SYNTHESES AND REACTIVITY OF BRIDGED BINUCLEAR IRON COMPLEXES

by

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11/4/81

Date

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I wish to thank my parents for their continual encouragement and support of my educational advances. I also thank Janet for her friendship and love throughout my work. I am grateful to Professor G. O. Nelson for his patience and support as my friend and research director.

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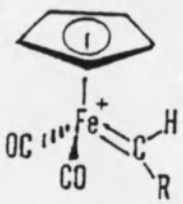
ABSTRACT

Reduction of $Me_2Si[(C_5H_4)(Fe(CO)_2]_2$ (21) to the dianion $(Me_2Si[(C_5H_4)Fe(CO)_2]_2)^{-2}$ and reaction with allylic chlorides gave the di(n^1-allyl) species, $Me_2Si[(C_5H_4)Fe(CO)_2(n^1\text{-allyl})]_2$. Treatment of the latter with fluoroboric acid afforded the dication diolefin complexes, $(Me_2Si[(C_5H_4)Fe(CO)_2(n^2\text{-olefin})]_2)(BF_4)_2$. Complex 21 was converted with iodine in refluxing chloroform to $Me_2Si[(C_5H_4)Fe(CO)_2I]_2$ (28). Treatment of 28 with silver tetrafluoroborate and several different olefins gave only $(Me_2Si[(C_5H_4)Fe(CO)_2]I)BF_4$ (29) as product. The photolysis of 21 with bis-(diphenylphosphino)ethane (dppe) gave two products, a bis-bridged binuclear complex $Me_2Si[(C_5H_4)Fe(CO)]_2$dppe (36), and a tetranuclear species $(Me_2Si[(C_5H_4(FeCO]_2$dppe (37). When 21 was photolyzed with bis-(diphenylphosphino)methane (dppm) a single, bis-bridged, crystalline product was obtained and identified as $Me_2Si[(C_5H_4)Fe(CO)]_2$dppm (41). The photolyses of di(n^1-alkyl) and di(n^1-allyl) derivatives of 21 with dppm were studied and are reported.

CHAPTER 1

INTRODUCTION

There are many examples of reactive complexes having the general formula $[Fp\text{-}un]^+$ ($Fp = (n^5\text{-}C_5H_5Fe(CO_2)$ where "un" represents an unsaturated ligand. Various functionalities such as a carbene (1) [1], olefin (2) [2-8], alkyne (3) [9-11], and vinylidene (4) [9] are possible. These cationic-iron complexes have been shown to be useful intermediates in the formation of new carbon-carbon bonds.



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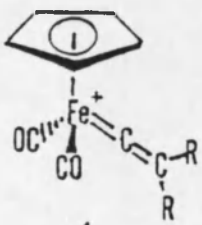
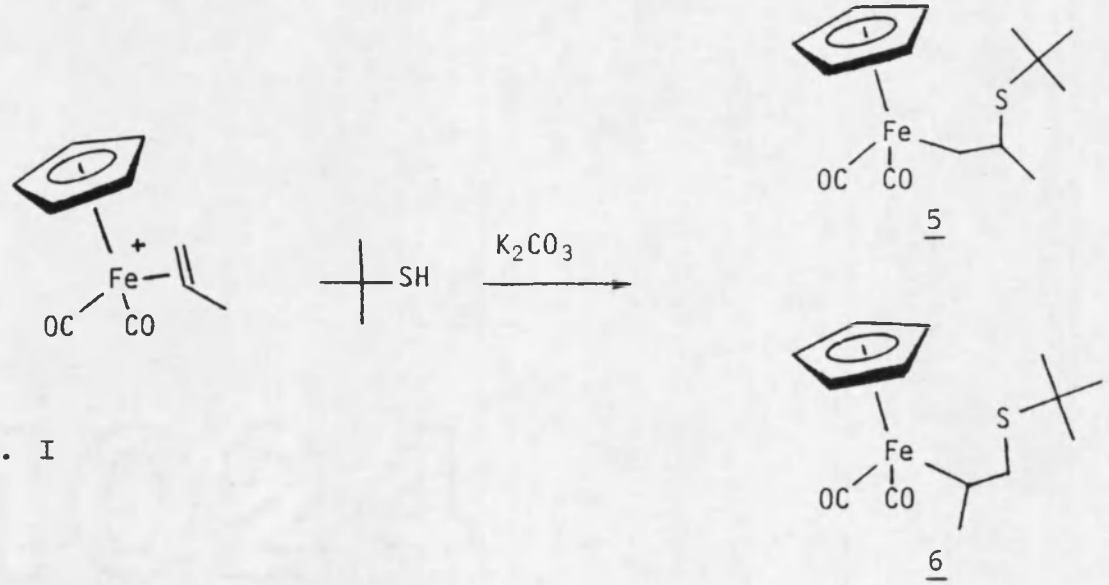


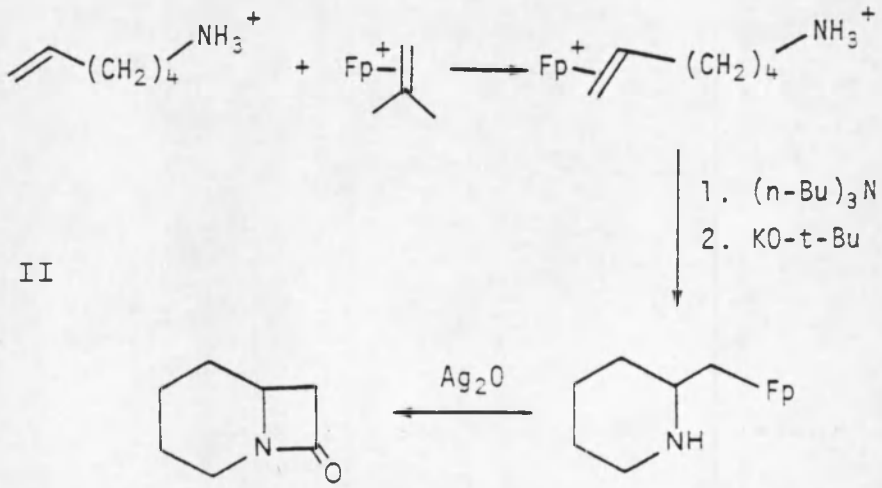
4

The reaction chemistry of $[(\pi\text{-}C_5H_5)Fe(CO)_2(n^2\text{-}olefin)]^+$ complexes has been extensively studied by Rosenblum, and he has developed the compounds into versatile synthons [2-8]. Several heteroatom and carbon-nucleophiles have been reacted with the above iron-olefin complexes to yield σ-alkyl iron compounds (Eq. I) [3].



Eq. I

The olefin complexes have been shown to demonstrate some regioselectivity and yielded products that are the result of trans addition of the nucleophile with respect to the iron [3]. Rosenblum has also reported that certain olefin complexes are attractive intermediates in lactam ring formation (Eq. II) [6].

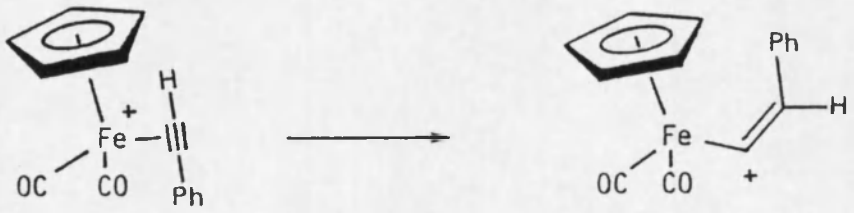


Eq. II

Fp = $(C_5H_5)Fe(CO)_2$.

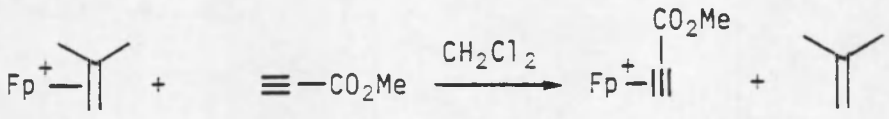
The alkyne complexes of type 3 have been shown by Reger and his co-workers to be precursors to substituted alkenes [11]. The alkyne complexes that have terminal acetylenic protons have been observed to rearrange, affording the vinylidene compounds (Eq. III) [12].

Eq. III



8 9

Rosenblum has also reported that RXN of methyl propiolate with Fp(isobutylene)BF_4 in refluxing dichloromethane generated the alkyne complex 10 [12]:



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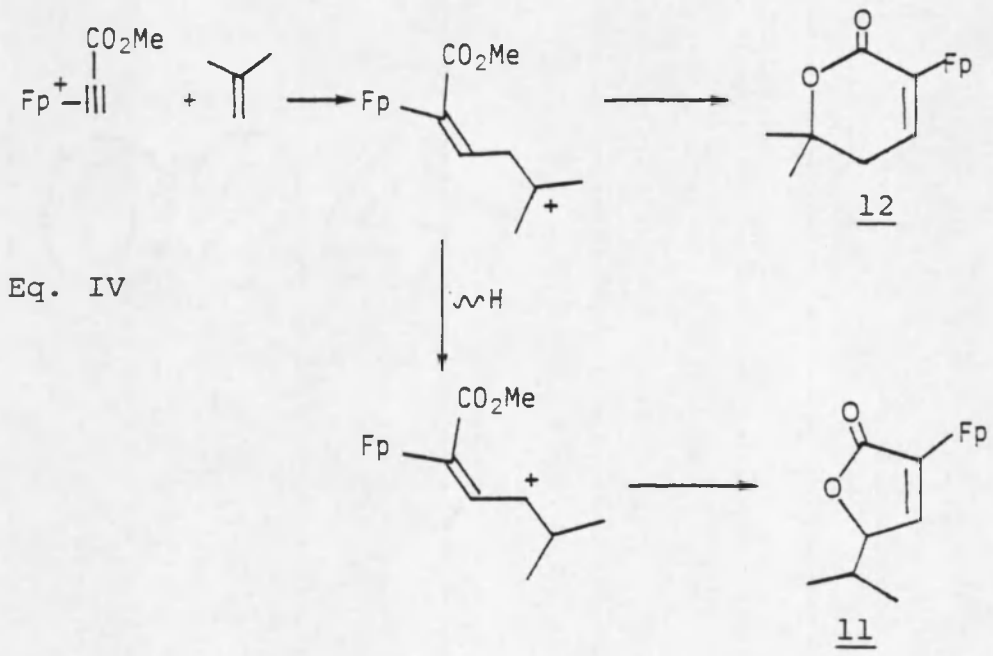
Compound 10 exhibits strong electrophilic character which has been demonstrated by the formation of the lactones 11 and 12 (Eq. IV). Even when the isobutylene was removed from the solution by purging with nitrogen the lactone products were formed [12].

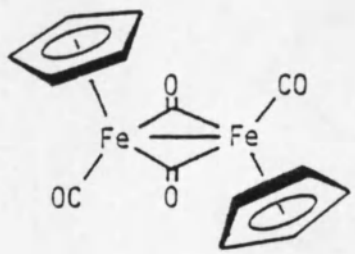


Eq. IV

1.1 Synthesis of Cationic Olefin and Alkyne Complexes

Cationic olefin and alkyne iron complexes have been synthesized by several routes as illustrated in Equations V through VII:

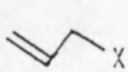
Eq. V

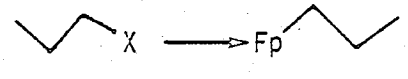
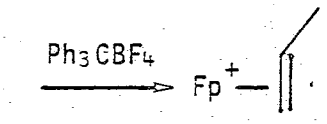


13

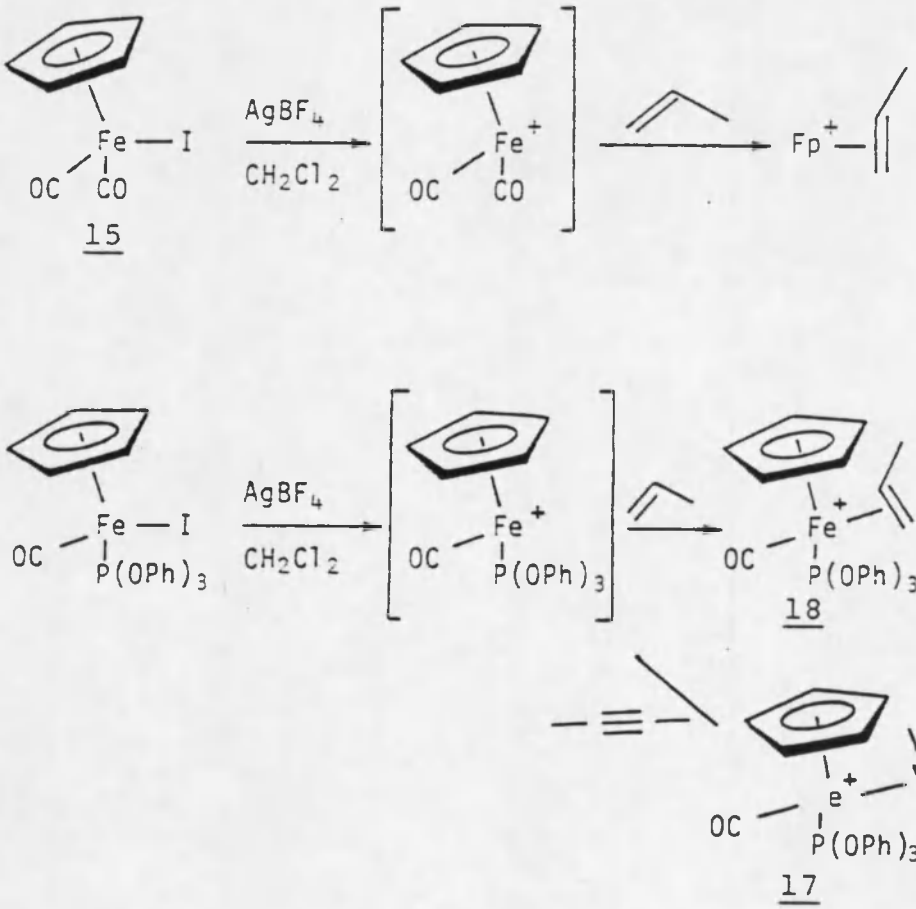
$\xrightarrow[\text{THF}]{\text{Na(Hg)}}$ $2[C_5H_5Fe(CO)_2]^-$ $\xrightarrow[\text{2. } HBF_4]{\text{1.}}$ Fp^+

14

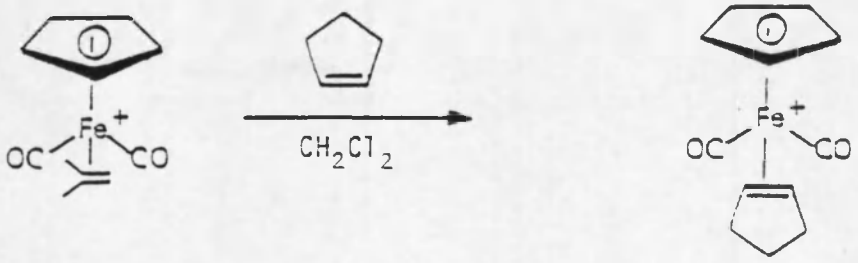
Eq. VI $[C_5H_5Fe(CO)_2]^- +$  $\longrightarrow$  $\xrightarrow{HBF_4}$ 

Eq. VII $[C_5H_5Fe(CO)_2]^-$ +  $\xrightarrow{Ph_3CBF_4}$ 

The $[CpFe(CO)_2]_2$ (13) complex can be readily reduced using sodium amalgam (Eq. V) to yield the $[CpFe(CO)_2]^{\ominus}$ (14) anion [13]. The latter has been shown to be a very strong nucleophile [14]. Epoxide ring opening by 14 was followed by protonation and loss of water to yield the cationic olefin complex (Eq. V) [15]. These complexes were also synthesized by reacting the anion with allylic halides followed by protonation with fluoroboric acid (Eq. VI) [2]. When a primary or secondary alkyl halide was reacted with 14 the n^1-alkyl iron complexes were isolated and when these were treated with trityltetrafluoroborate, a β-hydrogen was removed, yielding the cationic olefin complex (Eq. VII) [16]. Another route was recently discovered through reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2I$ (15) with silver tetrafluoroborate which produced the $Fp^{\oplus}$ cation, a sixteen electron species, that quickly combined with olefin or alkyne in solution [9]. It has also been reported that $(n^5\text{-}C_5H_5)Fe(CO)[P(OPh)_3]I$ (16) reacts analogously with silver tetrafluoroborate and olefins or alkynes to afford the corresponding complexes 17 and 18 [10]. Finally, it was observed that the $[(C_5H_5)Fe(CO)_2(n^2\text{-isobutylene})]BF_4$ (19) complex exchanged olefins [17] or alkynes [12] with loss



of isobutylene when heated (Eq. VIII):

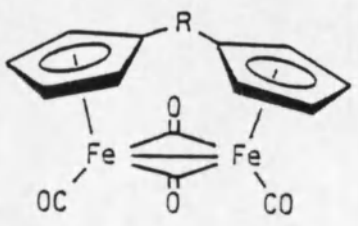


Thus using these simple routes to the necessary precursor complexes, the above iron olefin and alkyne compounds have been made readily available for use in organic syntheses.

1.2 Syntheses and Chemistry of Bridged Binuclear Iron Complexes

1.2.1 Cyclopentadienyl Bridged Compounds

The syntheses of a number of binuclear, non-ferrocene, bis-cyclopentadienyl bridged iron complexes have been reported in the literature (Fig. 1) [18-21]. Weaver and Woodward [19] and also Wegner et al. [18] have obtained an X-ray structure of 20, R = $SiMe_2$. Wegner et al. [18] also reported reduction of $(CH_3)_2Si[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ (21) to the dianion $(CH_3)_2Si[(\pi\text{-}C_5H_4)Fe(CO)_2]_2^{-2}$ (22) by a two step (E° = -1.54; -2.20 V) process, while the unbridged system reduces by a single two-electron mechanism at -2.22 V [22].



