

UNIVERSITY OF SOUTHAMPTON

ACETYLENE TRANSITION METAL COMPLEXES

by

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To  
Hossein and Babak  
&  
My Mother and My Father

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ABSTRACT

FACULTY OF SCIENCE

CHEMISTRY

Master of Philosophy

ACETYLENE TRANSITION METAL COMPLEXES

by Fatima Behkish

Acetylene iron complexes of general formula  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{L}$  acetylene  $]\text{BF}_4$  ( $\text{L} = \text{PPh}_3$  or  $\text{P}(\text{OPh})_3$ , acetylene =  $\text{Ph}_2\text{C}_2$ ,  $(\text{CH}_3)_2\text{C}_2$  and  $(\text{CH}_3\text{OOC})_2\text{C}_2$  and  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{bis}(\text{diphenylphosphinoethane}$  acetylene  $)]\text{BF}_4$  (acetylene =  $(\text{CH}_3)_2\text{C}_2$ ,  $(\text{CH}_3\text{OOC})_2\text{C}_2$ ) have been prepared in order to calculate energy barriers and free energy and entropy of activation of rotation of the acetylene.  $\Delta G^\ddagger = 75.3, 69.2, 74.0$  and  $63.8$  KJ/mol for complexes of  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{PPh}_3\{(\text{CH}_3\text{OOC})_2\text{C}_2\}]\text{BF}_4$ ,  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{PPh}_3\{(\text{CH}_3)_2\text{C}_2\}]\text{BF}_4$ ,  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OPh})_3\{(\text{CH}_3\text{OOC})_2\text{C}_2\}]\text{BF}_4$  and  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OPh})_3\{(\text{CH}_3)_2\text{C}_2\}]\text{BF}_4$  respectively,  $\Delta H^\ddagger = 47.0 \pm 2.0, 53.0 \pm 2.0$  and  $47.0 \pm 1.0$  KJ/mol and  $\Delta S^\ddagger = -63.5 \pm 7.0, -32 \pm 7.0$  and  $-32 \pm 4.0$  J/deg/mol for complexes of  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{PPh}_3\{(\text{CH}_3\text{OOC})_2\text{C}_2\}]\text{BF}_4$ ,  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{PPh}_3\{(\text{CH}_3)_2\text{C}_2\}]\text{BF}_4$  and  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OPh})_3\{(\text{CH}_3)_2\text{C}_2\}]\text{BF}_4$  respectively have been calculated.

### Acknowledgements

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## Abbreviations

I.R.	infra red
n.m.r.	nuclear magnetic resonance
u.v.	ultra violet
TMS	tetramethylsilane
$\pi$ -Cp	$\eta^5$ -cyclopentadienyl
acac	acetylacetonate
P-P	dppe = bis(diphenylphosphino)ethane
P'-P'	dmpe = bis(dimethylphosphino)ethane
THF	tetrahydrofuran
P.E.	petroleum ether
TCNE	tetracyanoethylene
un	olefin or acetylene
MO	Molecular orbital
Mp	( $\pi$ -Cp) M(CO) <sub>2</sub>
CNDO	Complete neglect of differential overlap
SCF-X $\alpha$ -SW	Self consistent field X $\alpha$ Scattered wave
IEH	Iterative extended Hückel
EHT	extended Hückel Theory
HOMO	highest occupied Molecular orbital
LUMO	lowest unoccupied Molecular orbital

ACETYLENE TRANSITION

METAL COMPLEXES

CHAPTER 1

INTRODUCTION



## 1.1 Introduction

The interest in studying olefin and acetylene transition metal complexes increased since it was found that they modified their chemistry, promoting catalytic synthesis of organic compounds.

## 1.2 Structure and Bonding

The most widely accepted theoretical model for describing bonding between a transition metal atom and an olefin has been explained by Dewar (1), Chatta and Duncanson (2). This model describes the bonding by a two-way donor-acceptor mechanism.

- (a) A  $\sigma$ -donation from the bonding  $\pi$ -electrons of the olefin to the empty orbital hybrid levels of the metal.
- (b) A  $\pi$ -back donation from the d orbital of metal to the empty  $\pi^*$  (antibonding orbital) level of the ligand (Figure 1.1).

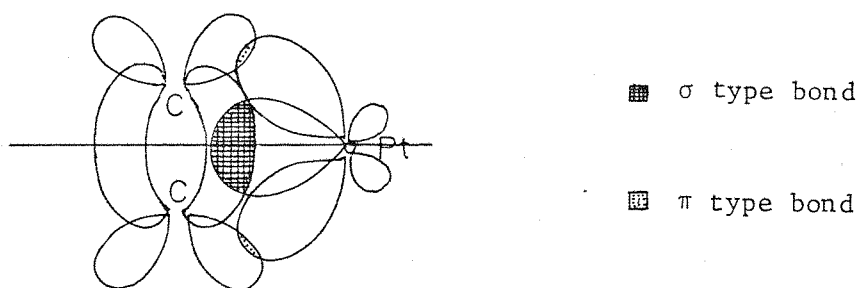
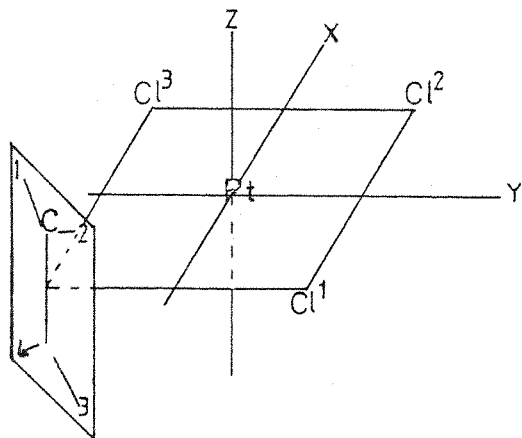


Figure 1.1. The structure of  $\sigma$ -donation and  $\pi$ -back donation of the olefin coordinated to transition metal complexes.

Such an interpretation is in a good agreement with X-ray data for Zeise's salt (3) with the monoolefin ligand occupying one coordination site and arranged perpendicularly to the Cl Pt Cl plane.



The plane of the hydrogen atoms is parallel to the plane  $Cl^1Cl^2Cl^3$  but is displaced slightly from co-planarity with the carbon atoms by repulsion of the hydrogen atoms by the platinum atom.

Quantitative data on bond strength has been reported for silver complexes. From dissociation equilibrium constants the estimated enthalpy change for the reaction  $B + Ag^+_{Aq} \xrightleftharpoons{K_o} B Ag^+_{Aq}$  (B is unsaturated group, here  $C_5H_{10}$ ,  $K_{o0}/K_{o25} = 2.35$ ) (4) is about 28.9 KJ/mol, which suggested a silver-olefin bond energy about 144 KJ. Thermochemical properties of some silver olefin complexes have been interpreted as showing that  $\pi$ -acceptor properties are more important than  $\sigma$ -donor properties.

Cramer in following of Dewar's work, showed by X-ray studies of  $[(C_2H_4)PdCl_2]_2$ ,  $[(C_2H_4)PtHN(CH_3)_2Cl_2]$  and  $K[Pt(C_2H_4)Cl_3] \cdot H_2O$  and other platinum complexes, that the olefin double bond was perpendicular to the coordination plane, i.e. the  $d_{xz}$  filled orbital of metal is involved in the back donation  $\pi$ -bond in (a) (Figure 1.2), and also in this configuration it is conceivable that the  $d_{xy}$  also participates in a similar bond (b) (Figure 1.2). Cramer, observing the fluxional behaviour of  $(\pi-Cp)Rh(C_2H_4)_2$  (5) by n.m.r. studies, has indicated that structure (b) is accessible for this complex because of the low energy barrier to rotation for coordinated ethylene molecules.

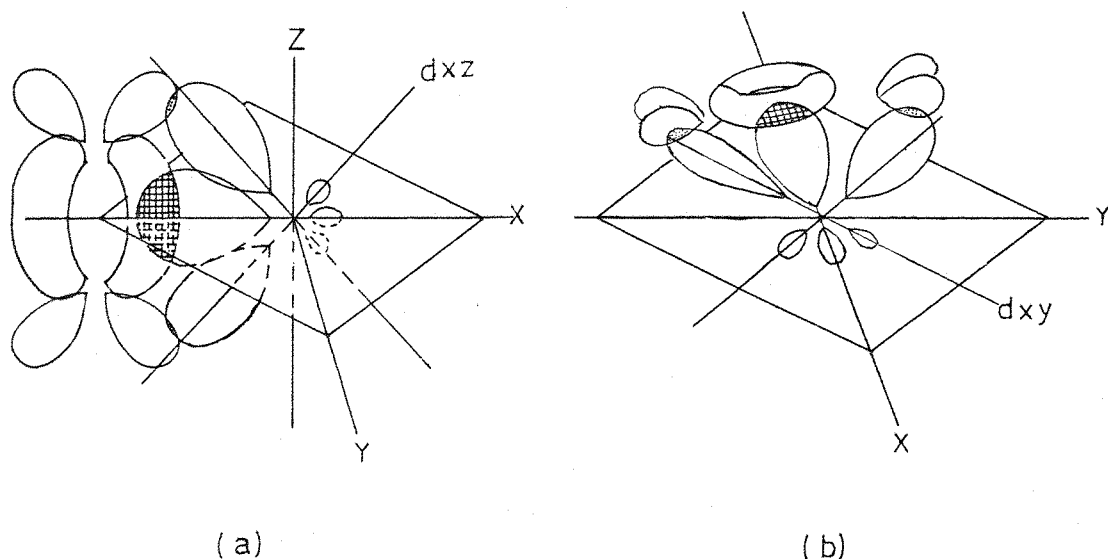


Figure 1.2. The two possible directions in which an olefin can coordinate with platinum in a planar complex (e.g. Ziese's salt).

This model can explain the structure and bonding as well as other properties of such complexes in a qualitative manner. But quantitative contribution of  $\sigma$  and  $\pi$  components are more difficult to establish. Although Gramlen (6), Mulliken and Pearson (7), Pettit (8) have worked on this explanation, this is still a matter of considerable discussion.

