)(CH ₃ CN)(η ² -dppm) ₂][BF ₄], 3	37
Synthesis of <i>trans</i> -[Fe(CH ₃ CN) ₂ (η ² -dppm) ₂][BF ₄] ₂ •2CH ₂ Cl ₂ , 4	38
Synthesis of <i>trans</i> -[Fe(η ² -H ₂) ₂ (η ² -dppm) ₂][BF ₄] ₂ , 5	39
Synthesis of <i>trans</i> -[Fe{NC(CH ₂) ₂ CN}(η ² -dppm) ₂][BF ₄], 6	39
Synthesis of <i>trans</i> -[Fe(H)(pyridine)(η ² -dppm) ₂][BF ₄], 7	40
Synthesis of <i>trans</i> -[Fe(H)(CO)(η ² -dppm) ₂][BF ₄], 8	41
Synthesis of <i>trans</i> -[Fe(H)(N ₂)(η ² -dppm) ₂][BF ₄], 9	42
Synthesis of <i>trans</i> -[Fe(H)(η ² -CH ₂ =CH ₂)(η ² -dppm) ₂][BF ₄] ₂ •0.5CH ₂ Cl ₂ , 10	43
The reactivity of compound 2 toward propene	44
The reactivity of compound 2 toward <i>cis</i> -2-butene	44

The reactivity of compound 2 toward styrene	44
Results and Discussion	45
I. Syntheses and Characteristics of the Complexes	45
I.1. <i>trans</i> -[Fe(H) ₂ (η ² -dppm) ₂], 1	46
I.2. <i>trans</i> -[Fe(H)(η ² -H ₂)(η ² -dppm) ₂][BF ₄], 2	47
I.3. <i>trans</i> -[Fe(H)(CH ₃ CN)(η ² -dppm) ₂][BF ₄], 3	49
I.4. <i>trans</i> -[Fe(CH ₃ CN) ₂ (η ² -dppm) ₂][BF ₄] ₂ •2CH ₂ Cl ₂ , 4	51
I.5. <i>trans</i> -[Fe(η ² -H ₂) ₂ (η ² -dppm) ₂][BF ₄] ₂ , 5	55
I.6. <i>trans</i> -[Fe{NC(CH ₂) ₂ CN}(η ² -dppm) ₂][BF ₄], 6	64
I.7. <i>trans</i> -[Fe(H)(pyridine)(η ² -dppm) ₂][BF ₄], 7	67
I.8. <i>trans</i> -[Fe(H)(CO)(η ² -dppm) ₂][BF ₄], 8	68
I.9. <i>trans</i> -[Fe(H)(N ₂)(η ² -dppm) ₂][BF ₄], 9	70
I.10. <i>trans</i> -[Fe(H)(η ² -CH ₂ =CH ₂)(η ² -dppm) ₂][BF ₄] ₂ •0.5CH ₂ Cl ₂ , 10	71
I.11. The reactivity of 2 toward propene, <i>cis</i> -2-butene and styrene	74
II. Electronic Interactions of Different Substituents with Iron	74
III. The Nature of the H ₂ Site and the Stability of Complexes Derived Therefrom	78
IV. The Equilibrium between 1 and 2 and Intramolecular H Exchange between Dihydrogen and <i>trans</i> Hydride Ligands	79

V.	The Mechanism for the Formation of Complexes 4 and 5	81
VI.	Explanation of the Formation of <i>cis</i> -[Fe(CH ₃ CN) ₂ (η ² -dppm) ₂][BF ₄] ₂	83
VII.	Explanation of the Reactions of 1 toward CO, N ₂ and Succinonitrile in the Presence of an Excess of HBF ₄ •Et ₂ O	87
	Suggestions for Further Work	90
	References	92

List of Figures

Figure 1	The three membered ring structure of η ² -H ₂ complexes	5
Figure 2	Structure of M(H ₂), M(H...H) and M(H) ₂	12
Figure 3	Structure of <i>trans</i> -[Fe(H)(η ² -H ₂)(meso-tet-1)] ⁺	15
Figure 4a	ORTEP drawing of the cation of 4	56
Figure 4b	Structure of the disordered anions BF ₄ ⁻	57
Figure 5	ORTEP drawing of the cation of 3	58
Figure 6	FTIR of 4 in Nujol	60
Figure 7	Structure of 6	65

List of Tables

Table 1	Dihydrogen complexes of iron and their main spectroscopic properties	20
Table 2	$\nu_{N\equiv N}$ values for some N_2 complexes	27
Table 3	$\nu_{C\equiv N}$ values for some organonitrile complexes	30
Table 4	Selected bond lengths and angles for 4 and 3	59
Table 5	Spectral data for <i>trans</i> -[Fe(H)(L)(η^2 -dppm) $_2$] $^{n+}$ (n=0 or 1)	75

List of Spectra

Spectrum 1	$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CD_2Cl_2 , room temperature) of the three component mixture obtained initially from reactions of 1 with an excess of $\text{HBF}_4\cdot\text{Et}_2\text{O}$ and CH_3CN	53
Spectrum 2	$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 4 in CD_2Cl_2 at room temperature...	54
Spectrum 3	$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN) spectrum of the mixture obtained initially from the reaction of 1 with large excess of $\text{HBF}_4\cdot\text{Et}_2\text{O}$ (molar ratio 1:10) at room temperature	63

Spectrum 4	The invariant ^1H NMR spectrum of 2 over the temperature range 220 K to 299 K	80
Spectrum 5	$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN) spectrum of the mixture obtained initially from the reaction of 1 with a moderate excess of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (molar ratio 1:5) at room temperature	84

List of Schemes

Scheme 1	An associative mechanism for intramolecular H atom exchange in dihydrogen complexes	15
Scheme 2	Structural changes of <i>trans</i> - $[\text{Fe}(\text{H})(\text{H}_2)\{\text{PPh}(\text{OEt})_2\}_4]^+$ with temperature variation	24
Scheme 3	A possible mechanism for the formation of 4 and 5	82
Scheme 4	A possible mechanism for the formation of <i>cis</i> - $[\text{Fe}(\text{CH}_3\text{CN})_2(\eta^2\text{-dppm})_2][\text{BF}_4]_2$	85
Scheme 5	Another possible mechanism for the formation of <i>cis</i> - $[\text{Fe}(\text{CH}_3\text{CN})_2(\eta^2\text{-dppm})_2][\text{BF}_4]_2$	86

Abbreviations

Bu	butyl
Cp	cyclopentadienyl
Cp*	1,2,3,4,5-pentamethylcyclopentadienyl
Cy	cyclohexyl
dbpe	$(\text{PhCH}_2)_2\text{PCH}_2\text{CH}_2\text{P}(\text{PhCH}_2)_2$
dedppe	1-(diethylphosphino)-2-(diphenylphosphino)ethane
depe	1,2-bis(diethylphosphino)ethane
dmpe	1,2-bis(dimethylphosphino)ethane
d(i-Pr)pe	1,2-bis(diisopropylphosphino)ethane
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane
dtfpe	1,2-bis{bis(p-trifluoromethylphenyl)}ethane
dtpe	1,2-bis(di-p-tolylphosphino)ethane
en	ethylenediamine
Et	ethyl

HB(3,5 Me ₂ -pz)	3,5-dimethylpyrazolylhydroborato
Me	methyl
meso-tet-1	meso-tetraphos-1, (R,S)-Ph ₂ PCH ₂ CH ₂ PPhCH ₂ CH ₂ PPhCH ₂ CH ₂ PPh ₂
Ph	phenyl
pp ₃	P(CH ₂ CH ₂ PPh ₂) ₃
ⁱ Pr	isopropyl
py	pyridine
Pz	pyrazolyl
THF	tetrahydrofuran
tolyl	-C ₆ H ₄ CH ₃

Introduction

Since the first report of a molecular hydrogen complex of tungsten by Kubas^[1] in 1984, considerable attention has been given to dihydrogen complexes of transition metals because of their relevance to homogeneous and heterogeneous catalysis. The study of these dihydrogen complexes has opened a new branch of coordination chemistry, resulting in the discovery of several hundred stable complexes of this type and the current better understanding of this unusual coordination chemistry process^[2,3,4].

Most of the known dihydrogen complexes have been synthesized with phosphine ligands as the supporting scaffold. However, only a few^[5,6a] of these contain the very versatile ligand bis(diphenylphosphino)methane (dppm), which has been shown to play an important role in coordination chemistry. In this context, a very useful one step route for the formation of the metal (I) and (0)-carbonyl-dppm complexes^[7] has been developed in this laboratory. This procedure involves reductions of the +2 states of several metal salts, e.g., Co^[8] and Ni^[9], by NaBH₄ in the presence of CO and dppm. However, when this reductive procedure was applied to iron (III) in the absence of CO, the reduction of iron stopped at the +2 state to give a dihydride complex, *trans*-[Fe(H)₂(dppm)₂], which can be further protonated to form the corresponding molecular dihydrogen complex^[6a]. As will be seen later in this thesis, similar results have been obtained for Fe(III) reductions using the more powerful reducing agent LiAlH₄^[6b].

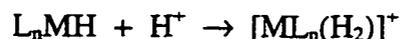
This thesis reports an extension of the Fe work noted above and is concerned mainly with the synthesis, characterization, structure and reactivity of the dihydride and dihydrogen complexes of iron(II) with dppm as the supporting ligand. The following sections of this chapter outline the background chemistry and current approaches in the field of dihydrogen complex chemistry upon which the research reported in the Results and Discussion section was based.

I. Molecular Hydrogen Complexes of Transition Metals

(I) Synthetic methods

Two general methods are often used to prepare dihydrogen complexes^[3]. One, which was used by Kubas to synthesize the first dihydrogen complex^[1] and, later, for the neutral complexes $ML_n(H_2)$, is the reaction of a coordinatively unsaturated metal fragment with hydrogen gas. This method was also employed by Morris and other workers in the synthesis of the compounds, $[MH(H_2)(L_2)_2]^+$, where $M = Fe, Ru, Os$ and L_2 is a variety of chelating diphosphines. Details of dihydrogen complexes synthesized by this method can be found in a review by Morris^[3].

Another widely used method of preparation is the protonation of hydride complexes by acid to give cationic dihydrogen complexes as shown below; $HBF_4 \cdot Et_2O$ is the preferred source of protons.^[3]



Other methods^[3], including preparations of dihydrogen complexes under reducing conditions or by modifying existing dihydrogen complexes, are less common and rarely employed now.

(II) Electronic structure of dihydrogen complexes of transition metals

The known molecular hydrogen complexes can be roughly divided into two groups. One is the neutral complexes with the form of $ML_n(H_2)$ while the others are cationic and take the form of $[ML_nL'(H_2)]^+$. Complexes with more than one dihydrogen ligand are rare and will be discussed later in this chapter.

There are two main aspects to the electronic interactions in such complexes:

1. Bonding between H_2 and the transition metal (M)

The metal-dihydrogen bonding is usually described as a σ - π interaction^[10]. A three-membered ring model (Figure 1) was suggested^[10] to represent the metal- H_2 interaction, which is widely accepted as the general structural feature of dihydrogen complexes^[11,12a]. The H-H σ bond donates electron density to an empty metal d-orbital in such a way that the resulting bonding molecular orbital is spread over the three atoms (Figure 1). This necessarily results in a weakening of the H-H bond since the two electrons

originally in this bond are now spread over 3 atoms. In addition, π back-bonding from a filled d-orbital of the M to the σ^* orbital of H_2 is possible and therefore the σ -donation and the π back-donation will reduce the interaction of the two hydrogen atoms causing an elongation, or eventually, splitting of the H-H bond. For a dihydrogen complex, the σ - π interaction must be in a delicate equilibrium in order to keep the H_2 unit intact. It is possible for the H_2 ligand to rotate in a plane perpendicular to the M- H_2 axis. The extent of the rotation will depend on the extent of any π -backbonding since this has directional properties whereas the σ component to the bonding does not. In other words, the weaker the π -backbonding, the shorter the H-H distance and the lower the barrier to rotation. There is considerable discussion on this topic in the literature^[2,3,10,11].

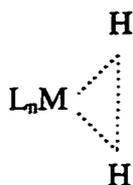


Figure 1 The three-membered ring structure of η^2 - H_2 complexes

Recent experimental evidence^[13,14] has shown that H_2 is a very weak σ -donor ligand but a strong π -acid ligand. Though the least amount of π backbonding would

ensure the strongest H-H bond, the coordination of H_2 to transition metals also needs a relatively strong M- H_2 interaction which will inevitably increase the π backbonding. All these suggest that the degree of π backbonding from M will determine the stabilities of both the dihydrogen ligand with respect to the ligand's splitting and the dihydrogen complex with respect to dihydrogen loss.

2. Bonding between M and the supporting ligand L

Here L is specified as a phosphine ligand. The bonding between M and phosphorus can be also viewed as a result of σ - π interaction^[15], i.e., electron donation from the phosphorus lone pair orbital to an empty metal d orbital and back-donation from a filled metal orbital to vacant ligand orbitals (which were suggested to be the hybrid orbitals contributed from phosphorus 3d and 3p orbitals and the P-R σ^* orbitals^[16]). Theoretical studies indicate that the balance between the σ and π interactions depends on the electronegativity of the substituents (R) bonded to the phosphorus atoms^[17]. This balance will affect the net electron density at M and thus change the amount of π back-donation from ML_n to H_2 .

(III) Factors affecting the stability of the dihydrogen ligand

1. The effects of the phosphine ligand

Depending upon the substituents bonded to the phosphorus atoms, the phosphine ligand can modulate the electron density at the metal and thus affect the π back-bonding from M to the H₂ ligand. These factors are crucial to the stability of H₂ complexes and have been fully confirmed by systematic studies on dihydrogen complexes. For example, Kubas showed from investigations on complexes of the type Mo(CO)₃(PR₃)₂(H₂)^[18] and Mo(CO)(H₂)(R₂CH₂CH₂R₂)₂^[19] that when R was changed from Ph to alkyl (Et or i-Bu), the dihydrogen complex changed to its corresponding dihydride form. However, the degree to which phosphines affect the stability of the dihydrogen ligand depends largely on the nature of the metal and the ligand *trans* to the dihydrogen ligand. For example, in systematic studies on the complexes *trans*-[MH(H₂)(R₂CH₂CH₂R₂)]⁺[X⁻] (M=Fe, Ru; X=BPh₄ or BF₄)^[20,21], no H-H cleavage was observed and the H-H distance changed little when R was changed from Ph to the same alkyl as was used in studies on the complexes Mo(CO)(H₂)(R₂CH₂CH₂R₂)₂^[19]. The dihydrogen-dihydride interconversion will be discussed later in this chapter.

In addition to the electronic effect noted above, it has been found that geometrical changes in the phosphine also can affect the nature of η^2 -H₂ complexes. Recently, Morokuma and coworkers^[22] reported that [(diphosphine)₂Ru(H₃)] [BF₄] complexes can adopt three different forms, i.e., *trans*-hydrido-dihydrogen, classical trihydride (for definition, see section IV.1 of this chapter) and *cis*-hydrido-dihydrogen depending upon the bite angle of the diphosphine^[22]. Kranenburg has also reported that the structure and

stability of certain ruthenium dihydrogen complexes dramatically changes with increasing bite angle of the diphosphines^[23]. However, it should be noted that these geometrical changes may affect the nature of the dihydrogen complexes indirectly through the electronic effect because diphosphines with different bite angles could cause different splitting of the levels of the d-orbitals and thus affect the π back donation from the metal to the dihydrogen ligand.

2. The effect of transition metals M

The transition metals in most of the synthesized dihydrogen complexes prefer an octahedral structure. There is clear evidence to show that the energy levels of the d electrons will affect the nature of the dihydrogen ligand. For example, $\text{Mo}(\text{CO})\text{H}_2(\text{R}_2\text{CH}_2\text{CH}_2\text{R}_2)_2$ has been confirmed to be a molecular hydrogen complex^[19] but its tungsten analogue, $\text{W}(\text{CO})\text{H}_2(\text{R}_2\text{CH}_2\text{CH}_2\text{R}_2)_2$, adopts a typical dihydride form^[24]. It appears from experimental evidence^[25] that increasing the energy of the d-electrons (down the group) will increase the π backbonding from M and thus cause the splitting or elongation of the dihydrogen ligand. For example, in the complexes, $[\text{M}(\text{H})(\text{H}_2)(\text{L}_2)][\text{BF}_4]$ (M=Fe, Ru, Os, L=dppe or dtfpe), $d_{\text{H-H}}$ increases from Fe to Os^[25]. Theoretical studies^[26] have also shown that a dihydrogen ligand prefers contracted metal d orbitals, i.e., the dihydrogen complexes of the first-row transition metals are more preferred than those of the second- and third-row transition metals.

3. The effect of ligands *trans* to H-H

It is well known that *trans* ligands in transition metal complexes can strongly interfere with each other. For dihydrogen complexes, investigations on the system *trans*-[OsL(η^2 -H₂)(en)₂]ⁿ⁺ have shown^[14,27] that the *trans*-ligand L (with different donor/acceptor abilities) can deeply affect the properties of the dihydrogen ligand. For example, it was found that when L is a π -acid ligand, *trans*-[OsL(η^2 -X₂)(en)₂]⁺ (X=H₂, HD) has a high J_{HD} value, i.e., such ligands result in a short H-H distance. When L is a very strong π -acid ligand such as PhCH₂NC, the H₂ of the corresponding dihydrogen complex is very easily lost^[27]. When L was changed to the strong σ -donor ligand CH₃CO₂⁻ (acetate), a long H-H distance of 1.34(2) Å was determined by neutron diffraction studies^[14]. Theoretical studies on the complexes *trans*-ML(H₂)(CO)₄^[28] also indicate that the M→L back-donation competes with the M→H₂ back-donation if L is a π acceptor ligand. It is apparent from the above evidence that the ligand *trans* to dihydrogen can modulate the net electron density of the metal center and thus the amount of π back donation to H₂.

It appears that for a stable dihydrogen complex, an electron-poor metal center requires a good σ -donor *trans* to the dihydrogen whereas a more electron-rich center requires a good π acid ligand. This is consistent with the results^[29] of theoretical calculations on the three membered ring structure (Figure 1) which indicated that the

electron density within the three membered ring should be no more than two electrons. This point can also be illustrated by considering the corresponding dinitrogen complexes. Morris suggested^[3] that the $\nu_{\text{N=N}}$ of a dinitrogen complex with an electron-poor metal center will exceed 2150 cm^{-1} and that with an electron-rich center will be less than 2060 cm^{-1} .

4. The effect of counter anions

A large number of dihydrogen complexes exist as cations in solution and the solid forms require suitable counter-ions. The σ - π interaction in dihydrogen complexes is so delicate that different types of counter-ions may affect the stability of the H-H ligand. An example of this has been provided by Bianchini and coworkers^[30], who reported that the different counter-ions used to crystallize a cationic cobalt complex, $[\text{CoPP}_3(\text{H}_2)]^+$, influence the structure observed. When PF_6^- is used as the counter-ion, the H_2 complex is formed but when the counter-ion is changed to BPh_4^- , the complex is in the dihydride form. In solution the H_2 complex is always formed whatever the counter-ion is. Furthermore, $[\text{Fe}(\eta^2\text{-H}_2)(\text{H})(\text{dppe})_2][\text{BF}_4]$ reacts with NaBPh_4 ^[20] to form $[\text{Fe}(\eta^2\text{-H}_2)(\text{H})(\text{dppe})_2][\text{BPh}_4]$ in which the BPh_4^- anion has been found to be significantly distorted from tetrahedral geometry. This reflects that there is a significant interaction between the anion and cation and this interaction can affect the H-H bonding.

(IV) Characteristics of dihydrogen complexes

1. The H-H distance

It has been found that the H-H bond in dihydrogen complexes can adopt different distances from a minimum of 0.82 \AA ^[19,20,31,32] to the much longer distance of 1.357 \AA ^[33]. Investigations on the change of bond energy of H-H with the different distances showed^[34] that a relatively high bond energy can still be kept at long distances (e.g., about 50% of the maximum at 1.35 \AA). This possibly explains why H-H ligands in dihydrogen complexes can remain intact at a distance longer than that in free H_2 (0.76 \AA). For a stable three-membered ring system (Figure 1), there appears to exist an optimum H-H distance to ensure both a reliable M-H₂ interaction and strong H-H bonding. This is perhaps why the stabilities of $[\text{M}(\text{H})(\text{H}_2)(\text{L}_2)][\text{BF}_4]$ (M=Fe, Ru, Os, L=dppe or dtfpe) with respect to the H_2 loss is in the order Os > Fe > Ru and the $d_{\text{H-H}}$ sequence in their corresponding complexes is Fe > Ru > Os^[25].

Coordination of hydrogen in the form of M-(H₂) is often referred to as nonclassical while the corresponding dihydride form is referred to as classical. Dihydrogen complexes can be divided into two groups according to the H-H distances^[2,3]. The first contains typical dihydrogen complexes (0.82 \AA to 1.0 \AA) and the second collects together intermediate or elongated dihydrogen complexes M(H \cdots H) (1.1 \AA to 1.6 \AA). Distances greater than 1.6 \AA are found in classical dihydride complexes, as illustrated in Figure 2.