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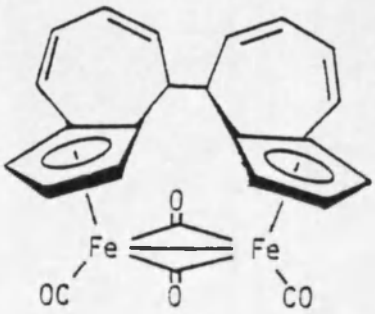
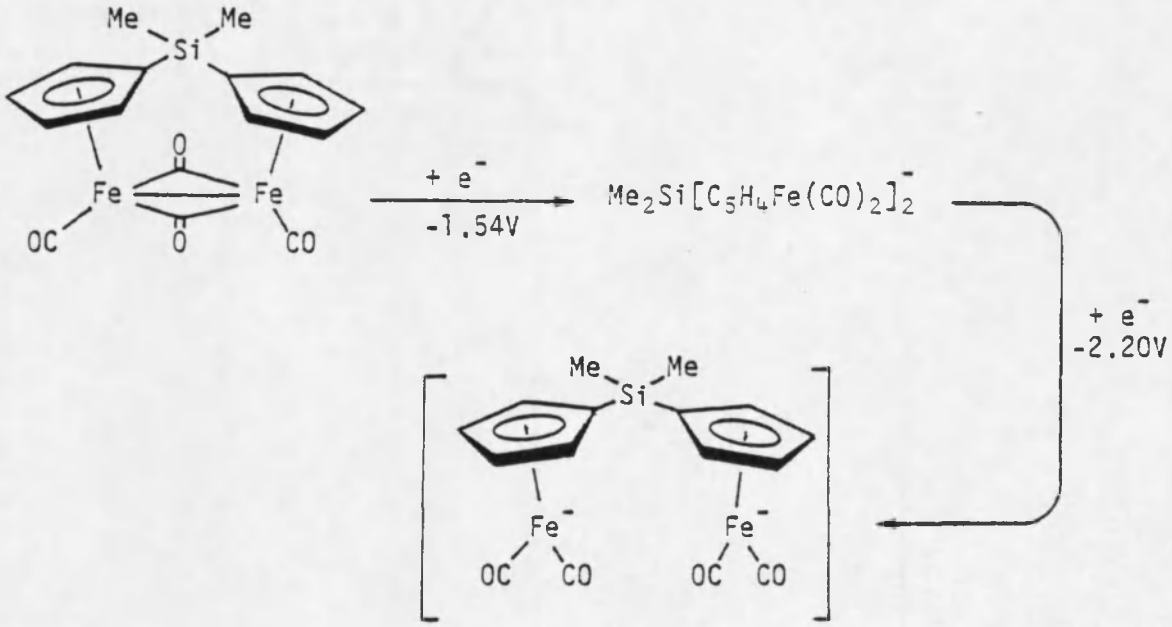


21

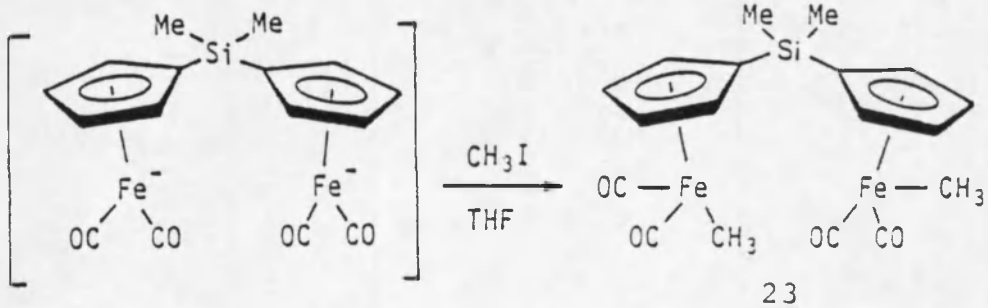
R = -N-N- , $SiMe_2$, $-Me_2C\text{-}CMe_2-$
Me Me

Fig. 1. Bis-cyclopentadienyl bridged iron complexes.



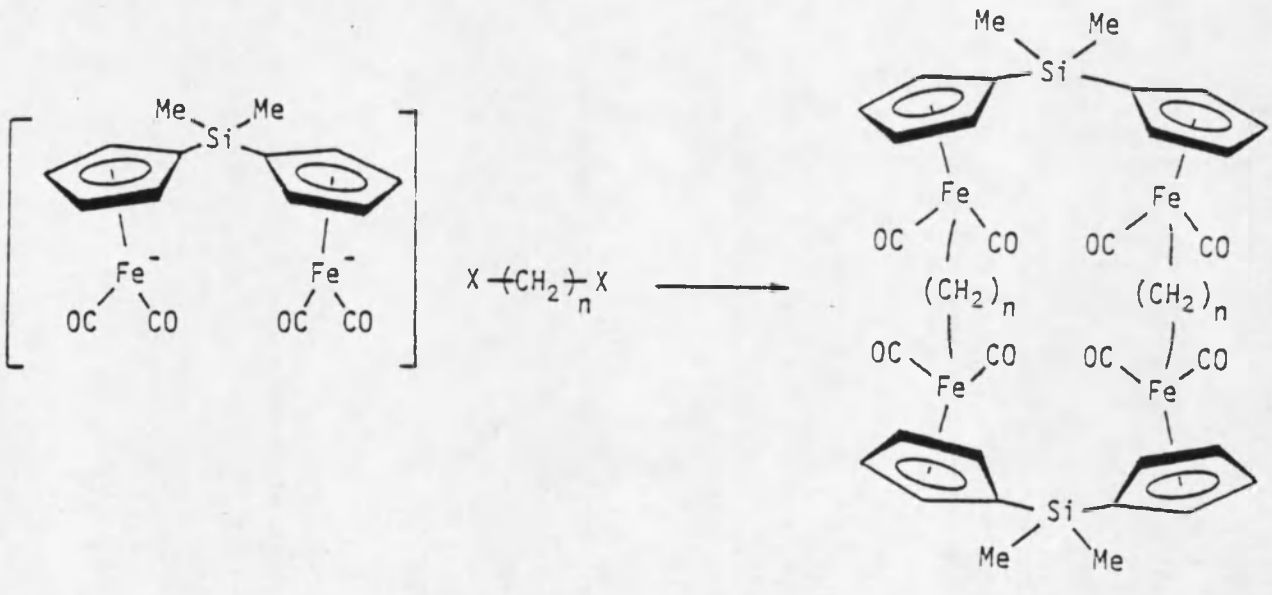
22

Dianion 22 was also prepared by the chemical reduction of 21 using sodium amalgam. The dianion was then reacted with alkyl halides to prepare derivatives of the type $(CH_3)_2Si[(C_5H_4)Fe(CO)_2R]_2$, where R = CH_3 (23) and CH_2CH_3 [23]:



23

Thermal decomposition of these complexes has been studied [24]. Reaction of the above dianion with α, ω-alkyl dihalides gives tetranuclear products $[(CH_3)_2Si[\pi\text{-}C_5H_4\text{-}Fe(CO)_2]_2(CH_2)_N]_2$ for N = 3, 4, and 5 (18):



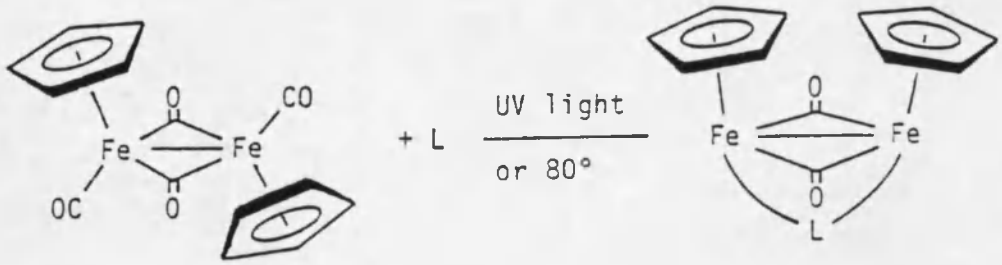
X = Br, Cl

1.2.2 Bis-phosphine Bridged Complexes

The two iron centers have also been bridged by means of a bis-phosphine or bis-arsine ligand to afford derivatives of the type $[(\pi\text{-}C_5H_5)Fe(CO)]_2L$ [25]. These can be prepared by treatment of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ with L in benzene under thermal or photolytic conditions (Scheme I) [25].

Ferguson and Meyer [26] described a study on the electrochemical oxidation of $[(\pi\text{-}C_5H_5)Fe(CO)]_2Ph_2PCH_2CH_2Ph_2$ (24) and reported the latter complex to undergo a two-electron oxidation. Removal of the first electron was both a chemically and an electrochemically reversible process in all compounds that were studied. From spectral data obtained the mono-cation (25) was apparently

Scheme I:

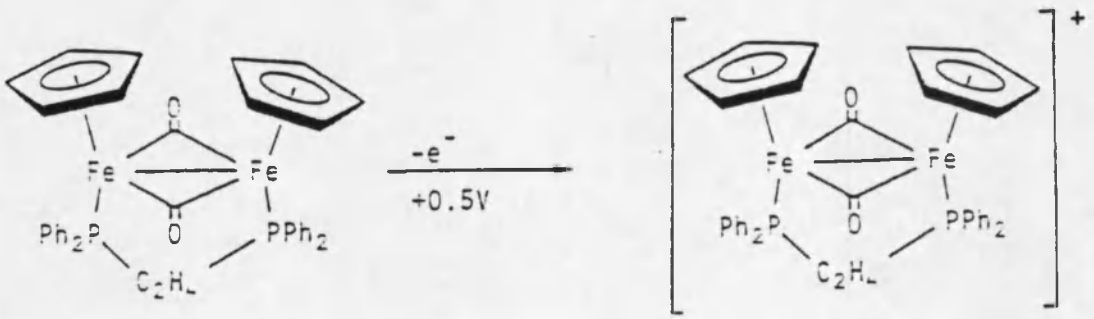


L = $Ph_2P(CH_2)_nPPh_2$, n=1,2,3

Ph_2PNPPh_2 , $Ph_2PC_2H_2PPh_2$
|
Et

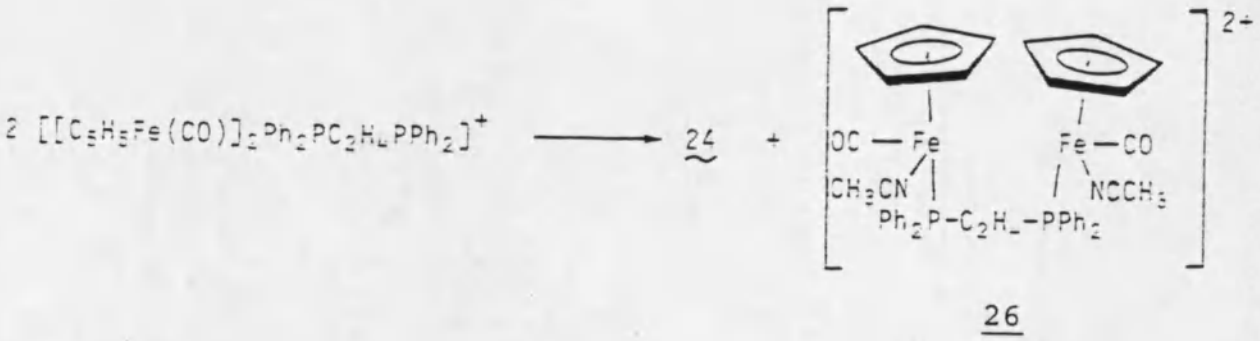
$Ph_2As(CH_2)_nAsPh_2$, n=1,2

isostructural with 24 and contained a "one-electron" metal-metal bond [26]:



24 25

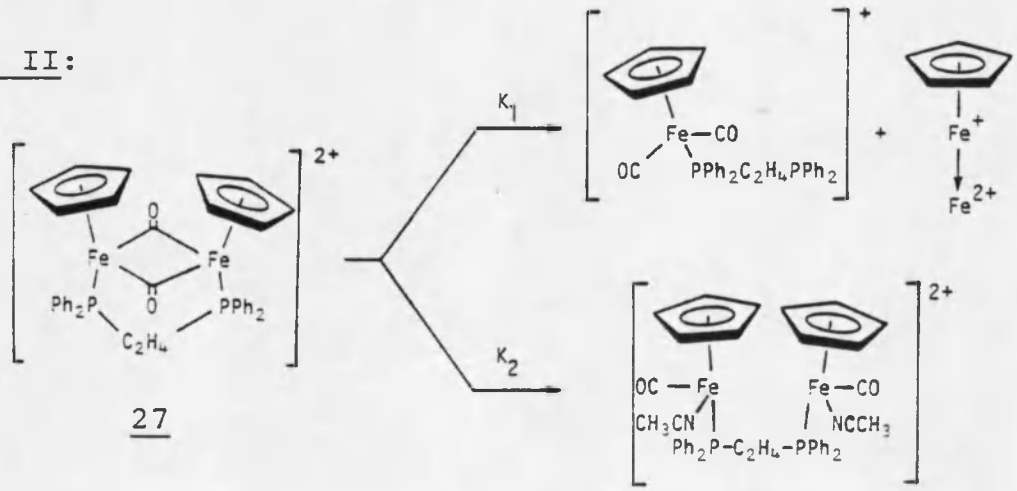
Complex 25 decomposed through a disproportionation mechanism to give 24 and the dication $[[(\pi\text{-}C_5H_5)Fe(CO)(CH_3CN)]_2\emptyset_2PCH_2\text{-}CH_2P\emptyset_2]^{+2}$ (26) in acetonitrile [26]. When a potential of 1.2 V was applied to 25 in solution one additional electron was removed irreversibly. The electrochemical reaction was believed to proceed through an initial dication intermediate,



26

containing no metal-metal bond but isostructural to 24. Complex 27 reacted further by either asymmetric (K_1 path) or symmetric (K_2 path) cleavage of the diphosphine and carbonyl bridges (Scheme II) [26].

Scheme II:

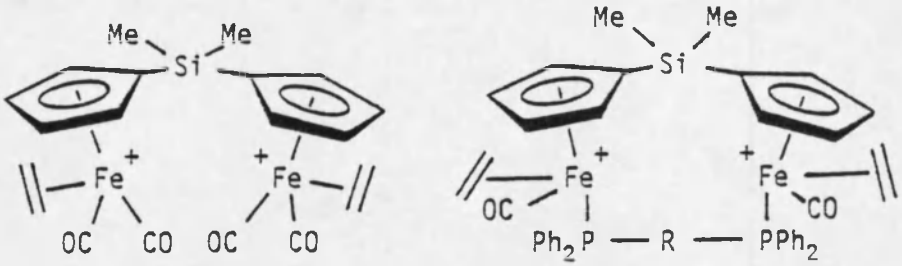


27

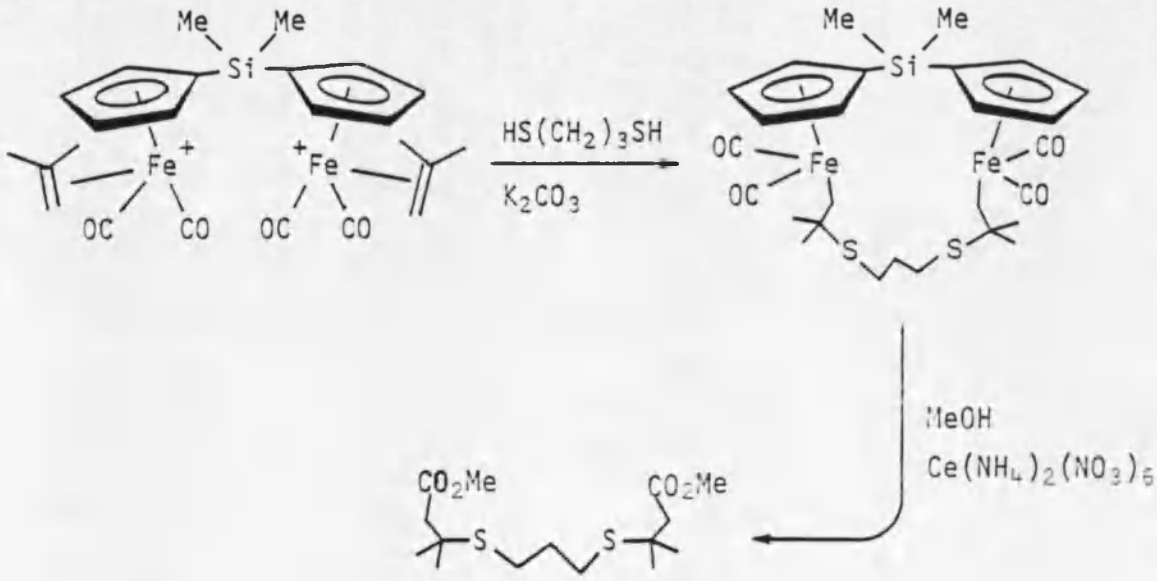
26

The path taken by 27 was dependent upon temperature and solvent used. In the better coordinating solvent acetonitrile, the symmetric cleavage (K_2) was important and at high temperatures the K_2 path dominated. Reaction at 75° in acetonitrile gave quantitatively the symmetrical cleavage product 26 which could be isolated as its dihexafluorophosphate salt [26].

Comparison of the chemical and electrochemical behavior of bridged binuclear iron complexes to that of the unlinked derivatives has demonstrated distinct differences. It was the purpose of this work to study the synthesis of new mechanically linked binuclear-iron complexes with development of the chemistry associated with them. We are interested specifically in synthesizing single and doubly linked olefin and alkyne complexes:



The bridged olefin complexes would then be reacted with various difunctional nucleophiles in a presumably regio-selective manner, to yield the bridged bis-(n'-alkyl) derivatives:



The bis(n^1-alkyl) complexes could then be reacted with $Ce(NH_4)_2(NO_3)_6$ to yield the diesters [3]. Analogous chemistry as above could be performed on the bis-bridged systems.

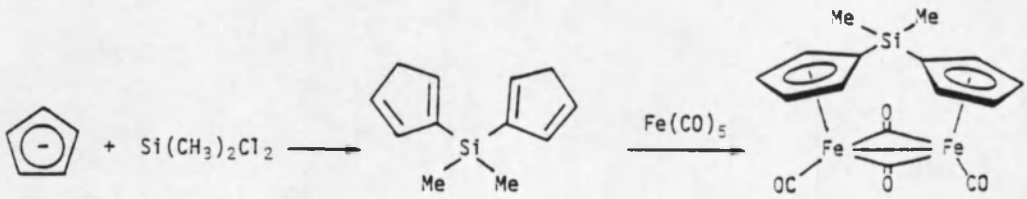
CHAPTER 2

RESULTS AND DISCUSSION

2.1 Monobridged Binuclear-Iron Complexes

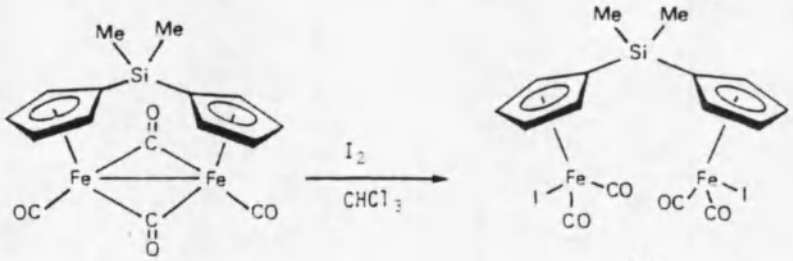
2.1.1 Monobridged Diiodo Complexes

Reaction of two equivalents cyclopentadienyl anion with one equivalent of dichlorodimethylsilane followed by reaction with iron pentacarbonyl in refluxing tetrahydrofuran-xylene (1:5) afforded complex 21 in 15% isolated yield [18]:



21

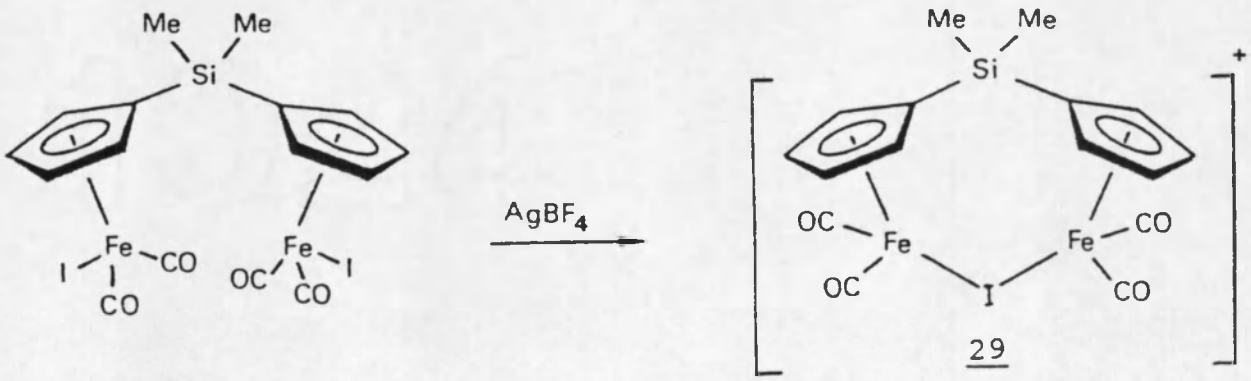
Compound 21 was then reacted with iodine in refluxing chloroform (degassed) to yield the diiodo complex $[(\pi\text{-}C_5H_4)Fe(CO)_2I]_2SiMe_2$ (28):



28

Compound 28 has been fully characterized by spectroscopic, analytical, and single crystal X-ray methods [27]. The numbering scheme used in this X-ray diffraction study is given in Fig. 2, and a stereoscopic view of the molecule is shown in Fig. 3. Selected bond lengths and bond angles are collected in Tables 1 and 2.