Experimental evidence shows that back donation should be accompanied by an increase in olefin C-C bond distance and a decrease in bond force constants. Back donation is also accompanied by an increase in olefin-metal bond strength, and a decrease in interatomic distances. These effects are evident in the X-ray studies of  $[(\pi\text{-Cp})\text{Fe}(\text{CO})_2(\text{allene})]^+$ . The variations in C-C bond length are similar to those observed for  $d^8$ -metal-allene complexes (9), thus, bond lengths are  $1.367 \text{ \AA}$  for  $\text{C}_3\text{-C}_4$  and  $1.335 \text{ \AA}$  for  $\text{C}_4\text{-C}_5$ . However, the  $\text{C}_3\text{-C}_4\text{-C}_5$  angle is  $145.7^\circ$ , one of the smallest angles observed for other than  $d^{10}$ -metal-allene complexes (Figure 1.3) (10). It has been suggested that changes in the C-C bond strength on coordination are accompanied by a decrease in stretching frequency of about  $80\text{-}150 \text{ cm}^{-1}$

but this is not exact because the I.R. frequency is from a mixture of two vibrations, and it is difficult to assign the change to one of them (Figure 1.4).

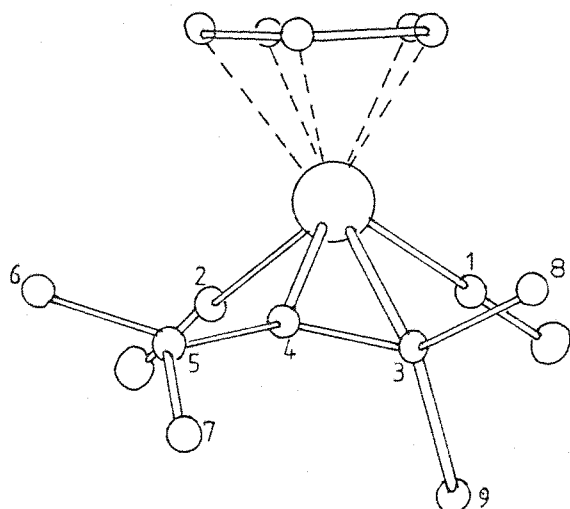


Figure 1.3

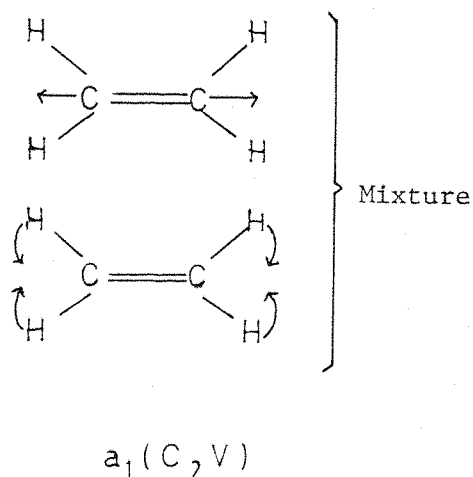
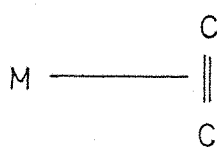
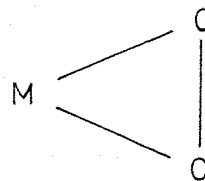


Figure 1.4

The neutron study of Zeise's anion shows a slightly longer C-C bond ( $1.354 \text{ \AA}$ ), than the equivalent bond in ethylene ( $1.338 \text{ \AA}$ ). The decrease in C-C strength may depend on the formation of a three-membered ring [(b) (Figure 1.5)].



(a)



(b)

Figure 1.5

But another explanation is that the electron population in  $\pi$ -bond of olefin is reduced on coordination and it would be accompanied by a population in the  $\pi^*$  antibonding orbital (Figure 1.6). Those

electronic changes induce C-C bond lengthening.

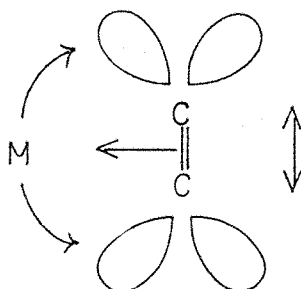
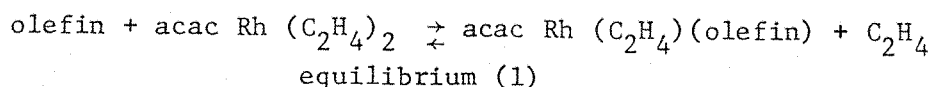


Figure 1.6

### 1.2.1 Substituents and Stability

It is expected that the strength of both the  $\sigma$ -bond and  $\pi$ -back bonding are affected by olefin structure. In spite of that, all electronic changes mentioned above can be affected by changes in the electronegativity of other ligands in the complex. An electronegative olefin substituent on ethylene, by reducing the electron density of the olefin, would weaken the  $\sigma$ -bond and strengthen the  $\pi$ -back bonding, which induces a longer C-C bond, and stabilizes the complex; and an electropositive olefin substituent can affect complex in the opposite way. Depending upon the contributions of each, the complex of substituted ethylene might be more or less stable than ethylene itself (11). Denning and Hartley showed (12) that the stability of platinum complexes increases with structure modifications which reduce the electron density of the olefin bond.

The equilibrium constants and the enthalpies for equilibrium (1) experimentally show increasing stability for olefin complexes with increasing electronegative substituents, and reduce the stability of olefin complexes with increasing substitution of hydrogen by alkyl groups.



The ( $K_E$ ) equilibrium constants increase in the order:  $\text{CH}_2 = \text{CHCH}_3$  (0.078) <  $\text{CH}_2 = \text{CHC}_2\text{H}_5$  (0.092) <  $\text{CH}_2 = \text{CHF}$  (0.320) <  $\text{trans -CHF} = \text{CHF}$

(1.290) < cis - CHF = CHF (1.590).

Displacement of ethylene by propene or butene is endothermic, but reaction with vinyl fluoride is slightly exothermic. It is known that stability constants for olefin complex formation generally decrease in order: ethylene > 1-olefins > cis-2-olefins > trans-2-olefins (13). If back donation is generally important in stabilizing metal-olefin bonds, then it is reasonable that substitution of olefinic hydrogens by alkyl groups should have a destabilizing effect.

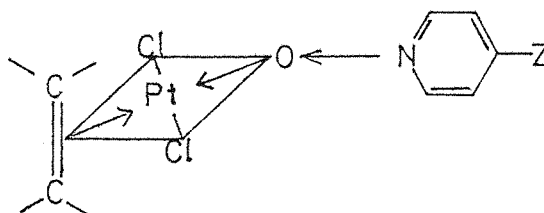
Olefinic carbon-13 resonances shift upfield on coordination to metal (14,15). Coordination shifts of olefins with electronegative substituents in effect move the olefinic resonances upfield towards the positions of saturated aliphatic carbons. Aris and his co-workers (16) have suggested that upfield shifts are a result of  $\pi$ -back bonding. Laycock and Baird (17) have compared  $^{13}\text{C}$  n.m.r. data for free and coordinated olefins and found the largest change in chemical shift on coordination of the ethylene carbon, compared with alkyl substituted olefins in  $[(\pi\text{-Cp})\text{Fe}(\text{CO})_2(\text{olefin})]^+$  derivatives.

It was suggested that the bonding interaction is strongest for ethylene, and is somewhat stronger for  $\text{C}_1$  than for  $\text{C}_2$  of unbranched terminal olefins. In the case of 2,2-disubstituted terminal olefins, the methylene carbon appears to interact with the metal much more strongly than  $\text{C}_2$ , but somewhat less strongly than  $\text{C}_1$  of unbranched terminal olefins.

Steric factors have an important role in the determination of the strength of bonding in complexes and can explain differences in strength of the  $\text{C}_1$  and  $\text{C}_2$  bonds with the metal. In  $[(\pi\text{-Cp})\text{Fe}(\text{CO})_2(\text{olefin})]^+$  complexes, the  $\text{C}=\text{C}$  axis is preferred parallel to the cyclopentadienyl ring, but substituents on the olefin will be oriented away from this bulky group. As a result the  $\text{C}=\text{C}$  axis is prevented from being parallel to the Cp ring and then the substituted olefinic carbon ( $\text{C}_2$ ) would move further away from Cp ring than  $\text{C}_1$ .

This distortion can be effected by other ligands in the complex. The steric effect is greater for trans- than for cis-2-butene because in the latter case both methyl groups can be directed away from the Cp ring.

The C-C length and C-M bond strength can be affected by changes of electronic character of other ligands in the complex (18)(19), as shown in complexes of type No. 1. The effect of strong electron-releasing groups (e.g.  $Z = \text{OCH}_3$ ) appears to be the strengthening of



Complex No. 1

the platinum-olefin bonds at the expense of the C-C bond as a result of the enhanced population of antibonding  $\pi^*$  orbitals of the olefin. With strong electron withdrawing groups (e.g.  $Z = \text{NO}_2$ ) the opposite effects are seen. This effect was confirmed by I.R. While the C=C stretch absorbs at about  $1510 \text{ cm}^{-1}$  for the ethylene complex, when  $Z = \text{H}$ , this vibration was reported at  $1490 \text{ cm}^{-1}$  for  $Z = \text{OCH}_3$ , and  $1545 \text{ cm}^{-1}$  for  $Z = \text{NO}_2$ .

The geometry of coordinated double bonds changes compared with the free ligand. Hence coordinated  $\text{CS}_2$  (20) or alkynes (21) are no longer linear and ethylene in Zeise's salt is no longer planar. This has been confirmed by X-ray and the neutron diffraction studies for ethylene. The displacement of the carbon atoms toward the platinum with respect to the plane defined by the four hydrogen atoms amounts to  $0.18 \text{ \AA}$ . Hence the geometries of coordinated  $\pi$ -bonded molecules support the view that both  $\sigma$ -donations and  $\pi$ -back donation properties are important. When the ligand is a very strong  $\pi$ -acid, such as tetracyanoethylene (TCNE), the C=C bond length

increases to a normal C-C bond length (from  $1.31 \text{ \AA}$  to  $1.54 \text{ \AA}$ ) on coordination in  $\text{Pt}(\text{PPh}_3)_2\text{TCNE}$ . In such an extreme case, the ligand can be readily regarded as an approximative to the  $\sigma$ -bonded donor similar to (b) (Figure 1.5). Because TCNE is one of the strongest  $\pi$ -acids known, the complex can be described as containing a  $d \rightarrow \pi^*$  bond with no  $\sigma$ -bond, and C-C single bond can explain as a result of M-L charge transfer (Figure 1.6).

### 1.3 Nature of Acetylene Bonding on the Acetylene Complexes (3)

The model interaction of acetylene in complexes discussed by Maitlis (22), Jonassen et al. (23-26), Bennett (27) and in Temkin and Flid's monograph (28). The acetylene coordination can be explained as four orbital interactions, illustrated in Figure 1.7.