$d(\text{H-H})$ 0.82\AA° to 1.0\AA° 1.1\AA° to 1.6\AA° $> 1.6\text{\AA}^\circ$

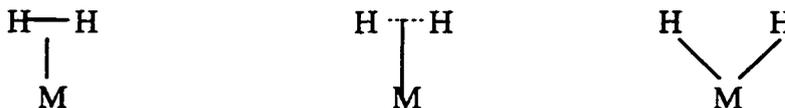


Figure 2 Structure of $\text{M}(\text{H}_2)$, $\text{M}(\text{H} \cdots \text{H})$ and $\text{M}(\text{H})_2$

2. Spectroscopic properties

Because of difficulties in accurately locating H atoms close to metal atoms by X-ray diffraction, and because of the (often impractical) requirement of large crystals for neutron diffraction, IR and NMR properties of dihydrogen complexes are normally used to authenticate their presence. The dihydrogen vibrational mode $\nu(\text{H-H})$ is, as would be expected from its symmetrical nature, very weak. It occurs in the range of 2300 cm^{-1} to 2700 cm^{-1} and can only be occasionally observed^[1,35] by IR methods. Most dihydrogen complexes are characterized by NMR methods.

^1H NMR spectra of H_2 complexes usually display a broad singlet in the negative region due to rapidly relaxing protons in the H_2 ligand^[36]. When one hydrogen of the H-H ligand is replaced by D, the HD complexes usually give large values for J_{HD} . This is a very useful criterion for establishing dihydrogen coordination because J_{HD} for classical HD complexes is usually very small ($<1\text{ Hz}$). For nonclassical HD complexes, J_{HD} is often found within the range of 12 to 34 Hz ^[11] although a value as low as 1.6 Hz has been found

in the cationic complex $[\text{Os}(\text{en})_2(\text{H}_2)(\text{X})]^{n+}$ ^[37]. As would be expected, the magnitude of J_{HD} is directly related to $d_{\text{H-H}}$. Recently, a linear relationship between J_{HD} and $d_{\text{H-H}}$ has been established both experimentally^[2] and theoretically^[38]:

$$d(\text{H-H}) = 1.42 - 0.0167 (J_{\text{HD}})$$

For dihydrogen complexes, the T_1 (proton relaxation time) values are usually found to be very short because of the dipole-dipole interaction of two very close protons and this has made T_1 measurements another efficient criterion for the examination of H_2 complexes. This method was first suggested by Crabtree^[39] and the idea has undergone some subsequent modifications^[12]. For typical dihydrogen complexes $\text{M}(\text{H}_2)$ -, T_1 was suggested to be less than 40 ms at 250 MHz whereas for hydrides, T_1 is usually >100 ms. T_1 measurements cannot be used to evaluate elongated dihydrogen complexes^[11]. For deductions to be reliable, the T_1 method requires that dipole-dipole relaxations from other sources be eliminated and this requirement is often difficult to meet in NMR experiments. Relatively large measurement errors may exist and this sometimes makes the T_1 method less useful in some cases.

Currently, the best proof for the existence of a dihydrogen complex in solution is the observation of a large H-D coupling for the corresponding HD complex.^[2]

3. Equilibrium between dihydrogen and dihydride complexes

It is generally accepted that there exists an equilibrium between a dihydrogen complex and the corresponding dihydride complex in solution^[3] as shown below:



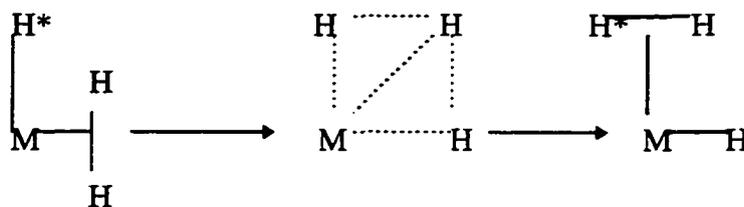
The equilibrium is normally observed by the changes in the broad dihydrogen peak with variation of temperature in ^1H NMR spectra. Normally, the characteristic broad singlet will change to a multiplet with appropriate change of temperature.

Though there are many experimental reports^[12b,36,40-42] of this phenomenon, it is a fact that this equilibrium is normally found among complexes with the form of $\text{ML}_n(\text{H}_2)$ or $[\text{ML}_n(\text{H}_2)]^+$ and is not often observed in dihydrogen complexes which contain more than two hydrogen atoms^[19]. The reason for this is still under investigation. It is apparently unreasonable to relate this phenomenon to the H-H distance since it has been found in the first reported dihydrogen complex $\text{W}(\text{CO})_3(\text{PPr}_3)_2(\text{H}_2)$ with the short H-H distance (0.82A°)^[35] but has not been observed for the apparently elongated dihydrogen complex $\text{ReH}_7\{\text{P}(\text{p-tolyl})_3\}_2$ which contains one dihydrogen ligand shown by neutron diffraction to have an H-H distance of 1.357A° ^[32]. Since dihydrogen complexes prefer octahedral

geometry (six coordinate) and a change to the dihydride form (seven coordinate) would require rearrangement of the supporting phosphine ligands, the energy barrier for this rearrangement may play the dominant role on whether or not the equilibrium can be observed.

4. Intramolecular H atom exchange between dihydrogen and hydride ligands

There is strong evidence^[3] to indicate that exchange of H atoms between dihydrogen and other hydrogen-donor ligands can occur in dihydrogen complexes. An associative mechanism with the $\eta^3\text{-H}_3$ intermediate has been suggested^[3,11] (Scheme 1) to explain this phenomenon and there is clear evidence^[11] to confirm the existence of this type of intermediate:



Scheme 1

For complexes where the hydride ligand is *trans* to the H_2 , the formation of such a $\eta^3\text{-H}_3$ intermediate apparently needs the migration of the *trans* hydride. This would require site exchange of the hydride with the supporting ligands. This site exchange could

be temporary and dynamic and not require the rearrangement of the phosphine ligands. The energy barrier could then be much less than that needed for the dihydrogen/dihydride equilibrium. This possibly explains why only intramolecular H atom exchange can be observed in some systems with no observable equilibrium between dihydrogen and the corresponding dihydride complexes.

The rate of H atom exchange can be established from an observation of changes in the variable temperature ^1H NMR spectra in the hydride region and is normally determined quantitatively by the line shape analysis method^[3].

5. The acidity of dihydrogen complexes

Dihydrogen complexes have been found to be more acidic than their dihydride counterparts^[2,3] and they can transfer a proton to a base more rapidly :



The factors which affect the stability of dihydrogen ligands also affect their acidity. The effects are very complicated and still under investigation, but it appears from current experimental evidence that the acidity has some relation to the H-H distance. Normally, dihydrogen complexes with shorter $d_{\text{H-H}}$ are more acidic than those with longer $d_{\text{H-H}}$. For example, in the complexes $[\text{CpRu}(\text{H}_2)(\text{R}_2\text{CH}_2\text{CH}_2\text{R}_2)][\text{BF}_4]$, when R is changed from

C₆H₄CF₃ to Me the complexes change from the dihydrogen forms to the dihydride complexes (i.e., H-H distances become longer) and values of pK_a change from 4.5 to 10^[42d]. However, there seems to exist an optimum H-H distance at which the dihydrogen complex has the most acidity. Recently, what is currently the most acidic but stable H₂ complex known, *trans*- [Os(H₂)(CH₃CN)(dppe)₂][BF₄], has been synthesized with an H-H distance of 1.1 Å and it can be deprotonated by treatment with a very weak base such as ether^[43].



(V) The reactions of dihydrogen complexes

By far the most observed and studied reactions for dihydrogen complexes are substitution reactions. Thus, the usually labile H₂ ligand can be replaced by other small ligands, which may include CO, phosphines, amines, nitriles, N₂, O₂, D₂, water, alkynes and alkenes^[3]. When the substitution reactions occur with unsaturated reagents, e.g., alkynes, RNN⁺, CO₂ and CS₂, the substitution is often followed by insertion of the unsaturate into the M-H bond^[44]. It is rare for alkenes to enter into further insertion reactions.

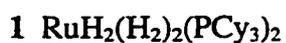
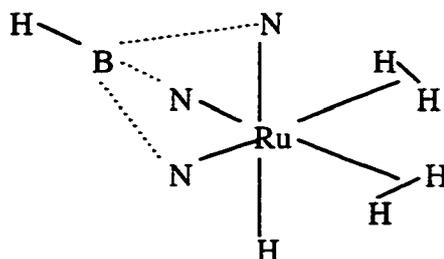
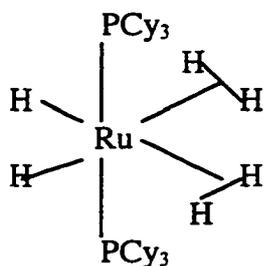
Substitution reactions also appear to be a unique property of dihydrogen complexes since no such reactions have been found for dihydride complexes. Different

dihydrogen complexes can show different reactivities toward substitution, probably depending upon $d_{\text{H-H}}$ in the dihydrogen complexes. For example, $[\text{ReH}_4(\text{H}_2)\{\text{PPh}(\text{CH}_2\text{CH}_2\text{PCy}_2)_2\}]^+$ with an H-H distance of 1.08 \AA cannot be displaced by CO, N_2 and $i\text{-BuNC}$ ^[45]. This inertness of dihydrogen ligands toward substitution has also been found for $[\text{ReH}_4(\text{H}_2)\{\text{PPh}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2\}]^+$ ^[46] which contains an elongated H_2 ligand.

(VI) Bis-dihydrogen complexes of transition metals

Compared with the large number of studies on mono-dihydrogen complexes, studies on bis-dihydrogen complexes are more limited since only a few have yet been characterized. Most such complexes have been prepared by protonation of their corresponding polyhydride complexes. To the knowledge of this author, only three thermally stable bis-dihydrogen complexes have been found and only two of them, *cis*- $\text{RuH}_2(\text{H}_2)_2(\text{PCy}_3)_2$ ^[47], **1**, and *cis*- $\text{LRuH}(\text{H}_2)_2$, $\{\text{L}=\text{HB}(3,5\text{-Me}_2\text{-pz}), \text{HB}(3\text{-}^i\text{Pr},4\text{-Br-pz})\}$ ^[48], **2**, have been isolated. Other bis-dihydrogen complexes have been characterized either in a matrix^[49] or in solution at very low temperature^[50].

Bis-dihydrogen complexes appear to be highly labile even in the solid state and no crystal structures have yet been reported. The structures of **1** and **2** were deduced from their IR and NMR characteristics. The third bis-dihydrogen complex, *cis*- $[\text{IrH}_2(\text{H}_2)_2(\text{PCy}_3)_2]$, **3**, is stable only at -80°C although the structure can be maintained at room temperature under a dihydrogen atmosphere^[51].



Studies on the reactivity of these complexes showed that the two dihydrogen ligands have almost the same reactivities. For example, the dihydrogen ligands in **1** can be replaced by N_2 or CO to give the corresponding $\text{RuH}_2(\text{L})_2(\text{PCy}_3)_2$, $\text{L}=\text{N}_2$ or CO ^[47], and **3** reacts with MeCN to give a cationic species $[\text{IrH}_2(\text{MeCN})_2(\text{PCy}_3)_2]^+$ ^[51]. Complex **3** also shows high acidity and can be deprotonated by NEt_3 to return to its polyhydride form ^[51].

II. The Current Situation Concerning Dihydrogen Complexes of Iron

Since the new work described later in this thesis concerns the chemistry of an iron-dppm-dihydrogen complex, a brief survey of what has so far been published on Fe-(H₂) complexes in general is given here.

(I) Characteristics of dihydrogen complexes of iron

The currently known Fe-(H₂) complexes and their characteristics are summarized in Table 1. The listed complexes display apparently different properties (see below) from those of ruthenium and osmium analogues. Such properties, including $d_{\text{H-H}}$ and J_{HD} , acidities, intramolecular exchange of H atoms between dihydrogen and hydride ligands, equilibrium between dihydrogen and hydride complexes and reactivities toward H₂ substitution, will be discussed in the following subsections.

1. The magnitudes of $d_{\text{H-H}}$, J_{HD} and T_1

The available $d_{\text{H-H}}$ data for dihydrogen complexes of iron show quite short H-H distances despite widely differing phosphine ligands and different measuring methods. The J_{HD} values are also very similar at around 30 Hz. If we apply the J_{HD} and $d_{\text{H-H}}$ relation^[2,38] mentioned earlier, the listed Fe complexes (Table 1) all have $d_{\text{H-H}}$ smaller than 1 Å. All the

Table 1 Dihydrogen complexes of iron and their main spectroscopic properties

Cationic Complexes	$\delta(^1\text{H})^a$ ppm	$\delta(^1\text{H}_2)$ ppm	$\nu_{\text{Fe-H}}$ cm^{-1}	J_{HD}^b Hz	$d_{\text{H-H}}$ Å°	T_1 ms	ref
$[\text{FeH}(\text{H}_2)(\text{dppe})_2]^+$	-12.9	-8.0	1919	32	0.89 ⁿ	8.5(200)	21a
$[\text{FeH}(\text{H}_2)(\text{depe})_2]^+$	-14.6	-10.5		29.5	0.86	12(200)	21b
$[\text{FeH}(\text{H}_2)(\text{dmpe})_2]^+$	-17.4	-11.6	1856	31	0.86 ^x		52
$[\text{FeH}(\text{H}_2)(\text{dedppe})_2]^+$	-13.6	-9.2		32		7(200)	21c
$[\text{FeH}(\text{H}_2)(\text{dbpe})_2]^+$	-14.4	-10.1					6a
$[\text{FeH}(\text{H}_2)(\text{meso-tet-1})]^+$	-16.7	-9.8		32	0.88	32(200)	6a, 53
$[\text{FeH}(\text{H}_2)(\text{dppm})_2]^+$	-7.2	-4.0					6a
$[\text{FeH}(\text{H}_2)(\text{d}(i\text{-Pr})\text{pe})_2]^+$							54
$[\text{FeH}(\text{H}_2)\{\text{PPh}(\text{OEt})_2\}_4]^+$	-10.34	-7.2	1715			3(80)	55
$[\text{FeH}(\text{H}_2)\{\text{P}(\text{OEt})_3\}_4]^+$	-10.4	-9.6	1720			4(80)	55
$[\text{FeH}(\text{H}_2)(\text{dtfpe})_2]^+$	-12.55	-7.7		32	0.86	15(400)	22
$[\text{FeH}(\text{H}_2)(\text{dtpe})_2]^+$	-12.5	-8.2			0.84	15(400)	22
$\text{Fe}(\text{H})_2(\text{H}_2)(\text{PEtPh}_2)_3$	-11.7				0.821 ⁿ	24(250)	31, 56
$\text{Fe}(\text{H}_2)(\text{CO})_2(\text{C}_4\text{H}_4)$							57
$\text{Fe}(\text{NO})_2(\text{CO})(\text{H}_2)$							58
$[\text{FeCp}^*(\text{H}_2)(\text{dppe})]^+$		-12.39		27		7(300)	59
$[\text{FeCp}(\text{H}_2)(\text{dppe})]^+$		-12.5		30.7		5(300)	60
$[\text{FeCp}(\text{H}_2)(\text{dppp})]^+$		-12		29		7(300)	60
$[\text{Cp}(\text{CO})(\text{PEt}_3)\text{Fe}(\text{H}_2)]^+$		-11.8		31.6			61
$[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}(\text{H}_2)]^+$		-10.8		31.7			61
$[\text{FeH}(\text{H}_2)(\text{pp}_3)]^+$				28.3			3
$[\text{Fe}(\text{H}_2)(\text{CO})(\text{dppe})_2]^{2+}$		-6.8		33.1	0.86	11.1(300)	62

X-ray and neutron diffraction data are indicated by x or n, respectively.

^a Center values of the multiplet ^b For the H-D analogues

complexes also have T_1 values less than 40 ms.

The d_{H-H} , J_{HD} and T_1 values suggest that all the currently known Fe dihydrogen complexes possess typical structures with little elongation of the H-H distance, i.e., no elongated Fe-(H₂) complex has been found. This is quite different from the situation observed for complexes of ruthenium and osmium since there have been quite a few reports of elongated dihydrogen complexes for Ru^[63] and Os^[25,40].

Considering ¹H chemical shift data, it is noteworthy that almost all dihydrogen complexes of iron show a broad singlet within the range δ -4 to -13 which was concluded by Kubas^[36] to be the type of signal characteristic of the dihydrogen ligand.

2. The acidity of dihydrogen complexes of iron

Systematic studies on the complexes $[MH(H_2)(L_2)][BF_4]$, M=Fe, Ru, Os, L = diphosphines, have shown^[25] that dihydrogen complexes of iron are slightly more acidic than their ruthenium and osmium analogues. The following pK_a^{cis} values cited from these studies^[25] illustrate this:

Diphosphine	pK_a (Fe)	pK_a (Ru)	pK_a (Os)
dtfpe	7.8	9.0	8.4
dppe	12.0	14	12.7
depe	16	16.5	16.3

It appears from the experimental evidence^[25] that the changing of the diphosphine ligand has a relatively large effect on the acidities of the iron complexes even though there is little change in the $d_{\text{H-H}}$ distances.

3. The intramolecular exchange of H atoms

The intramolecular exchange of H atoms between H_2 and other hydrides has been observed^[6a,21a,21b,21c,24,52-55] for almost all the investigated dihydrogen complexes with more than two hydrogens, including the cationic complexes $[\text{FeH}(\text{H}_2)\text{L}_2]^+$ {L=dppe, depe, dmpe, dedppe, d(i-Pr)pe, dtfpe, dtpe}, $[\text{FeH}(\text{H}_2)\{\text{PPh}(\text{OEt})_2\}_4]^+$ and $[\text{FeH}(\text{H}_2)\{\text{P}(\text{OEt})_3\}_4]^+$. However, it is not observed for the *cis*-hydride- η^2 -dihydrogen complex $[\text{Fe}(\text{H})_2(\text{H}_2)(\text{PEtPh}_2)_3]^{\text{[31,56]}}$ or for *trans*- $[\text{FeH}(\text{H}_2)(\text{meso-tet-1})][\text{BF}_4]^{\text{[6a,53]}}$ which has a rather unusual phosphine environment (Figure 3).

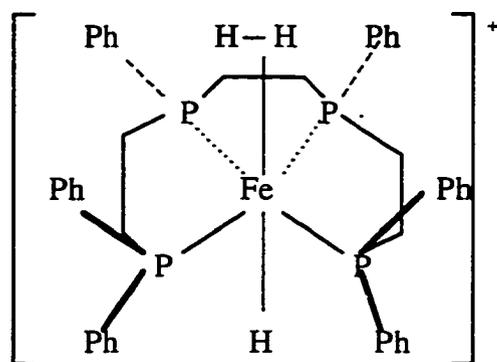
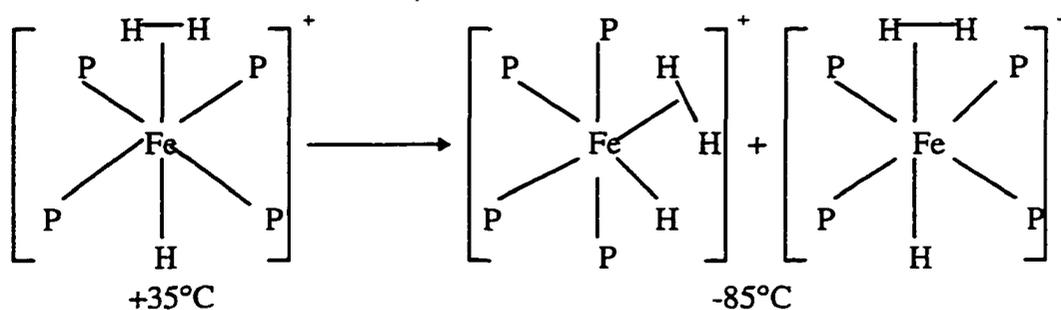


Figure 3. *trans*- $[\text{FeH}(\text{H}_2)(\text{meso-tet-1})]^+$ with four phenyl groups on the H_2 side

The barrier for this intramolecular exchange differs with different complexes. For example, the coalescence temperatures for *trans*-[FeH(H₂)(depe)₂][BPh₄], *trans*-[FeH(H₂)(dppe)₂][BF₄], *trans*-[FeH(H₂)(dmpe)₂][BPh₄] and *trans*-[FeH(H₂)(dedppe)₂][BPh₄] are 293 K^[21b], 313 K^[21a], >273 K^[52] and >325 K^[21c], respectively.

The ³¹P{¹H} NMR spectrum of [FeH(H₂){PPh(OEt)₂]₄⁺ varies with the temperature. At +35°C, only one singlet is observed which corresponds to the *trans*-structure. At -85 °C, however, the NMR signal changes to a singlet and a multiplet, consistent with the presence of a mixture of *cis* and *trans* isomers (Scheme 2)^[61].



Scheme 2

Since variable-temperature monitoring of ³¹P {¹H} NMR spectra is not the normal procedure in the investigation of dihydrogen complexes, it is likely that this phenomenon may exist for other systems, especially those which have a low barrier for the intramolecular exchange. The presence of the *cis* and *trans* isomers accompanying the intramolecular exchange^[61] noted above shows that site exchange of a phosphine with one

hydride could occur in solution for dihydrogen complexes of iron with monodentate phosphine ligands. For complexes with chelating diphosphines, the site exchange probably requires a temporary dissociation of one end of the diphosphine from the iron center. The possibility of this fast opening of the chelating ring has been confirmed in mechanistic studies on *trans*-[FeH(X)(L)₂], X=Cl or Br, L=dppe or depe,^[64] and *trans*-[FeH(N₂)(depe)₂][BPh₄]^[65].

For *trans*-[FeH(H₂)(meso-tet-1)][BF₄], both the steric and electronic barriers for this site exchange are large because of the special environment (Scheme 2). For the *cis*-hydride-η²-dihydrogen complex [Fe(H)₂(H₂)(PEtPh₂)₃], a *cis* effect of hydride on H₂ has been suggested as a factor which could retard the intramolecular exchange^[32].