From the ORTEP diagram (Fig. 3) one can see the two metal centers are twisted away from one another, thus possibly decreasing the steric effect about the metal centers. When 28 was treated with two and one-half equivalents of silver tetrafluoroborate in dichloromethane with or without olefin present, the only product isolated was the bridging iodo species, complex 29:



The bridging iodonium complex has been fully characterized by spectroscopic and analytical data. The ^1H NMR (Fig. 4) clearly shows the two irons are chemically equivalent and by the downfield shift in the cyclopentadienyl protons, it appears the metals have become more electropositive.

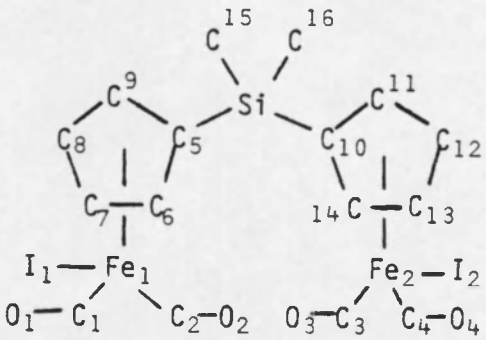


Fig. 2. Numbering scheme used for $Me_2Si[(C_5H_4)Fe(CO)_2I]_2$.

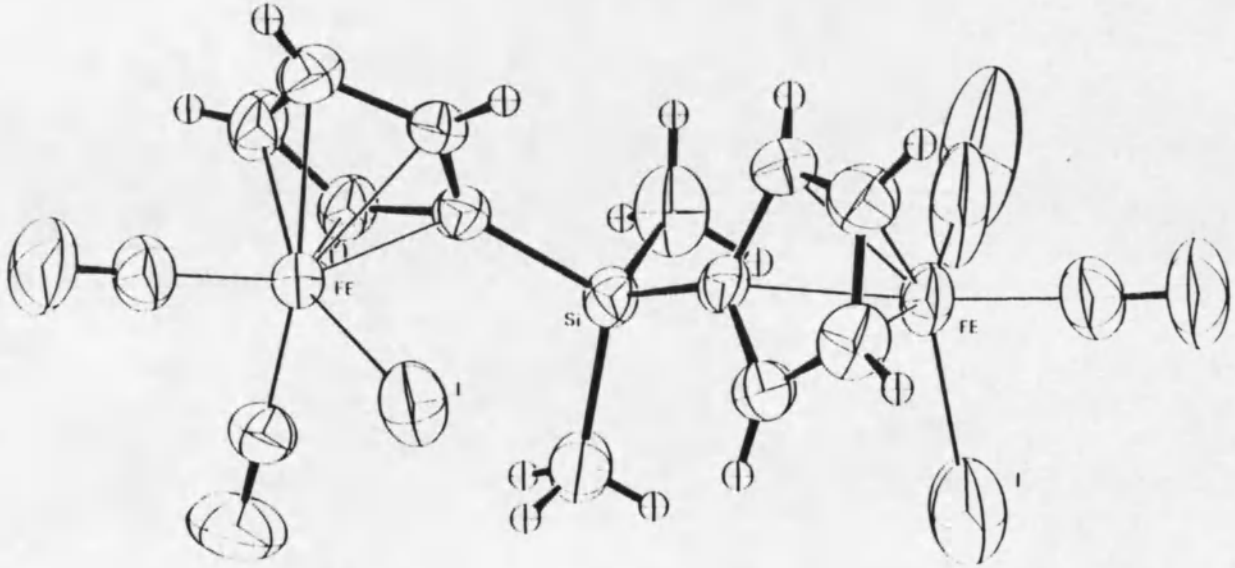


Fig. 3. ORTEP stereoscopic view of $Me_2Si[(C_5H_4)Fe(CO)_2I]_2$.

Table 1. Selected bond lengths (Å) for $Me_2Si[(C_5H_4)Fe(CO)_2I]_2$.

Fe(1)-I(1)	2.605	Fe(1)-C(9)	2.119
Fe(1)-C(1)	1.770	Si-C(5)	1.865
Fe(1)-C(2)	1.792	Si-C(15)	1.871
Fe(1)-C(5)	2.121	C(1)-O(1)	1.141
Fe(1)-C(6)	2.080	C(2)-O(2)	1.131
Fe(1)-C(7)	2.085	C(5)-C(6)	1.450
Fe(1)-C(8)	2.097	C(5)-C(9)	1.440

Table 2. Selected bond angles (deg) for $Me_2Si[(C_5H_4)Fe(CO)_2I]_2$.

C(1)-Fe(1)-I(1)	90.85	C(6)-C(5)-C(9)	105.27
C(2)-Fe(1)-I(1)	91.32	C(5)-C(9)-C(8)	109.48
C(1)-Fe(1)-C(2)	93.60	C(11)-C(10)-C(14)	105.40
C(5)-Si-C(15)	110.88	C(10)-C(11)-C(12)	109.65

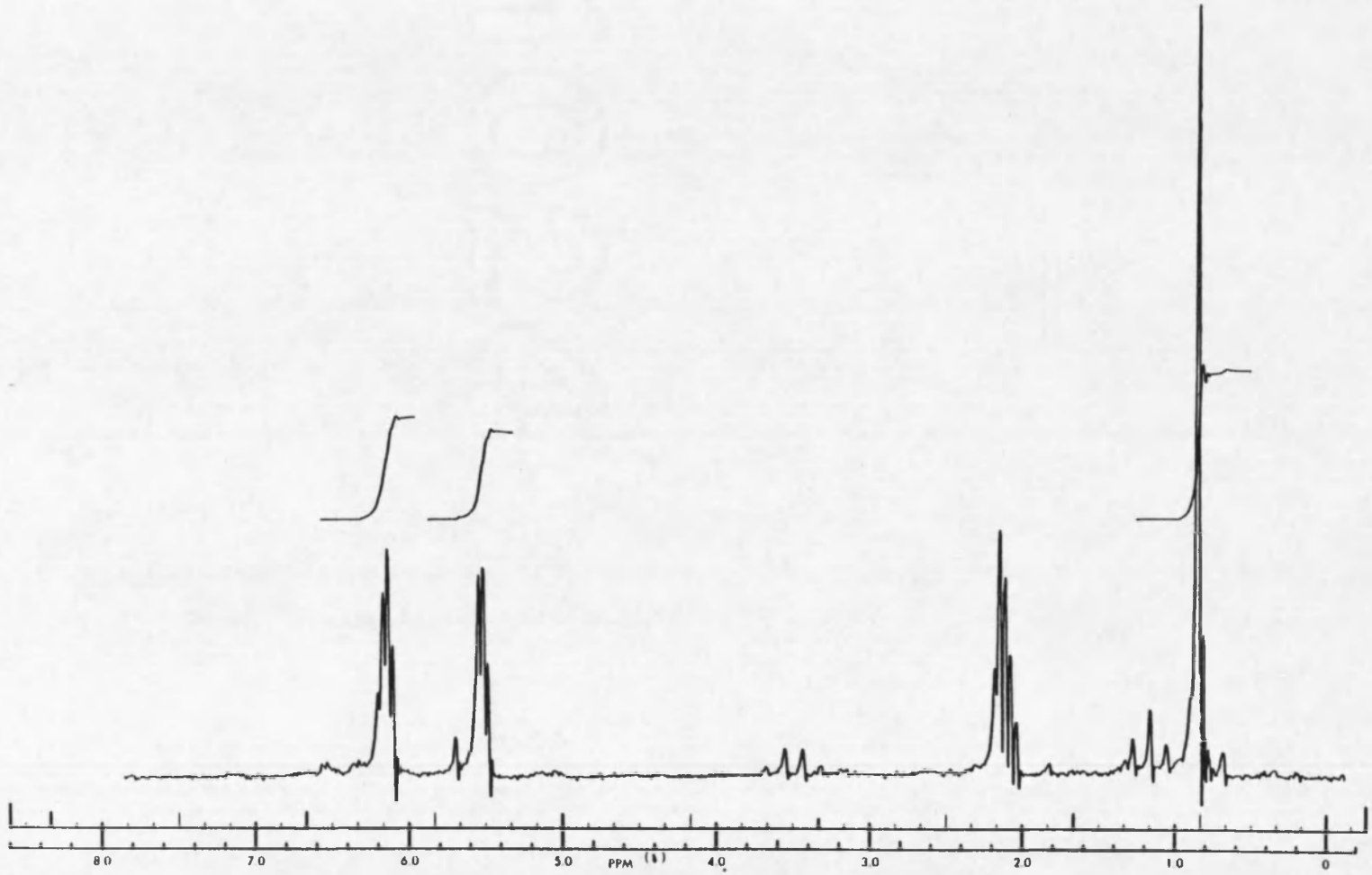
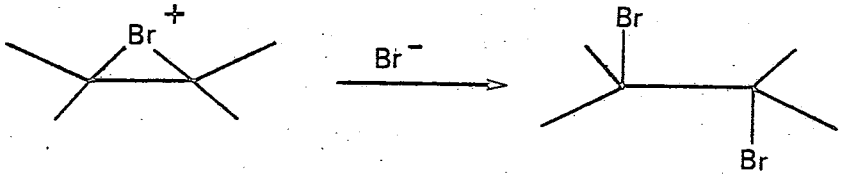


Fig. 4. ^{1}H NMR spectrum of $(Me_2Si[(C_5H_4)Fe(CO)_2]_2I)BF_4$ (29).

Complex 29 appears in pure form as brick red crystals which are obtained by recrystallization from dichloromethane-ether solutions. The bridging iodo complex was very stable in oxygen free solutions, and in solid form was air stable.

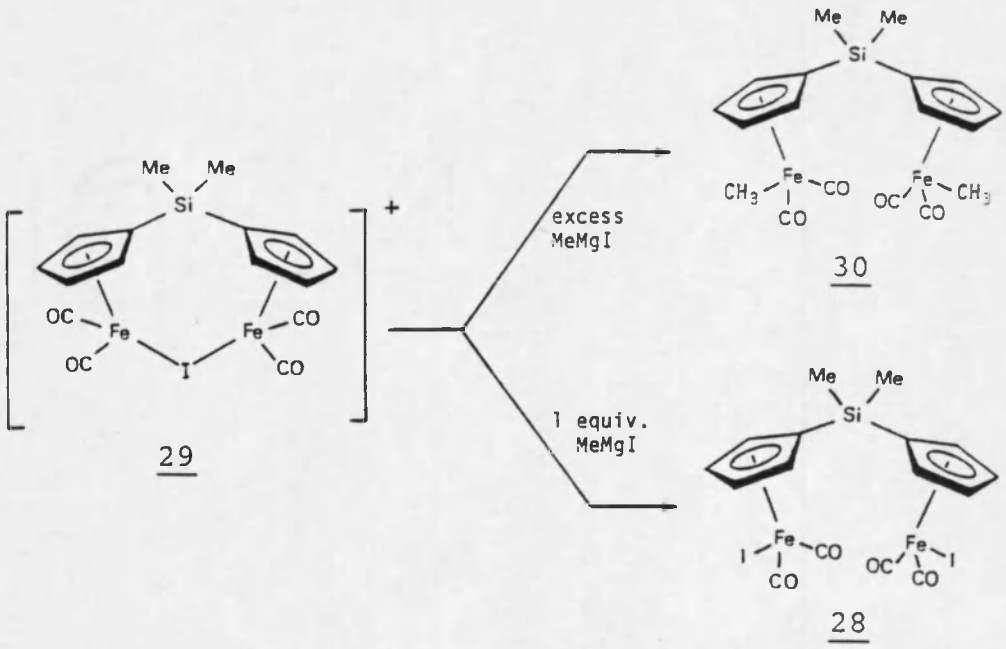
A bridging iodonium intermediate has been observed by Rosenblum when using high concentrations of $(\pi\text{-}C_5H_5)Fe(CO)_2I$ and silver tetrafluoroborate in preparations of cationic olefin complexes. Therefore one could conclude that the bridged complex 29 was behaving like a highly concentrated solution of the mononuclear species.

It has been well established in the literature that bridging iodonium and bromonium cations can readily undergo ring opening by nucleophilic attack [28]:



In comparison, a heterogeneous mixture of tetrahydrofuran (THF) and 29 was reacted with one equivalent of methylmagnesium iodide resulting in isolation of the diiodo complex 28 (Scheme III).

The formation of 28 from reaction of one equivalent of methylmagnesium iodide suggests the iron center was more susceptible to attack by the "soft" iodide versus the "hard"



29 30 28

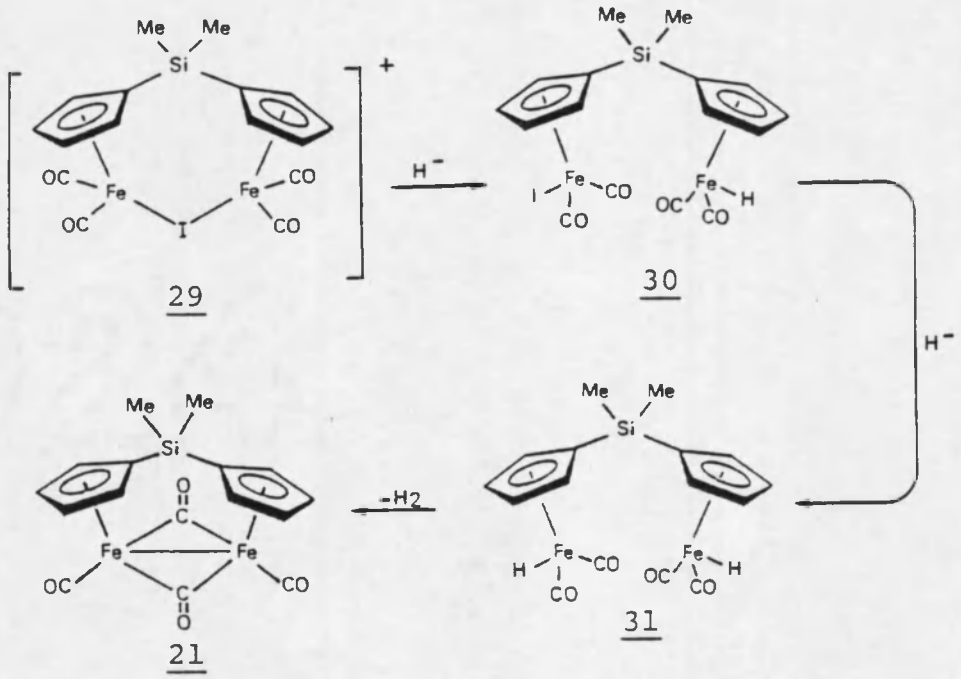
methyl carbon. The formation of 30 must arise from reaction of two equivalents methylmagnesium iodide with complex 28. It has been shown previously that reaction of alkyl carbanions with $CpFe(CO)_2I$ yielded n'-alkyl iron complexes [29].

Reaction of 29 with sodium borohydride in THF did not yield the mixed hydride iodo complex but rather the iron-iron bonded species 21. It is proposed that the dihydride compound 31 is an intermediate which undergoes rapid elimination of hydrogen gas leading to formation of the iron-iron bond (Eq. IX).

2.1.2 Monobridged Olefin Complexes

Through the known facile reduction of the iron-iron bond in complex 21 by sodium-amalgam [18] we have prepared

Eq. IX



n^1-allyl species which are precursors to cationic olefin compounds [2]. The n^1-allyl complexes, 32 and 33, were purified by chromatography on alumina (neutral, activity III) by elution with hexane. They were isolated usually as light brown oils; however, occasionally crystalline product was obtained. In the solid state the complexes were air stable but in solution decomposed if not oxygen free. The ^1H NMR spectra of both n^1-allyl complexes are shown in Figs. 5 and 6. They are in good agreement with the previously reported spectra for $(\pi\text{-}C_5H_5)Fe(CO)_2(n^1\text{-iso-butylene})$ and $(\pi\text{-}C_5H_5)Fe(CO)_2(n^1\text{-allyl})$ compounds [2]. When compounds 32 and 33 were reacted with 48% aqueous fluoroboric acid or a fluoroboric acid-ether complex, in THF

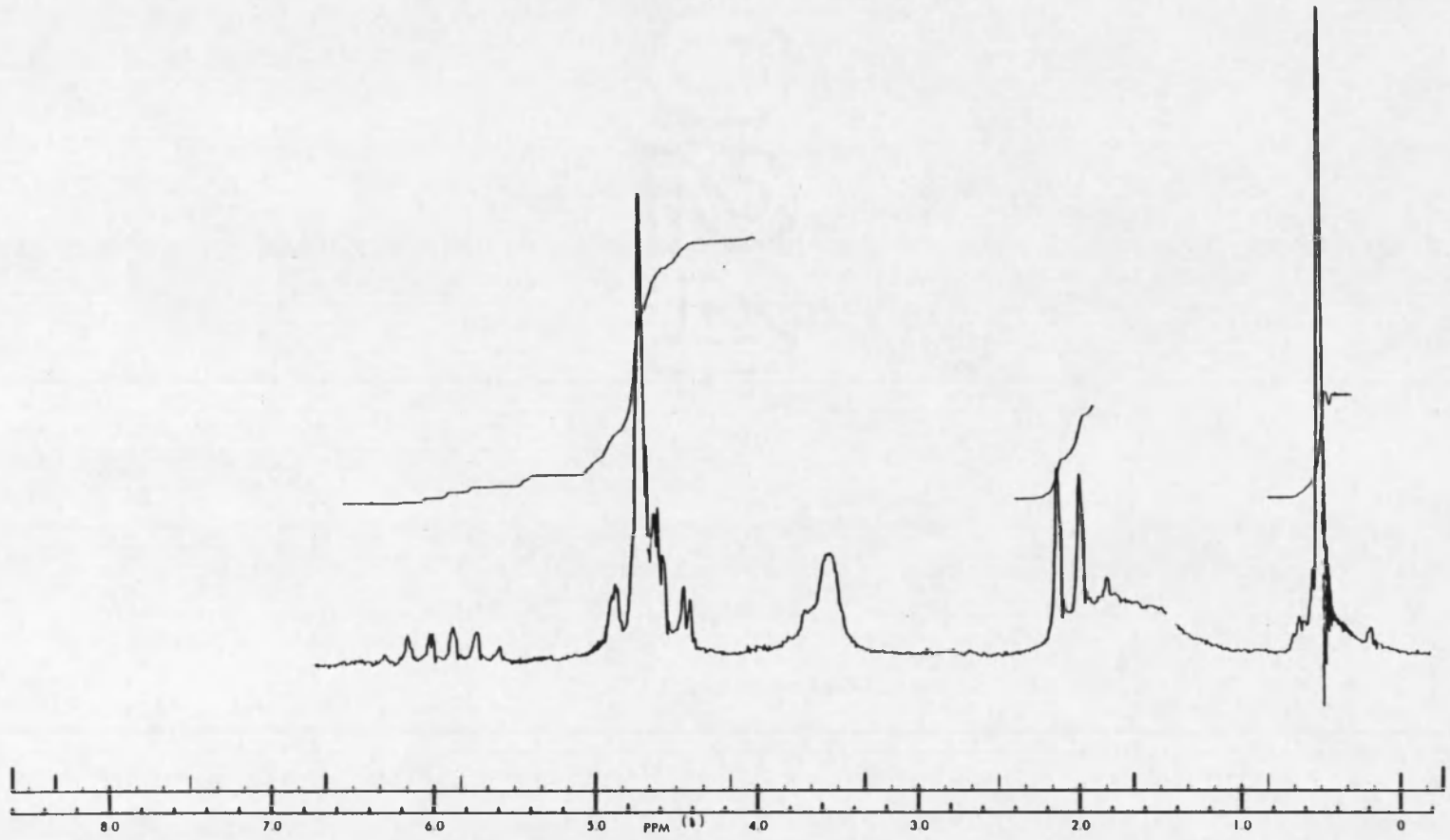


Fig. 5. ^{1}H NMR ($CDCl_3$) of $Me_2Si[(C_5H_4)Fe(CO)_2(n^1\text{-allyl})]_2$ (32).