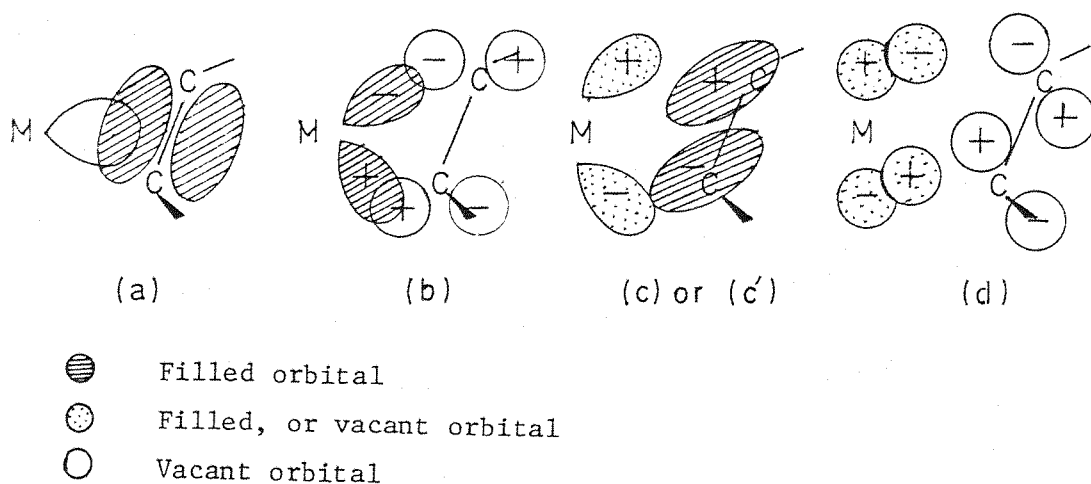


Figure 1.7. Molecular orbital interactions for coordinated acetylene: (a) Metal  $\sigma$  orbital ( $s$ ,  $p\sigma$ ,  $d\sigma$ ) and  $\pi_{||}$  orbital of acetylene molecular bond; (b) metal  $\pi_{||}$ -orbital ( $p\pi_{||}$ , or  $d\pi_{||}$ ) and the antibonding orbital of acetylene  $\pi_{||}^*$ ; (c) metal  $\pi_{\perp}$  orbital ( $p\pi_{\perp}$ , or  $d\pi_{\perp}$ ) and  $\pi$  bonding; (d) metal  $\delta$ -orbital ( $d\delta$ ) and  $\pi_{\perp}^*$ .

To explain the bonding in acetylene complexes, it is very important to find the extent of overlap in these orbitals and the energy level difference between the interacting orbitals. I - overlap decreases in the order (a) > (b) > (c) > (d), most overlap is for early transition metals. II - The energy levels are a function of three factors:



first effective oxidation state of metal, second the nature of auxiliary ligands, and third the substituents on acetylenic carbons (29)(30)(31).

The following comments can be made about those which are important for overall determination of the bond strength. (a) is a bonding interaction and (b) is bonding in most cases (it is acceptable for most transition metal ions or atoms to have d- electrons which may occupy  $\pi$  orbitals); like  $\text{Cp}_2\text{W} = \text{O}$  ( $\text{RC} \equiv \text{CR}$ ) (32),  $\text{Cp Nb}(\text{CO})(\text{PhC} \equiv \text{CPh})_2$  (33). (c) is bonding but here the strength of bond is less than (a), or (b). For later transition metals, and especially metals with  $d^{10}$  configuration, the electron contribution to the bond is unfavourable so in this situation the interaction would be repulsive and antibonding (c') between the metal and the ligand. Finally, interaction (d) can be eliminated for this determination because of poor overlap. (The most overlap is in the complex of metal centre with  $d^3 - d^4$ ).

The extent of the lengthening of the C-C bond and of the bending of  $\text{C} \equiv \text{C}-\text{C}$  angle has as a major contribution on  $\pi^*$  back donation; (interaction (b)) and a minor contribution from  $\sigma$  donation interaction (a) and  $\pi$  donation interaction (c).

### 1.3.1 X-ray Study

In two examples of Pt(II) and Pt(0) acetylene complexes, the result of an X-ray study shows that the length of the coordination  $\text{C} \equiv \text{C}$  bond is definitely shorter in Pt (II) than in Pt (0), as would be anticipated. The acetylene acts as an electron donor in the first complex and as a  $\pi$ -acidic acetylene in the second complex; in the latter complex, the Pt-acetylene bond is stronger and the complex will be more stable.

X-ray studies of bis (triphenylphosphine) diphenyl acetylene platinum (21), or dicobalt hexacarbonyl diphenyl acetylene (34), show clear changes in the geometry of coordinated molecule compared with free acetylenes.

The structure of  $(\text{PPh}_3)_2 \text{Pt}(\text{Ph}_2\text{C}_2)$  in the crystal lies between the two possibilities which have been postulated, i.e. a platinum (0) trigonal complex (35) (36) with acetylene occupying one coordination position and  $\pi$  bonded in a manner similar to ethylene in Zeise's salt. In valence bond terms, the electrons of the  $\pi_x$  orbital of the acetylene being donated to a  $\text{dsp}^2$  hybrid orbital of the metal with simultaneous back donation from the filled  $\text{dxz}$  or  $\text{dxz pz}$  hybrid - orbital of platinum into the  $\pi_x^*$  orbital of acetylene; or it could be four coordinate platinum (II) with each of the acetylenic carbons  $\sigma$ -bonded to a  $\text{dsp}^2$  hybrid of the metal (by use of approximately  $\text{sp}^2$  orbitals from acetylene, therefore reducing the triple bond to a double bond).

In the complex  $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{Ph}_2)$  the carbon carbon axis in the acetylenic group makes approximately a  $14^\circ$  angle with a plane consisting of the platinum and two phosphorus atoms. The benzene rings of the acetylene are bent away from the metal at angles of  $40^\circ$  confirming the suggestion made on the basis of dipole moment data of the analogous p-substituted diphenylacetylene platinum compounds (37). The C-C distance is  $1.32 \pm 0.09 \text{ \AA}$ .  $(\pi\text{-C}_5\text{H}_5)_2 \text{W}(\eta^2\text{C}_2\text{Ph}_2)(\sigma\text{Ph})$  shows a  $\text{C}\equiv\text{C}$  bond length  $1.29 \text{ \AA}$  and the  $\text{C}-\text{C}\equiv\text{C}$  angle  $142^\circ\text{-}145^\circ$  (32).

There is much evidence of such perturbation of the coordinated molecule. To explain this problem, it is very helpful to discuss the excited state of the acetylene molecule and look at the rearrangement of orbitals and their hybridisation in the coordinated acetylene molecule. This causes the triple bond to reduce to a double bond and become cis-bent in geometry.

### 1.3.2 Rearrangement of Orbitals in Coordinated Acetylene

The normal acetylene molecule is linear ( $D_{\infty h}$ ) and the highest occupied orbitals are those of the unsaturated shell, that is, the two equivalent bonding orbitals  $\pi_u$ , (a) in Figure 1.8. If we suppose the linear shape will remain in the excited state of molecule then the lowest unoccupied orbital into which an electron from a  $\pi_u$  orbital could be lifted is the antibonding  $\pi_g$  orbital [(b) in Figure 1.8].

Then this causes much steric repulsion between any electron occupying this orbital and the electron of the C-H bonds. An even worse position would arise if we should try to promote a  $\pi_u$  electron to the antibonding  $\sigma_u$  orbital, (which also has a nodal plane across the middle of the molecule, but is concentrated about the molecular axis, mainly outside the C-C span), since in this case an occupying electron would be very strongly interpenetrated with the C-H bond electrons. These high energy situations indicate there may be another possibility for the acetylene molecule to rearrange in the excited state so the excited electrons lie considerably further out of the way of the C-H bonds.

It is clearly possible that the linear ( $sp$ ) hybridisation, which determines the  $\sigma$ -bond framework of the normal acetylene molecule might change in the direction of a plane trigonal  $sp^2$  hybridisation, so that bond angles become reduced from  $180^\circ$  towards  $120^\circ$ . The simplest form which such an occurrence could take is that in which the change of hybridisation  $sp \rightarrow sp^2$  is complete. Hence the excited acetylene molecule assumes the shape of a normal ethylene molecule from which two hydrogen atoms have been removed (38).

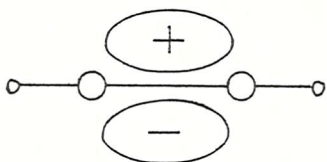


Figure 1.8(a)

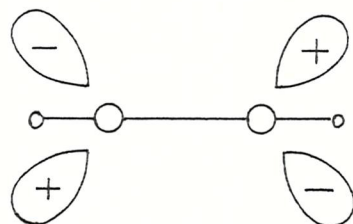


Figure 1.8(b)

Now there are the two possibilities of cis and trans configurations of the acetylene molecule (Figure 1.9). The difference of cis and trans bent acetylene would be more important in coordinated acetylene which is our interest. This problem has been studied by Blizzard and Santry (39). They calculated the energy changes of those effects by using CNDO molecular orbital theory.





Trans-bent excited state:  $sp^2$   
atomic orbitals constituting nearly  
non-bonding molecular orbitals

Cis-bent excited state:  $sp^2$   
atomic orbitals constituting  
nearly non-bonding molecular  
orbitals

Figure 1.9

As we explained before this change in geometry has been interpreted as evidence of metal-carbon  $\pi$  bonding, because such a process would be expected to lead to an electron distribution analogous to that of  ${}^1\text{Au}$  excited state of acetylene, which is known to be bent. But  ${}^1\text{Au}$  state probably correlates with the  $\Sigma^-u$  state of the linear molecule, which is derived from the electron configuration  $(\pi u^x)^1 (\pi u^y)^2 (\pi g^y)^1$  ( $D_{\infty h}$ ) (if the Z axis is taken to be along the molecular axis then ground-state  $\pi$ -electron configuration is  $(\pi u^x)^2 (\pi u^y)^2$  ( $D_{\infty h}$ ), where  $\pi u^x$  is the  $\pi u$  orbital in the ZX plane, the excitation of a  $\pi$  electron into an antibonding  $\pi$  orbital leads to a number of excited states,  ${}^1\Sigma^-u$ ,  ${}^1\Sigma^+u$ ,  ${}^1\Delta u$ , together with the corresponding triplet states), which becomes  $(au)^1 (bu)^2 (ag)^1$  ( $C_{2h}$ ) in the trans bent form of acetylene. In the acetylene complex the electron density is added to a  $\pi_g$  orbital in the same plane as the  $\pi u$  orbital from which the density is removed. This distribution would be of the type  $(\pi u^x)^1 (\pi u^y)^2 (\pi g^x)^1$  ( $D_{\infty h}$ ) which corresponds more closely to the  ${}^1\Delta u$  or  ${}^1\Sigma^+u$ , rather than to the  ${}^1\Sigma^-u$  excited state. But the analogy is not complete, because the excited states have open-shell electron configuration, with the appropriate coupling of the electron spins.