4. The equilibrium between dihydrogen and dihydride complexes

No such equilibria have been found for the iron dihydrogen complexes with the formula [FeH(H₂)L_n]⁺. This is perhaps due to the electronic nature of the iron center. As mentioned in the previous part, the electronic situation of iron centers for dihydrogen complexes can be deduced from the $v_{N=N}$ values of their corresponding dinitrogen complexes. The available $v_{N=N}$ values^[3] show that the metal fragments [FeHL_n]⁺ are not very electron rich, even when most of the dihydrogen complexes have the *trans*-hydride, and the formation of the seven coordinated dihydride complexes is not favored^[3]. The

energy barrier for this rearrangement could be so high that it cannot be compensated by the formation of iron hydride bonds^[21a].

Experimental evidence appears to support this conclusion. For example, this equilibrium is not observed for the complex $[\text{FeCp}(\text{H}_2)(\text{dppe})][\text{BF}_4]$ ^[59] but is observed for the ruthenium analogue $[\text{RuCp}(\text{H}_2)(\text{dppe})][\text{BF}_4]$ ^[66] in which the Ru site is more electron rich. When Cp is changed to the more electron donating ligand Cp*, the expected equilibrium is found between $[\text{Fe}^{\text{II}}\text{Cp}^*(\text{H}_2)(\text{dppe})]^+$ and $[\text{Fe}^{\text{IV}}\text{Cp}^*(\text{H})_2(\text{dppe})]^+$ ^[59].

5. The reactivity of the dihydrogen complexes toward replacement

It appears that H₂ replacement reactions are relatively easy with dihydrogen complexes of iron although there are differences in reaction rates depending upon the different phosphine ligands. For example, $[\text{FeH}(\text{H}_2)\{\text{PhP}(\text{OEt})_2\}_4]^+$ and $[\text{FeH}(\text{H}_2)\{\text{P}(\text{OEt})_3\}_4]^+$, are relatively stable under N₂ atmospheres^[55], $[\text{FeH}(\text{H}_2)(\text{dppe})_2]^+$ reacts slowly with N₂^[21a] and N₂ substitution with $[\text{FeH}(\text{H}_2)(\text{dmpe})_2]^+$ is very fast^[52].

Substitution reactions offer another efficient route for the synthesis of some interesting complexes. However, comparatively little attention^[52,55] has been paid to such syntheses compared with the huge effort devoted to the characterization of new dihydrogen complexes. Only the substitution reactions with *trans*- $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$ have been fully investigated. These include reactions with N₂, CO, C₂H₄, CS₂, MeCN, CO₂, alkenes and alkynes from which the products were characterized.^[44,52,67,68]

The characteristics of some important substitution derivatives of dihydrogen complexes of iron are described in the following section.

(II) Some substitution derivatives of iron dihydrogen complexes

1. Substitution by N₂

The replacement of H₂ by N₂ is the most observed reaction in dihydrogen complexes of iron. It is also important to recognize that N₂ complexes of Fe can also be made independently of the Fe-(H₂) complexes. In fact, the $\nu_{\text{N}=\text{N}}$ of dinitrogen complexes can be used to assess the possibilities of synthesizing the corresponding H₂ complexes. For example, it has been suggested^[3] that when $\nu_{\text{N}=\text{N}}$ falls in the range 2060 cm⁻¹ to 2150 cm⁻¹, the existence of stable dihydrogen complexes might be expected. This assumption correlates very well with the experimental facts on iron complexes (Table 2)^[3].

Table 2

Dihydrogen Cationic Complexes	$\nu_{\text{N}=\text{N}}$ (cm ⁻¹) for the corresponding N ₂ complex
[FeH(H ₂)(dmpe) ₂] ⁺	2094
[FeH(H ₂)(depe) ₂] ⁺	2090
[FeH(H ₂)(dppe) ₂] ⁺	2120
[FeH(H ₂)(meso-tet-1)] ⁺	2130
[FeH(H ₂)(pp ₃)] ⁺	2100

However, the coordination mode of N_2 to a transition metal is different from that of H_2 . It always adopts the mono-nuclear end-on mode ($M-N\equiv N$) and, furthermore, bridging dinitrogen complexes have never been found from N_2 replacement of H_2 although such compounds are known to exist and can be synthesized by other methods. *Trans*- $[(FeCl(depe)_2)_2(\mu-N_2)][BPh_4]_2$ ^[69] is typical of such a compound. Compared with H_2 , the π accepting ability of N_2 is weak^[13,14] and it can be very easily replaced by other neutral ligands such as CO or MeCN^[70]. Of course CO and MeCN are quite different coordinating ligands, the former being a good π -acceptor and a moderately good σ -donor while the later is a good σ -donor and a poor π -acceptor^[13,14,71].

2. Substitution by CO

Replacement of H_2 by CO occurs readily. The coordination of CO takes the end-on mode like N_2 ($M-C\equiv O$) and the corresponding substitution complexes show high stability. It has been found that the stabilities of the complexes $[FeH(L')(L)][BPh_4]$ ($L'=CO, MeCN$ and C_6H_5CN ; $L=pp_3, np_3$) follow the order $CO \gg MeCN = C_6H_5CN$ ^[70,72,73] although it is noteworthy that these complexes are not synthesized through the route of H_2 displacement.

The bonding between metal and carbonyl is via σ - π interaction. The σ -donation of electrons come from a filled orbital centered on carbon and π interaction is via the π^*

orbital of CO. Consequently, CO is a relatively poor σ donor, but a strong π acceptor.

Thus, $\nu_{\text{C=O}}$ in the complexes, $[\text{FeH}(\text{CO})(\text{dmpe})_2][\text{BPh}_4]$ ^[52], $[\text{FeH}(\text{CO})(\text{pp}_3)][\text{BPh}_4]$ ^[70] and $[\text{FeH}(\text{CO})(\text{depe})_2][\text{BPh}_4]$ ^[73], is greatly reduced (1926, 1930 and 1915 cm^{-1}) compared with that for free CO ($\nu_{\text{C=O}} = 2143 \text{cm}^{-1}$). Here, only the complex $[\text{FeH}(\text{CO})(\text{dmpe})_2][\text{BPh}_4]$ was synthesized by a replacement reaction using the dihydrogen complex.

3. Substitutions by organonitriles

As relatively strong σ -donor ligands, organonitriles generally use the lone pair of electrons on the nitrile nitrogen atom to coordinate to a transition metal. Thus, the value of $\nu_{\text{C=N}}$ in the complex is usually raised.^[74] However, when back donation from the metal to the nitrile is present, especially when the metal is in a low oxidation state, $\nu_{\text{C=N}}$ is generally lowered because of relatively strong π -back-bonding^[75].

Some organonitrile complexes of iron, together with their $\nu_{\text{C=N}}$ values are listed in Table 3 (Note that only $[\text{FeH}(\text{NCMe})(\text{dmpe})_2][\text{BPh}_4]$ was synthesized through the replacement of H_2 of the dihydrogen complex by MeCN).

It is apparent that back donation from the d-orbitals of iron to nitriles occurs in the relevant iron complexes. It is an interesting fact that organonitrile complexes prefer the *trans*- coordination mode.

Table 3

Cations (<i>trans</i> -)	$\nu_{\text{C}\equiv\text{N}}$ (Free Ligand, cm^{-1})	$\nu_{\text{C}\equiv\text{N}}$ (Complex, cm^{-1})	Reference
$[\text{FeH}(\text{NCMe})(\text{dmpe})_2]^+$	2254(s), 2293(w)	2231	52
$[\text{FeH}(\text{NCMe})(\text{depe})_2]^+$	2254	2228	73
$[\text{Fe}(\text{NCMe})_2(\text{depe})_2]^{2+}$	2254	2254	76
$[\text{Fe}(\text{succn})_2(\text{depe})_2]^{2+}$	2257	2236, 2222	76
$[\text{FeCl}(\text{NCPh})(\text{depe})_2]^+$	2231	2179	76
$[\text{FeH}(\text{NCPh})(\text{depe})_2]^+$	2231	2168	73

4. Substitution by $\text{CH}_2=\text{CH}_2$

The coordination of ethylene to transition metals is generally through the side-on (η^2 -bonded) mode which is the same as that of H_2 in a dihydrogen complex. However, ethylene donates its π electrons to form the metal-ethylene bond and at the same time the filled d-orbital of the metal returns electrons to the π^* -orbital of the ethylene. This interaction weakens the C=C bond and affects the properties of the coordinated ethylene (e.g., the chemical shift of the ethylene protons^[77]).

There are only a few studies^[52,78] on ethylene substitution reactions with dihydrogen complexes of iron. The chemical shift of the protons in coordinated ethylene

has been found to be quite large and towards higher magnetic fields in both *trans*- $[\text{FeH}(\text{C}_2\text{H}_4)(\text{dmpe})_2][\text{BPh}_4]^{[52]}$ and *cis*- $[\text{FeH}(\text{C}_2\text{H}_4)(\text{pp}_3)][\text{BPh}_4]^{[78]}$. These ethylene derivatives are unstable when exposed to air or moisture and no crystal structures of such iron complexes have been reported yet.

III. Summary and Research Proposals

The synthesis and characterization of molecular hydrogen complexes of transition metals in general have been well developed. Compared with major efforts on the synthesis of new M-(H₂) complexes, relatively little work has concentrated on the chemistry of these complexes, especially on those of iron.

The synthesis and chemistry of both the dihydride and the dihydrogen complexes of iron with dpmm as the supporting ligand have only been briefly touched upon^[6]. For example, no NMR information has been given on the dihydride complex *trans*-Fe(H)₂(dpmm)₂ because no suitable solvent could be found. The ¹H NMR spectrum of the dihydrogen complex [Fe(H)(H₂)(dpmm)₂][BF₄] has been reported^[6a] but the solid has not been characterized and there has been no discussion of this system in the literature. What is more, no reactivity studies have been carried out on this dihydrogen product. It is surprising that, considering the many derivatives of analogous compounds of Fe of the type [Fe(H)(H₂)(phosphine)₂]⁺[X⁻] with other phosphines, made either by substitution of H₂ or by other methods, derivatives of the dpmm-containing compound are very rare. For example, no iron-ethylene, iron thioformato or iron-dinitrogen complexes with dpmm as the supporting ligand have been reported.

Based upon the above information, it was thought to be desirable to design a research program concerning the synthesis and chemistry of both the dihydride and the dihydrogen complexes of iron with dpmm since dpmm usually behaves quite differently

from other bidentate phosphines. Because of time constraints, the proposed research concentrates on the following areas:

1. Synthesis of the pure starting material *trans*-[Fe(H)₂(η²-dppm)₂].
2. Synthesis of the pure dihydrogen complex *trans*-[FeH(η²-H₂)(η²-dppm)₂]⁺[X⁻].
3. Investigation of the intramolecular exchange between H₂ and hydride.
4. Investigation of the equilibrium between *trans*-[Fe(H)₂(η²-dppm)₂] and *trans*-[FeH(η²-H₂)(η²-dppm)₂]⁺[X⁻] by monitoring both the ¹H and ³¹P {¹H} NMR spectra over a range of temperatures.
5. Investigation of the chemistry of *trans*-[FeH(η²-H₂)(η²-dppm)₂]⁺[X⁻], mainly with respect to substitution reactions. The H₂-displacing ligands will include the small ligands used in the research on the related *trans*-[FeH(η²-H₂)(η²-dmpe)₂][BPh₄] for comparison purposes. Representative small ligands to be used initially for these studies are: N₂, CO, CH₂=CH₂, MeCN. This preliminary list will be revised according to the experimental results.

Experimental

Reagents and Solvents FeCl₃, dppm, LiAlH₄ and HBF₄•Et₂O were purchased from Aldrich and kept in a dry, N₂ filled glove box at all times after their opening. THF and benzene were obtained from Aldrich; ether, pyridine, CH₂Cl₂ were obtained from BDH Inc.; succinonitrile was obtained from Kodak; hexane and acetonitrile were obtained from Caledon Laboratories, Ltd. Benzene, THF and ether were dried by distillation from sodium wire and kept in a glove box under dry N₂. It was usually necessary to use these within three days, especially during periods of high humidity. CH₂Cl₂ and CH₃CN were dried by distillation from P₂O₅ just before their use. Other reagents and solvents were reagent grade and were kept in the glove box without further purification. All the deuterated solvents used were dried over Linde type 4 A° molecular sieves activated for 24 h before their use. In addition, all solvents were degassed prior to use by appropriate gases.

Physical Measurements Infrared spectra were recorded on a Bruker IFS-66 FTIR spectrometer as Nujol mulls between NaCl plates. ¹H and ³¹P{¹H} NMR spectra were recorded on a Bruker AC-E 200 spectrometer. ¹H chemical shifts were measured relative to tetramethylsilane (TMS) and the ³¹P chemical shifts were reported relative to a

reference of 85% H₃PO₄. For the ³¹P{¹H} NMR spectra, a coaxial D₂O insert was used for frequency lock in the situations where undeuterated solvents were used. Micro-analyses for C, H and N were performed in our laboratories using a Control Equipment Corporation model 240XA analyzer with V₂O₅ as a combustion aid.

Synthesis of the Compounds All the syntheses were performed in a glove box filled with carefully dried (P₂O₅) inert gas at all times. N₂ was normally used to control the atmosphere for syntheses except those specified. When a specific gas atmosphere was needed, the reactions were carried out in a 100 mL three-necked flask under a flow of the particular gas. When nitrogen-free conditions were required, the glove box was filled with Ar.

Synthesis of *trans*-[Fe(H)₂(η²-dppm)₂], 1

FeCl₃ (0.45 g, 2.8 mmol) dissolved in THF (10 mL) and dppm (2.1 g, 5.5 mmol) in benzene (15 mL) were mixed to form a dark green solution. A suspension of LiAlH₄ (0.19 g, 5.0 mmol) in THF (5 mL) was added drop by drop to the stirred solution over a 2 min. period. The mixture was filtered immediately and the filtrate was kept in the glove box. Red crystals formed in the filtrate within 24 h. The product was filtered off and washed successively with ether, benzene and ether (10 mL each) and then dried under reduced pressure for about 1 h. Yield: 10-16%. Crystals of **1** produced in this manner were found

to be suitable for a single crystal X-ray structure determination. Anal. Calcd for **1** ($\text{FeP}_4\text{C}_{50}\text{H}_{46}$): C, 72.7%; H, 5.6%. Found: C, 72.9%; H, 5.6%. IR: $\nu_{\text{Fe-H}}=1711\text{ cm}^{-1}$. $^{31}\text{P}\{^1\text{H}\}$ NMR (25°C, CD_2Cl_2): δ 24 (singlet). ^1H NMR (25°C, CD_2Cl_2): δ -7 (Fe-H, broad). Complex **1** decomposes quickly in the presence of water. However, it is stable for at least one week in the solid state if kept in a dry, inert atmosphere. It has limited stability in dry CH_2Cl_2 and is either insoluble or decomposes quickly in other solvents.

Synthesis of *trans*- $[\text{Fe}(\text{H})(\eta^2\text{-H}_2)(\eta^2\text{-dppm})_2][\text{BF}_4]$, **2**

Freshly prepared **1** (0.25 g, 0.30 mmol) was suspended under an atmosphere of H_2 in THF (10 mL) which had been degassed by Ar or H_2 . To this stirred suspension, an excess of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (70-100 μL , 0.48-0.68 mmol) was added dropwise. A pale yellow precipitate was produced either immediately or within 1-2 min. Ether (10 mL) was added immediately and this precipitated out the pure yellow solid. The product was filtered off and washed three times with ether (5 mL each) and then dried under reduced pressure. Yield: 95-100%. Anal. Calcd for **2** ($\text{FeF}_4\text{P}_4\text{BC}_{50}\text{H}_{47}$): C, 65.7%; H, 5.2%. Found: C, 65.5%; H, 5.5%. IR: $\nu_{\text{Fe-H}}=1708\text{ cm}^{-1}$ (very weak). $^{31}\text{P}\{^1\text{H}\}$ NMR (25°C, CD_2Cl_2): δ 32.5 (singlet). ^1H NMR (25°C, CD_2Cl_2): δ -7.21 (Fe-H, quintet, $^2J_{\text{PH}}=44\text{ Hz}$); δ -4.0 (Fe-H₂, broad singlet). Complex **2** is very sensitive to traces of water but it is stable for at least one week in the solid state in a dry Ar atmosphere. In solution it decomposes quickly in acetone, benzene, ethanol and chloroform but is stable at least 6 hours in dry CH_2Cl_2 .

Recrystallization of **2** is possible from CH₂Cl₂/hexane under a strictly anhydrous Ar atmosphere.

Synthesis of *trans*-[Fe(H)(CH₃CN)(η²-dppm)₂][BF₄], **3**

Method A Compound **2** (0.037 g) was dissolved in CH₃CN (10 mL) to form an orange-red solution. After 10 min, ether (50 mL) was carefully layered over the solution and the crystalline product which was produced over a 24 h period was separated, washed with ether (10 mL) and dried under reduced pressure. Yield: >90%. Anal. Calcd for **3** (FeF₄P₄BNC₅₂H₄₈): C, 65.5%; H, 5.1%; N, 1.5%. Found: C, 65.5%; H, 4.9%; N, 1.3%. IR: ν_{Fe-H}=1880 cm⁻¹ (w), ν_{CN}=2250 cm⁻¹. ³¹P{¹H} NMR (25°C, CD₂Cl₂): δ 29.8 (singlet). ¹H NMR (25°C, CD₂Cl₂): δ -13.7 (Fe-H, quintet, J_{PH}=44.0 Hz); δ 4.31 and 4.79 (PCH^aH^bP, poorly resolved); δ 1.44 (Fe-NCCH₃). Complex **3** is stable in air. It is soluble and stable in acetone, chloroform, methylene chloride and acetonitrile. Crystals of **3** for X-ray diffraction can very easily be obtained by slow diffusion from CH₂Cl₂/hexane.

Method B Compound **1** (0.21 g, 0.26 mmol) was suspended in CH₃CN (10 mL) and stirred at -30°C (dry ice and acetone) for 20 min. An excess of HBF₄•Et₂O (200 μl, 1.36 mmol) was added dropwise to the stirred solution to form an orange red solution. Ether (50 mL) was added to precipitate out the orange yellow solid which was filtered off and dried under reduced pressure. Yield: 86%.

Synthesis of *trans*-[Fe(CH₃CN)₂(η²-dppm)₂][BF₄]₂•2CH₂Cl₂, **4**

To a stirred suspension of compound **1** (0.19 g, 0.22 mmol) in CH₃CN (6 mL), HBF₄•Et₂O (150 μL, 1 mmol) was added dropwise. Compound **1** dissolved to give a clear deep-red solution. Ether (70 mL) was added immediately to precipitate out a peach colored solid (0.21 g) which was filtered off and washed with ether (10 mL) and dried under reduced pressure. ³¹P{¹H} NMR (25°C, CD₂Cl₂): δ 29.8 (singlet); δ 14 (singlet); δ 12.3 (triplet) and δ 1.08 (triplet) (see discussion). The mixture of products (0.21 g) was redissolved in CH₃CN (8 mL) and stirred overnight. Ether (70 mL) was then added to precipitate out a pink solid (0.14 g) which was collected and dried the same way as described above. CH₂Cl₂ (or CH₃CN) (4 mL) was added to this mixture and the insoluble residue removed by filtration. Hexane (or ether) (16 mL) was carefully layered over the filtrate. The final crystalline product **4**, suitable for the X-ray structure determination, was formed within 24 h. The crystals were filtered off and washed with ether (10 mL) and dried under reduced pressure. Yield : 31%. Anal. Calcd for **4** (FeB₂N₂F₈P₄C₅₆H₅₄Cl₄): C, 53.69%; H, 4.35%; N, 2.24%. Found: C, 53.07%; H, 4.77%; N, 2.23%. IR: ν_{CN} = 2249, 2269, 2289, 2317 cm⁻¹. ³¹P{¹H} NMR (25°C, CD₂Cl₂): δ 14.2 (singlet). ¹H NMR (25°C, CD₂Cl₂): δ 2.37 {Fe-(CH₃CN)₂}. Complex **4** is stable in air and is soluble and stable in methylene chloride, chloroform and acetonitrile.

Preparation of *trans*-[Fe(η^2 -H₂)₂(η^2 -dppm)₂][BF₄]₂, **5**

Method A To a stirred suspension of compound **1** (0.11 g, 0.13 mmol) in THF (10 mL), HBF₄•Et₂O (150 μ L, 1 mmol) was added dropwise to give a clear yellow solution.

³¹P{¹H} NMR (25°C): δ 3.32 (singlet).

Method B Compound **2** (10 mg, 0.01 mmol) was dissolved in CD₂Cl₂ (0.6 mL) under an Ar atmosphere. HBF₄•Et₂O (15 μ L, 0.1 mmol) was added dropwise with shaking.

³¹P{¹H} NMR (25°C, CD₂Cl₂): δ 3.32 (singlet).

A pale yellow solid, **2**, was obtained by adding ether or hexane (50 mL) to the solution noted above (see discussion). Attempts to obtain solid **5** were not successful (see discussion).

Synthesis of *trans*-[Fe(H){NC(CH₂)₂CN}(η^2 -dppm)₂][BF₄], **6**

Method A A solution of succinonitrile (0.1 g, 1.25 mmol) in THF (4 mL) was added to a stirred suspension of compound **2** (0.13 g, 0.14 mmol) in THF (10 mL) and an orange red solution was formed immediately. After 40 min, ether (30 mL) was added to the solution and an orange solid precipitated out. The product was filtered off and washed twice with ether (10 mL each time) and dried under reduced pressure. Yield: 80%. Anal. Calcd for **6** (FeF₄P₄BN₂C₅₄H₄₉): C, 65.35%; H, 4.94%; N, 2.82%. Found: C, 65.72%; H,

5.16%; N, 2.64%. IR: $\nu_{\text{Fe-H}}=1881 \text{ cm}^{-1}$ (w), $\nu_{\text{CN}}=2228$ (very weak), 2239 cm^{-1} (weak).