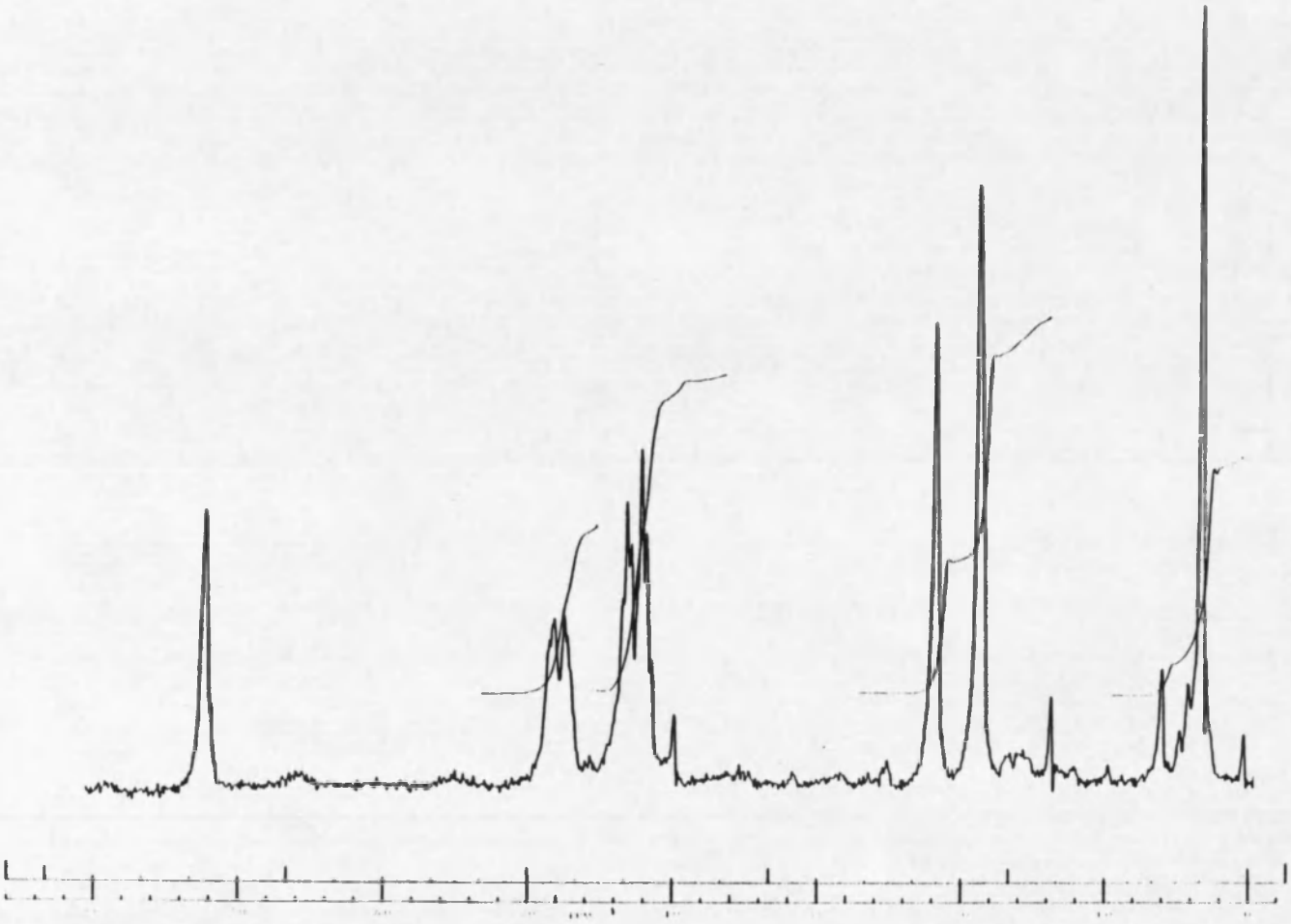
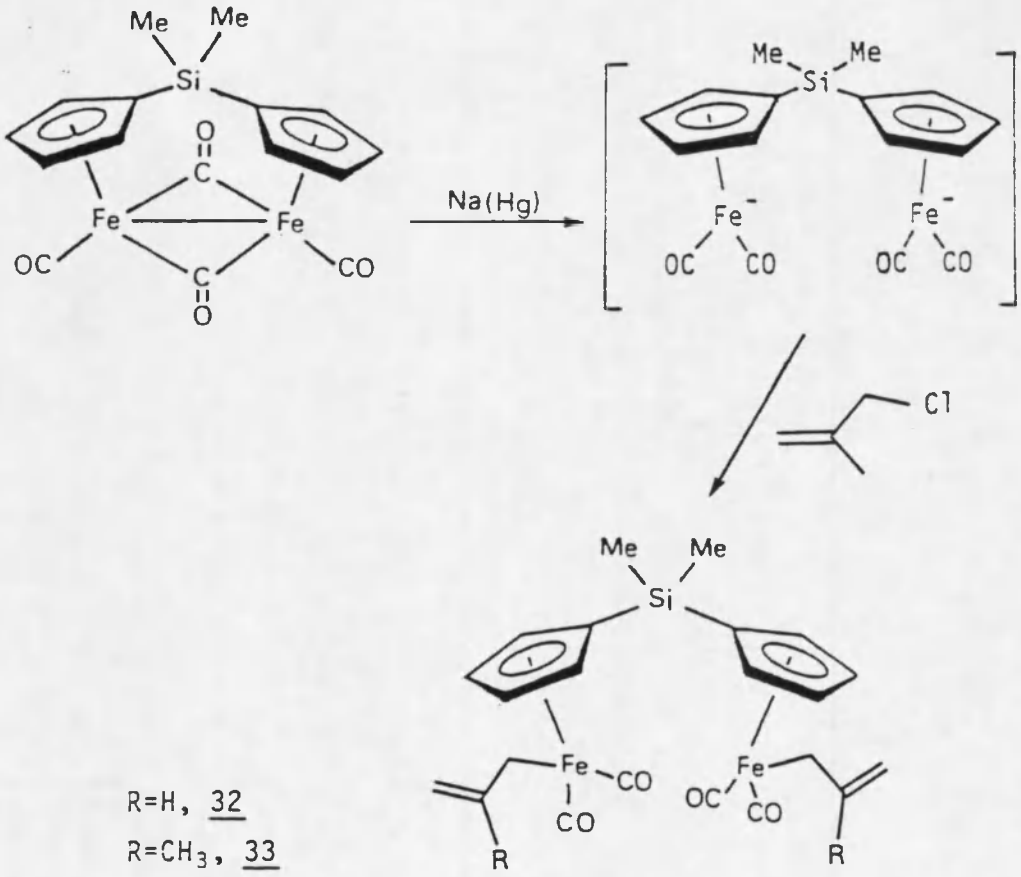


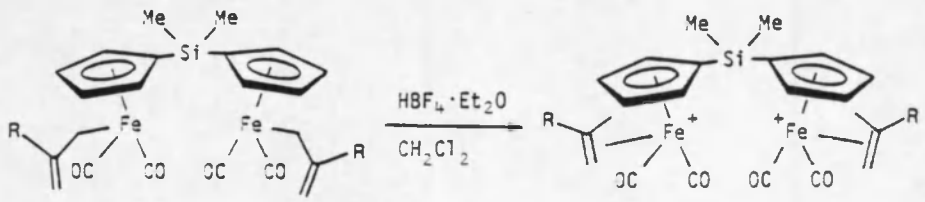
Fig. 6. ^{1}H NMR (C_6D_6) of $Me_2Si[(C_5H_4)Fe(CO)_2(n^1\text{-isobutylene})]_2$ (33).



R=H, 32

$R=CH_3$, 33

or dichloromethane, the corresponding cationic-olefin complexes were isolated:



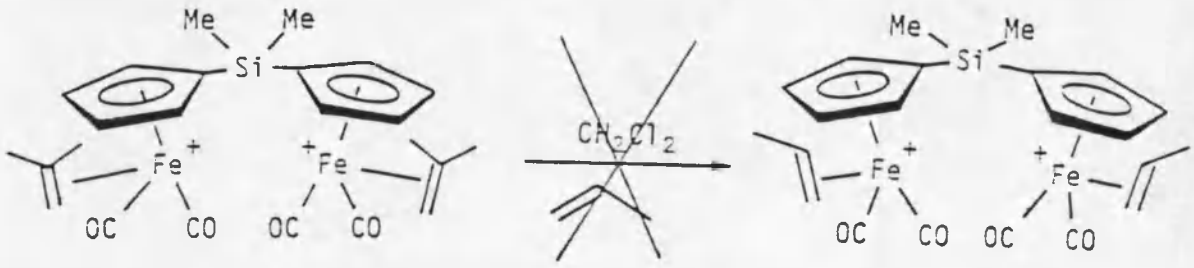
R=H, 34

$R=CH_3$, 35

The above n^2-olefin compounds 34 and 35 were obtained as yellow-orange solids by recrystallization from acetone-ether

or dichloromethane-ether mixtures. The structures of 34 and 35 are based on comparison of proton chemical shifts and integration values to those of the mono-nuclear analogs [2]. The ^1H NMR spectra for 34 and 35 are shown in Figs. 7 and 8 respectively. Upon conversion from the n^1-allyl to the cationic n^2-olefin species, the cyclopentadienyl ^1H NMR signals were shifted downfield while the chemical shifts for the olefins were moved upfield.

As discussed earlier, the $[(\pi\text{-}C_5H_5)Fe(CO)_2(n^2\text{-}$isobutylene$)]^+$ complex undergoes exchange with olefins such as cis-2-butene and cyclopentene to yield the new corresponding n^2-olefin species. When 35 was reacted with cyclopentene in 1,2-dichloroethane at 60° for times ranging from fifteen minutes to three hours, no exchange of cyclopentene for isobutylene was observed. The starting isobutylene species (35) was isolated after each attempted exchange reaction. Other olefins such as propene, 1,5-hexadine, and cis-2-butene also failed to exchange. Finally, complex 35 was heated with 3-hexyne for twenty-four hours in dichloromethane, again only yielding starting complex 35 as product (Eq. X).



Eq. X

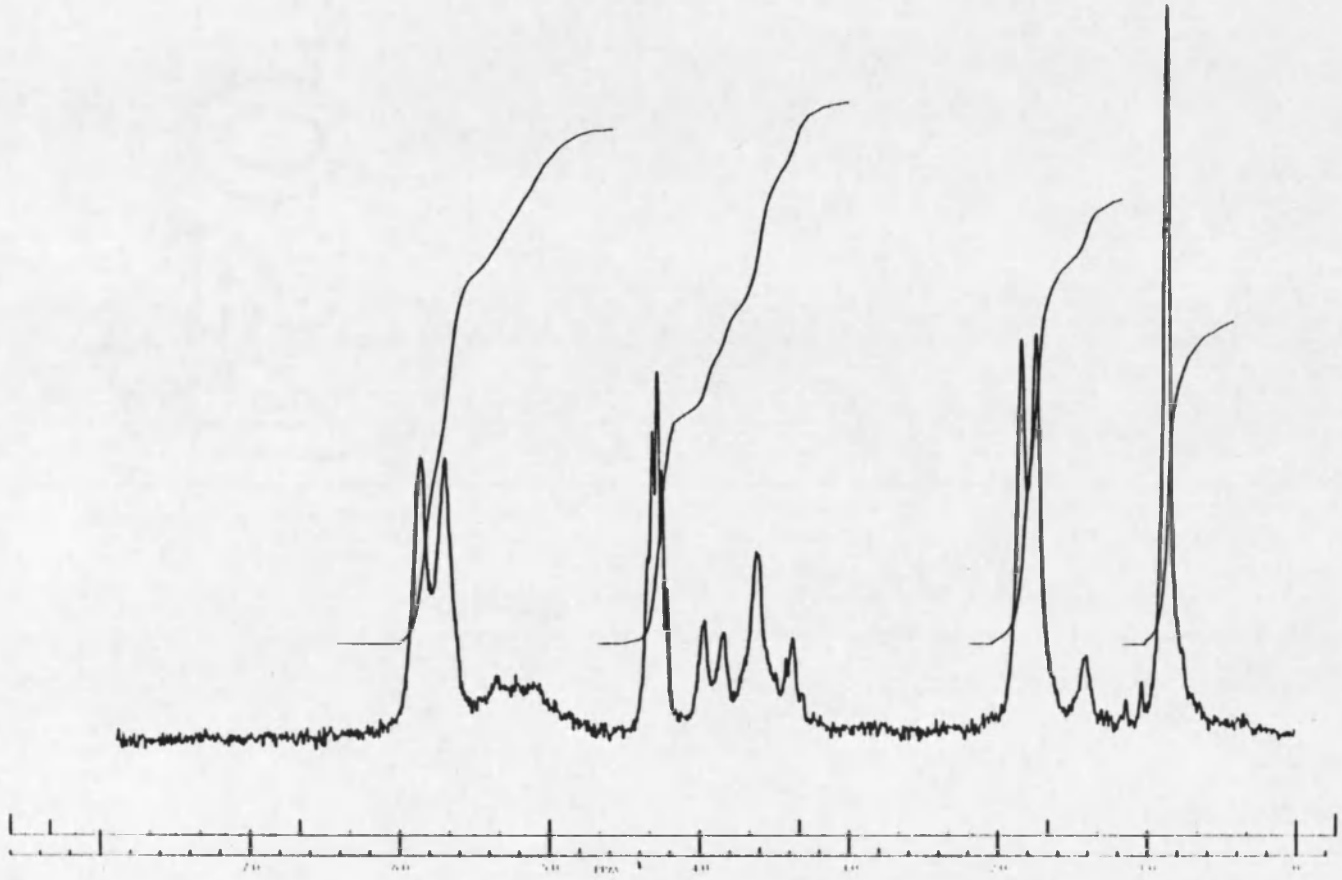


Fig. 7. ^{1}H NMR (CD_3NO_2) spectrum of $(Me_2Si[(C_5H_4)Fe(CO)_2(n^2\text{-propene})]_2)^{+2}$ (34).

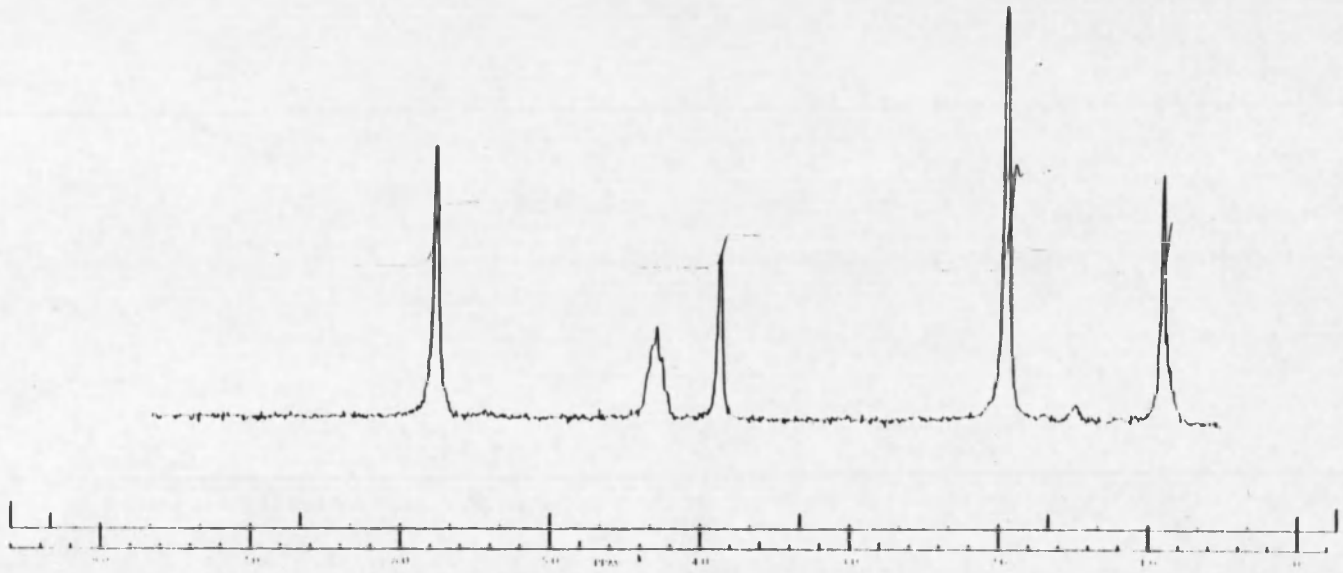


Fig. 8. ^{1}H NMR (CD_3NO_2) spectrum of $(Me_2Si[(C_5H_4)Fe(CO)_2(n^2\text{-isobutylene})]_2)^{+2}$

2.2 Bisbridged Binuclear Iron Complexes

2.2.1 Syntheses and Reactivity of Iron-Iron Bonded Bisbridged Complexes

Photolysis of a red solution of $[(\pi\text{-}C_5H_4)Fe(CO)_2]_2\text{-}SiMe_2$ (21) and bis-diphenylphosphinoethane (dppe) in benzene for fourteen hours with a four hundred and fifty watt mercury lamp resulted in generation of a dark green solution. Removal of the solvent and several washes with acetone left a light green powder. Chromatography on alumina (III) using benzene gave an initial green band followed by a blue-green band. The green complex was shown to be the bis-bridged species 36 by spectroscopic and analytical data. The blue-green band was identified as the tetranuclear complex 37 [30] (Scheme IV). The ^1H NMR spectrum of 36 is shifted upfield relative to complex 21 due to the electron donation from the phosphine ligand (Fig. 9). In complex 37 there are two types of bridged cyclopentadienyl rings, one in which the iron has a phosphine attached and a second ring which has an iron with a terminal carbonyl group. The ^1H NMR spectrum of 37 clearly shows the two different cyclopentadienyl rings and also an integration ratio of four rings to one bis-phosphine unit (Fig. 10).