On the other hand, as mentioned above, the excited-state geometry is trans bent, whereas the complexed acetylene is always cis bent.

Although some theoretical evidence exists for a cis-bent excited state of acetylene (40), the necessity of explaining why the trans-bent geometry is suppressed in favour of the cis-bent structure remains a barrier to the general acceptance of this theory. The bond angles of acetylene are a function of the electron densities in the  $\pi_u$  and  $\pi_g$  orbitals. The removal of electron density from  $\pi_u$  causes an increase in energy, but removal to  $\pi_g$  causes an energy increase and the acetylene to bend. CNDO calculations have been carried out (39) following the variation of acetylene energy with change in electron distribution. The energy relative to the linear molecule was plotted against the number of electrons added to  $\pi^*$  ( $\pi_g$ ) and subtracted from  $\pi_u$ . This shows that the increase of energy would be greater for trans-bent acetylene than cis-bent. Another explanation of cis-bent coordinated acetylene is to look at the bond strength between the metal and acetylene which is dependent upon the symmetry of all orbitals of the acetylene suitable for bonding. As mentioned above, the most important interactions responsible for bonding between metal and acetylene are  $\sigma$  and  $\pi$ , that is an acetylene-metal  $\sigma$ -bond from a filled  $\pi_u$  and hybrid orbital of metal and  $\pi$  from empty  $\pi_g$  and filled  $d\pi$  of metal, also the acetylene-metal  $\sigma$  bond contains interaction between filled  $\sigma_g$  and hybrid orbital of metal which is not very important. But the acetylene-metal  $\pi$  bond which also contains another interaction between the  $\sigma_u$  and  $d\pi$  is very important in making the acetylene-metal bond weaker or stronger. By looking at the orbital symmetry of trans and cis-bent acetylene (Figure 1.10 and Figure 1.11) we can see that the interactions explained above are repulsion for trans-bent and attraction for the cis-bent form. This symmetry argument then tells us that there is a force within the complex opposing to the trans-bent geometry.

The orbitals (of acetylene) which are responsible for bonding between acetylene-M are the bonding  $\pi$  orbital ( $\pi_u$ ) donation and antibonding  $\pi$  orbital ( $\pi_g$ ) back donation as shown in Figure 1.10 for the trans-bent form of acetylene and in Figure 1.11 for the cis-bent form of acetylene.

Figure 1.10 shows the relative signs of the 2s and 2p $\pi$  atomic orbital components of the  $\pi$ - and  $\sigma$ - bonding molecular orbitals for trans-bent acetylene: ( $C_2h$ ), and in Figure 1.11, the relative signs of the 2s and 2p $\pi$  atomic orbital components of the  $\pi$  and  $\sigma$ -bonding molecular orbitals for cis-bent acetylene: ( $C_2v$ ) is presented.

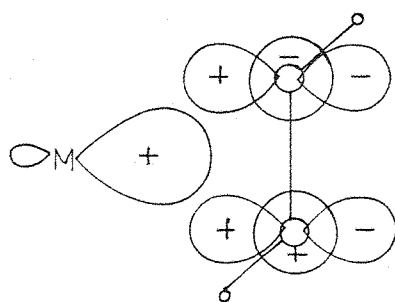


Figure 1.10(a)  $\pi_u$  orbital with metal  $\sigma$  orbital

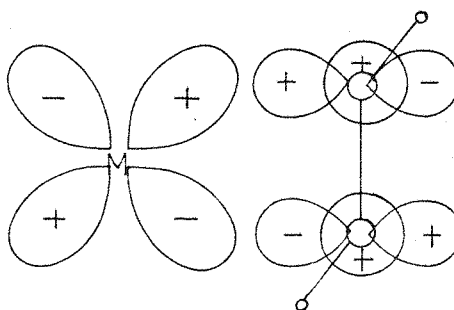


Figure 1.10(b)  $\pi^*$  orbital with metal  $d_{\pi}$  orbital.

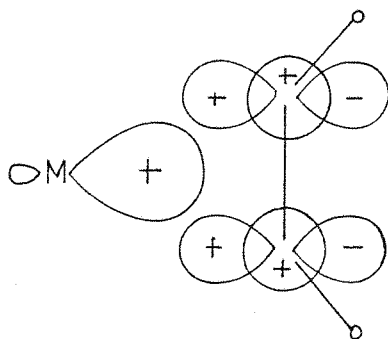


Figure 1.11(a).  $\pi_u$  orbital with metal  $\sigma$  orbital

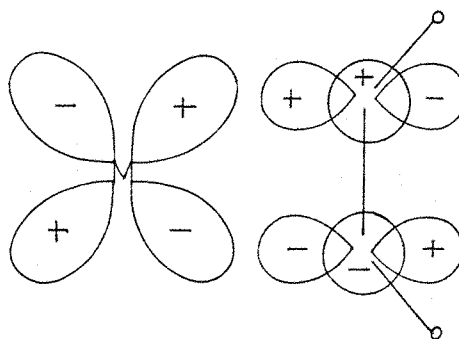


Figure 1.11(b).  $\pi^*(\pi_g)$  orbital with metal  $d_{\pi}$  orbital.

As shown in Figure 1.11, if the hydrogens and metal are on

opposite sides of the C-C bond, on all atomic overlaps will have be the same sign and will combine to yield a large net metal-acetylene overlap. If hydrogens and metal are on the same side of C-C bond then the atomic overlap will have opposite signs and will yield a small net metal-acetylene overlap. Then this is a strong force favouring a hydrogens cis-bent form away from the central metal.

There are also steric interactions of the acetylene hydrogen with other ligands in the complex; this effect is greater for larger acetylene substituents. Thus the substituted group has a very important effect on the magnitude of the change of geometry of the acetylene in the complex.

On the other hand, the extent of the lengthening and bending of  $C \equiv C - R$  angle reflects a major contribution by  $\pi^*$  back donation interaction (b) in Figure 1.7 and a minor contribution of  $\sigma$  and  $\pi$  donation (interaction (a) and (c)). The density of electron in  $\pi^*$  of the acetylene can be affected by the electron donating ability or electron withdrawing ability of the central metal, substituents of the acetylene and auxiliary ligands.

For this reason there are definitely shorter C-C bond lengths in Pt (II) complexes (the C-C length is  $1.24 \text{ \AA}$  in Pt (II)  $Cl_2$  (P-toluidine) (t-Bu  $C \equiv C$ -t-Bu) which contains an electron-donating acetylene) than in Pt(0) which has more ability to donate electrons to  $\pi^*$  of the acetylene. In Pt(II) which has much less ability to donate electrons to the  $\pi^*$  of acetylene the bending angle would be much smaller than Pt(0) complexes, (in the Pt(II) complex mentioned above, C-C-C angle is  $(162^\circ - 165^\circ)$ ; that angle in Pt(0) complexes is mostly around  $140^\circ$ ).

The effects of the auxiliary ligands have also been noted (41) (42)(43). In Figure 1.12, two Pt(II) acetylene complexes are shown with a change in one of the ligands around central metal,  $PtCl_2$  (P-toluidine)(t-Bu  $C \equiv C$ -t-Bu)(a) and  $PtCl_2$ (piperidine) (t-Bu  $C \equiv C$ -t-Bu) (b). In the first complex, C-C length is  $1.24 \text{ \AA}$  and the C-C-C angle

162-165° while in the second one these values are 1.27 Å and 165° respectively.

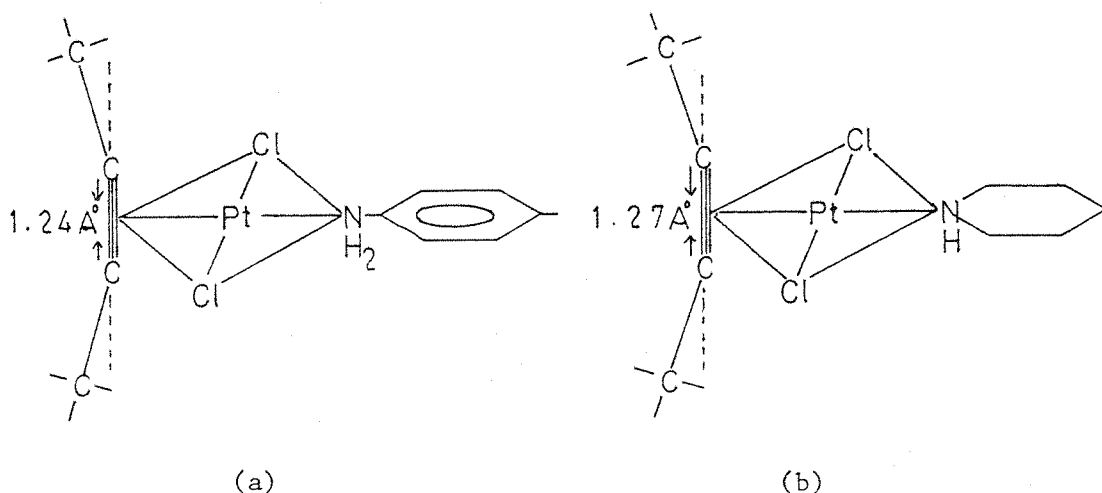


Figure 1.12

In the above example, we can see the effect of ligands on acetylene bonding, now in the following example we can see the ligand effects on back donation to  $\pi^*$  of acetylene. In the complexes Pt(II)  $\text{Cl}(\text{CF}_3\text{C}_2\text{CF}_3)(\text{AsMe}_3)_2$  and Pt(II) (tripyrazolylborate)  $(\text{CF}_3\text{C}_2\text{CF}_3)$ , the C-C lengths are 1.32 and 1.292 Å respectively, and the latter shows the smaller back donation. The C-C angle in the second case is 145.6° which still shows a large interaction (b) (Figure 1.7). In the first complex, the longer C-C bond results from greater back donation, it having less electronegative auxiliary ligands.

As mentioned above, the substituted group plays an important role in these geometry changes. In  $(\text{PPh}_3)_2$  Pt(0) acetylene complexes like  $\text{Pt}(\text{CF}_3\text{C}_2\text{CF}_3)(\text{PPh}_3)_2$ ,  $\text{Pt}(\text{PhC}_2\text{Ph})(\text{PPh}_3)_2$  and  $\text{Pt}(\text{NCC}_2\text{CN})(\text{PPh}_3)_2$ , the C-C lengths are 1.255, 1.32 and 1.42 Å respectively, in which the first and second ones give largely  $\sigma$  substituent effects to the acetylene, but in the last one there are  $\sigma$  and  $\pi$  substituent effects. In the same way as electronegative groups carry electron density away from the C-C bond, the  $\pi$  effect causes more electron



removal from the  $\pi_u$  and more ability to back donate to  $\pi_g$ , which is accompanied by longer C-C distances and a more bent acetylene. After all, when the central metal is a very good electron donor, the geometry changes cannot be affected very much by the electronegativity of substituents, and when substituent group causes a great electron density removal from the C-C bond the geometry cannot be effected very much by different ligands (40).