$^{31}\text{P}\{^1\text{H}\}$ NMR (25°C, CD_2Cl_2): δ 30.3 (singlet). ^1H NMR (25°C, CD_2Cl_2): δ -13.1 (Fe-H, quintet, $J_{\text{PH}}=47 \text{ Hz}$); δ 4.34 and 4.81 ($\text{PCH}^{\text{a}}\text{H}^{\text{b}}\text{P}$, poorly resolved); δ 2.22, 1.93 (Fe- $\text{NCCH}_2\text{CH}_2\text{CN}$) (broad singlets, overlapped and poorly resolved). Complex **6** is stable in air. It is soluble and stable in methylene chloride and chloroform.

Compound **6** (0.11 g) was recrystallized from CH_2Cl_2 (4 mL) /hexane (12 mL) by slow diffusion over 24 h. The orange crystals were filtered off, washed with ether (10 mL), dried under reduced pressure and used for the X-ray structural determination.

Method B A solution of succinonitrile (0.055 g, 0.69 mmol) in THF (4 mL) was added to a stirred suspension of compound **1** (0.18 g, 0.22 mmol) in THF (10 mL). $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (200 μL , 1.36 mmol) was added dropwise and **1** dissolved immediately to give a clear yellow solution which gradually became orange-red. After 20 min, ether (30 mL) was added to stop the reaction and the orange solid which precipitated out was filtered off, washed twice with ether (10 mL each time) and dried under reduced pressure. Yield: 81%.

Synthesis of *trans*-[Fe(H)(pyridine)(η^2 -dppm) $_2$][BF $_4$], **7**

To a stirred suspension of compound **2** (0.11 g, 0.12 mmol) in THF (10 mL), pyridine (0.1 mL, 1.24 mmol) was added. A clear red solution was formed and after 50

min, ether (30 mL) was added to precipitate out a blood-red solid which was washed twice with ether (10 mL each time) and dried under reduced pressure. Yield: 66%. Anal. Calcd for **7** ($\text{FeF}_4\text{P}_4\text{BNC}_{55}\text{H}_{45}$): C, 66.99%; H, 4.56%; N, 1.42%. Found: C, 62.49%; H, 5.35%; N, 1.97. IR: $\nu_{\text{Fe-H}}=1853\text{ cm}^{-1}$ (w). $^{31}\text{P}\{^1\text{H}\}$ NMR (25°C, deuterated pyridine): δ 22.67 (singlet). ^1H NMR (25°C, deuterated pyridine): δ -17 (Fe-H, quintet, $^2J_{\text{PH}}=46\text{ Hz}$). In solution, complex **7** only has limited stability in pyridine and it decomposes quickly in acetone or methylene chloride. This makes analyses difficult and recrystallization impossible.

Synthesis of *trans*- $[\text{Fe}(\text{H})(\text{CO})(\eta^2\text{-dppm})_2][\text{BF}_4]$, **8**

Method A^[6b] The procedure is the same as that used for **2** except that the reaction was carried out under CO. The final product is a pale yellow solid. Yield: $\approx 100\%$. Anal. Calcd for **8** ($\text{FeF}_4\text{P}_4\text{BOC}_{51}\text{H}_{45}$): C, 65.1%; H, 4.8%; Found: C, 65.4%; H, 4.4%. IR: $\nu_{\text{Fe-H}}=1710\text{ cm}^{-1}$ (w), $\nu_{\text{CO}}=1944\text{ cm}^{-1}$ (s), 1904 cm^{-1} (w, sh). $^{31}\text{P}\{^1\text{H}\}$ NMR (25°C, acetone- d_6): δ 31.6 (singlet). ^1H NMR (25°C, acetone- d_6): δ -2.03 (Fe-H, quintet, $^2J_{\text{PH}}=44.4\text{ Hz}$); δ 5.05 and 4.69 (PCH^aH^bP, poorly resolved). Complex **8** is stable in air and is soluble and stable in acetone, acetonitrile, chloroform and methylene chloride. Crystals of **8** can be easily obtained by recrystallization from CH_2Cl_2 /hexane.

Method B Compound **1** (0.13 g, 0.15 mmol) was suspended in THF (20 mL). An excess of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (100 μL , 0.68 mmol) was added dropwise with stirring to form a yellow solution. CO was passed through the solution for one hour after which ether or hexane (20 mL) was added to precipitate out a pale yellow product. It was washed twice with ether (10 mL each time) and dried under reduced pressure. Yield: 83%.

Synthesis of *trans*-[Fe(H)(N₂)(η^2 -dppm)₂][BF₄], **9**

Method A Into a suspension of compound **2** (0.12 g, 0.13 mmol) in THF (20 mL), N₂ was passed at a rate of 3-5 bubbles/second for 5 h. Ether (20 mL) was then added to precipitate out a yellow solid which was washed twice with ether (10 mL each time) and dried under reduced pressure. Yield: 77%. Anal. Calcd for **9** ($\text{FeF}_4\text{P}_4\text{BN}_2\text{C}_{50}\text{H}_{45}$): C, 63.91%; H, 4.79%; N, 2.98%. Found: C, 64.0%; H, 4.99%; N, 2.52%. IR: $\nu_{\text{Fe-H}}=1713 \text{ cm}^{-1}$ (w), $\nu_{\text{NN}}=2116 \text{ cm}^{-1}$. $^{31}\text{P}\{^1\text{H}\}$ NMR (25°C, CD_2Cl_2): δ 24.2 (singlet). ^1H NMR (25°C, CD_2Cl_2): δ -9.38 (Fe-H, quintet, $^2J_{\text{PH}}=43.6 \text{ Hz}$). Complex **9** gradually changes its colour in air. In solution **9** is only stable in dry CH_2Cl_2 . It decomposes very quickly in acetone or chloroform. Recrystallization of **9** is possible from CH_2Cl_2 /hexane under a strictly anhydrous N₂ atmosphere.

Method B Freshly prepared compound **1** (0.11 g, 0.13 mmol) was suspended in THF (10 mL) and $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (100 μL , 0.68 mmol) was added dropwise with stirring.

Compound **1** dissolved to form a clear yellow solution into which N₂ was then passed at a rate of 3-5 bubbles/second for 5 h. During this time a yellow precipitate was formed.

Addition of ether (20 mL) completed the precipitation of the yellow product which was filtered off and washed twice with ether (10 mL) and dried under reduced pressure. Yield: >60%.

Synthesis of *trans*-[Fe(H)(η^2 -CH₂=CH₂)(η^2 -dppm)₂][BF₄] \bullet 0.5CH₂Cl₂, **10**

Method A Ethylene was passed into a stirred suspension of **2** (0.091 g, 0.10 mmol) in THF (20 mL) at a rate of 3 bubbles/second for three hours. Ether (20 mL) was added to precipitate out an orange red product which was filtered off, washed with ether (10 mL) and dried under reduced pressure. Yield: 89%. Crystals of **10** were obtained by recrystallization from CH₂Cl₂/hexane under a dry Ar atmosphere. Anal. Calcd for **10** (FeF₄P₄BC_{52.5}H₅₀Cl): C, 64.52%; H, 5.15%. Found: C, 64.70%; H, 5.12%. IR: $\nu_{\text{Fe-H}}=1714$ cm⁻¹ (w, sh). ³¹P{¹H} NMR (25°C, CDCl₃): δ 32.8 (singlet). ¹H NMR (25°C, CDCl₃): δ -1.78 (Fe-H, quintet, ²J_{PH} = 50.6 Hz); δ 5.29 and 4.39 (PCH^aH^bP, poorly resolved); δ 3.18 {Fe-(η^2 -CH₂=CH₂)}. Complex **10** is very sensitive to moisture. It is stable in dry acetone, chloroform and methylene chloride.

Method B Compound **1** (0.11 g, 0.137 mmol) was suspended in THF (10 mL) under ethylene. An excess of HBF₄ \bullet Et₂O (100 μ L, 0.68 mmol) was added dropwise with stirring

to form a yellow solution through which ethylene was passed at a rate of 3 bubbles/second for three hours. An orange precipitate slowly formed and precipitation was completed by addition of ether (20 mL). The orange red solid was filtered off, washed twice with ether (10 mL each time) and dried under reduced pressure. Yield: 72%.

The reactivity of compound 2 toward propene ($\text{CH}_3\text{CH}=\text{CH}_2$)

The procedure was almost the same as **Method A** for the synthesis of compound **10** (starting with **2** and ethylene) except that propene was used instead of ethylene. No evidence that **2** reacted with the propene was detected from NMR measurements.

The reactivity of compound 2 toward *cis*-2-butene (*cis*-2- $\text{CH}_3\text{CH}=\text{CH}_2\text{CH}_3$)

The procedure was almost the same as **Method A** for compound **10** except that *cis*-2-butene was used instead of ethylene. No evidence that **2** reacted with the *cis*-2-butene was detected from NMR measurements.

The reactivity of compound 2 toward styrene ($\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$)

To a stirred suspension of compound **2** (0.13 g, 0.14 mmol) in THF (10 mL), a large excess of styrene (1.62 mL, 14 mmol) was added under Ar. The mixture was stirred for 3 h. No evidence that **2** reacted with the olefin was observed from ^{31}P NMR measurements.

Results and Discussion

This chapter is an account of the approaches used for the synthesis of Fe-dppm hydride and dihydrogen complexes and also the H₂ displacement reactions of the dihydrogen complex. Stability, electronic, geometrical and mechanistic considerations are also discussed.

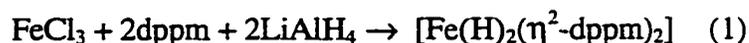
I. Syntheses and Characteristics of the Complexes

I.1. *Trans*-[Fe(H)₂(η²-dppm)₂], **1**

While several preparative approaches to dihydrogen complexes are known (see the introduction chapter of this thesis), hydride complexes of transition metals are perhaps the most widely used starting materials for the synthesis of such complexes. Accordingly, a convenient synthesis of compound **1** had to be devised. Compound **1** was first synthesized in 1988 by Bautista^[6a] from FeCl₂ and dppm using NaBH₄ as the source of H⁻. The only spectroscopic information reported was ν_{Fe-H} (1710 cm⁻¹) and the low frequency of ν_{Fe-H} was explained by the high *trans* effect of two *trans* hydrogens.

Since the above Fe(II)-NaBH₄-dppm reactions apparently lead to no reduced Fe compounds, in contrast to the production of many low valent complexes of Co, Ni, Pd and Pt under similar conditions^[7], work was started in this laboratory on reactions between Fe(II) / (III) - dppm and the stronger reducing agent LiAlH₄. In the course of this work^[6b],

it was found that the $\text{FeCl}_3/\text{dppm}/\text{LiAlH}_4$ reaction is a very convenient source of compound **1** which can be produced as outlined in reaction (1) and in the previous chapter by controlling the molar ratio of $\text{FeCl}_3:\text{dppm}:\text{LiAlH}_4$ at 1:2:2.

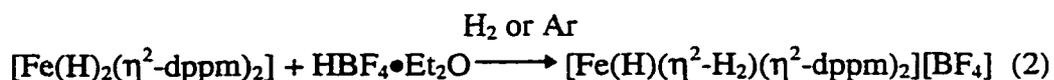


A crystal structure of **1** has been obtained and this confirmed a *trans* arrangement of the two hydrogens^[6b]. Compound **1** is highly sensitive to traces of water and its successful use in the synthesis of $[\text{FeH}(\text{H}_2)(\text{dppm})_2][\text{BF}_4]$, **2**, depends greatly upon the purity of **1**. Thus, all the solvents used in the synthesis and examination of **1** were carefully dried and, under these conditions, **1** is both soluble and stable in dry dichloromethane for at least one hour. This solution shows a sharp singlet at δ 24 in the ^{31}P { ^1H } NMR spectrum which is consistent with the *trans* geometry^[6b] shown by X-ray data. A broad unresolved singlet, attributed to the hydride ligand, occurs at δ -7 in the ^1H NMR spectrum. The value for $\nu_{\text{Fe-H}}$ of **1** was found to be 1711 cm^{-1} . *Trans*- $[\text{Fe}(\text{H})_2(\eta^2\text{-dppm})_2]$ is either insoluble or unstable in solvents other than dichloromethane.

It is noteworthy that dihydride complexes of iron with different chelating di-phosphines assume different geometries and quite a few adopt a *cis* structure^[6a], including *cis*- $[\text{Fe}(\text{H})_2(\eta^2\text{-dppe})_2]$.

I.2. *Trans*-[Fe(H)(η^2 -H₂)(η^2 -dppm)₂][BF₄], **2**

Under an atmosphere of either Ar or dihydrogen, complex **1** reacts according to reaction (2) with HBF₄•Et₂O to produce *trans*-[Fe(H)(η^2 -H₂)(η^2 -dppm)₂][BF₄] **2**.



Once again, complex **2** was first synthesized by Bautista^[6a] in 1988 by the same reaction, but the complex was not fully characterized. Only the ¹H spectrum with a broad singlet (δ -4) and a quintet (δ -7.2) was reported. The two peaks were assigned to the dihydrogen and the hydride ligands respectively. Further investigations on substitution reactions of compound **2** were precluded because of its apparent instability.

The initial attempts to repeat or modify the published method^[6a] in this laboratory were frustrated by the non-reproducibility of the reactions, low yields and the apparent lability of the final product.

In the work reported herein, by monitoring the ³¹P {¹H} NMR spectra of **2** under different conditions, we found that **2** is, like **1**, very sensitive to traces of water in solution, especially during its formation. The procedure was therefore further modified by ensuring that all the solvents used were strictly anhydrous. Pure product **2** was then obtained and characterized by IR, NMR and elemental analytical data. The solid **2** is stable under

reduced pressure and can be kept in a dry inert atmosphere for at least one week. Also, in the solid form, replacement of the dihydrogen ligand by N₂ (see later discussion) is very slow. In solution, **2** is stable only in dry CH₂Cl₂.

The complex exhibits a sharp singlet at δ 32.5 in the ³¹P {¹H} NMR spectrum which is consistent with a *trans*-arrangement of H/H₂ and the chelating dppm ligand. The ¹H NMR spectrum of complex **2** agrees with the published data^[6a], with δ -4 (broad singlet) due to H₂ and the δ -7 (quintet) signal due to the hydride split by 4 equivalent P atoms. These signals are at lower field than those exhibited by the dppe analogue (δ -8, -12.9, respectively)^[6a]. This can be explained in terms of the somewhat different donor character of dppe relative to dppm. The corresponding H-D complex was prepared by another worker in this laboratory and J_{HD} was found to be 30.0 Hz^[6b]. From this, an H-H distance of 0.92 Å was calculated by an empirical correlation^[2].

A weak and sharp peak at 1708 cm⁻¹, not at 1645 cm⁻¹ as previously reported^[6b], in the IR spectrum of **2** was assigned to $\nu_{\text{Fe-H}}$. Compared with **1**, $\nu_{\text{Fe-H}}$ is only very slightly reduced. This reflects a similar electronic environment of the hydride in the two complexes.

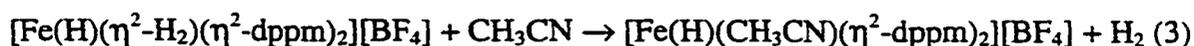
Though samples of complex **2** are pure enough for further reactions, most samples exhibited a small additional peak (δ 24) in ³¹P {¹H} NMR spectra. This is most probably due to contamination by *trans*-[Fe(H)₂(η^2 -dppm)₂]. The reason for this is not clear since

no equilibrium between $[\text{Fe}(\text{H})_2(\eta^2\text{-dppm})_2]$ and $[\text{Fe}(\text{H})(\eta^2\text{-H}_2)(\eta^2\text{-dppm})_2][\text{BF}_4]$ has been found (see later discussion). However, it was found in these experiments that the presence of traces of water will cause splitting of the dihydrogen ligand to give the dihydride form. Thus, a trace of water in either the THF or the ether may be responsible for this contamination. It is also possible that this additional signal is caused by the presence of the dinitrogen complex (δ 24.2 in the ^{31}P { ^1H } NMR spectrum). If that is the case, this contamination must have been introduced during the formation of complex **1** since the **1** to **2** conversion occurs in the absence of N_2 . It is also possible that $[\text{FeHCl}(\text{dppm})_2]$ is an intermediate in the synthesis of **1** and if so, it is reasonable to assume that it may react with N_2 to give the dinitrogen complex because such reactions of its dppe and depe analogues have already been well established^[62].

Complex **2** can undergo H_2 displacement reactions with a variety of molecules and these will be discussed in the following sections. Reactions will be discussed where the H_2 in **2** is replaced directly by other ligands and where substitution products are made directly from **2** generated *in situ* by reacting **1** with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ in the presence of the additional ligands.

I.3. *Trans*- $[\text{Fe}(\text{H})(\text{CH}_3\text{CN})(\eta^2\text{-dppm})_2][\text{BF}_4]$, **3**

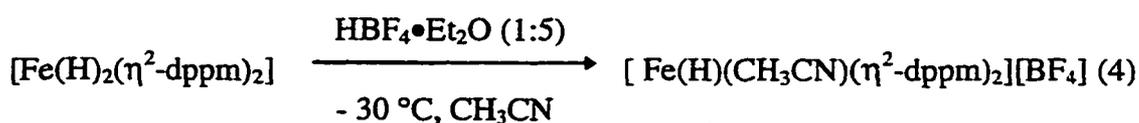
Complex **2** can be very easily and irreversibly converted into complex **3** by treatment with CH_3CN according to reaction (3).



Complex **3** is very stable to both moisture and air. It is also soluble and stable in a variety of polar solvents and both ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra can be obtained in several deuterated solvents, including acetone, chloroform, methylene chloride and acetonitrile. The $^{31}\text{P}\{^1\text{H}\}$ spectrum of compound **3** in CD_2Cl_2 shows a sharp singlet at δ 29.8 which clearly indicates that the compound possesses a *trans*-phosphine stereochemistry. This geometry has been confirmed by another worker in our laboratories using X-ray crystallography^[79]. The hydride signal in the ^1H NMR spectrum is a quintet at δ -13.7 which is much more downfield than that shown by the dmpe analogue (δ -24). Since dmpe is a much stronger electron-donating ligand than dppm, it appears that the electron-density on the iron site in the dmpe compound is higher than that for the dppm analogue. This also probably affects both the σ -donor and π -acceptor character of the CH_3CN ligand. This is reflected in the $\nu_{\text{C=N}}$ values in the two IR spectra. Thus, ν_{CN} (2231 cm^{-1}) for $[\text{Fe}(\text{H})(\text{CH}_3\text{CN})(\eta^2\text{-dmpe})_2][\text{BPh}_4]$ is lower than that of $[\text{Fe}(\text{H})(\text{CH}_3\text{CN})(\eta^2\text{-dppm})_2][\text{BF}_4]$ (2250 cm^{-1}) and the latter value is only slightly lower than that of free CH_3CN (2254 cm^{-1}). This suggests a weak back-bonding from iron to CH_3CN which is also consistent with the slight upfield shift of the signal (δ 1.44) due to the methyl hydrogens of the coordinated CH_3CN in the ^1H NMR spectrum.

The increase of $\nu_{\text{Fe-H}}$ (1880 cm^{-1}) for **3** relative to both **1** and **2** shows a relatively stronger Fe-H interaction which will be further discussed in a later section.

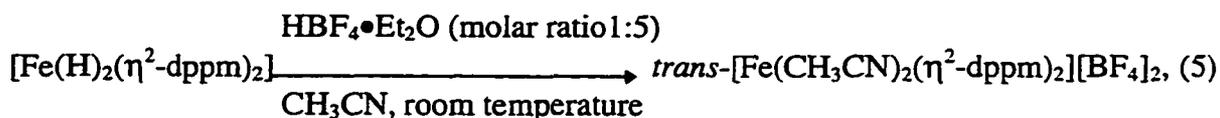
Complex **3** can also be synthesized directly from $[\text{Fe}(\text{H})_2(\eta^2\text{-dppm})_2]$ in the presence of acetonitrile and a large excess of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (molar ratio 1:5) at low temperature.



At room temperature, this reaction also produces the complex *trans*- $[\text{Fe}(\text{CH}_3\text{CN})_2(\eta^2\text{-dppm})_2][\text{BF}_4]_2$ which will be further discussed in the following section.