Complex 37 must arise as the result of the intermolecular reaction of the substituted intermediate 38 [25]

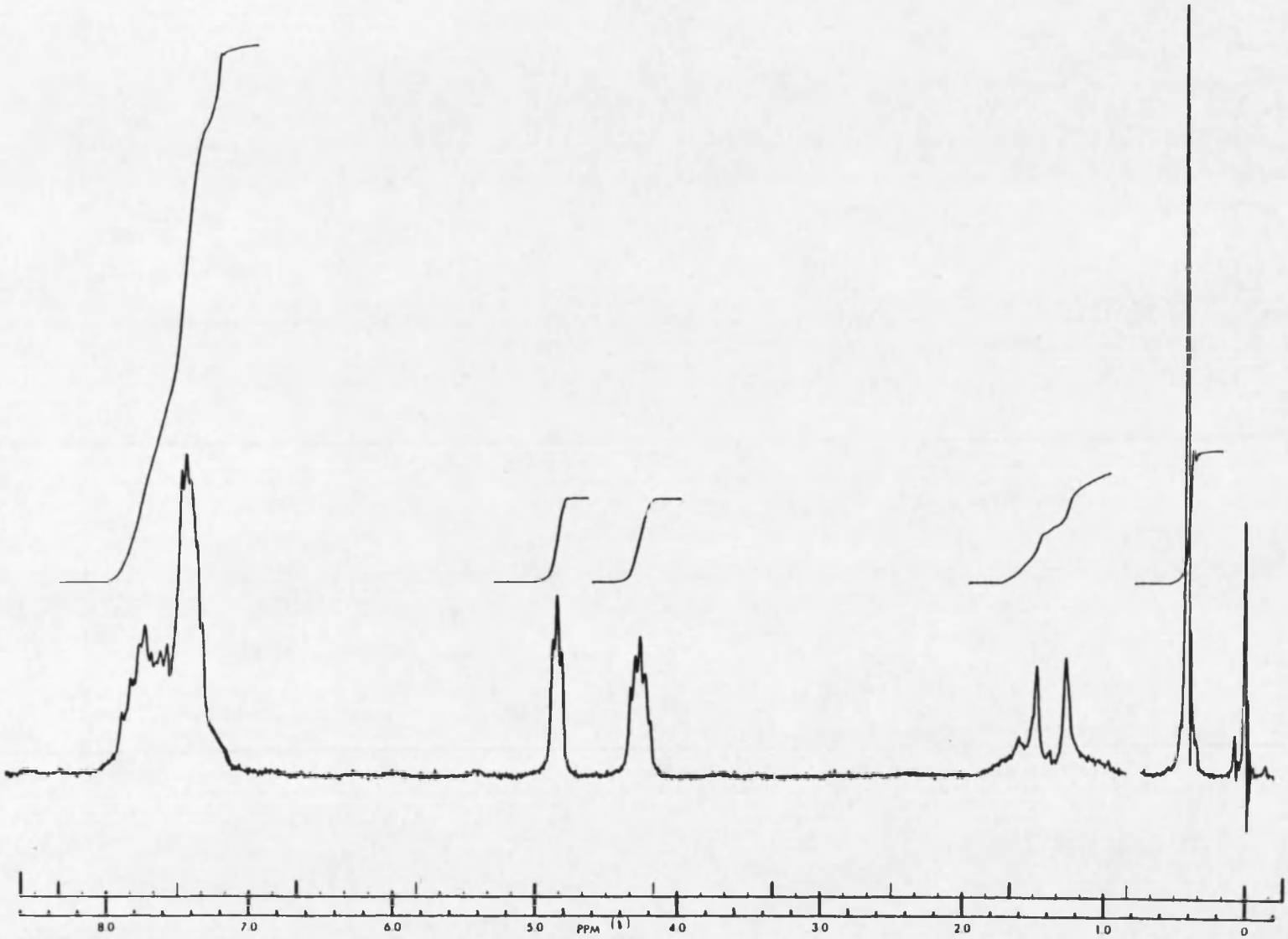


Fig. 9. ^1H NMR ($CDCl_3$) spectrum of $Me_2Si[(C_5H_4)Fe(CO)]_2dppe$ (36).

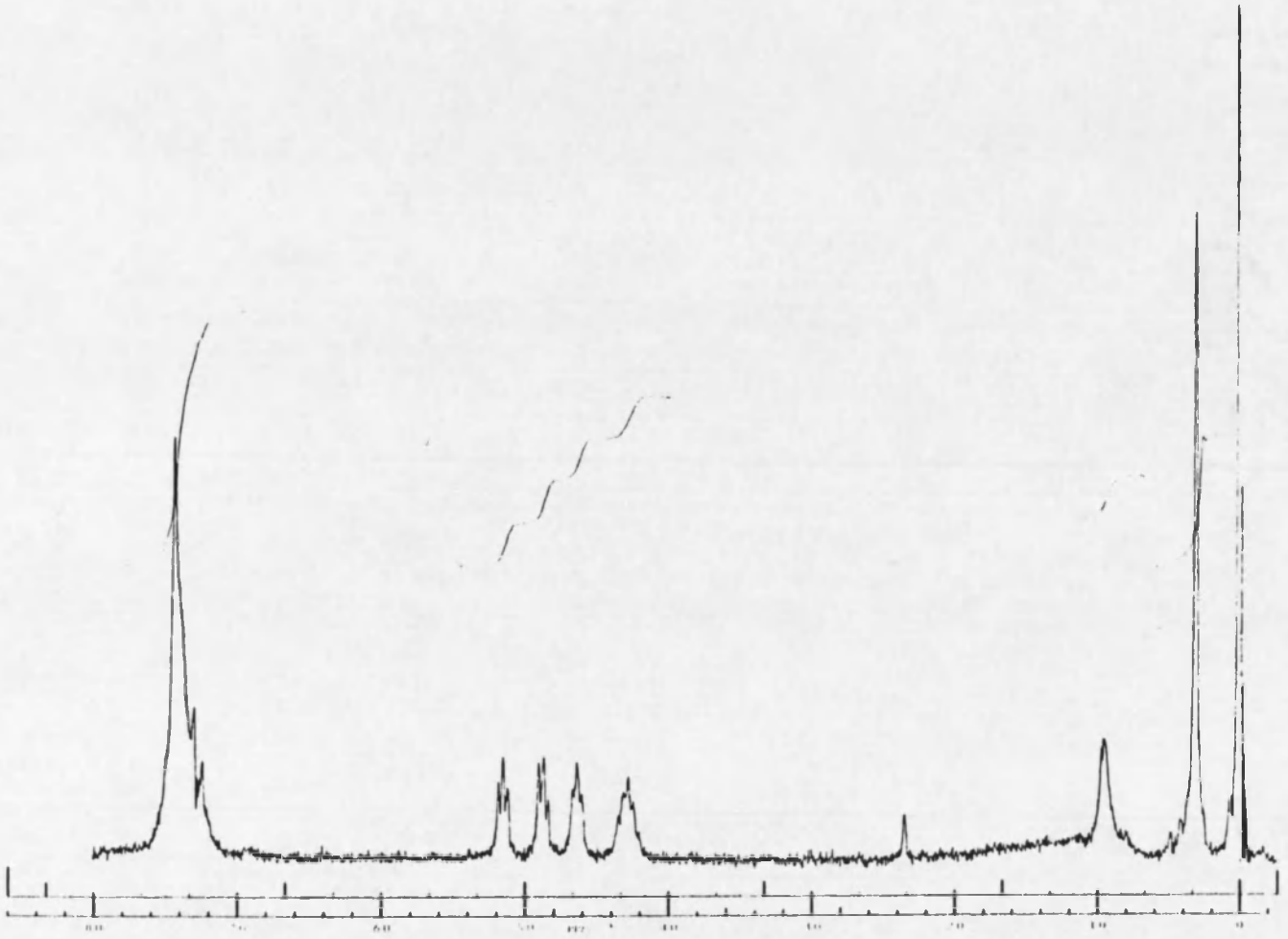
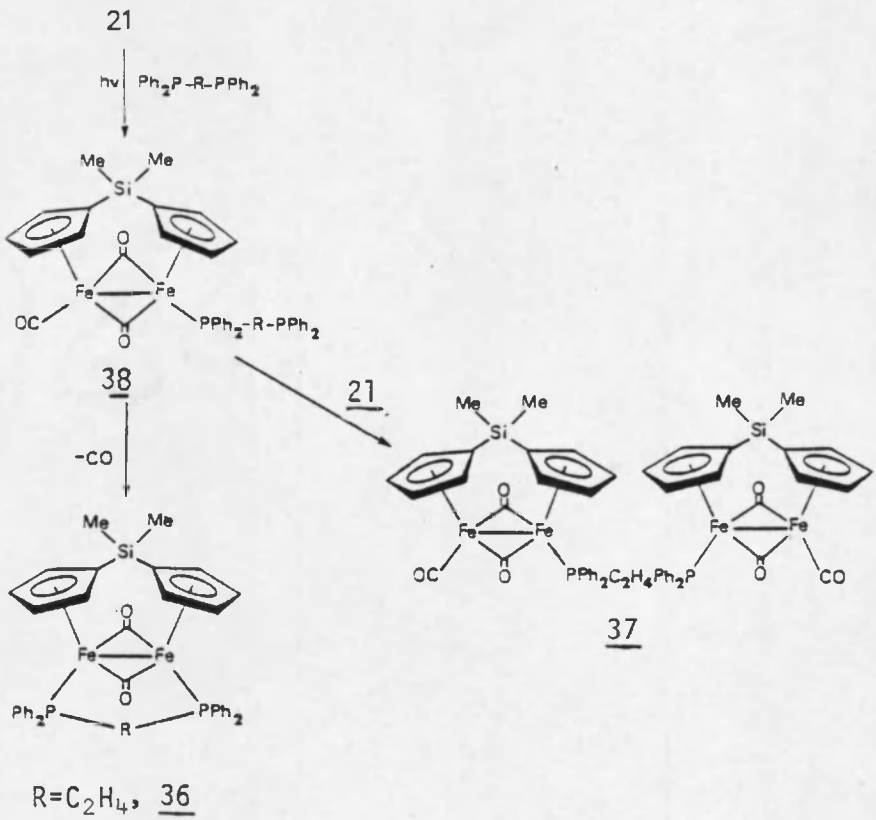


Fig. 10. ^{1}H NMR ($CDCl_3$) spectrum of $(Me_2Si[(C_5H_4)Fe(CO)]_2CO)_2dppe$ (37).

Scheme IV:



with another molecule of 21. Complex 36 would come from the same intermediate by intramolecular substitution by the free end of the complexed bis-phosphine unit. Thus as expected, when the concentration of the reacting photolysis solution was increased, complex 37 became the major isolated product.

When 36 was reacted with 48% aqueous fluoroboric acid in dichloromethane the bridging hydride species (39) was isolated. The bridging hydride can be observed in the ^1H NMR spectrum as a triplet approximately 36 ppm upfield from tetramethyl silane (TMS) (Fig. 11). In the infrared spectrum only terminal carbonyl absorptions were observed.

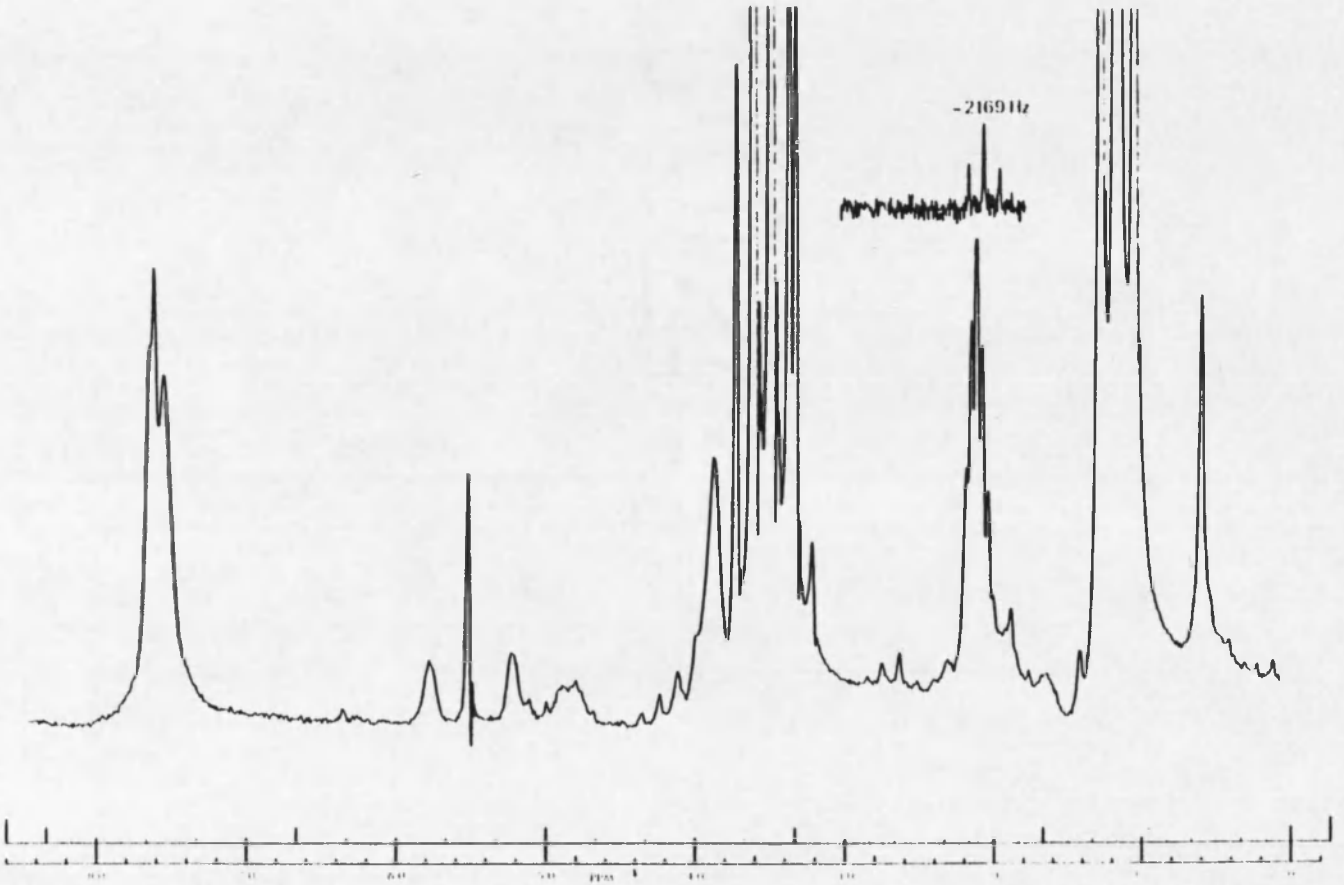
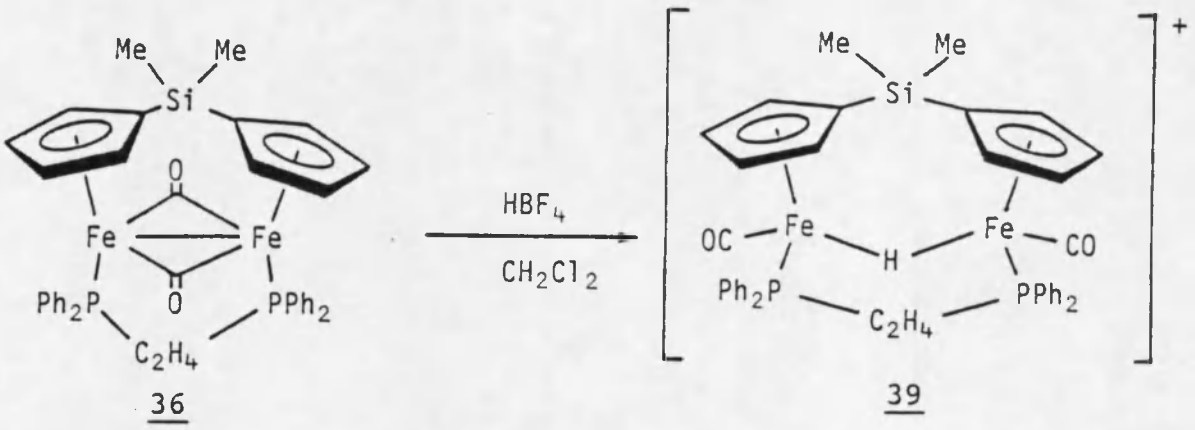
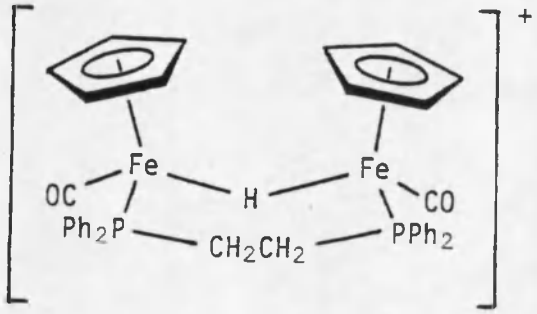


Fig. 11. ^{1}H NMR (d_6-acetone) spectrum of $(Me_2Si[(C_5H_4)Fe(CO)]_2(H)dppe)BF_4$ (39).



36 39

The spectroscopic data for an analogous mono-bridged complex (40) is nearly identical to the bis-bridged hydride 39 [31].



40

The photolysis of complex 21 with bis-diphenylphosphinomethane (dppm) gave more rapidly and in higher yield (compared to 36), a single, dark green, highly crystalline compound identified as the bis-bridged species 41.

A single crystal X-ray diffraction study [27] of 41 has been completed, the numbering scheme used in this study is given in Fig. 12, and a stereoscopic view of 41 is shown in Fig. 13. Selected bond lengths and bond angles are collected in Tables 3 and 4. From the ORTEP of 41 (Fig. 13)

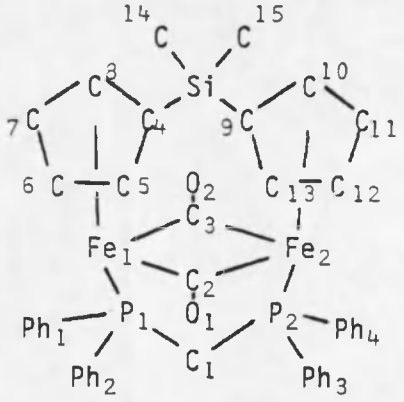


Fig. 12. Numbering scheme used for $Me_2Si[(C_5H_4)Fe(CO)]_2dppm$ (41).