### 1.3.3 I.R. Study

Another way to investigate the effect of those factors mentioned above is by looking at the C-C stretching frequency of the coordinated acetylene, comparing it with free acetylene and with other coordinated acetylenes.

In acetylene coordinated to a metal we can consider three different vibrations, in an isolated triatomic unit (Figure 1.13) ( $C_{2v}$  local symmetry). The infrared active modes are  $2A_1 + B_1$ . Then in this unit

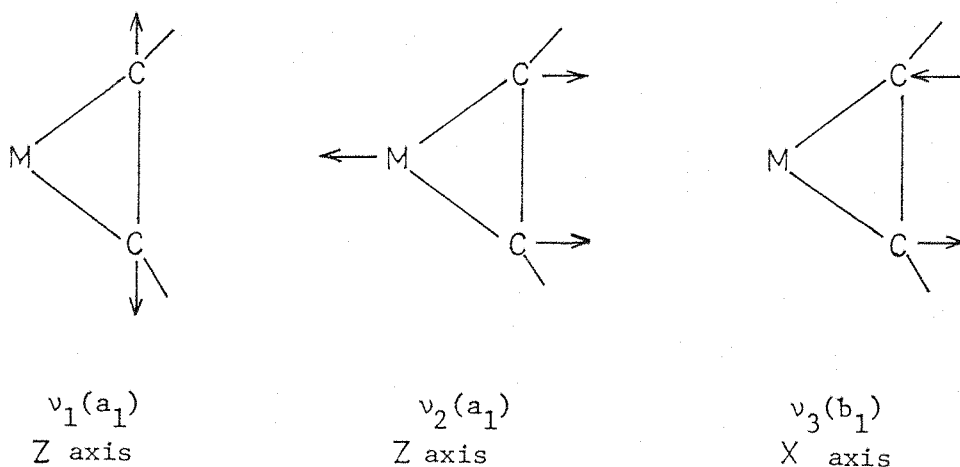


Figure 1.13. Three different vibrations in the three element system ( $C_2v$ )

we can expect coupling between three vibrations and the vibrations of the rest of the molecule.

The vibration which is very important for this system is  $\nu_1$  which has a lower frequency than that of the free acetylene. The

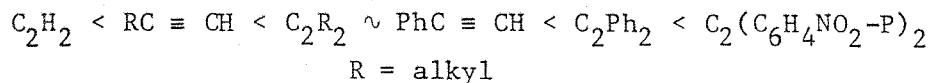
( $\nu_1$ ) vibration frequency would be decreased with an increase in the electron donating ability of an auxiliary ligand which induces increased electron back donation to the  $\pi^*$  of acetylene. Conversely  $\nu_1$  would be decreased by an increase of electronegativity of substituted groups in the acetylene. With a very strongly electronegative group substituted in acetylene, the former factor cannot be very effective to change ( $\nu_1$ ) vibration frequency. However, the trend in  $\text{Pt}(\text{CF}_3\text{C}\equiv\text{CCF}_3)\text{L}_2$  is obscure. The electron donating ability increases down a triad of metals as shown by the I.R. of the Ni(O) and the Pt(O) analogues of  $\text{M}(\text{Ph}_2\text{C}_2)(\text{PPh}_3)_2$ .  $\nu_1$  is observed at  $1800\text{ cm}^{-1}$  and  $1768\text{ cm}^{-1}$  for Ni and Pt respectively. Also for  $\text{M}[\text{C}_2(\text{CF}_3)_2](\text{PPh}_3)_2$   $\nu_1$  is at  $1790\text{ cm}^{-1}$  for Ni and  $1775\text{ cm}^{-1}$  for Pt. On crossing the row from left to right in the transition metals block, the d orbitals are more filled. There is an  $18\text{ cm}^{-1}$  difference between the complexes  $\text{V}(\eta^5\text{C}_5\text{H}_5)_2(\text{CF}_3\text{C}_2\text{CF}_3)(d^3)$ , and  $\text{Mo}(\text{Cp})_2[\text{C}_2(\text{CF}_3)_2](d^4)$ , whose I.R. frequencies are respectively  $1800\text{ cm}^{-1}$  and  $1782\text{ cm}^{-1}$  (44)(45)(46).

The electron donation ability of an auxiliary ligand would affect the ( $\nu_1$ ) vibration frequency as explained above, and for  $[\text{Ir}(\text{CO})_2\text{L}_2(\text{MeO}_2\text{CC}_2\text{CO}_2\text{Me})]^+$  complexes when  $\text{L} = \text{PPh}_3, \text{PMePh}_2, \text{PEt}_3$ , the frequency of  $\nu_1$  is  $1814\text{ cm}^{-1}$ ,  $1808\text{ cm}^{-1}$  and  $1791\text{ cm}^{-1}$  respectively (47). This shows an increase in ( $\nu_1$ ) frequency with decreased electron donating ability of an auxiliary ligand. Considering the series of complexes of the type  $\text{Pt}(\text{RC}\equiv\text{CR})(\text{PPh}_3)_2$  ( $\text{R} = \text{Ph}, \text{CF}_3, \text{CO}_2\text{Me}$ ), ( $\nu_1$ ) frequencies are  $1740\text{--}1768$ ,  $1775$  and  $1782\text{ cm}^{-1}$  respectively (48) (49). This shows an increase in ( $\nu_1$ ) frequency with a decrease in electron withdrawal ability of the substituted group.

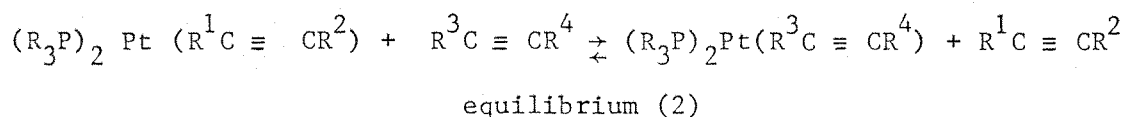
After all a delicate dependence of complex stability on the identity of the metal oxidation state, auxiliary ligands, and the nature of the substituents on the acetylene has been reported (72).

### 1.3.4 Substituent of Acetylenes

In Pt-acetylene complexes, the acetylene ligand can be readily substituted by other ligands. The following general order of stability has been stabilised (50):



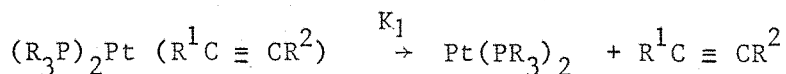
Relatively high stability in ligand substitution reactions is associated with the rather high ability of platinum to form retrodonative bonds. Thus the acetylene is a  $\pi$ -acceptor and should therefore facilitate the trans-ligand A-type substitution (51). This has been confirmed by the data of Allen and Theophanides (52) on the hydrolysis of  $K[(acetylene)PtCl_3]$ . With a strong trans donor a D-type mechanism of substitution of the acetylenic ligand might be expected; evidence for this is obtained from the kinetic data of the reaction



It has been found (53) that the reaction rate is independent of both the nature and the concentration of the attacking ligand.

Dependence of the equilibrium constant upon the character of the substituents in the acetylene obeys the Hammett (54) equation  $\log K/K_0 = \rho\sigma$ , where  $K$  and  $K_0$  are the equilibrium constant of the substituted and unsubstituted phenylacetylenes, respectively Figure 1.14. The electron-attractive effect of the substituents shifts the equilibrium to the side of the reactants (equilibrium 2). The first-order rate constant decreases in the same direction. Since the stability of complexes is defined by the same factors, the way in which the Pt-acetylene bond splits is probably the rate-determining step. The effects of phenyl ring substituents in triarylphosphines on the reaction rate have also been studied (53). Electron-releasing substituents slow down the reaction and behave similarly to the electronegative ones in the acetylenic part of the molecule. These results are interpreted in terms of a dissociative mechanism.

The decomposition of the complex proceeds according to the following scheme as a limiting step (54):



The reverse reaction is determined by the nature of R. The  $[Pt(PR_3)_2]$  generated is a rather stable intermediate. A comparison of the results obtained with the n.m.r. data (55) of substituted phenylacetylenes leads to the conclusion that there is a relation between equilibrium constant, first-order rate constants, and chemical shifts of the acetylenic proton. They all depend on substituent effects on the electron density in the triple bond.

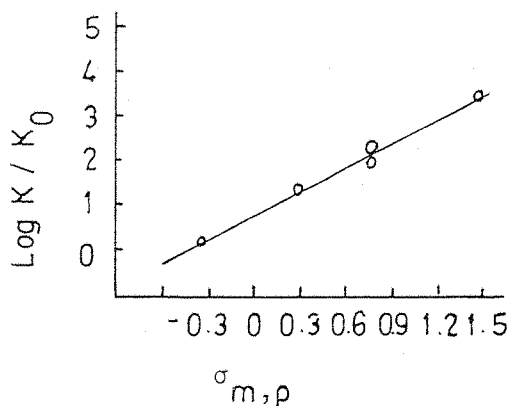
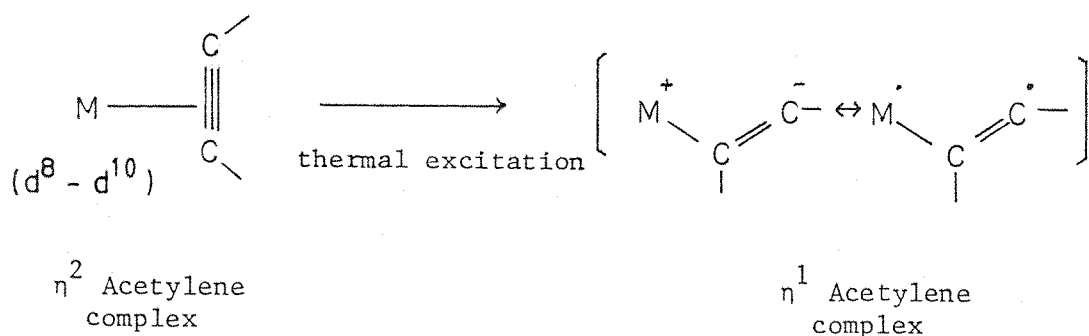


Figure 1.14.  $\log K/K_0$  vs.  $\sigma(x)$  for the exchange reaction of the complexes  $(R_3P)_2Pt(HC \equiv CC_6H_4x)$ , from Temkin and Flid (28).