I.4. *Trans*- $[\text{Fe}(\text{CH}_3\text{CN})_2(\eta^2\text{-dppm})_2][\text{BF}_4]_2 \cdot 2\text{CH}_2\text{Cl}_2$, **4**

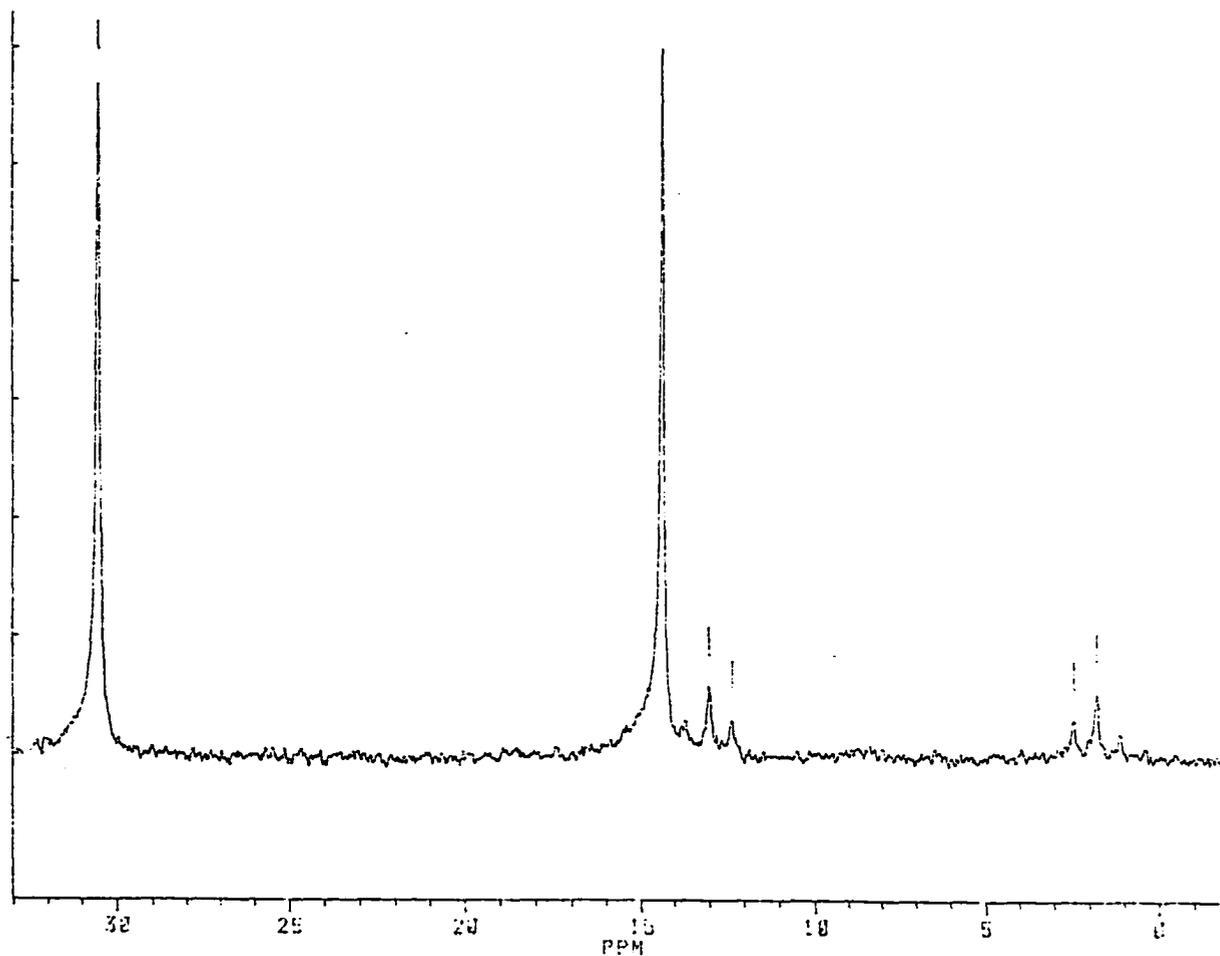
The reaction outlined in reaction (4), at room temperature, was monitored by NMR methods and it was found that after 2 to 3 hours only a sharp singlet at δ 14, which was later determined to be the signal due to **4**, was present in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum.



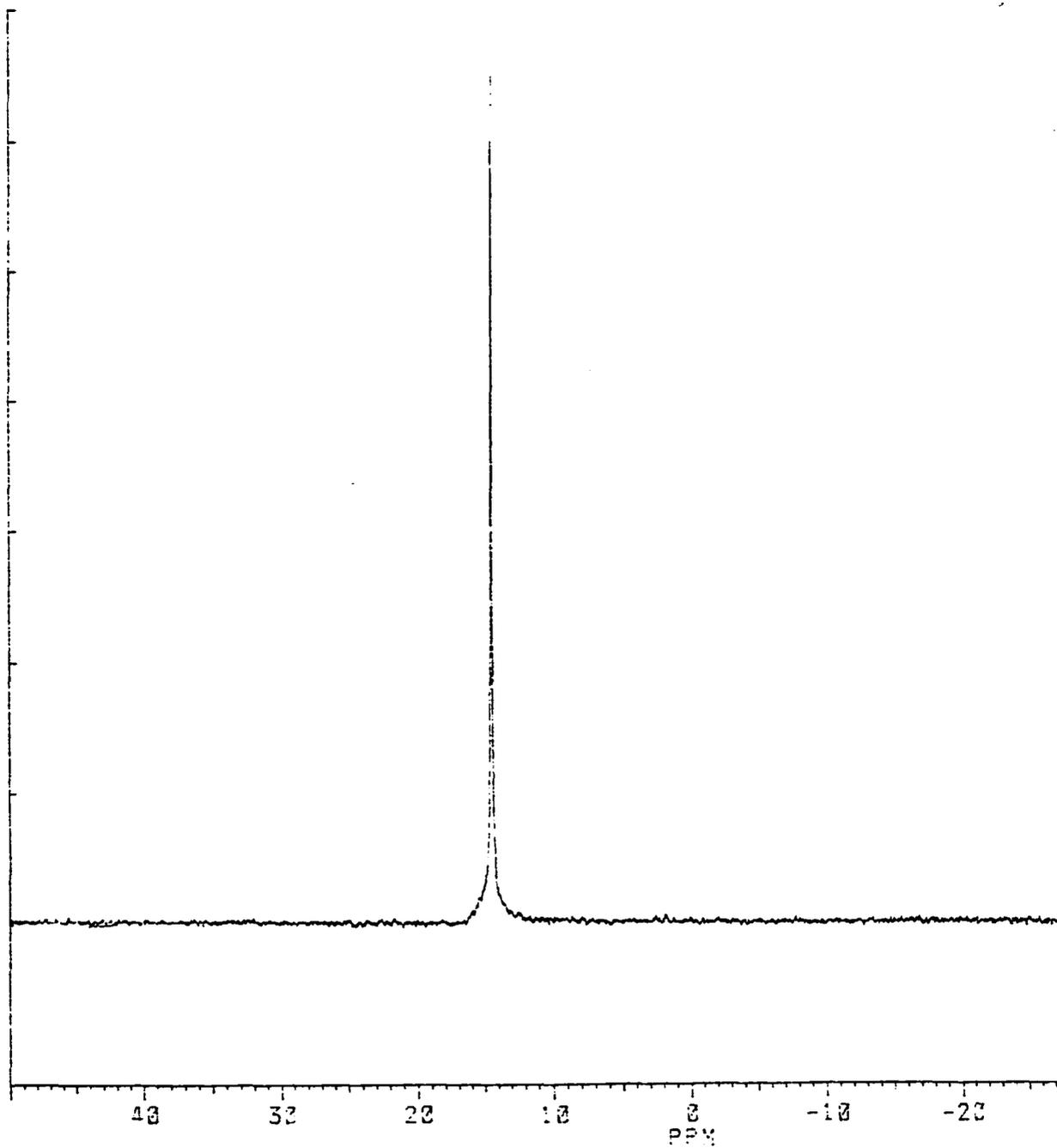
However, it was difficult to isolate the pure product in the presence of an excess of acid. A method with several steps was, therefore, developed to obtain the complex. First, the reaction (5) was stopped quickly (by precipitating the reaction products from solution) after adding the $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ and the product obtained was found to contain three components. One showed a singlet (δ 29.8), a second appeared as two triplets (δ 12.3, 1.08) and the third also exhibited a singlet (δ 14) in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (Spectrum 1). The singlet at δ 29.8 was identified as being due to complex 3 while the two triplets and the other singlet were tentatively assigned to the signals of *cis*- and *trans*- $[\text{Fe}(\text{CH}_3\text{CN})_2(\eta^2\text{-dppm})_2][\text{BF}_4]_2$. The mixture was redissolved in CH_3CN and after 24 hours, ether was added to precipitate out another mixture. More than 50% of this mixture is soluble in CH_2Cl_2 from which 4 was recrystallized as a dichloromethane solvate by layering hexane or ether over the solution. Complex 4 gives a sharp singlet (δ 14) in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (Spectrum 2). The insoluble residue was not characterized in this work.

No hydride peak was observed in the ^1H NMR spectrum of the final product. One broad singlet at δ 2.37 in this spectrum was identified as being due to the hydrogens of the coordinated CH_3CN . This reflects the equivalent electronic situation of the two CH_3CN ligands in this complex. The downfield shift of the signal due to the methyl hydrogens of

Spectrum 1 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CD_2Cl_2 , room temperature) of the three component mixture obtained initially from reactions of **1** with an excess of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ and CH_3CN



Spectrum 2 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4** in CD_2Cl_2 at room temperature



the acetonitrile ligands relative to that of the free ligand, together with the large ^{31}P chemical shift upfield relative to complex **3**, probably indicates that σ -donation dominates the iron-nitrile interaction in this complex and that the donor character of the nitrile ligands appears to have more effect upon the *cis*-phosphorus than on the *trans* ligand.

The highly symmetrical *trans*-arrangement of the two CH_3CN ligands in **4** was also confirmed by a crystal structure (Figure 4) and its bonding parameters (Table 4).

The Fe-N bond length is shorter in **4** than **3** (Figure 5 and Table 4) because of the strong *trans* effect of the H^- in **3**. The four weak peaks in the $\nu_{\text{C}\equiv\text{N}}$ region of the IR spectrum of **4** (Figure 6) are probably caused by the different vibrational modes^[80]. Again, the higher $\nu_{\text{C}\equiv\text{N}}$ values compared with that of the free ligand supports that σ -donation from the coordinated CH_3CN to Fe dominates the iron and acetonitrile interaction. Only one very weak vibrational mode due to $\nu_{\text{C}\equiv\text{N}}$ was observed in the IR spectrum of complex **3**.

I.5. *Trans*- $[\text{Fe}(\eta^2\text{-H}_2)_2(\eta^2\text{-dppm})_2][\text{BF}_4]_2$, **5**

The unexpected production of complex **4** from the procedure outlined in reaction (5) prompted this author to investigate further what happens when an excess of $\text{HBF}_4\cdot\text{Et}_2\text{O}$ is added to a suspension of complex **1** in the absence of CH_3CN .

Figure 4a ORTEP drawing of the cation of **4**

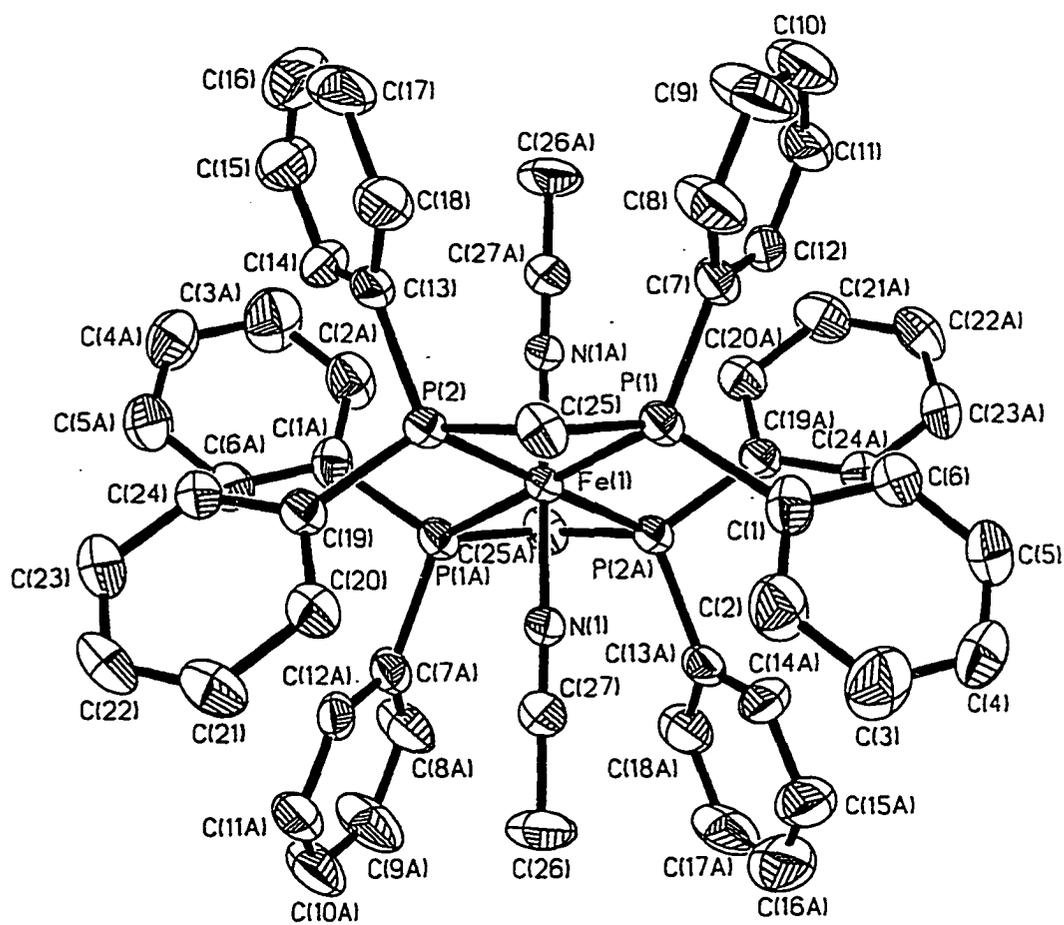


Figure 4b Structure of the disordered anions BF_4^- of 4

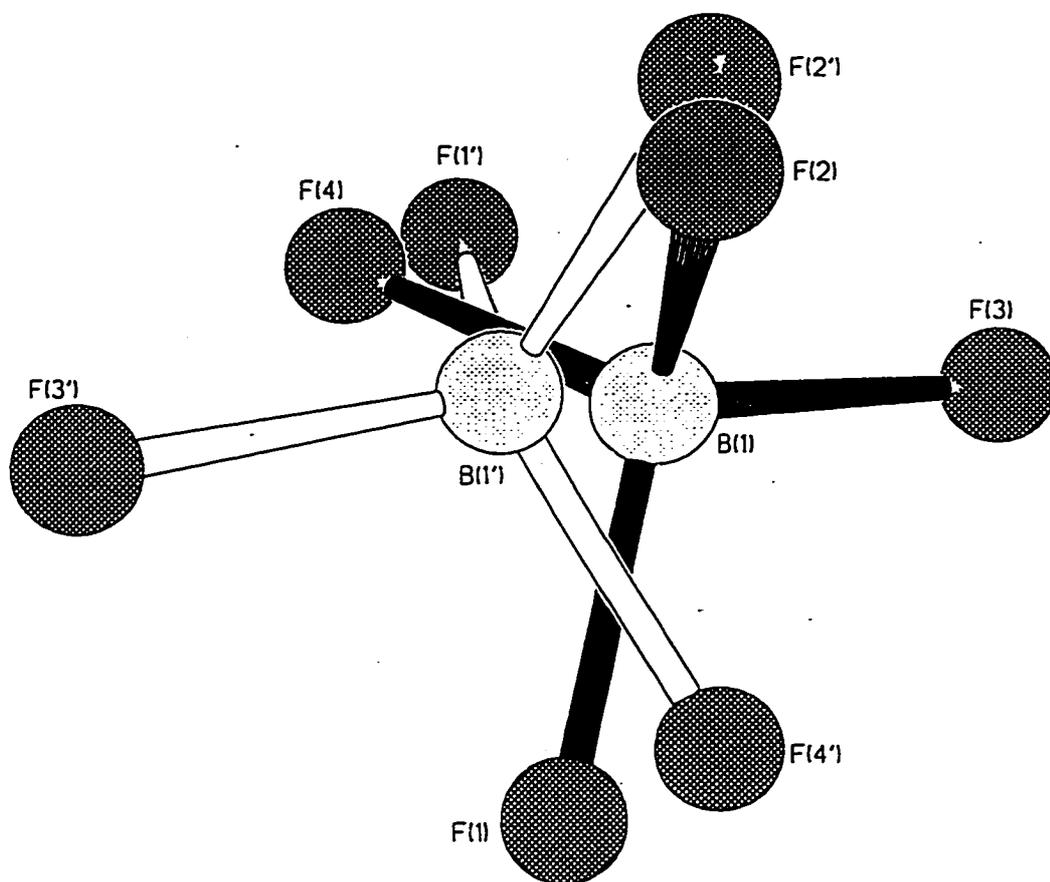


Figure 5 ORTEP drawing of the cation of **3**^[79]

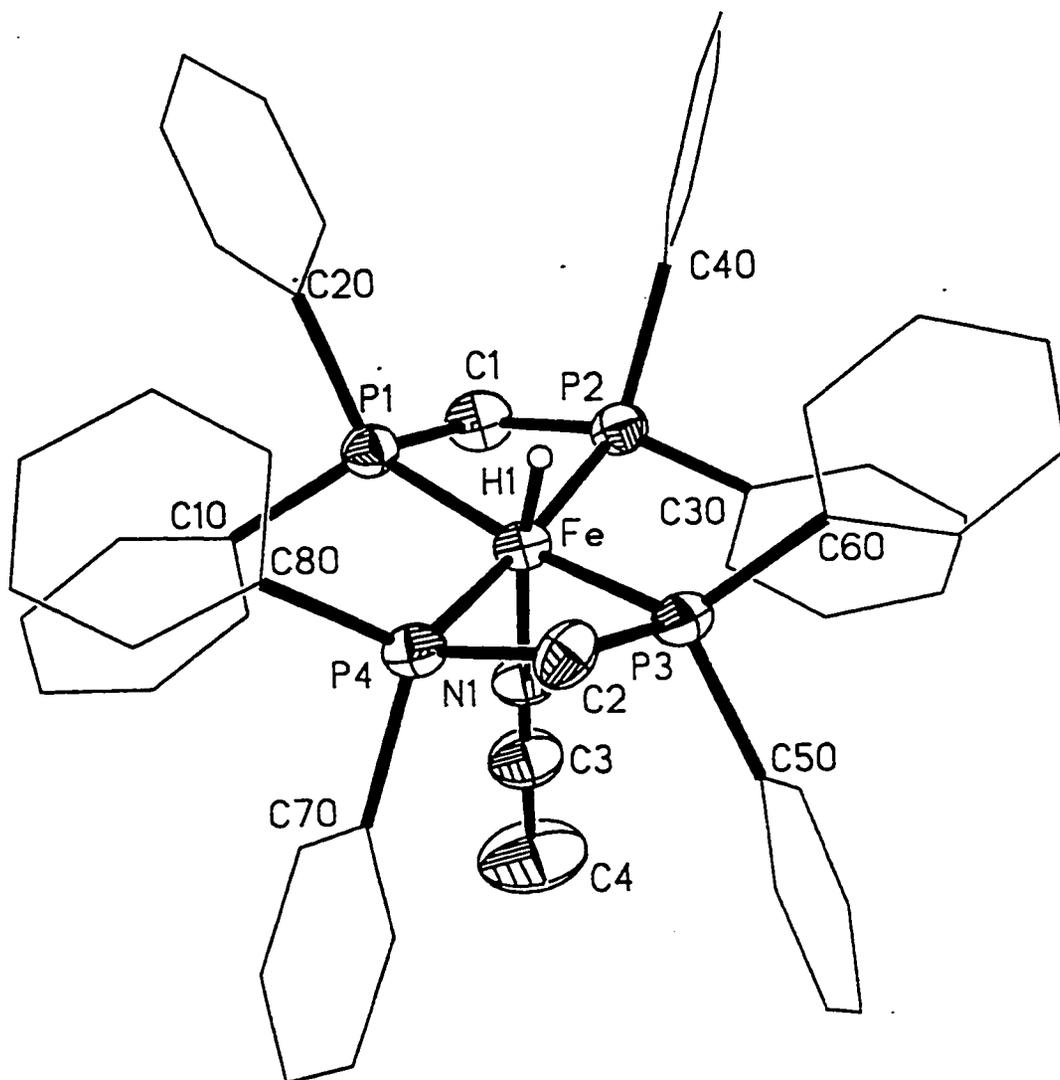


Table 4 Selected bond lengths (Å) and angles (°) for **4** and **3**^[79]