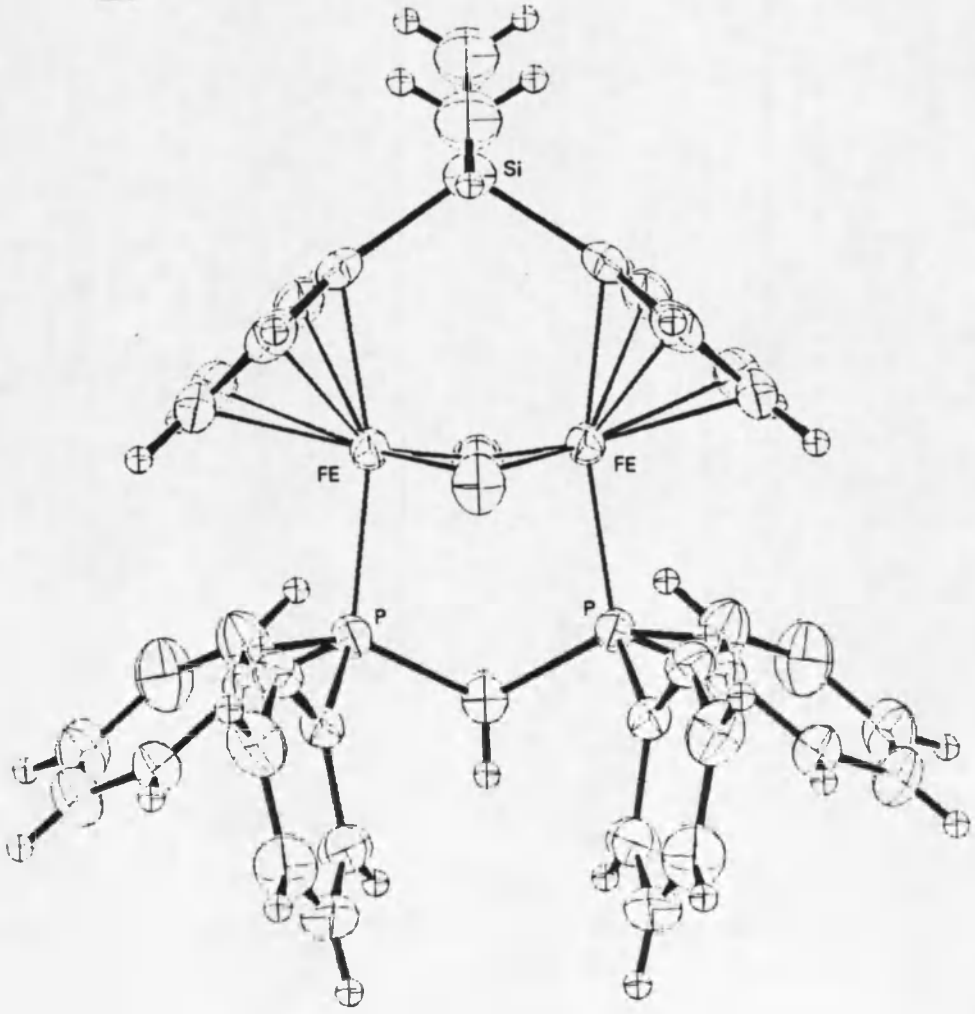


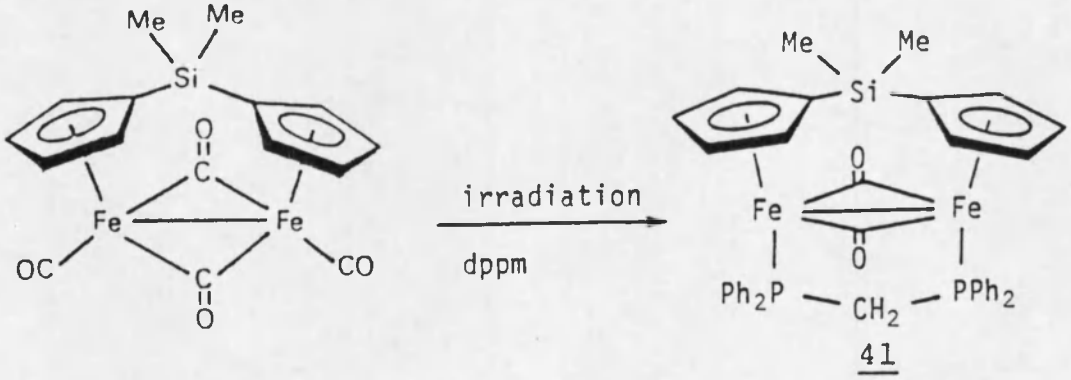
Fig. 13. ORTEP stereoscopic view of $Me_2Si[(C_5H_4)Fe(CO)]_2dppm$ (41).

Table 3. Selected bond distances (Å) for $Me_2Si[(C_5H_4)Fe(CO)]_2dppm$.

Fe(1)-Fe(2)	2.497	P(1)-C(1)	1.847
Fe(1)-P(1)	2.185	Si-C(14)	1.866
Fe(1)-C(4)	2.127	Si-C(15)	1.836
Fe(1)-C(5)	2.110	Si-C(4)	1.875
Fe(1)-C(6)	2.114	C(3)-O(2)	1.181
Fe(1)-C(7)	2.117	C(4)-C(5)	1.431
Fe(1)-C(8)	2.124	C(4)-C(8)	1.422
Fe(1)-C(3)	1.916	C(8)-C(7)	1.410
Fe(1)-C(2)	1.916	C(7)-C(6)	1.414
P(1)-Ph(1)	1.831	C(6)-C(5)	1.388
P(1)-Ph(2)	1.839		

Table 4. Selected bond angles for $Me_2Si[(C_5H_4)Fe(CO)]_2dppm$.

C(3)-Fe(1)-C(2)	98.68	C(4)-Si-C(9)	109.39
C(3)-Fe(1)-P(1)	88.78	C(14)-Si-C(4)	108.54
Fe(1)-P(1)-C(1)	110.07	C(15)-Si-C(4)	109.46
C(1)-P(1)-Ph(1)	103.13	P(1)-C(1)-P(2)	111.50
C(1)-P(1)-Ph(2)	102.33	Fe(1)-C(2)-Fe(2)	81.32
Fe(1)-P(1)-Ph(1)	119.21	C(5)-C(4)-C(8)	105.37
Fe(1)-P(1)-Ph(2)	117.13		

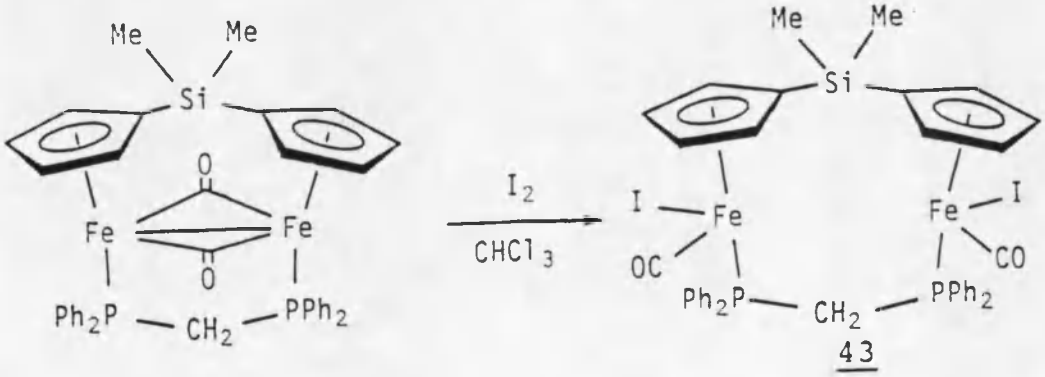


41

one can see that the irons will be held in close proximity even when the iron-iron bond is broken.

Reaction of 41 with fluoroboric acid in CH_2Cl_2 affords the bridging hydride complex (42). The bridging hydride appeared as a triplet in the 'H NMR spectrum at approximately -35 ppm(δ) from TMS.

Complex 41 was reacted with iodine in refluxing chloroform for thirty minutes to yield after work-up a single, dark brown, air stable solid. By analytical analysis the formula of $Me_2Si[(\pi\text{-}C_5H_4)Fe(CO)I]_2Ph_2PCH_2PPh_2$ was verified, and the structure assigned as 43:



43

Spectroscopic data indicated that only terminal carbonyls were present, in support of structure 43. The ^{1}H NMR spectrum of 43 (Fig. 16, p. 51) has some features which we have not yet been able to explain. In the spectrum there are two singlets at 0.52 and 0.82 δ ppm, each integrating to six protons relative to the cyclopentadienyl protons at 4.7 ppm which was set at 8 protons. Only one of the two singlets can be accounted for in structure 43. The ^{13}C spectrum of 43 showed five non-equivalent cyclopentadienyl ring carbons which could be explained by the chirality of the iron center and the assumption that the ring was not free to rotate.

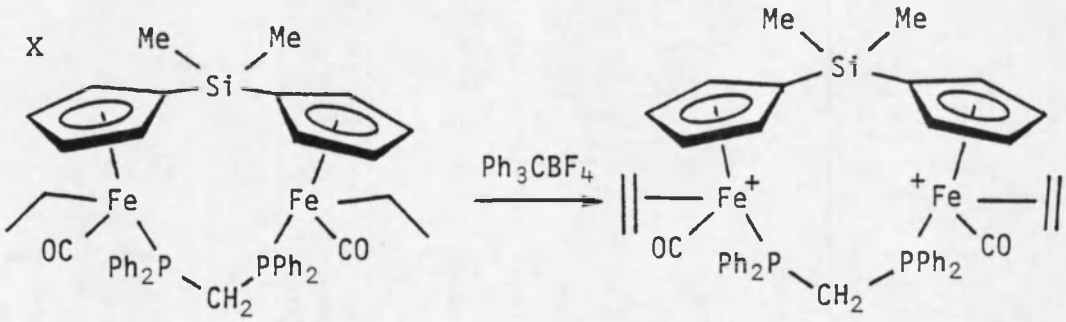
Complex 43 has been recrystallized by slow evaporation of solvent from a chloroform or acetone solution. Crystals of 43 from acetone have been shown to diffract X-rays and a single crystal X-ray study is in progress.

Reaction of 43 with silver tetrafluoroborate in dichloromethane for one hour at room temperature gave only complex 43 back after work-up. The lack of reactivity of the iodides in 43 must arise from steric interactions around the iron nucleus. Also reaction of 43 with allylmagnesium chloride in THF for several hours did not result in substitution of the iodides.

2.2.2 Attempted Syntheses of di-(n^1-alkyl and n^1-allyl) Bis-Bridged Complexes

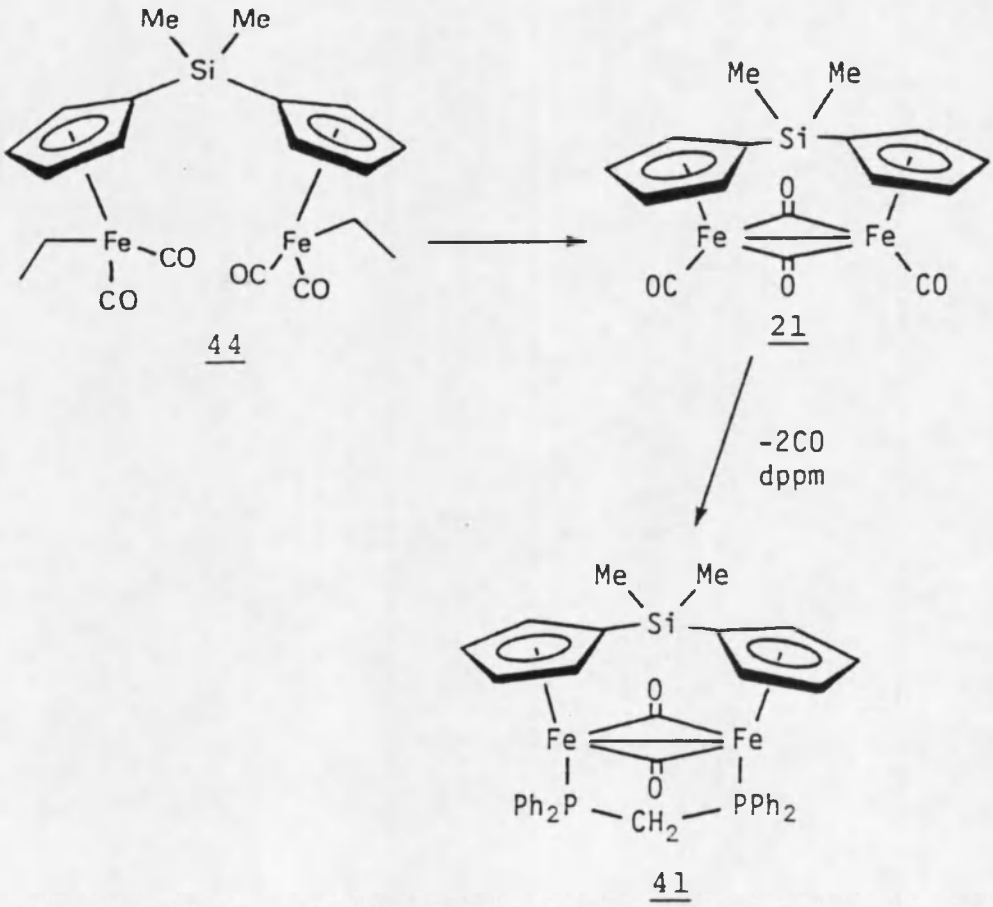
Preparation of olefin complexes can be carried out by β-hydride abstraction from n^1-alkyl iron complexes (Eq. VII). Therefore if we could synthesize bis-bridged di(n^1-alkyl) derivatives, the conversion to the cationic n^2-olefin compounds could be accomplished by the above method (Eq. X).

Eq. X

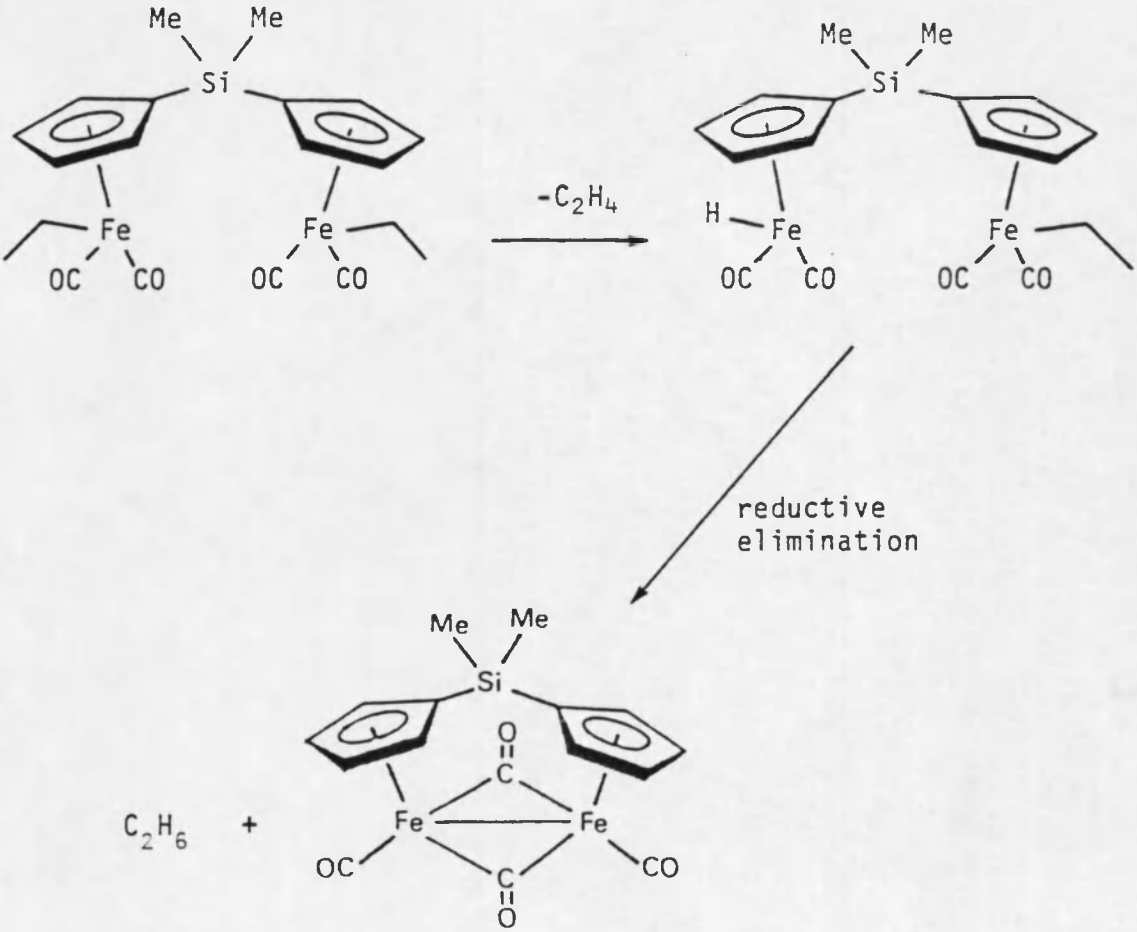


When the di(n^1-ethyl) derivative (44) [18] of complex 21 was photolyzed with dppm (Scheme IV) only compound 41 was isolated as a product. By withdrawal of aliquots at one hour intervals, complex 21 was observed by ^1H NMR as an intermediate in the formation of 41. When 44 was photolyzed in a sealed ^1H NMR tube, without dppm, the reaction was completed in ten minutes. The three products in the ^1H spectrum were 21, ethane, and ethylene. The production of ethylene and ethane can be explained by a mechanism involving β-hydrogen abstraction with loss of ethylene followed by reductive elimination across the two irons to yield 21 and ethane (Scheme V).

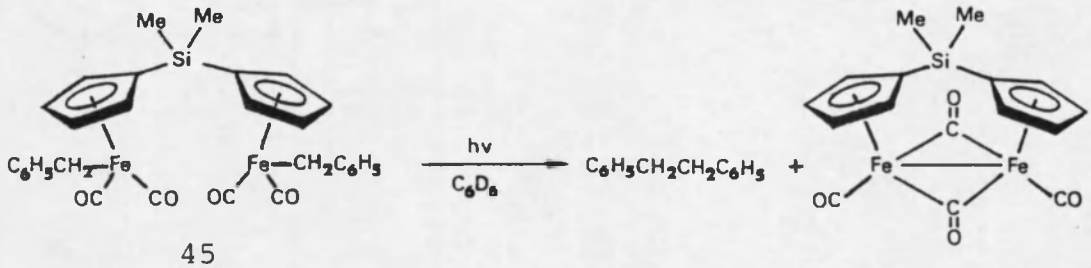
Scheme IV:


Me
Me
Si
Fe
CO
CO
Fe
OC
CO
44
Me
Me
Si
O
Fe
Fe
OC
O
CO
21
-2CO
dppm
Me
Me
Si
O
Fe
Fe
O
Ph2P
CH2
PPh2
41

Scheme V:



To eliminate the possibility of β-hydrogen abstraction we synthesized the di(n^1-benzyl) derivative of 21. Photolysis of the n^1-benzyl compound in d_6-benzene for eight hours yielded the coupled product bibenzyl in 90% and 21 in 85% conversion:



45

The per cent conversion was based on integration values in the ^{1}H NMR spectra using hexamethylbenzene as an internal standard. It was possible to monitor both reactant disappearance and product formation as shown in Fig. 14. The photolysis of n^1-benzyl iron complexes was much slower than the n^1-alkyl complexes, suggesting different mechanisms. The n^1-benzyl iron compounds are proposed to go through a radical type mechanism. Both n^1-methyl and n^1-phenyl iron complexes failed to give any coupled products after extended periods of photolysis. This was reasonable since neither complex has β-hydrogens or resonance stabilized radicals.