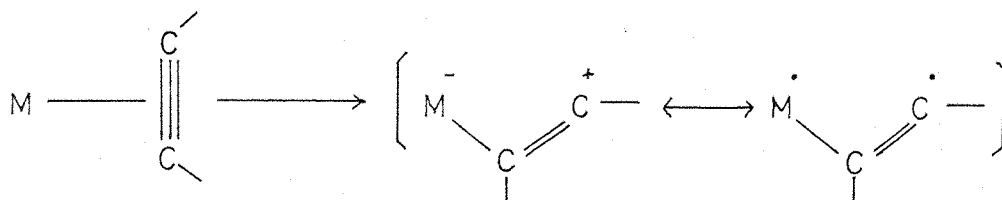
#### 1.4 Activation of Coordinated Acetylene

Studies on elementary reactions of acetylene with metal complexes are now beginning to explain the nature of activation of coordinated acetylene. Acetylene activation is not a simple process. Some metals with high oxidation state such as  $d^1-d^2$  complexes and many low-valent metals ( $d^8-d^{10}$  complexes) are capable of making active acetylene complexes. For the latter case interaction (c') (Figure 1.7) would lead to activation of an  $\eta^2$  acetylene ligand to an  $\eta^1$  acetylene having some radical as well as some anionic character:



Scheme 1.1

In the complexes of a high oxidation state, strong  $\sigma$ -donor interaction (a) of Figure 1.7 and weak  $\pi$ -back donation (b) of Figure 1.7 would lead to the formation of apparently similar  $\eta^1$  acetylene complexes by thermal activation (Scheme 1.2). Here the species, however, have some cationic character as manifested by their preferential reactions with electron-donating acetylenes (56)(57).



Scheme 1.2

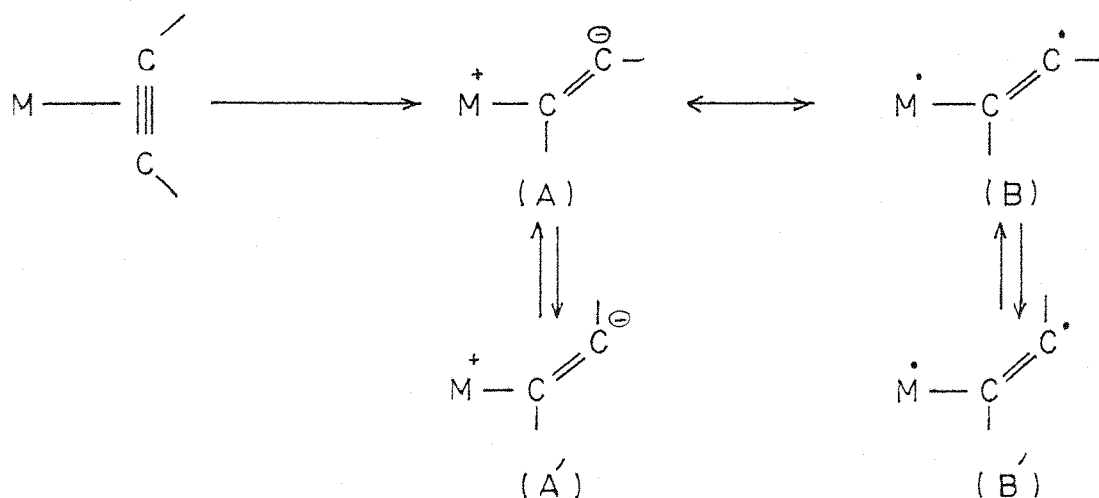
In sharp contrast to these activations, an  $\eta^2$ -acetylene complex is stabilized when all the interactions (a), (b), and (c) of Figure 1.7 are bonding, as in some electron-deficient  $d^6$  complexes, for example,  $W(RC \equiv CR)_3(CO)$  (58)(59)(60).

#### 1.4.1 Insertion Reactions

##### A - Metalocyclization

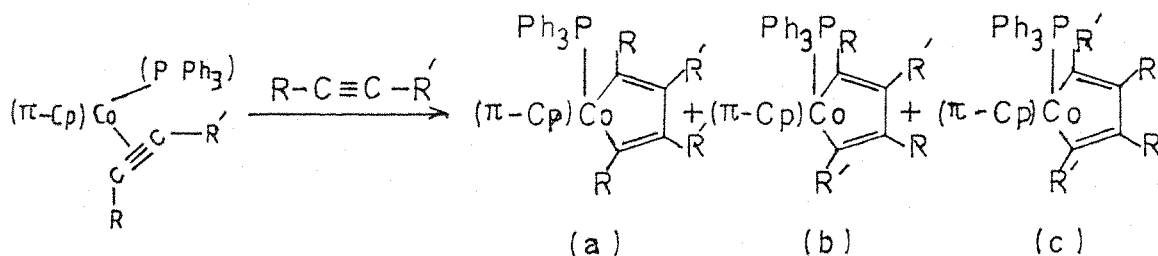
Metal  $\eta^2$  acetylene complexes react with further molecules of

acetylene in two ways, i.e. ligand exchange or substitution and insertion reaction which gives metalocyclization. There is no way to predict which way may be followed in any particular case. But most metals with ( $d^8-d^{10}$ ) acetylene complexes follow insertion reactions. In these complexes, repulsive interaction (c') of Figure 1.7 is operating in addition to interactions (a) and (b) of Figure 1.7. Thermal excitation then either causes these complexes to lose the acetylene or gives rise to a thermally excited molecule in which there is a change in coordination state (61).



Scheme 1.3

Three factors - the effective oxidation state of metal, identity of the metal and auxiliary ligand determine the radical or ionic character (A),(B) Scheme 1.3, and also determine the reactivity, stereo and regioselectivity toward acetylene insertion. The mixture of isomeric products in reaction of  $(\pi\text{-Cp})\text{Co}(\text{PPh}_3)$  ( $\text{RC} \equiv \text{CR}'$ ) with  $(\text{RC} \equiv \text{CR}')$  illustrates these points, Scheme 1.4.



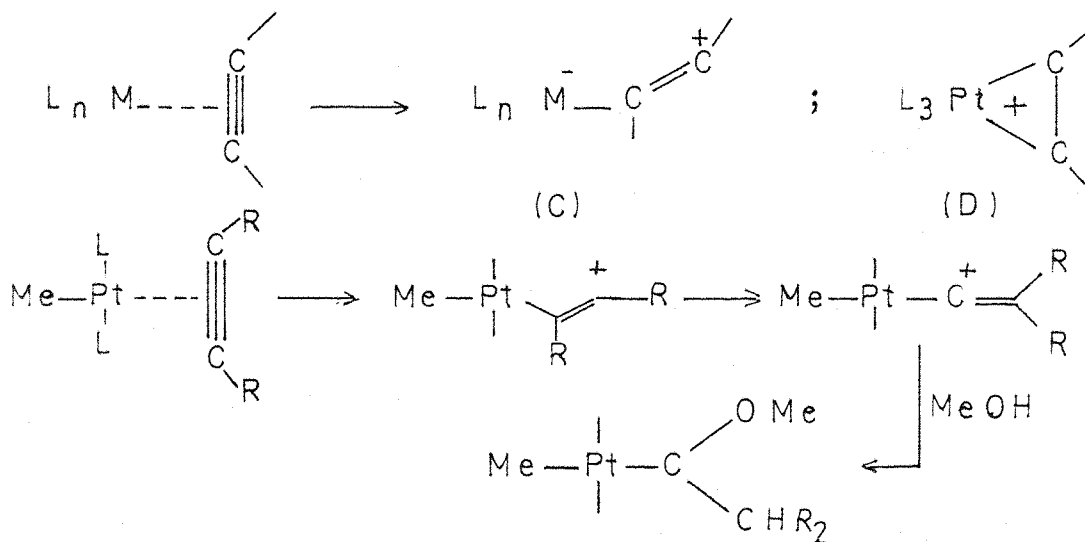
Scheme 1.4

(i)  $\text{R} = \text{CO}_2\text{CH}_3$ ,  $\text{R}' = \text{CH}_3$  : a.9% b.50%

(ii)  $\text{R} = \text{Ph}$ ,  $\text{R}' = \text{CO}_2\text{CH}_3$  : a.13% b.20%

A preponderance of isomer (b) and absence of isomer (c) (i) indicates a polarized intermediate of the  $\eta^1$  acetylene complex (62) and that the intermediate  $(\pi\text{-Cp})(\text{PPh}_3)\text{Co}^+ - \text{C}(\text{CH}_3) = \bar{\text{C}}\text{-CO}_2\text{CH}_3$  would be more acceptable. But in the case of (ii), the radical character may be more reasonable.

For reactions of cationic Pt-acetylene complexes (63), another polar monohaptoacetylene complex (c) may be postulated:



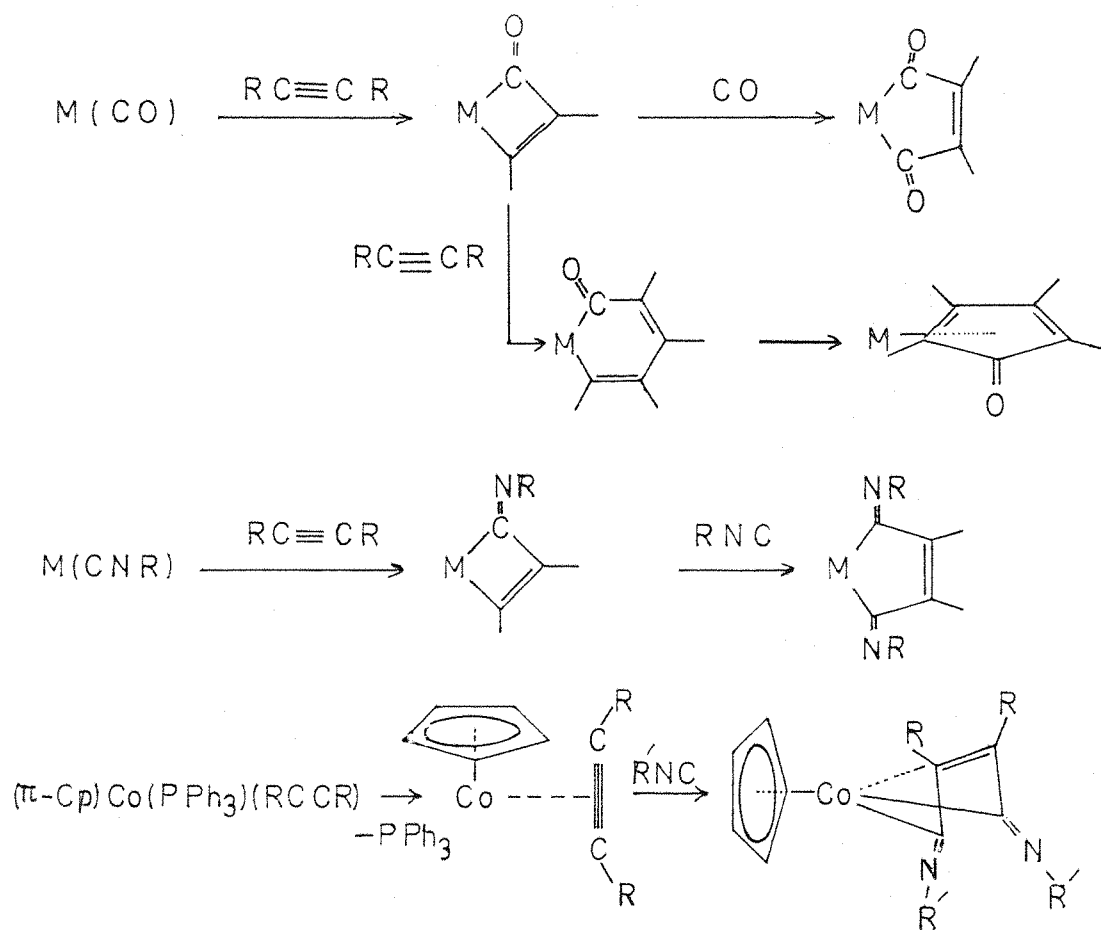
Scheme 1.5

Chisholm and Clark proposed (63) that the electrophilic reactions of  $[\text{PtCH}_3\text{L}_2(\text{RC}\equiv\text{CR})]^+$  can be explained with the intermediate mode (D). Since the positive  $\beta$ -carbon has a vacant  $p\pi$ -orbital, the rearrangement to alkoxy carbene complexes can be regarded as a carbonium ion rearrangement.

The early transition metals are not capable of acetylene cyclization, for e.g.  $(\eta^5\text{C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{RC}\equiv\text{CR})$ , in contrast to later transition metals (64).

#### B - Metalocyclization of Acetylene with CO, RNC

Metalocycles are also formed from reaction between acetylene and  $\text{M}(\text{CO})$  or  $\text{M}(\text{CNR})$ .



Scheme 1.6

Their formation may involve monohapto-acetylene intermediates.

Metalocyclopentadiene complexes have received considerable attention as intermediates in transition metal catalyzed cyclotrimerization of acetylenes. Several groups have prepared metallocyclopentadienes and shown that they react with acetylenes to give substituted benzenes (65).

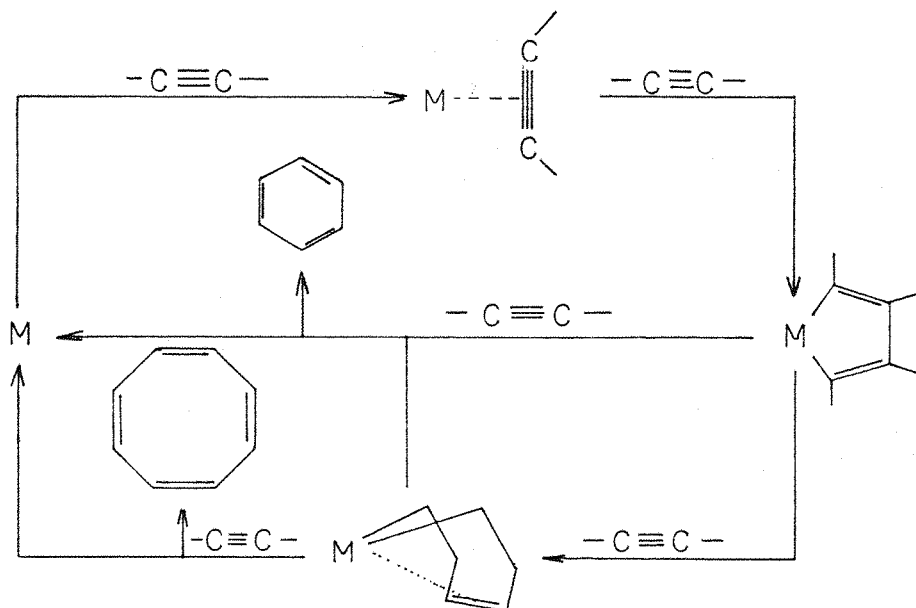
#### 1.4.2 Catalytic Reactions

##### A - Catalytic cyclooligomerization

Transition metal acetylene complexes can catalyze the formation of cyclic aromatic compounds. The insertion reaction can proceed as

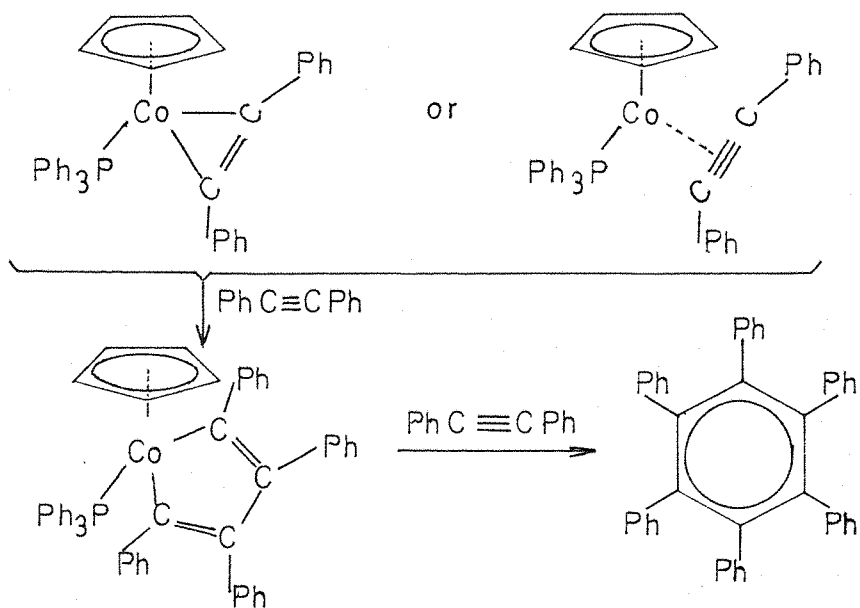


discussed above via an intermediate like (A) or (B) (Scheme 1.3) similar to that of Scheme 1.4 (66,67).



Scheme 1.7

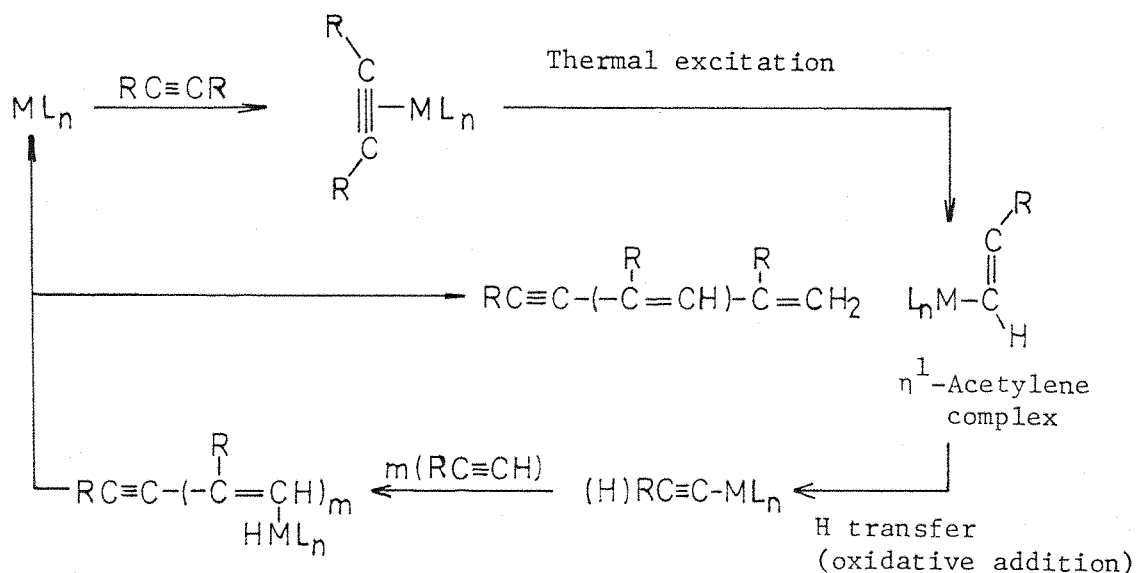
In those examples acetylenes are catalytically cyclized to benzene and cyclooctatetraene Scheme 1.7. In another example substituted acetylene gives substituted benzene (65) Scheme 1.8.



Scheme 1.8

### B - Linear Oligomerization

Transition metal acetylene complexes may also catalyse linear oligomerization. Meriweather et al. (68) (69) proposed hydrido- $\sigma$ -alkynylnickel complexes as active intermediates in catalytic linear oligomerization (scheme 1.9). Subsequent insertion of acetylene into an M- $\sigma$ -alkynyl bond has been assumed.



Scheme 1.9

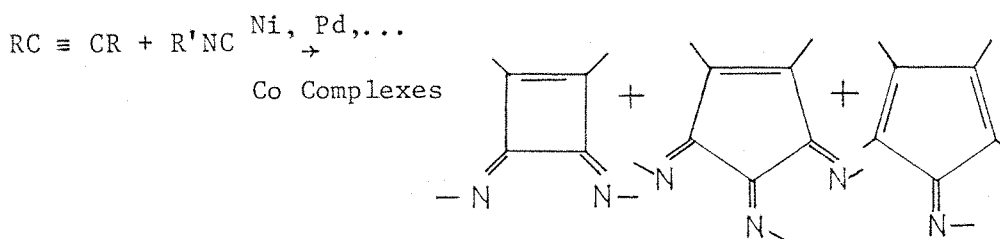
Another report of linear polymerization of an acetylene with a nickel-carbonyl-phosphine catalyst is due to Cairns and co-workers (70) who copolymerized acetylene and acrylonitrile to 2, 4, 6-heptatrienenitrile. In the series of  $\text{Ni}(\text{CO})_2(\text{PR}_3)_2$  complexes the activation of catalyst varied with the substituent R in the following general way:  $\text{C}_2\text{H}_4\text{CN} > \text{C}_6\text{H}_5 > \text{H} > \text{OC}_2\text{H}_5 > \text{n alkyl} \gg \text{OC}_6\text{H}_5 \sim \text{Cl}$ .