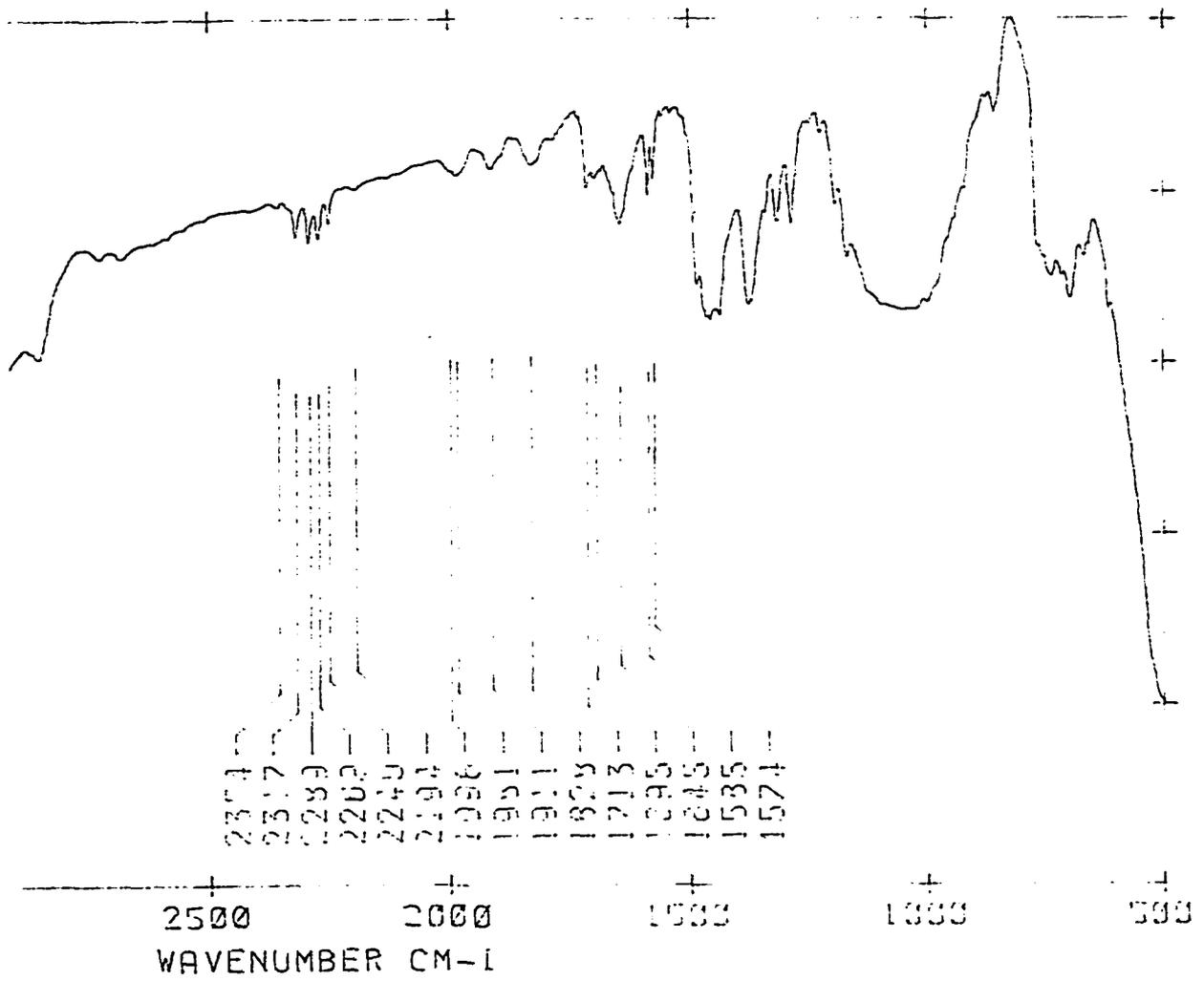
For 4

Fe—N	1.909 (4)	N—Fe—N	180°
Fe—P(2)	2.2715(14)		
Fe—P(1)	2.2841(13)		
C—N	1.133(7)		

For 3

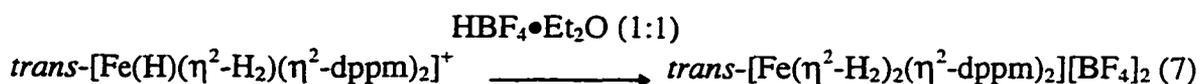
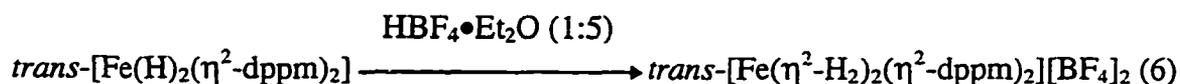
Fe—N	1.927 (4)	H—Fe—N	172(3)°
Fe—P(1)	2.206(2)		
Fe—P(2)	2.214(2)		
Fe—P(3)	2.203(2)		
Fe—P(4)	2.203(2)		
Fe—H	1.35(6)		
C—N	1.133(7)		

Figure 6 FTIR of 4 in Nujol



It was found that when a suspension of complex **1** in THF or CH₂Cl₂ was mixed with an excess of HBF₄•Et₂O (molar ratio 1:5) (**Method A**), a clear yellow solution was obtained which showed only a sharp singlet (δ 3.32) in the ³¹P{¹H} NMR spectrum. The same singlet also occurs in the ³¹P{¹H} NMR spectrum upon adding a slight excess of HBF₄•Et₂O to a solution of complex **2** in CD₂Cl₂ (molar ratio 1:1) (**Method B**). The ¹H NMR spectra of the solution offer no useful information because of the presence in the spectra of two very strong signals, probably from HBF₄•Et₂O.

Since the presence of CH₃CN in **Method A** leads ultimately to the formation of *trans*-[Fe(CH₃CN)₂(η²-dppm)₂][BF₄]₂, it is not unreasonable to believe that the singlet at δ 3.32 is due to *trans*-[Fe(η²-H₂)₂(η²-dppm)₂][BF₄]₂, **5**, formed in solution in both **Method A** [reaction (6)] and **Method B** [reaction (7)].



What is thought to be solutions of complex **5** are very stable in THF or CH₂Cl₂ in the presence of an excess of HBF₄•Et₂O. Also in the presence of a very large excess of

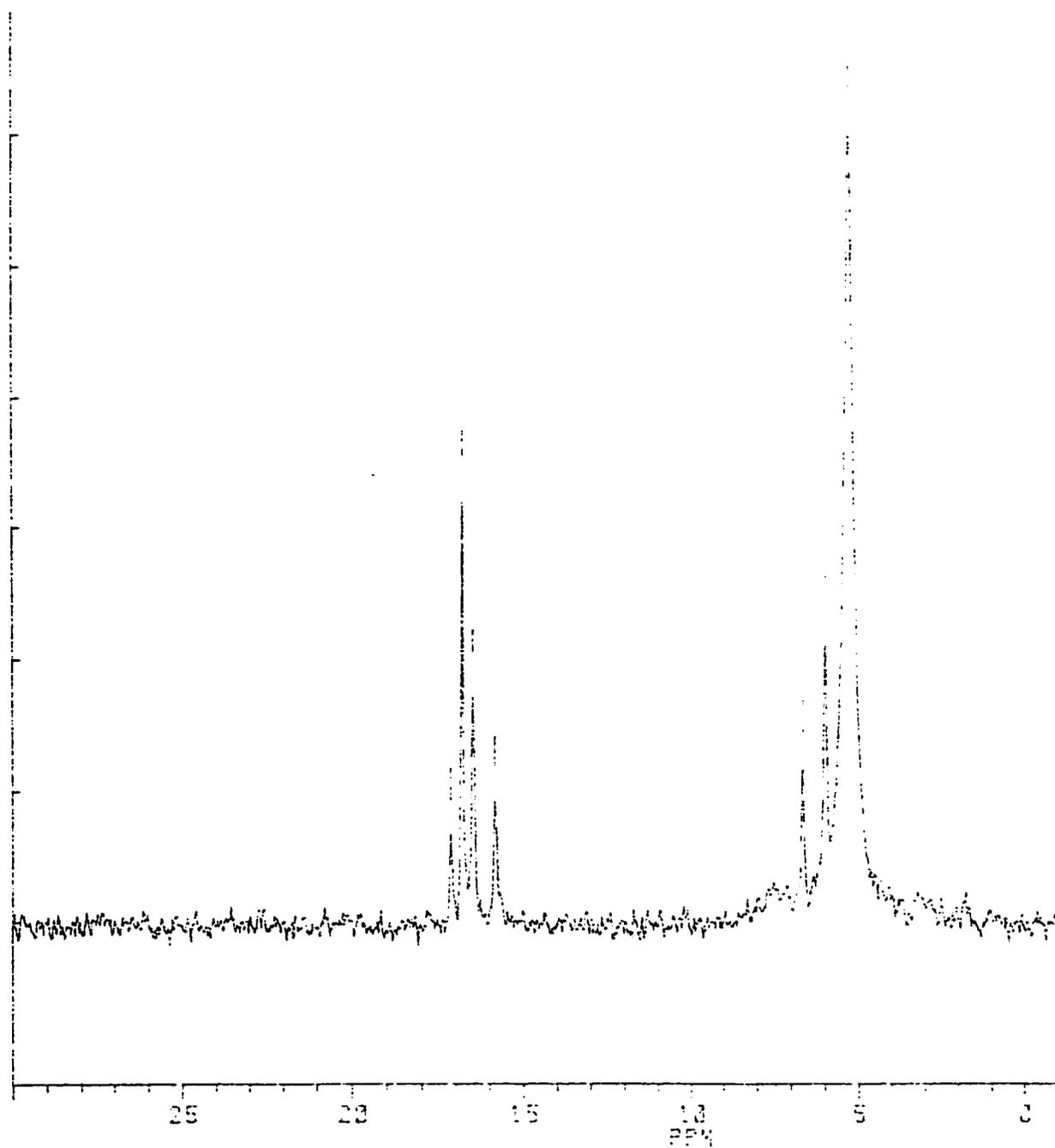
$\text{HBF}_4 \bullet \text{Et}_2\text{O}$ (molar ratio 1:10), the replacement of a dihydrogen ligand in complex **5** by CH_3CN is very slow and, furthermore, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the solution shows that it contains, initially, complex **5** and a mixture of *cis*- and *trans*- $[\text{Fe}(\text{CH}_3\text{CN})_2(\eta^2\text{-dppm})_2][\text{BF}_4]_2$ (Spectrum 3). The formation of the *cis*-isomer is discussed in section VI of this chapter.

Based upon the above evidence, it is reasonable to conclude that a bis-dihydrogen complex of Fe(II) (complex **5**) is formed under these conditions. An extensive literature search indicates that no bis-dihydrogen complexes of iron have ever been reported.

Since protonation of dihydride complexes by $\text{HBF}_4 \bullet \text{Et}_2\text{O}$ is the normal method for the preparation of the corresponding dihydrogen complexes of transition metals and the use of a small excess of $\text{HBF}_4 \bullet \text{Et}_2\text{O}$ was emphasized in almost each synthesis, it occurred to this author that bis-dihydrogen complexes may be found (at least to some degree) in other analogous systems when the protonating acid is present in a large excess. It is noteworthy that *cis*- $[\text{Ru}(\text{CH}_3\text{CN})_2(\text{dppm})_2][\text{BF}_4]_2$ has been characterized in this laboratory^[81] as being formed under the same conditions as reaction (6) and that *cis*- $[\text{Ru}(\text{H}_2)_2(\text{dppm})_2][\text{BF}_4]_2$ was suggested to be the possible intermediate.

Attempts were made to isolate pure **5** in the solid state. However, when a large amount of ether or hexane was added to the solutions obtained under the conditions of reaction (6), the main solid product obtained is complex **2**. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of

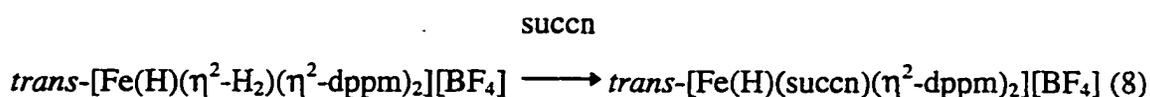
Spectrum 3 $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN) spectrum of the mixture obtained initially from the reaction of **1** with large excess of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (molar ratio 1:10) at room temperature



the product also showed a small residual peak at δ 24. The reasons why deprotonation occurs during the precipitation process are not clear at this time. Efforts to obtain crystals of **5** in the presence of a large excess of acid were also unsuccessful. It appears that **5** is only stable in solution in the presence of acid.

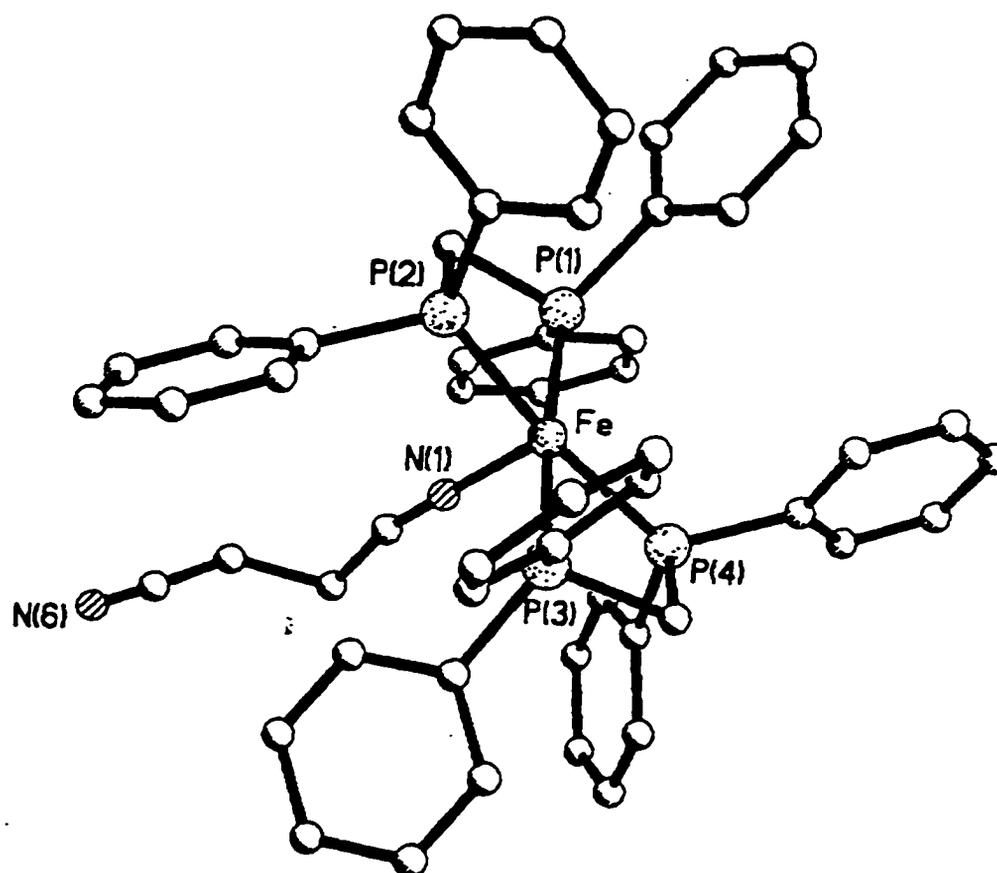
I.6. *Trans*-[Fe(H){ η^1 -NC(CH₂)₂CN}{ η^2 -dppm)₂][BF₄], **6**

The dihydrogen ligand of complex **2** can be easily replaced by succinonitrile under almost the same conditions as those used for acetonitrile in reaction (3).



Complex **6** is very stable towards moisture and air. It is soluble in acetone, chloroform and methylene chloride to form stable solutions. The ¹H NMR spectrum of compound **6** shows the hydride quintet at δ -13.1 while the ³¹P{¹H} NMR spectrum shows a sharp singlet at δ 30.3 which confirms a *trans* geometry for the hydride and NC(CH₂)₂CN ligands. Two broad unresolved peaks (δ 2.22, 1.93) due to the methylene hydrogens of the succinonitrile ligand located in the ¹H spectrum suggest monodentate coordination and this has been confirmed by X-ray diffraction (Figure 7). The data set for the structure was very poor due to the fact that **6** crystallizes in exceptionally thin plates

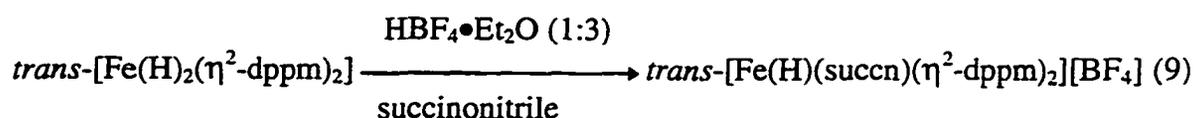
Figure 7 Structure of 6



and therefore, while the overall structure is valid, high R values mean that no accurate bond lengths and angles are available.

The coordinated succinonitrile shows a single, weak, broad and unsymmetrical signal in the IR spectrum which appears to be made up of at least two peaks at 2239 cm^{-1} and 2228 cm^{-1} due to $\nu_{\text{C}\equiv\text{N}}$. The $\nu_{\text{C}\equiv\text{N}}$ values are considerably reduced from that of the free ligand (2257 cm^{-1}) and also compared with the acetonitrile analogue. This suggests that there is relatively more π back-bonding from the iron fragment to the succinonitrile ligand. However, the fact that **3** and **6** show almost the same chemical shifts for the Fe-H multiplet in ^1H NMR spectra and for the singlets in ^{31}P $\{^1\text{H}\}$ NMR spectra, together with their very similar $\nu_{\text{Fe-H}}$ values, probably indicates the σ -donation also dominates the iron-succinonitrile interaction in **6**.

Compound **6** can also be obtained directly from $[\text{Fe}(\text{H})_2(\eta^2\text{-dppm})_2]$ in the presence of succinonitrile and an excess of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ at room temperature.

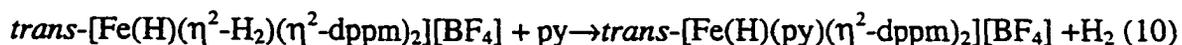


The initial purpose of employing succinonitrile instead of acetonitrile in this reaction was to attempt to trap out a *cis* complex with a chelating nitrile since there was clear evidence to suggest that *cis*- $[\text{Fe}(\text{CH}_3\text{CN})_2(\eta^2\text{-dppm})_2][\text{BF}_4]_2$ was formed early in

reaction (5). Possible reasons for the absence of a *cis* product will be discussed in a later section.

I.7. *Trans*-[Fe(H)(py)(η^2 -dppm)₂][BF₄], **7**

Replacement of the dihydrogen ligand of complex **2** by pyridine [reaction (10)] is slower than that for the corresponding acetonitrile and succinonitrile reactions, possibly for steric reasons. The ¹H NMR spectrum of complex **7** shows a quintet (Fe-H) at δ -17 while the ³¹P{¹H} NMR spectrum shows a sharp singlet at δ 20.3 which again reflects a *trans* arrangement of the hydride and pyridine.

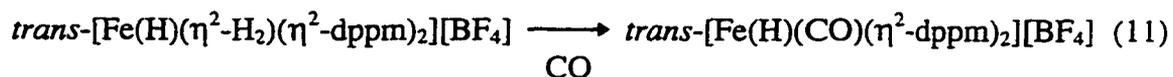


Unlike the nitrile complexes described above, product **7** is very labile and the pyridine ligand can quickly be replaced by CH₃CN. It was also found that, surprisingly, dinitrogen can compete with pyridine for the coordination site if the reaction is carried out under a N₂ atmosphere and for this reason, the synthesis of **7** must be carried out under Ar. Complex **7** is stable in pyridine for about 40 minutes after which replacement of the dppm ligand occurs. Good elemental analyses of **7** were not obtained because of its lability.

The much higher field location of the hydride peak relative to that of complexes **3** and **6** in the ^1H spectrum of **7** possibly indicates that σ -donation dominates the iron-pyridine interaction in this complex. In addition, because the chemical shift of the phosphorus singlet in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum was also found to move upfield relative to those of the CH_3CN and succinonitrile analogues, it can be concluded that pyridine is a stronger σ donor than nitrile ligands where the N atom is sp rather than sp^2 hybridized. The strong σ -donor ability of pyridine apparently displaces electron density from the iron center toward the P atoms of the chelating dppm ring. This, in turn, may cause first the dissociation of Fe-P linkages and, finally, replacement of the dppm ligand by pyridine as observed in this experiment.

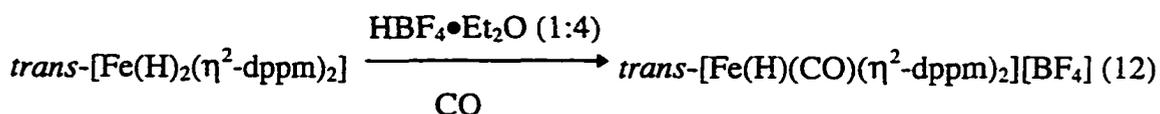
I.8. *Trans*- $[\text{Fe}(\text{H})(\text{CO})(\eta^2\text{-dppm})_2][\text{BF}_4]$, **8**

The synthesis of complex **8** by a direct substitution reaction [reaction (11)] was initially developed by another worker in these laboratories^[6b]. It is a very easy reaction to carry out and the final product is very stable.



In complex **8**, $\nu_{\text{C=O}}$ is greatly reduced from 2143 cm^{-1} (free ligand) to 1944 cm^{-1} which reflects the strong π -backbonding from the iron site to CO. The ^1H NMR chemical shift of the hydride ($\delta -2.03$) downfield compared with that of complex **1**, together with the large downfield phosphorus shift ($\delta 31.6$) in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, are also consistent with this effect. However, $\nu_{\text{Fe-H}}$ (1710 cm^{-1}) in the IR spectrum of **8** remains at almost the same value as that of complex **1**. It seems that the iron-hydride interaction has changed little when hydride is replaced by CO. Considering the apparently different characters of these two ligands, these phenomena are not easily explained (see Section II of this chapter).

It has been found by this author that complex **8** can also be synthesized by direct reaction of CO with **1** in the presence of an excess of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ [reaction (12)].

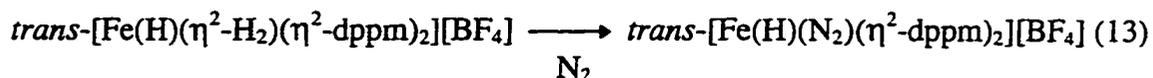


There was also a small residual peak at $\delta 24$ in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the solution of the product, and contamination of this type has been discussed in section I.2.

In spite of the presence of a large excess of H^+ , it is interesting that only the mono-carbonyl complex was obtained. The possible reasons for this result will be discussed in a later section.

I.9. *Trans*-[Fe(H)(N₂)(η²-dppm)₂][BF₄], **9**

Complex **9** was synthesized [reaction (13)] by the direct substitution of the dihydrogen ligand of complex **2** by N₂ in solution.