The di(n^1-methyl) complex was photolyzed with dppm in benzene for 12 hours resulting in a complicated array of products. The product mixture was chromatographed on alumina (III) with benzene and gave two bands, the first being red followed by a second red-green band. By ^{1}H NMR

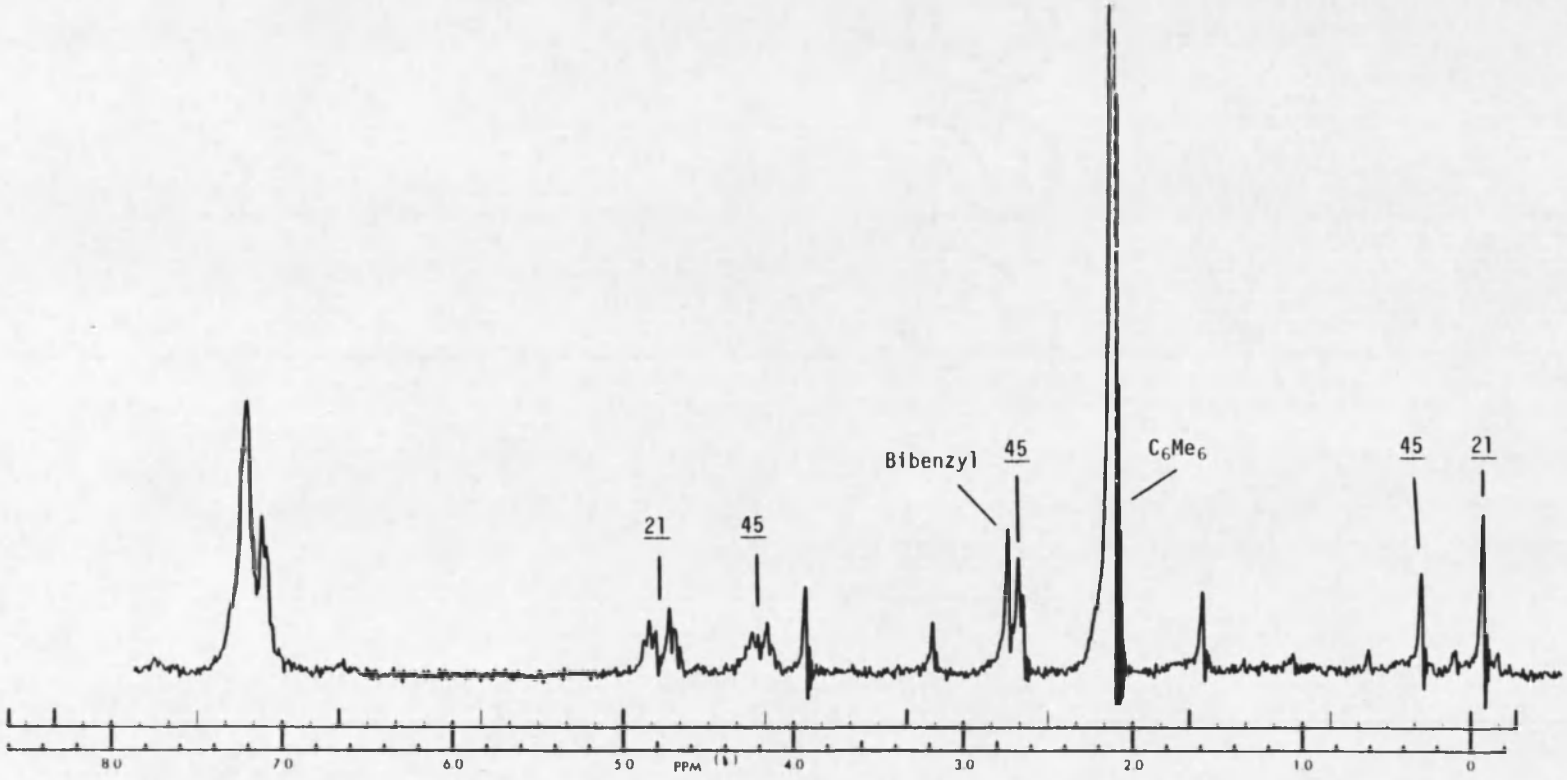
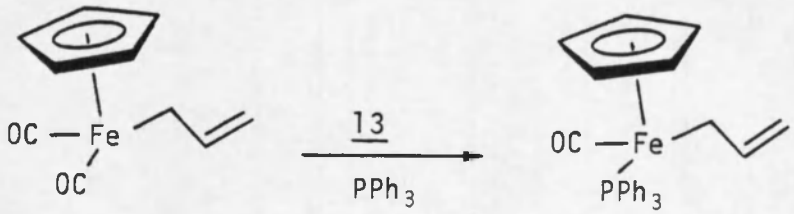


Fig. 14. ^1H NMR (C_6D_6) spectrum of $Me_2Si[(C_5H_4)Fe(CO)_2(n^1\text{-}CH_2C_6H_5)]_2$ after 30 min photolysis.

spectroscopy the initial red band was identified as complex 21 and the red-green band as a mixture of 21 and 41.

Finally, it was recently reported [32] that substitution of triphenylphosphine for a molecule of carbon monoxide on iron-n^1-allyl systems was catalyzed by $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ (13):

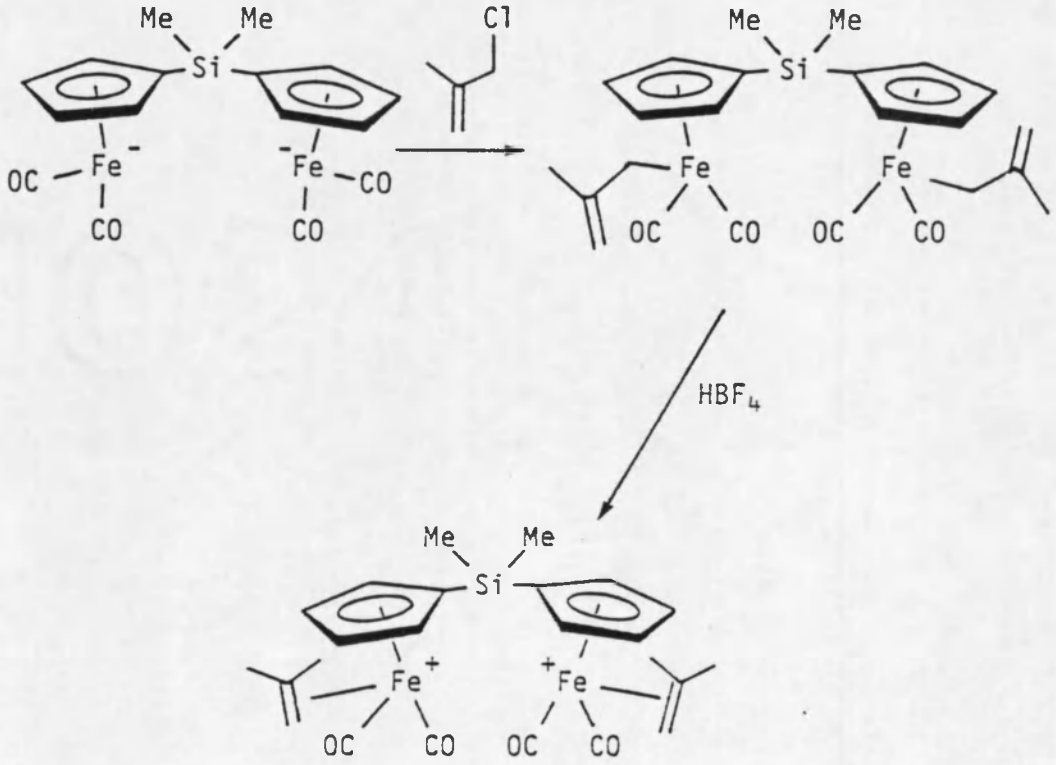


When $Me_2Si[(\pi\text{-}C_5H_5)Fe(CO)_2(n^1\text{-isobutylene})]_2$ was photolyzed with dppm and 0.1 equivalents of 13 only complex 46 was isolated (by ^1H NMR spectrum). The di(n^3-isobutylene) species (46) was reacted with dppm for several hours under irradiation, showing no decomposition or substitution of the carbonyls by dppm.

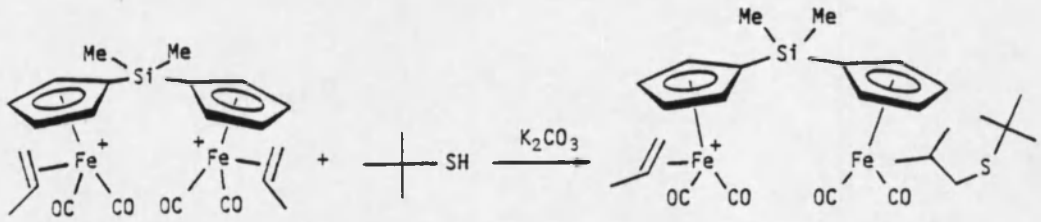
CHAPTER 3

CONCLUSION

Mono-bridged binuclear diolefin complexes have been synthesized through reaction of the dianion with allylic halides and subsequent treatment with fluoroboric acid:



These complexes could now be used in a study involving addition of various nucleophiles, and applying high dilution techniques, several new and interesting complexes could be realized:



Treatment of the diiodide complex (28) with silver-tetrafluoroborate and olefins gave only the bridging iodonium compound 29. Attempts to open the ring and isolate a mono-iodo, mono-(alkyl or hydride) have been unsuccessful.

Three bis-bridged binuclear analogs have been synthesized in our work; the reactivity of these bis-bridged systems appears to be limited by steric effects about the iron center. The chemistry of these systems is part of a detailed study in progress.

CHAPTER 4

EXPERIMENTAL

The ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on either a Varian T-60 or EM-360L spectrometer. The ^{13}C NMR spectra were recorded on a Bruker 250 MHz FT or WH-90 FT spectrometer. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS). Infrared spectra were recorded on a Perkins-Elmer 398 spectrometer. Elemental analyses were performed by Atlantic Microlab Inc., Atlanta, Georgia. Solvents were dried, degassed, and stored under nitrogen in schlenk glassware. All other reagents were purified by standard methods. All manipulations of chemicals were done under a purified nitrogen atmosphere using schlenkware and cannulation techniques.

4.1 Preparation of $Me_2Si[(\pi\text{-}C_5H_4)Fe(CO)_2]_2$ (21)

To a dry, degassed 500 ml round-bottom flask equipped with stopcock side arm, serum cap, and magnetic stir bar, 12.0 g (0.5 mole) sodium hydride and 125 ml THF were added under positive nitrogen flow. An addition funnel was inserted onto the flask and charged with 40 ml (0.56 mole) freshly distilled cyclopentadiene (dried over

molecular sieves) and 40 ml THF by cannulation. The side arm was attached to a bubbler and the cyclopentadiene solution was added dropwise while stirring. Evolution of hydrogen occurred after a few minutes; the rate of addition was such that a layer of bubbles existed. If necessary, additional cyclopentadiene was added until all sodium hydride was used. Five minutes after addition was complete, the purple sodium-cyclopentadienyl anion solution was added onto 30 ml (.25 mole) dichlorodimethylsilane and 30 ml THF at 0°C contained in a dry 500 ml round bottom flask. A precipitate of sodium chloride formed immediately and required manual agitation for complete mixing. To the resulting yellow mixture was added 250 ml xylene (degassed), and the mixture was filtered (10 cm diameter, medium frit) onto 300 ml xylene in a 1000 ml round bottom schlenk flask. To the yellow filtrate was added 67 ml (0.50 mole) iron pentacarbonyl via syringe and the resulting mixture was heated at reflux for 14 h. The mixture was cooled, and filtered; and then the solvent was evaporated under reduced pressure. To the residue was added 300 ml petroleum ether and the product was collected by filtration, washed with pet ether until the filtrate was clear, and then air dried to yield 14 g (14%) of 21 as dark purple crystals: IR(CH_2Cl_2) 1995, 1953, 1775 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.47, 5.03 (2t, 8, C_5H_4), 0.38 (s, 6, CH_3); ^{13}C NMR ($CDCl_3$) 262.29 (CO), 98.84, 87.18, 86.37 (C_5H_4), -3.94 (CH_3).

4.2 Preparation of $Me_2Si[(\pi\text{-}C_5H_4)Fe(CO)_2I]_2$ (28) and $Me_2Si[(\pi\text{-}C_5H_4)Fe(CO)I]_2Ph_2PCH_2PPh_2$ (43)

$Me_2Si[(\pi\text{-}C_5H_4)Fe(CO)_2I]_2$ was prepared by dissolving 1.00 g (2.4 mmole) 21 and 1.25 g (5.0 mmole) I_2 in 50 ml of degassed chloroform and the resulting mixture was refluxed for 30 min. The mixture was cooled, washed once with 10% sodium thiosulfate, and dried over anhydrous calcium chloride, the solvent was then removed in vacuo. The residue was recrystallized from $CHCl_3$/pet ether (30-60) to give 1.2 g (75%) of product: IR($C_6H_5CH_3$) 1992, 2015 cm^{-1}; ^1H NMR ($CDCl_3$) (Fig. 15) δ 5.15 (m, 8, $2C_5H_4$), 0.73 (s, 6, CH_3); ^{13}C NMR ($CDCl_3$) 212.92 (CO), 94.60, 84.57, 83.36 (C_5H_4), -1.22 (CH_3).

Anal. Calcd for $C_{16}H_{14}Fe_2O_4SiI_2$: C, 28.95; H, 2.13; I, 38.23. Found: C, 28.86; H, 2.17; I, 37.80.

Similar treatment of 41 with I_2 gave 43 in 80% yield: IR($CHCl_3$) 1960 cm^{-1}; ^1H NMR ($CDCl_3$) (Fig. 16) δ 7.5-6.9 (C_6H_5), 4.70 (bs, 8, C_5H_4), 2.03 (m, 4, CH_2), 0.80 (s, 6), 0.53 (s, 6); ^{13}C NMR ($CDCl_3$) 221 (CO), 134.86-127.78 (C_6H_5), 106.00, 93.07, 86.31, 81.13, 79.52 (C_5H_4), 32.15 (CH_2), 0.95, -3.22 (not assigned).

Anal. Calcd for $C_{39}H_{36}Fe_2O_2P_2I_2Si$: C, 47.21; H, 3.66; I, 25.58. Found: C, 47.11; H, 3.70; I, 25.48.

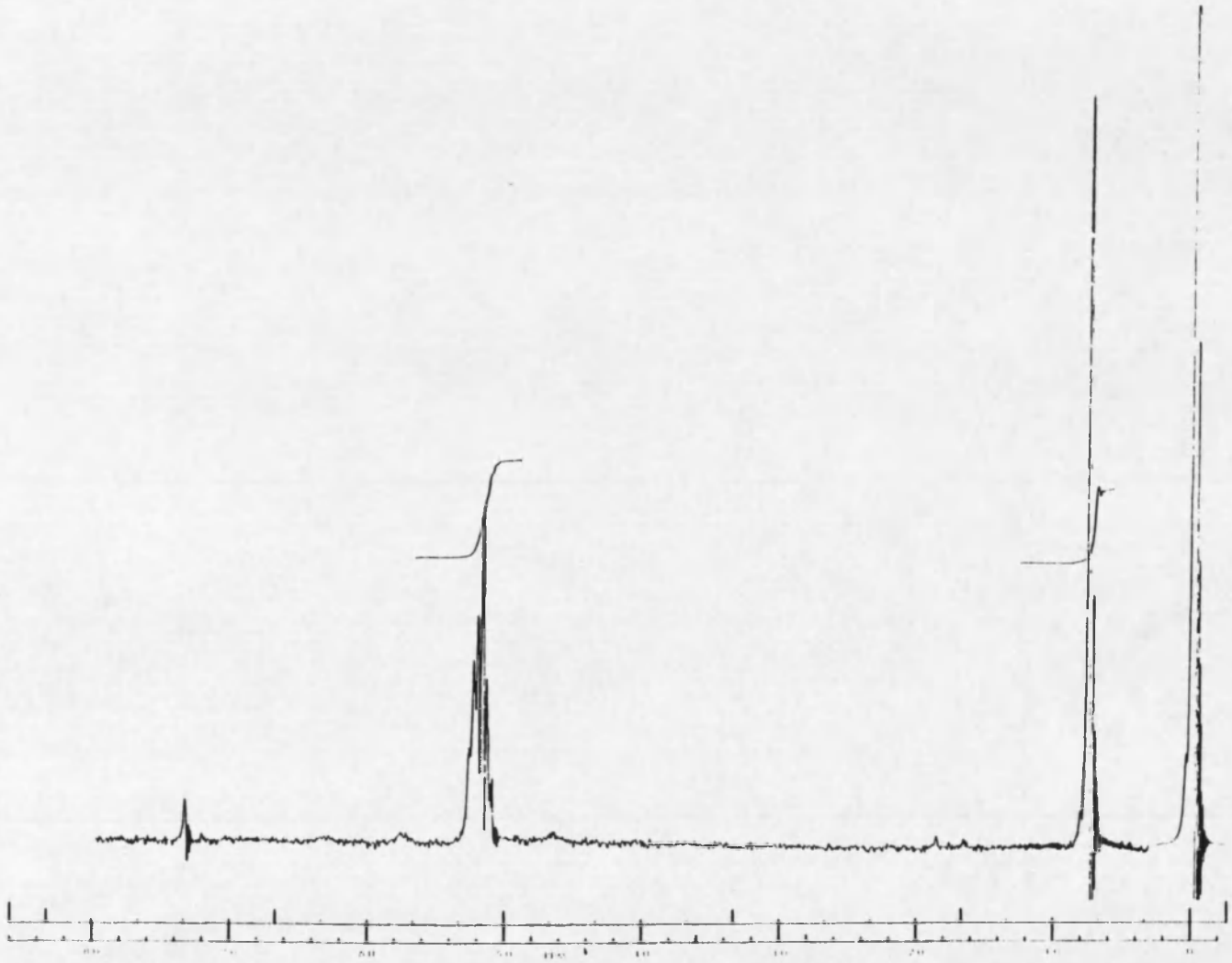


Fig. 15. ^{1}H NMR ($CDCl_3$) spectrum of $Me_2Si[(C_5H_4)Fe(CO)_2I]_2$.

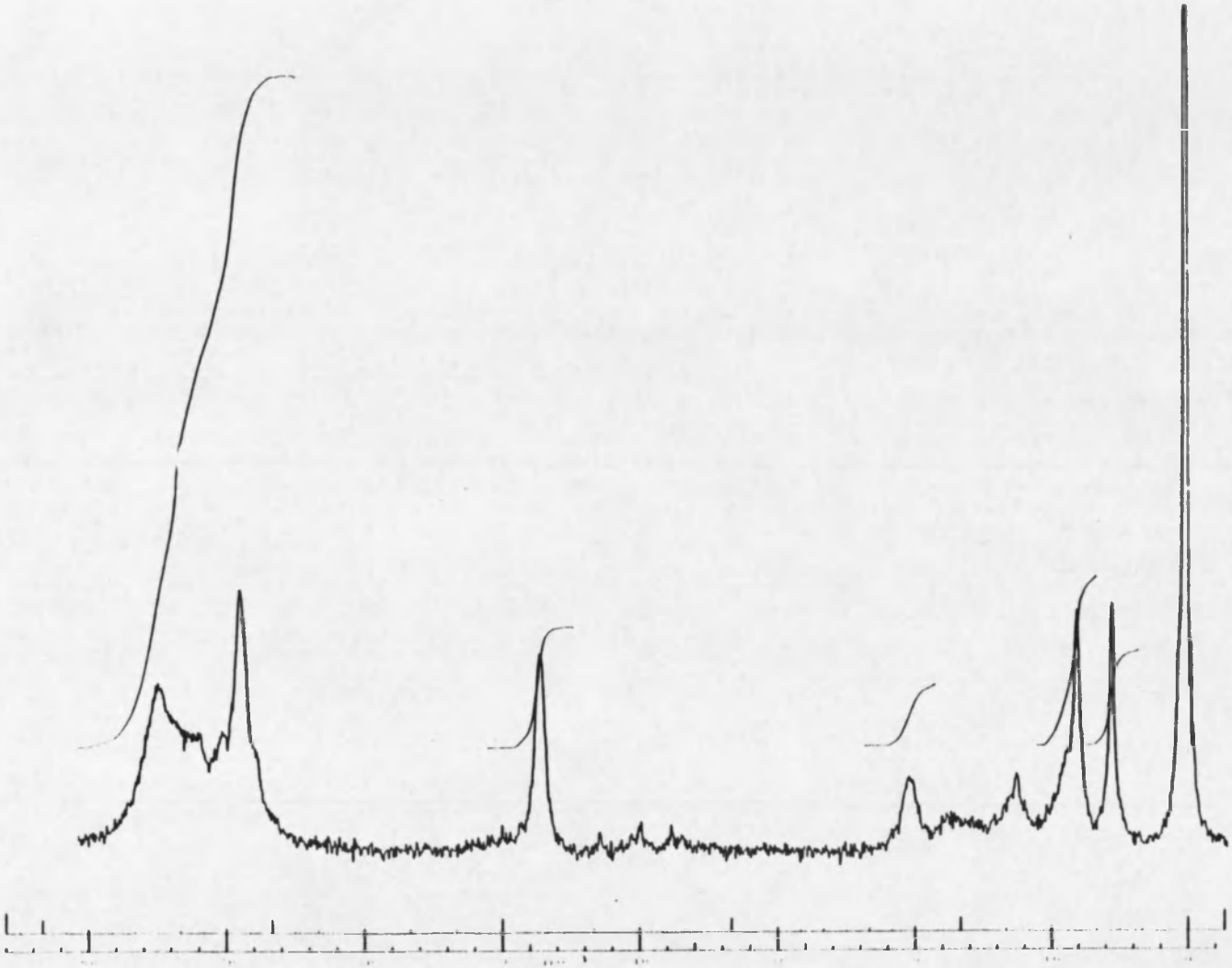


Fig. 16. ^{1}H NMR ($CDCl_3$) spectrum of $Me_2Si[(C_5H_4)Fe(CO)I]_2dppm$.