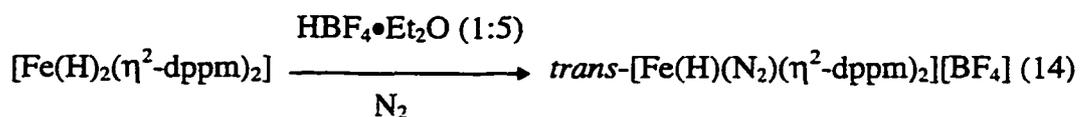


Complex **9** is very sensitive to moisture and decomposes in anhydrous acetone or chloroform to release dppm. It is stable for 24 hours in dry CH₂Cl₂ solutions when kept under a dry N₂ atmosphere. The expected hydride quintet for **9** is located at δ -9.38 in the ¹H spectrum. The *trans*-arrangement of the hydride and the dinitrogen ligand was confirmed by the presence of a singlet at δ 24.2 in the ³¹P{¹H} NMR spectrum.

Replacement of the H₂ ligand by N₂ shifts the signal due to the phosphorus atoms from δ 32.5 for **2** to δ 24.2 for **9** and shifts the hydride quintet in ¹H NMR spectra from δ -7 for **2** to δ -9.38 for **9**. It appears at first sight that N₂ is a relatively strong σ-donor and a poor π-acceptor here. However, this is not consistent with the IR data. The ν_{N≡N} (2116 cm⁻¹) for **9** is greatly reduced relative to that of free N₂ (2331 cm⁻¹) and this reflects the existence of considerable π-backbonding from iron to dinitrogen since the σ-donation from N₂ can only cause the strengthening of the N≡N bond^[82]. The ν_{Fe-H} (1713 cm⁻¹) for **9**

is close to that for **8** in which CO is an apparently strong π -acceptor and this seems to support the strong π -accepting ability of the N_2 ligand in **9**.

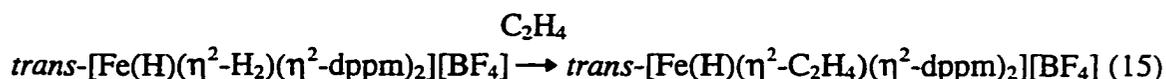
Complex **9** can also be obtained by the direct reaction of N_2 with complex **1** in the presence of an excess of $HBf_4 \cdot Et_2O$ [reaction (14)].



Note again that there is a large excess of acid in this reaction, and even though the presence of complex **5** in the initial solution was confirmed, no evidence for the formation of a bis- (N_2) product was obtained. The possible reasons for this are discussed in a later section.

I.10. *Trans*- $[Fe(H)(\eta^2\text{-CH}_2\text{=CH}_2)(\eta^2\text{-dppm})_2][BF_4] \cdot 0.5CH_2Cl_2$, **10**

As discussed in the introduction chapter of this thesis, ethylene is a good electron donor for the displacement of H_2 in dihydrogen complexes and several $[FeH(C_2H_4)(\text{bis-phosphine})_2]^+$ cations are known. Thus, when complex **2** is exposed to an ethylene atmosphere, the dihydrogen ligand is replaced gradually by C_2H_4 to give [reaction (15)] the product **10** which was identified mainly by its 1H and $^{31}P\{^1H\}$ NMR properties.

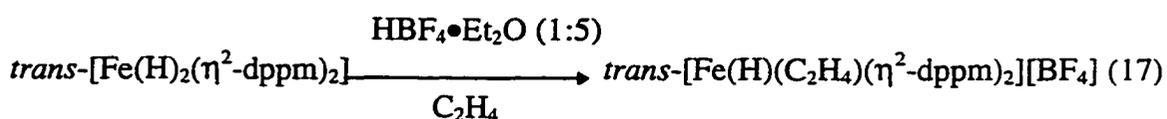


As with other substitution reactions involving **2**, the successful formation of **10** requires anhydrous conditions. The ethylene ligand of complex **10** can, in solution, be slowly replaced by N₂ when it is exposed to a dinitrogen atmosphere and therefore its synthesis requires a pure ethylene atmosphere. In solution, complex **10** can be quickly and irreversibly converted into complex **3** when CH₃CN is present even in trace amounts. The solid form of **10** is also very sensitive to moisture. Complex **10** also decomposes in undried deuterated solvents to release free dppm. However, it is soluble in dry solvents (acetone, methylene chloride and chloroform, for example), to form stable solutions. In methylene chloride, it was found to be stable for 24 hours when kept under a dry Ar atmosphere and crystals could be obtained by the layering of hexane over the solution. However, the needle shaped crystals obtained were too small for an X-ray crystallographic structure determination although good elemental analyses were obtained for the CH₂Cl₂-solvated crystalline product. Because of time constraints and because adequate structural information was available from spectroscopic studies, further efforts to obtain X-ray quality crystals were not made.

Considering now the spectroscopic information, the presence of a singlet at δ 3.18 for the protons in the coordinated ethylene ligand in the ¹H NMR spectrum indicates that

the coordination mode of ethylene in complex **10** is side-on which is analogous to the geometry of the dihydrogen complex **2**. The signal due to the hydrogens in coordinated $\text{CH}_2=\text{CH}_2$ is moved upfield relative to that of the free ligand (δ 5.3) and this may be due to the iron to C_2H_4 π -backbonding and the consequent change in hybridization at the C atoms. It has been established by X-ray structural studies^[83] on, for example, related tetracyanoethylene complexes, that the C=C bond is weakened as the backbonding from the metal to olefin increases and the hybridization of the carbon atoms in the complex may approach an sp^3 arrangement giving rise to the observed upfield shift of the ethylene protons in the ^1H NMR spectrum of **10**. The signal due to the *trans* Fe-H multiplet in the ^1H NMR spectrum is shifted significantly downfield compared with that of complex **2** (δ -7.21 to δ -1.78) and is also downfield relative to that of **8**. This might also suggest that π -backbonding is an important feature of the iron-ethylene interaction. The $\nu_{\text{Fe-H}}$ (1714 cm^{-1}) for **10** in the IR spectrum, close to that for **8**, seems to support this deduction.

As expected, complex **10** can also be obtained by the direct reaction of ethylene [reaction (17)] with complex **1** in the presence of an excess of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$.



A possible reason for the absence of a bis-ethylene product in this reaction will be discussed in a later section.

I.1.1. The reactivity of complex **2** toward propene, cis-2-butene and styrene

The H₂ of **2** is not displaced by propene, cis-2-butene or styrene under the same reaction conditions as have been described for complex **10**.

It is thought likely that the inertness of complex **2** towards propene, cis-2-butene and styrene is probably due to the steric interactions between these ligands and the phenyl groups on the dppm.

II. Electronic Interactions of Different Substituents with Iron

It is clear from experimental evidence that the iron-dppm fragment, $[\text{Fe}(\eta^2\text{-dppm})_2]^{2+}$, can accommodate different kinds of ligands and that the ligands prefer positions *trans* to each other. Two types of coordination mode of the *trans* ligands, side-on and end-on, were found in the new complexes. The complexes in which the *trans* ligands adopt the side-on mode are, as expected, *trans*- $[\text{FeH}(\text{H}_2)(\text{dppm})_2][\text{BF}_4]$ **2**, *trans*- $[\text{FeH}(\text{C}_2\text{H}_4)(\text{dppm})_2][\text{BF}_4]$ **10** and *trans*- $[\text{Fe}(\text{H}_2)_2(\text{dppm})_2][\text{BF}_4]_2$ **5**. The *trans* ligands in the remaining complexes were found to take the end-on mode.

Attempts have been made in the earlier sections to account for the spectral properties for each compound. At this point it is worthwhile to summarize the spectral variations for the complexes with the form of *trans*-[Fe(H)L(dppm)₂]ⁿ⁺ (n=0 or 1) and to include the closely related compound [Fe(H)(Cl)(dppm)₂] from previous work. This is done in Table 5.

Table 5 Spectral data for *trans*-[Fe(H)L(dppm)₂]ⁿ⁺ (n=0 or 1)

Complex		3	6	7	10	9	1	8	2
L	Cl ^a	MeCN	succn	py	C ₂ H ₄	N ₂	H ⁻	CO	H ₂
$\nu_{\text{Fe-H}}$ ^b	1889	1880	1881	1853	1714	1713	1711	1710	1708
$\delta^1\text{H}(\text{Fe-H})$ ^c	-21.2	-13.0	-13.1	-17.0	-1.8	-9.4	-7.0	-2.0	-7.2
$\delta^{31}\text{P}$ ^c	24.2	29.8	30.3	22.7	32.8	24.2	24.0	31.6	32.5

[^a ref 6b, ^b cm⁻¹, ^c CD₂Cl₂ or CH₂Cl₂, room temp]

As mentioned earlier in this thesis, there has been considerable discussion regarding the extent to which metal ions undergo π -backbonding to the dihydrogen ligand. It was hoped that the above series of compounds would allow changes in these spectral parameters to be related to changes in the iron-ligand bonding pattern. The above data (particularly concerning $\nu_{\text{Fe-H}}$ and $\delta^1\text{H}$) fall into two groups. First, when the Fe is coordinated to any of the four σ -donor ligands (Cl, MeCN, succn and py) with relatively weak *trans* effects, the *trans* hydride is both strongly bound (highest $\nu_{\text{Fe-H}}$, 1853 - 1889

cm⁻¹) and highly shielded (δ most upfield). In the second group, containing either H⁻ or good π -acceptor ligands (CO or C₂H₄) (all of which have a strong *trans* orientation ability), the $\nu_{\text{Fe-H}}$ values indicate a weaker Fe-H bond. The weakening of the Fe-H bond in **1** is most probably the direct result of the *trans* effect of the two hydrides^[6a]. For example, the Fe-H bond length changes from 1.35(6) Å in **3**^[79] to 1.56(8), 1.58(8) Å in **1**^[6b] consistent with the difference in the *trans* effect between MeCN and H⁻. The π -acceptor ligands cause a significant deshielding of the *trans* hydride, relative to the hydrides of the first group, consistent with the drain of electron density from the iron. It appears from the $\nu_{\text{Fe-H}}$ values that the bonding of N₂ in **9** behaves in a similar fashion to CO and C₂H₄ and this is further supported by the significant weakening of the N₂ bond ($\nu_{\text{N=N}}$ reduced from 2331 cm⁻¹ in free N₂ to 2116 cm⁻¹ in **9**) though the effects of these ligands on the chemical shifts of the *trans* hydride and the phosphorus atoms are quite different. The Fe-H bond in **2** appears comparable in strength to others in this second group. This suggests a relatively strong π acceptor role of H₂ in this complex which is also consistent with a lengthening of the H-H bond, calculated to be 0.92 Å in **2** (see previous section). It appears from experimental evidence that the formation of the dihydrogen ligand in complex **2** has little effect relative to the dihydride complex upon the Fe-H bond and the ¹H chemical shift of the *trans* hydride. Thus, the electronic environment around this *trans* hydride is still suitable for further protonation. This probably explains why the first bis-dihydrogen

complex reported for iron, **5**, can be synthesized. The great stability of complex **5** in solution confirms again that H₂ has little effect on its *trans* ligand. The large ³¹P chemical shift for **5** upfield relative to that of **2** may suggest that dihydrogen ligands can have a significant effect upon the electronic environment of neighbouring phosphorus atoms although the nature of this effect remains unclear.

Comparing this work with previous work, the Fe-phosphine interaction is found to change markedly with different types (i.e., different σ -donor and/or π -acceptor ability) of coordination ligand. For example, the Fe-P bond lengths decrease significantly from 2.316(3) - 2.290(2) Å^[6b] in *trans*-[Fe(Cl)(CO)(η^2 -dppm)₂][FeCl₄] to 2.2841(13)-2.2715(14) Å in *trans*-[Fe(CH₃CN)₂(η^2 -dppm)₂][BF₄]₂ **4** to 2.214(2)-2.203(1) Å^[79] in *trans*-[Fe(H)(CH₃CN)(η^2 -dppm)₂][BF₄] **3** to 2.172(2)-2.153(2) Å^[6b] in *trans*-[Fe(H)₂(η^2 -dppm)₂] **1**. In this series the overall increase in the σ -bonding capabilities of the *trans* ligands is accompanied by a corresponding decrease in the Fe-P bond length. This is probably due to the fact that *trans* ligands with strong σ -donation ability (e.g., two H⁻ in **1**) make the iron-center more electron-rich than those with weak σ -donor ligands (e.g., CO and Cl⁻ in *trans*-[Fe(Cl)(CO)(η^2 -dppm)₂][FeCl₄]). This could result in strengthened Fe-P d _{π} -d _{π} bonding arising from overlap of filled Fe 3d orbitals with vacant orbitals of the phosphorus atoms. The chemical shift of the P atoms in the same series is 10.3, 14, 29.8 and 24 respectively, which at first sight suggests a reverse trend although

the chemical shift of 29.8 for **3** is anomalous. However, since many factors can affect the electronic and magnetic environment of phosphorus atoms, this probably illustrates the difficulties of attempting to correlate electronic factors with ^{31}P $\{^1\text{H}\}$ NMR data.

III. The Nature of the H_2 Site and the Stability of Complexes Derived therefrom

The dinitrogen complex **9** shows $\nu_{\text{N}=\text{N}}$ at 2116 cm^{-1} . This is within the limits of 2060 to 2150 cm^{-1} suggested by Morris^[3] as an indication for the existence of a stable dihydrogen complex. Since $\nu_{\text{N}=\text{N}}$ is close to the upper limit, it appears that the electron density at the iron site in the fragment $[\text{Fe}(\text{H})(\eta^2\text{-dppm})_2]^+$ is somewhat poor.

Though a series of derivatives of the type $[\text{FeHL}(\text{dppm})_2][\text{BF}_4]$ can be obtained through simple H_2 replacement reactions, the resulting complexes exhibit quite different stabilities in solution. It was found in this work that the H_2 coordination site has an exceptional preference for nitriles and for example, acetonitrile quickly and irreversibly displaces H_2 , N_2 , C_2H_4 and pyridine from their corresponding complexes. The analogous substitution reactions of CO were not investigated in detail in this work but the complex $[\text{FeH}(\text{CO})(\text{dppm})_2][\text{BF}_4]$ is stable in CD_3CN for several days. This suggests that it is even more stable than the acetonitrile analogue (see the introduction to this thesis).

The relatively unstable ethylene complex (with respect to the replacement of ethylene by other ligands) suggests that side-on coordination may be sterically strained even with C₂H₄, and more bulky olefins do not coordinate at all.

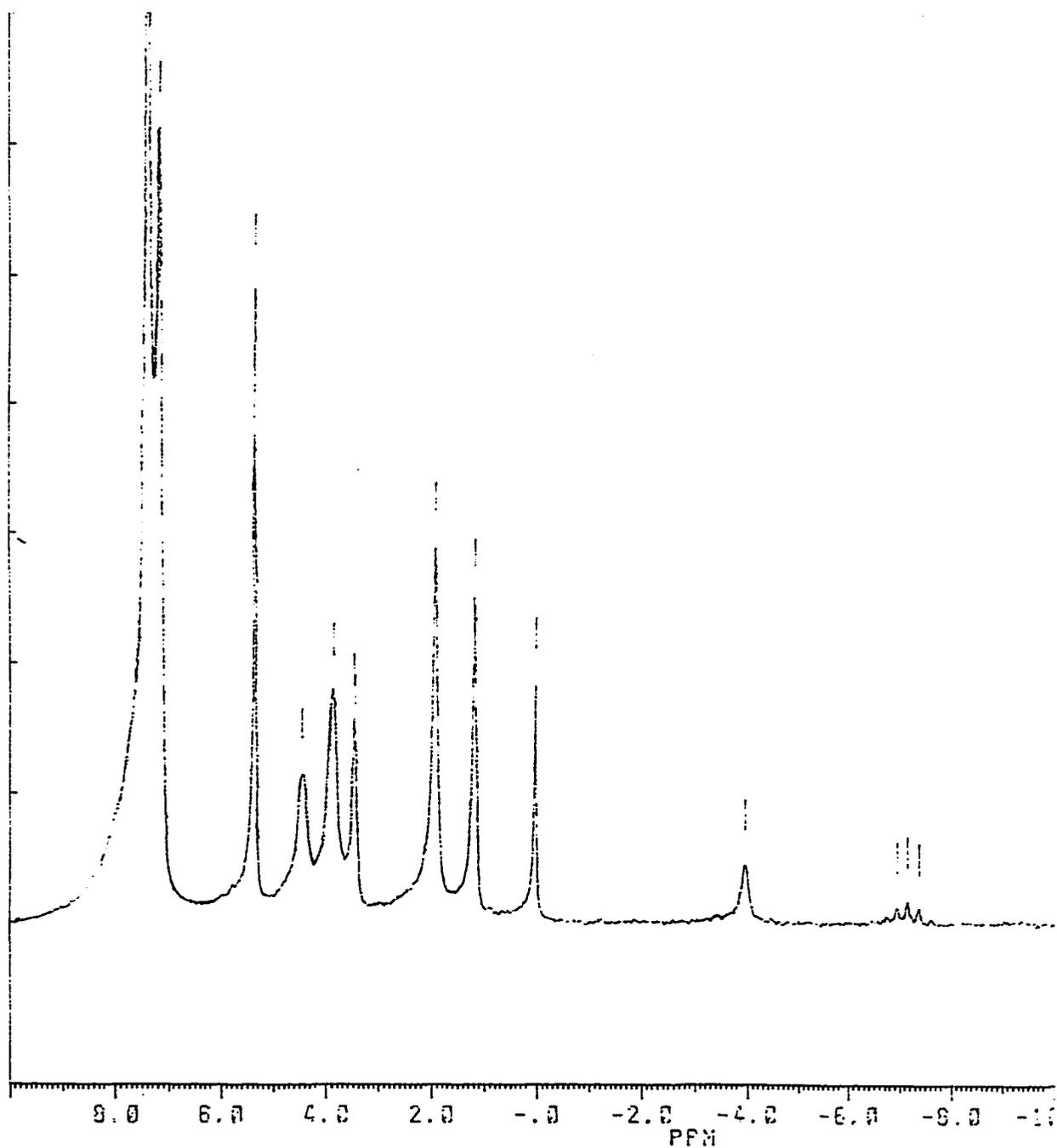
IV. The Equilibrium between Complexes 1 and 2 and Intramolecular H Exchange between Dihydrogen and *trans* Hydride Ligands

Both hydride-dihydrogen equilibria and site exchange between hydride and dihydrogen have been discussed in the introduction to this thesis. In this context, the ¹H and ³¹P{¹H}NMR spectra of complex 2 in CH₂Cl₂ were monitored at various temperatures in this work. The ¹H NMR spectra showed an unchanged picture, with a broad singlet at δ -4 and a clear quintet at δ -7.2, within the temperature range 220 K to 299 K (Spectrum 4). There were also no changes observable in the ³¹P{¹H}NMR spectra. Thus, within the investigated temperature range, it appears that neither an equilibrium between dihydrogen and dihydride complexes is present nor does the intramolecular hydrogen exchange between dihydrogen and hydride ligands takes place in solution for 1 and 2.

As mentioned in the early part of this thesis, no equilibria phenomena have been observed in iron-dihydrogen complexes with more than two hydrogen atoms and this is probably due to the high energy barrier to rearrangement of the phosphine ligands. However, intramolecular H exchange between H₂ and hydride were observed in almost all

Spectrum 4

The invariant ^1H NMR spectrum of **2** over the temperature range
220 K to 299 K



related systems, as mentioned before, including dppe, depe and dmpe complexes. The reason that it was not observed for the dppm analogue is probably because the energy barrier for this process is larger. A coalescence temperature of 340 K was reported in Morris' review^[3] for complex **2** which is higher than for the dppe analogue (313 K). However, in this work, it was found that complex **2** is only stable in CH₂Cl₂ for which the boiling point is 313 K. The coalescence temperature for this intramolecular H exchange was not measured in our instrumental lab because such a measurement may impair the equipment.

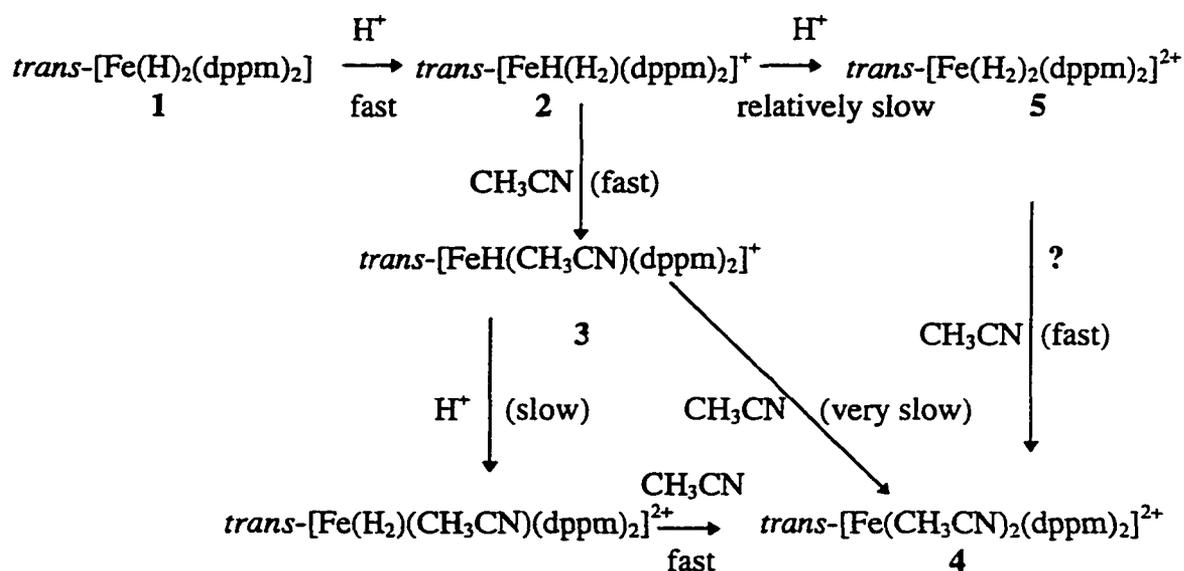
The high energy barrier to intramolecular H exchange in complex **2** probably indicates that chelation of the dppm ring to iron is more stable than for the dppe analogue. Considering the apparent strain of the four-membered dppm ring, it is reasonable to assume that the *cis* effect of the coordinated H₂, as discussed in Section II, should play an important role in stabilizing the ring through delocalizing the electron density on the phosphorus atoms.