4.3 Reaction of $Me_2Si[(\pi\text{-}C_5H_4)Fe(CO)_2I]_2$ (28) with Silver Tetrafluoroborate; Preparation of 29

A solution of complex 28 (0.50 g, 0.8 mmole) in 25 ml methylene chloride was treated with silver tetrafluoroborate (0.35 g, 1.9 mmole) at 30°C. After 5 min of reaction the color had changed from brown to deep red with contamination of the solution by silver iodide precipitation. The mixture was filtered, the solvent was evaporated under vacuo, and the residue recrystallized from CH_2Cl_2/ether to give pure product (29): ^1H NMR (d_6-acetone) (Fig. 4) δ 6.10, 5.47 (2t, 8, C_5H_4), 2.10 (m, d_6-acetone), 0.80 (s, 6, CH_3). ^{13}C NMR (d_6-acetone) 211.94 (CO), 208.59 ($CH_3\underline{C}OCH_3$), 97.08, 91.33, 84.24 (C_5H_4), -2.20 ($-CH_3$).

Anal. Calcd for $C_{16}H_{14}Fe_2O_4SiIBF_4$: C, 30.81; H, 2.26; I, 20.34. Found: C, 30.85; H, 2.27; I, 20.18.

4.4 Reaction of 28 and Cyclopentene with Silver Tetrafluoroborate

To a solution of 28 (0.5 g, 0.8 mmole) and 1 ml (11 mmole) of cyclopentene in 25 ml dichloromethane was added silver tetrafluoroborate (0.35 g, 1.9 mmole) at 30°C. After 5 min of reaction the solution became red in color. The reaction mixture was allowed to stir at 30° for 30 min. The mixture was then filtered, the solvent was evaporated under reduced pressure, and the residue was recrystallized

from CH_2Cl_2/Et_2O to give 29 as the only product (as shown by comparison of spectra).

4.5 Reaction of $[Me_2Si[(\pi\text{-}C_5H_4)Fe(CO)_2]_2I]BF_4$ (29) with Methylmagnesium Iodide

A suspension of 29 (0.50 g, 0.8 mmole) in 50 ml THF was treated with a solution of methylmagnesium iodide (0.16 g, 1 mmole) in 1 ml ether at 0°C. An immediate color change from red to brown occurred. After continued reaction at 0° for 30 min, the solvent was then removed in vacuo, and the residue chromatographed on alumina (III). Elution with benzene gave a single brown band identified by ^1H NMR spectroscopy as $Me_2Si[(\pi\text{-}C_5H_4)Fe(CO)_2I]_2$ (28): ^1H NMR ($CDCl_3$) δ 5.15 (m, 8, C_5H_4), 0.74 (s, 6, CH_3).

Anal. Calcd for $C_{16}H_{14}Fe_2O_4I_2Si$: C, 28.95; H, 2.13. Found: C, 31.3; H, 3.2.

Similar treatment of 29 with excess methylmagnesium iodide gave 30 as product: ^1H NMR ($CDCl_3$) δ 4.81 (s, 8, C_5H_4), 0.50 (s, 6, CH_3), 0.11 (s, 6, $Si(CH_3)$).

4.6 Preparation of $Me_2Si[(\pi\text{-}C_5H_4)Fe(CO)_2(n^1\text{-allyl})]_2$ (32) and $Me_2Si[(\pi\text{-}C_5H_4)Fe(CO)_2(n^1\text{-isobutylene})]_2$ (33)

To a mixture of sodium-amalgam prepared from 0.30 g (12 mmole) sodium and 2 ml (30 g) mercury were added 50 ml THF and 0.50 g (1.2 mmole) 21. The reaction was continued for 30 min, THF solution was cannulated away from the sodium-amalgam, and the resulting deep red solution was

reacted with excess 3-chloropropene for 15 min. The solvent was then removed in vacuo and the residue was chromatographed on alumina (III, neutral). Elution with hexane gave the product as a yellow-brown oil: ^{1}H NMR ($CDCl_3$) (Fig. 5) δ 6.32-4.2 (m, 6, $CH=CH_2$), 4.72 (s, 8, C_5H_4), 2.07 (d(J = 9 Hz), 4, $-CH_2$), 0.52 (s, 6, CH_3).

Similar treatment of 21 with sodium-amalgam and 2-(chloromethyl) propene gave 33 as product: ^{1}H NMR ($CDCl_3$) δ 4.73 (s, 8, C_5H_5), 4.51 (s, 4, $CH_2=$), 2.13 (s, 4, $-CH_2-$), 1.78 (s, 6, CH_3), 0.53 (s, 6H, $-CH_3$); ^{1}H NMR (d_6-benzene) (Fig. 6) δ 4.85, 4.77 (2m, 4, $CH_2=$), 4.33, 4.23 (2t, 8, C_5H_4), 2.20 (s, 4, $-CH_2-$), 1.90 (s, 6, $-CH_3$), 0.37 (s, 6, $Si-CH_3$).

4.7 Reaction of 32 and 33 with Fluoroboric Acid; Preparation of 34 and 35

A solution of the adduct 33 (0.45 g, 0.9 mmole) in 10 ml THF was treated with an excess of 48% aqueous fluoroboric acid at 0°C. Reaction was continued for 5 min, then dry ether was added, and the precipitate which separated was removed and recrystallized from acetone-ether to give 0.46 g of 35 (74%): ^{1}H NMR (CD_3NO_2) (Fig. 7) δ 5.78 (s, 8, C_5H_4), 3.90 (s, 4, $CH_2=$), 1.97 (s, 12, $-CH_3$), 0.93 (s, 6, CH_3); ^{13}C NMR (CD_3NO_2)[1] 206.06 (CO), 57.33 (CD_3NO_2), 48.86 ($CH_2=$), 23.92 ($-CH_3$), -7.91 ($Si-CH_3$).

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1. Some peaks in spectrum could not be assigned to their respective carbons.

Similar treatment of 32 with fluoroboric acid gave 34 in 50% yield: ^{1}H NMR (CD_3NO_2) (Fig. 8) δ 5.85, 5.68 (2bs, 8, C_5H_4), 4.1-3.4 (m, 6, $CH=CH_2$), 1.78 (d(J = 6 Hz), 6, CH_3), 0.85 (s, 6, Si-CH_3); ^{1}H NMR (d_6-acetone) (Fig. 17) δ 6.28, 6.10 (2m, 8, C_5H_4), 4.16 (s, 4, CH_2=), 2.05 (s, 12, -CH_3), 1.07 (s, 6, Si(CH_3)).

4.8 General Procedure for Attempted Olefin Exchange with 35

To a solution of olefin in 1,2-dichloroethane at 30°C was added 0.20 g of 35. The 1,2-dichloroethane suspension of 35 and olefin was heated to 60°C over various time lengths, ranging from 20 min to 24 h. The reaction mixture was allowed to cool, then dry ether was added. The precipitate was separated, dried under vacuo, and analyzed by ^{1}H NMR. Reactions with propene, cyclopentene, 1,4-hexadiene, 3-hexyne, cis-2-butene, and 1,4-hexadiene were unsuccessful: all exchange attempts gave back 35.

4.9 Preparation of Bisbridged Complexes 36, 37, and 41

A solution of 21 (0.50 g, 1.2 mmole) and 0.50 (1.3 mmole) bis(diphenylphosphino)ethane(dppe) in 250 ml of dry, degassed benzene was photolyzed in a Hanovia photochemical reactor by a 450 watt mercury lamp. The reaction was continued for 14 h, the solvent was removed in vacuo, and the residue was washed with acetone. The resulting green

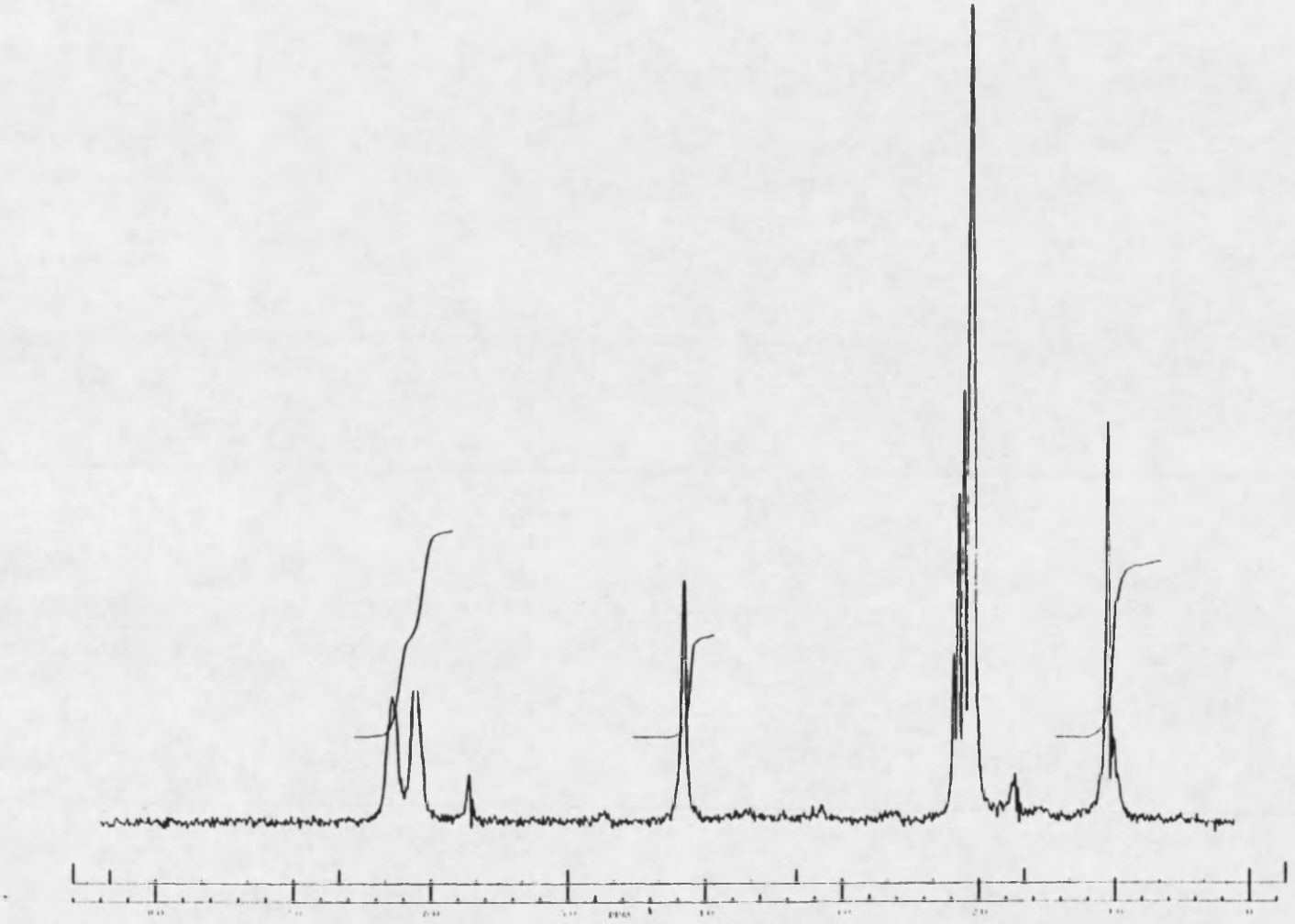

Fig. 17. ^{1}H NMR (d_6-acetone) spectrum of 34.

powder was chromatographed on activity III neutral alumina, elution with benzene gave an initial green band followed by a blue-green band. The green band was shown to be complex 36: IR(CH_2Cl_2) 1740 w, 1720 w, 1680 s cm^{-1}; ^1H NMR ($CDCl_3$) (Fig. 9) δ 7.25-7.90 (m, 20, C_6H_5), 4.83, 4.27 (2t, 8, C_5H_4), 1.37 (d(J = 12 Hz), 4, C_2H_4), 0.40 (s, 6, $-CH_3$); ^{13}C NMR ($CDCl_3$) 296.38 (t, CO), 137.75-127.96 (C_6H_5), 95.33, 88.07, 82.80 (C_5H_4), 23.17 (d(J = 29.31), C_2H_4), -2.91 ($-CH_3$).

Anal. Calcd for $C_{40}H_{38}Fe_2P_2O_2Si$: C, 63,89; H, 5.09. Found: C, 63.94; H, 5.17.

The blue-green compound was identified as complex 37: IR(CH_2Cl_2) 1937s, 1731s, 1680w cm^{-1}; ^1H NMR ($CDCl_3$) (Fig. 10) 7.4 (bs, 20, C_6H_5), 5.13(t), 4.87(t), 4.63(t), 4.28(m) (16, C_6H_4), 0.96 (bs, 4, C_2H_4), 0.30 (s, 6, CH_3); ^{13}C NMR ($CDCl_3$) 282.59(t), 216.08 (CO), 133.62-128.01 (C_6H_5), 96.22, 94.88, 89.99, 88.11, 86.23, 82.87 (C_5H_4), 23.07 (C_2H_4), -3.22 ($-CH_3$).

Anal. Calcd for $C_{56}H_{52}Fe_4P_2O_6Si_2$: C, 57.86; H, 4.51. Found: C, 57.75; H, 4.51.

Similar treatment of 21 with bis(diphenylphosphino)-methane(dppm) gave a green residue after removal of solvent. The residue was washed with acetonitrile and air dried to give 41 (70%) as dark green crystals: IR(CH_2Cl_2) 1960w, 1728w, 1682s cm^{-1}; ^1H NMR ($CDCl_3$) (Fig. 18) δ 7.30 (bs, 20,

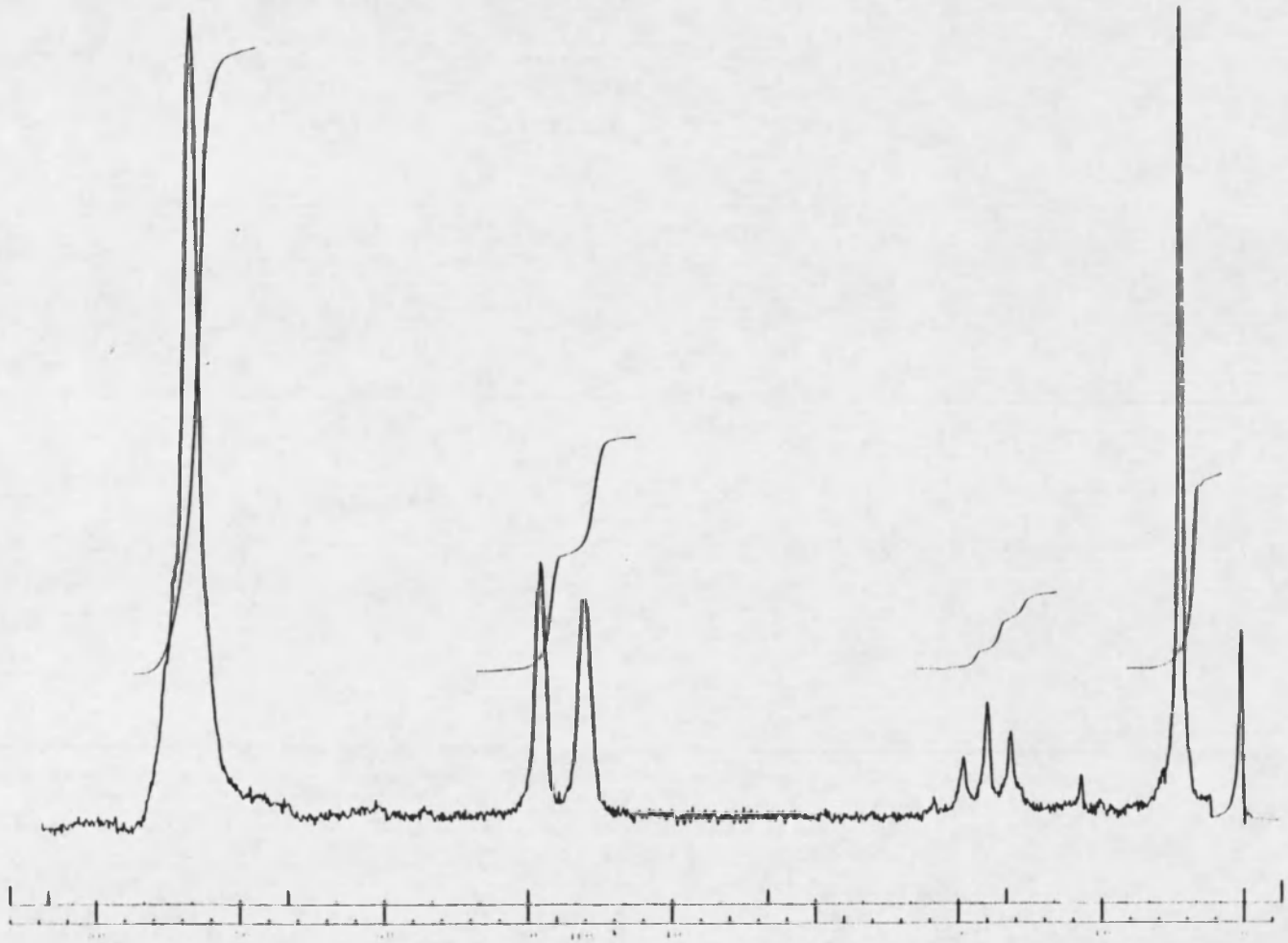

Fig. 18. ^{1}H NMR ($CDCl_3$) spectrum of $Me_2Si[(C_5H_4)Fe(CO)]_2dppm$.

C_6H_5), 4.88, 4.58 (2t, 8, C_5H_4), 1.78 (t(J = 10 Hz), 2 (CH_2), 0.42 (s, 6, $-CH_3$); ^{13}C NMR ($CDCl_3$) 298.29t(CO), 136.90-127.80 (C_6H_5), 98.22, 86.65, 78.13 (C_5H_4), 28.33 (CH_2), -3.22 ($-CH_3$).

Anal. Calcd for $C_{39}H_{36}Fe_2P_2O_2Si$: C, 63.43; H, 4.91. Found: C, 63.29; H, 4.97.

4.10 Preparation of $Me_2Si[(\pi-C_5H_4)Fe(CO)_2-CH_2C_6H_5]_2$ (45)

Complex 45 was prepared analogously to compounds 32 and 33 using benzyl chloride. ^1H NMR (C_6D_6) δ 7.20 (bs, 10, C_6H_5), 4.23 (m, 8, C_5H_4), 2.67 (s, 4, CH_2), 0.28 (s, 6, CH_3).

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