V. The Mechanism for the Formation of Complexes **4** and **5**

Experimental evidence acquired in this work seems to support the idea that the protonation of complex **1** to give complex **5** in the presence of an excess of HBF₄•Et₂O is a stepwise process.

The main evidence for this is (a) when the reaction outlined in reaction (4) is quickly stopped at the beginning, a mixture of products is obtained which includes *trans*-[FeH(CH₃CN)(dppm)₂][BF₄], **3**, and both *cis*- and *trans*-[Fe(CH₃CN)₂(dppm)₂][BF₄]₂ (Spectrum 1); (b) the initially formed complex **3** was found to change gradually into **4** (normally 2 to 3 hours under acid; 24 hours in the presence of an excess of CH₃CN) and (c) at low temperature (-30 °C), only the mono-acetonitrile complex **3** was obtained from the process outlined in equation (4).

It appears that the protonation of the second hydride is an endothermic process and that the rate is a little slower than for the first hydride's protonation. The probable mechanism for the formation of the cation complexes of **4** and **5** is outlined in Scheme 3.



Scheme 3 (showing only the cations)

It is worth noting that *trans*-[Os(H₂)(CH₃CN)(dppe)₂][BF₄]₂ has been synthesized through the protonation of *trans*-[Os(H)(CH₃CN)(dppe)₂][BF₄]^[43]. This seems to support the proposed stepwise protonation and substitution mechanism.

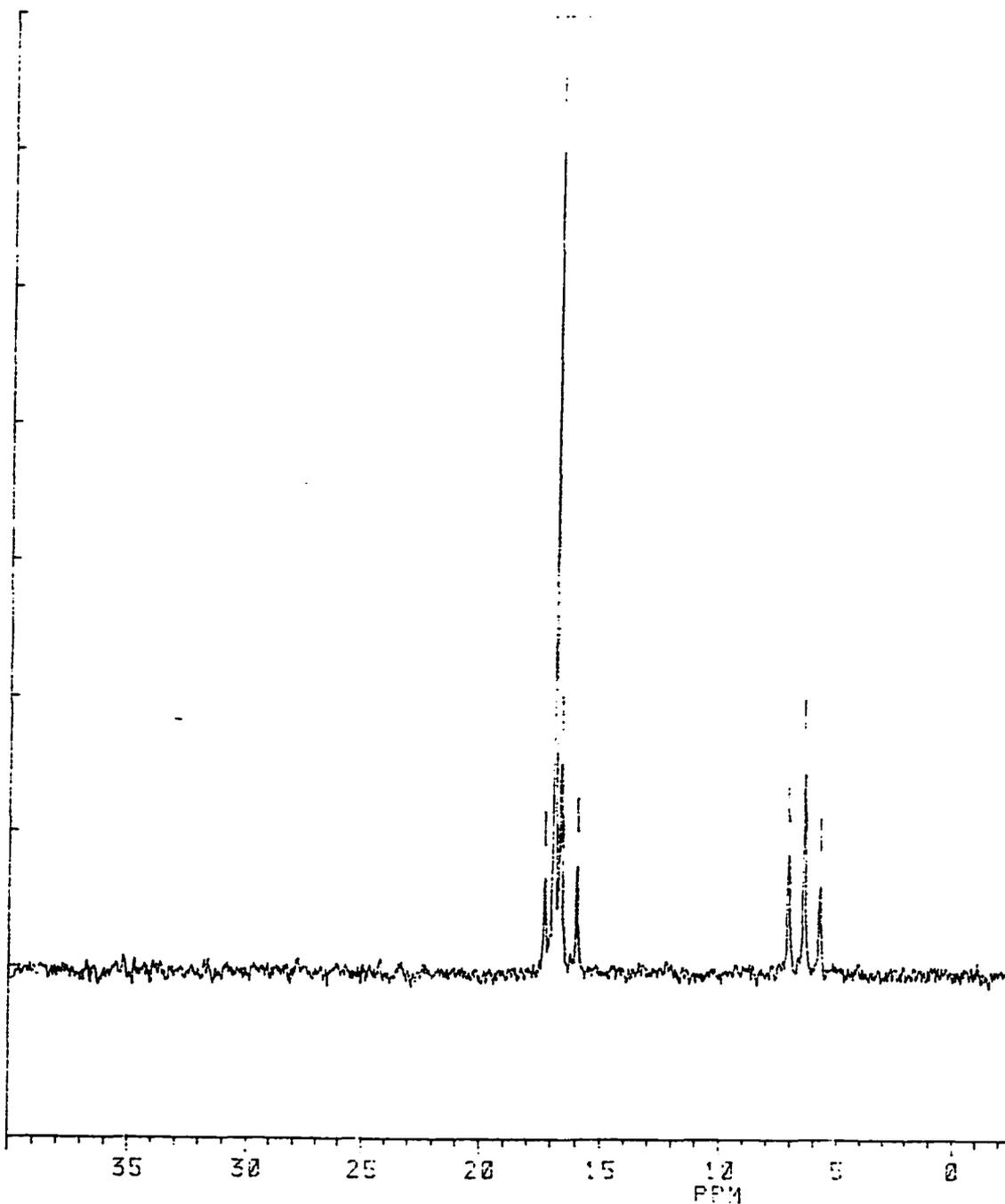
VI. Explanation of the Formation of *cis*-[Fe(CH₃CN)₂(dppm)₂][BF₄]₂

When the reaction outlined in reaction (4) was quickly stopped at the beginning, the resulting mixture, as noted earlier, also contained the unexpected complex *cis*-[Fe(CH₃CN)₂(dppm)₂][BF₄]₂ which was found to change quickly to *trans*-[Fe(CH₃CN)₂(dppm)₂][BF₄]₂ if it remained in the reaction solution or if the mixture of solid tetrafluoroborate salts was redissolved in an excess of CH₃CN. The same phenomenon was also observed when monitoring ³¹P NMR spectra of the reaction solutions without isolation of any of the products. This complex is the only *cis*-complex observed in all of the experiments described in this thesis though it appears to be a by-product with only limited life. Efforts to isolate the pure complex were not successful. However, it was found that when complex 1 was treated in an excess of CH₃CN and a moderate excess (molar ratio 1:5) of HBF₄•Et₂O, a mixture of only *cis*- and *trans*-[Fe(CH₃CN)₂(dppm)₂][BF₄]₂ was obtained and the percentage of the *cis*-isomer was significantly greater than that obtained in other reactions (Spectrum 5).

The formation of the *cis* isomer apparently requires the opening and rearranging of the dppm ring. Although, as discussed earlier, dppm shows a strong affinity for iron in the

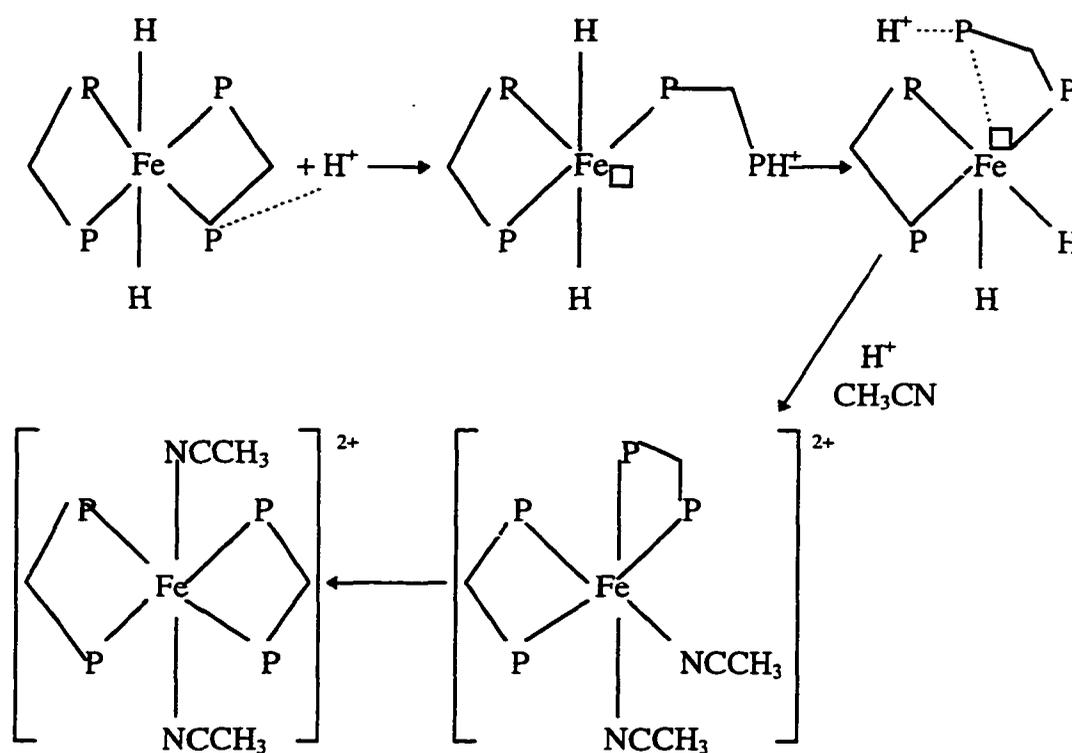
Spectrum 5

$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN) spectrum of the mixture obtained initially from the reaction of 1 with a moderate excess of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (molar ratio 1:5) at room temperature



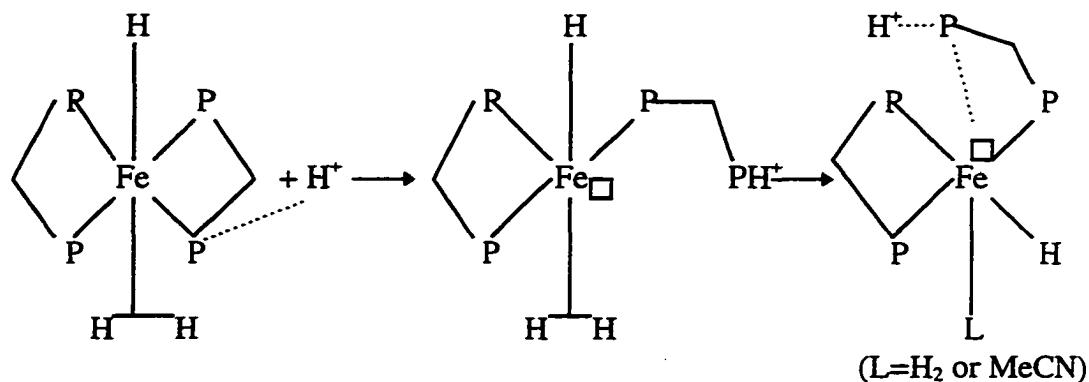
investigated systems, opening of an Fe-P bond could be possible in the presence of an excess of acid because H^+ may promote or stabilize this opening by protonating one phosphorus atom in *dppe*. It is noteworthy that in the presence of HX ($X=Cl$ or Br), the rapid opening of the chelating *dppe* ring with iron and further protonation of one pendant phosphorus atom have been observed during investigations of the complexes $[FeHX(dppe)_2]$ ($X=Cl$ or Br)^[62].

One possible mechanism for the formation of *cis*- $[Fe(CH_3CN)_2(dppe)_2][BF_4]_2$ is outlined in Scheme 4.



Scheme 4

Alternatively, ring opening and further rearrangement may occur after the first protonation forming the complex 2 (Scheme 5).



Scheme 5

Both Schemes 4 and 5 can well explain why the yield of the *cis* product can be improved in the presence of a large excess of acid. Since, in solution, complex 1 only has limited stability and appears to be more readily able to release dppm compared with complex 2, the strain in complex 1 may be larger than that in complex 2. Scheme 4 is therefore probably more reasonable than Scheme 5.

VII. Explanation of the Reactions of Complex 1 toward CO, N₂ and Succinonitrile in the Presence of an Excess of HBF₄•Et₂O

Under the same experimental conditions as those outlined in reaction (4) for the synthesis of complex 5, the reactions of complex 1 with L (L=CO, N₂ and succinonitrile) only produced the mono-substituted complexes *trans*-[Fe(H)L(dppm)₂][BF₄]. This result is unexpected because the bis-dihydrogen complex 5 was clearly present in the reaction solution under these conditions. In addition, it has been predicted from studies of Mössbauer spectroscopic quadrupolar splitting patterns for a series of six-coordinate low-spin iron(II) complexes containing bidentate phosphine ligands^[84] that at least the two complexes, *trans*-[Fe(CO)₂(dppm)₂][BF₄]₂ and *trans*-[Fe(N₂)₂(dppm)₂][BF₄]₂, should be stable.

One possible explanation why the bis substituted products were not observed is that both the formation and the substitution of complex 5 are stepwise reactions. After the substitution of the first H₂ ligand in 2 or 5 (see Scheme 3) by L (L=CO, N₂ and succinonitrile), L was polarized because of π-backbonding (or, more likely, the effect of the *trans* hydride) and a further protonation or strong interaction with H⁺ probably occurred at the more negative atom in L. Thus, the electronic situation of the site for *trans* hydride or dihydrogen ligands was changed to a more highly oxidized state and this made either the formation of the H₂ on the *trans* side unfavored or encouraged the

deprotonation of the *trans* H₂ ligand resulting in the impossibility of a second substitution by L.

As an example of the first of these explanations, it is known that protonation of coordinated dinitrogen occurs for several iron dinitrogen complexes^[52,85-87]. For example, *trans*-[Fe(H)(N₂)(dmpe)₂][BPh₄] ($\nu_{\text{N}=\text{N}}=2106 \text{ cm}^{-1}$) can react with HCl/alcohol to give ammonia^[52]. The $\nu_{\text{N}=\text{N}}$ (2116 cm⁻¹) for complex **9** is close to the dmpe analogue and so the protonation or at least the interaction between H⁺ and N^{δ-}≡N^{δ+}-Fe is possible in the dppm case.

The protonation of nitrile ligands in the complex [ReCl(NCR)(dppe)₂] (R=aryl) by HBF₄•Et₂O is preferred to protic attack on the metal center^[88]. Although there is no experimental evidence to show that the same protonation can also occur with these iron-nitrile complexes, it is not unreasonable in the succinonitrile complex since $\nu_{\text{C}=\text{N}}$ for one of the two C≡N bonds is 29 cm⁻¹ below that of the free ligand and it possesses non-bonding electrons. At the very least, a relatively strong attraction between H⁺ and the nitrile ligand may exist.

Although there is no direct evidence for strong interaction with H⁺ (or protonation) with the CO of **8**, this is again not unreasonable since CO behaves as a strong π-acceptor and the $\nu_{\text{C}=\text{O}}$ of **8** is greatly reduced compared with that of free CO.

Thus the interactions between H^+ and the substituent ligands may be responsible for the unexpected experimental results. This is also consistent with our current understanding that a proper electron density on the site is imperative for H_2 coordination.

It is noteworthy that although complexes **6**, **8** and **9**, synthesized by the direct reactions with complex **1** in the presence of an excess of $HBF_4 \cdot Et_2O$, only show a singlet in their $^{31}P\{^1H\}$ NMR spectra, the carbon content in their corresponding elemental analytical results are always lower than the calculated values. The presence of protonated substitution ligands is possibly responsible for this error.

Suggestions for Further Work

Although the dihydride and the dihydrogen complexes of iron with dppm as the supporting scaffold, and a series of their derivatives, have been synthesized and characterized in this work, attempts to elucidate details of the interactions between iron and some substituents (e.g. H_2 and N_2) have not been successful. Some meaningful work was not continued because of time constraints. Thus, the following points are suggested for further research work:

1. Further studies on Fe-L interactions (L= H_2 , N_2 and C_2H_4)

It was found in this work that complexes **2**, **9** and **10** are stable for at least 24 hours in dry CH_2Cl_2 under the appropriate gas atmosphere. It should be possible to obtain suitable crystals for X-ray diffraction studies. Details of some key bond lengths may help to clarify the interactions in these complexes.

2. Further efforts to obtain the solid form of complex **5**

While solutions of complex **5** are very stable in the presence of an excess of $HBF_4 \cdot Et_2O$, solid **5** was not isolated in this work. Additional crystallization methods, e.g.,

using different size anions or different protonation acids should be attempted in an effort to isolate this valuable product.

3. Characterization of the unknown residue during the synthesis of complex **4**

As mentioned in the Results and Discussion chapter, a filtration is needed during the synthesis of **4** to remove an uncharacterized peach-coloured product insoluble in CD_2Cl_2 . Most of this dissolves in CD_3CN to give **4**. The unknown residue may be significant since it is produced during the formation and the further substitutions of the dihydrogen ligands of complex **5**. Characterization of this residue may help in the further understanding of the bis-dihydrogen complex of iron.

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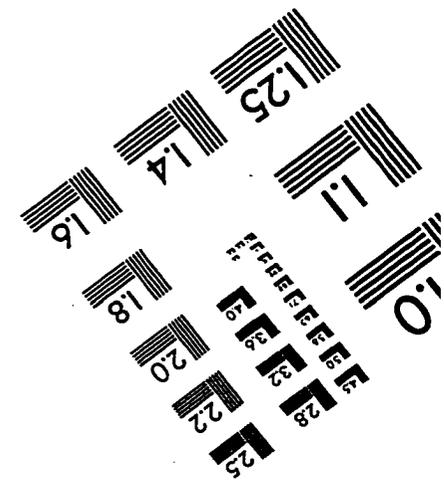
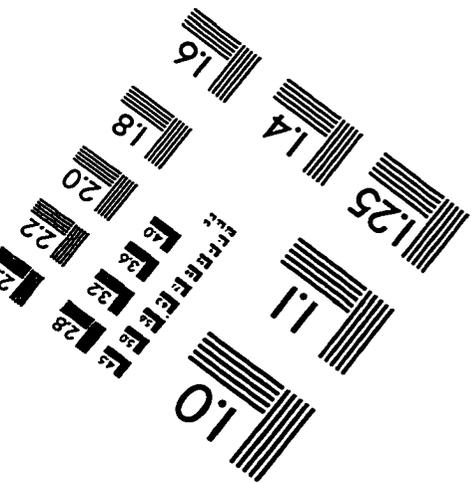
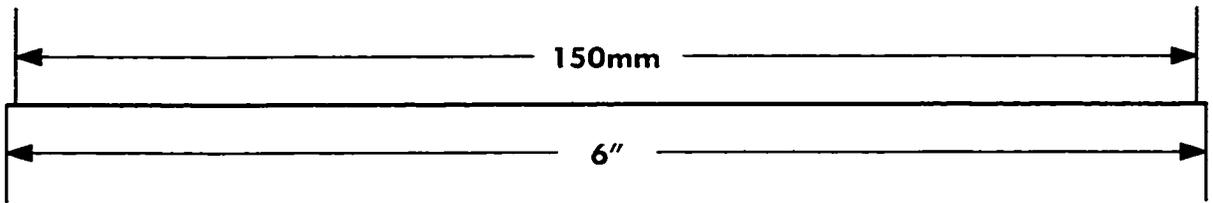
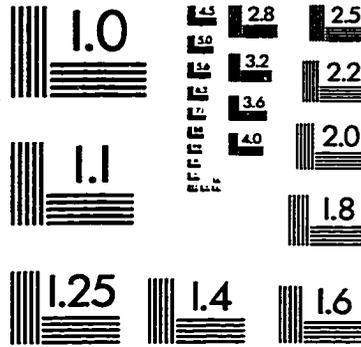
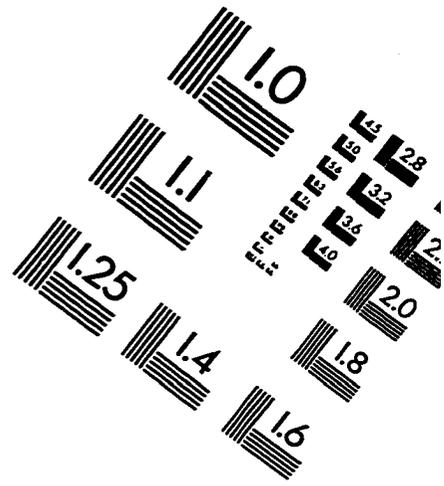
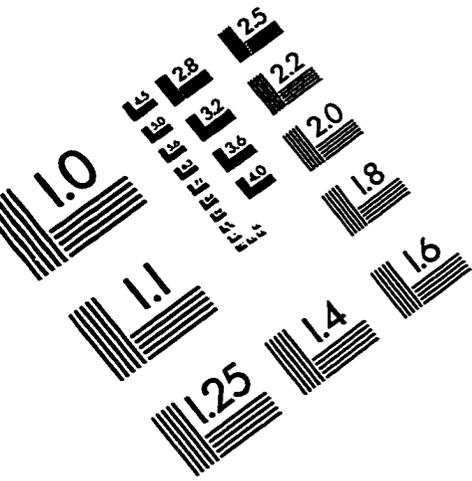
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IMAGE EVALUATION TEST TARGET (QA-3)



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