Brown and co-workers (71) showed that the rhodium and iridium complexes act as catalysts for the polymerisation of acetylenes. These give the same aromatic compounds but mainly a linear polymer having similar properties to that reported (72) to be formed under similar condition when  $\text{Pt}(\text{PhCC Ph}_2)(\text{PPh}_3)_2$  is used as catalyst. The mechanism of polymerisation may be similar in each case, involving insertion of a phenylacetylene molecule into the metal-carbon bond

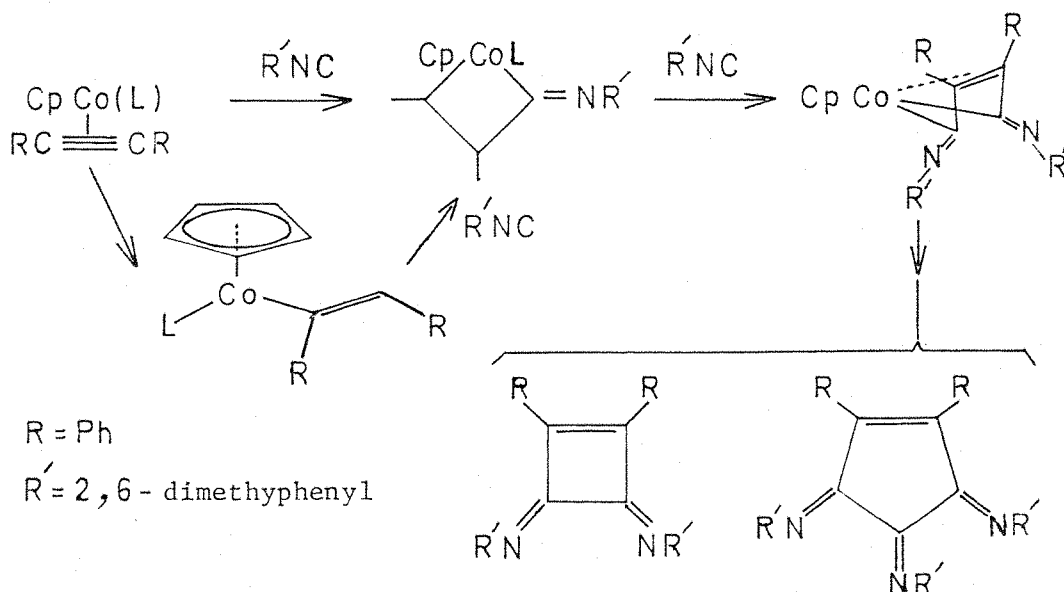
giving an intermediate vinylic species of the type  $L_nM-C(Ph) = CH-C \equiv C - Ph$  or  $L_nM-CH = C(Ph)-C \equiv C-Ph$ . Conversion of an  $\eta^2$ -acetylene complexes to the hydridoalkynyl complex will lead to linear oligomerization or polymerization. The tendency of some Rh or Pd complexes to form hydridoalkynyl complexes explains their catalytic activity towards linear oligomerization.

### C - Catalytic Cocyclization with Isocyanides

The cocyclizations of acetylenes and isocyanides are similar to cocyclization with carbon monoxide (73)(74)(75) (scheme 1.6). Low-valent nickel, palladium, or cobalt complexes are active in the following reaction (76)(73) for which intervention of acetylene complexes has been suggested:



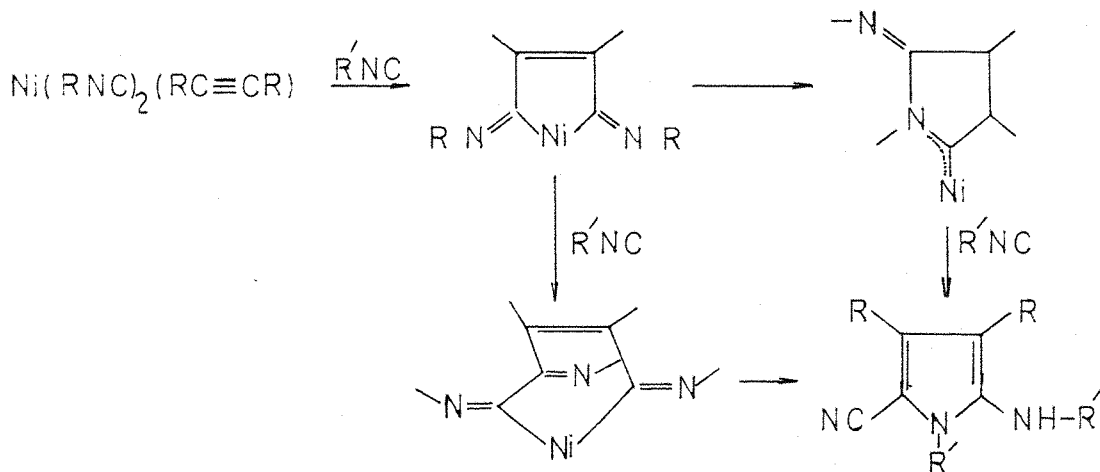
Intermediates of these reactions which were isolated by Yamazaki et al. and others (73)(74), Scheme 1.10, are metalocyclic complexes.



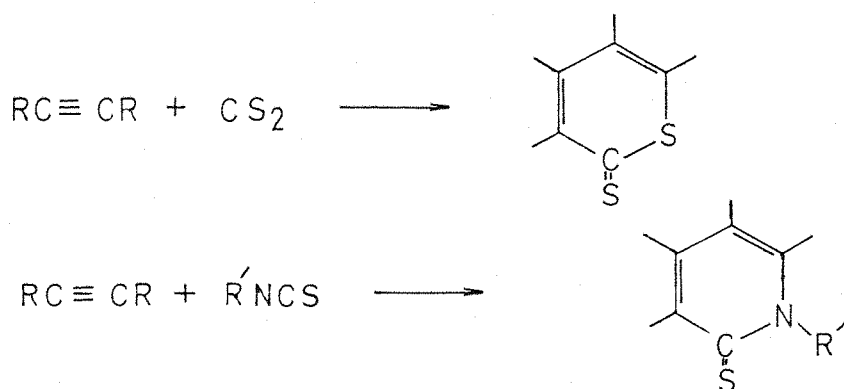
Scheme 1.10

D - Catalytic Cocyclization with Heterounsaturation

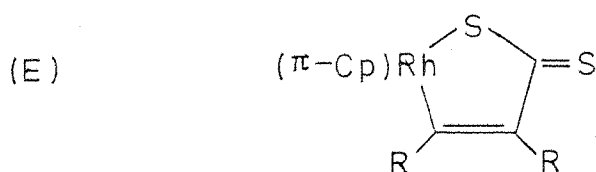
Various cobalt complexes reported by Yamazaki et al. (62) (77) and Bonnemann et al. (78) catalysed the syntheses of substituted pyridines from acetylenes and nitriles. Similar reaction is presented in Scheme 1.11 where a Ni complex plays the role.



The reaction with  $\text{CS}_2$  and  $\text{RNCR}$  act also in the similar way with acetylene (62) to give new heterocycles.  $\text{CpCo}(\text{PPh}_3)_2$  catalyzed those



reactions. An ionic intermediate  $\text{Cp}(\text{PPh}_3)\text{Co}^+ - \text{C}(\text{R}) = \bar{\text{C}}\text{R}$  has been suggested. The presence of this intermediate is supported by isolation of an intermediate complex (E) (79) from a similar reaction where Rh complex is the catalyst.



### 1.5 Olefin and Acetylene Rotation

There have been reported two different orientations for olefins or acetylenes within complexes like those in Figure 1.15 (which causes nonrigidity of an olefin or acetylene within the metal - un complexes) (14)(80)(81). The two orientations have different metal ligand bond strength and this difference in energy induces a barrier to rotation.



Figure 1.15. Possible orientation of ethylene in  $[(\pi\text{-Cp})\text{Fe L}_2 \text{ olefin}] \text{ X}$ .

The orientation preference is described in Cotton's review of olefin rotation (82). The abundance of one of those orientations is much greater than the other. The horizontal (a) structure is agreed to be more stable and is the orientation in the solid (Figure 1.15). This difference in abundance would be varied by changing the situation of the molecule. The scheme of metal-olefin bonding (83) which was described by Dewar, Chatt and Duncanson (1)(2) can explain most of the effects. Although this model has provided an explanation of the bonding and structure as well as other properties of such complexes

in a qualitative manner, the quantitative contribution of the  $\sigma$  and  $\pi$  components is still a matter of considerable discussion. Recent work suggests a somewhat more complicated bonding situation (83)(84) (85).

The barrier to rotation would be varied by several matters. Firstly, concerning the central metal, the barrier would increase by moving down a column in the periodic table and also increase by moving from left to the right of the row. In addition, it would decrease for each transition metal in a cationic state and gives lower barriers for higher oxidation states (14)(81)(86). Secondly, olefin substituents widely alter the barrier to rotation, e.g. in the complex  $(\pi\text{-Cp})\text{Rh}(\text{C}_2\text{H}_4)(\text{C}_2\text{F}_4)$  the rotation barrier is greater for  $(\text{C}_2\text{F}_4)$  than for  $\text{C}_2\text{H}_4$ , (96.3 and 65.5 KJ/mol respectively). Lastly steric factors would be important when a bulky group is cis to the unsaturated molecule. This tends to give bigger barriers when the olefin or the acetylene substituent also is a bulky group. Discussion of the rotation barrier begins best with square planar platinum complexes since they have been well studied experimentally and theoretically as these systems are relatively simple, e.g.  $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3] \cdot \text{H}_2\text{O}$  and other platinum complexes (83)  $\{\text{PtCH}_3(\text{RC}\equiv\text{CR}') [\text{P}(\text{CH}_3)_2\text{Ph}]_2\} \text{PF}_6$  (87).

As shown above, the bond between metal and olefin or acetylene contains contributions of  $\sigma$ -donation from the  $\pi$  molecular orbital of the olefin to the metal and  $\pi$ -back donation from the filled metal d orbital to the  $\pi$  antibonding orbital of the olefin (Figure 1.1). Then in this situation as far as the latter bond is concerned both the  $dxz$  and  $dxy$  are available to form the bond (Figure 1.2), allowing different orientations of the olefin or acetylene ligands. X-ray studies of platinum complexes (3) show that the olefin double bond (or the acetylene triple bond) is nearly perpendicular to the coordination plane (with an angle of  $5.9^\circ$  with the normal to the plan) (Figure 1.2) (a), so it is interaction of  $\pi^*$  bonding of olefin and  $dxz$  of metal (out of plane  $\pi$ -bond), that is evident in the more stable complex.

The complex of Zeise's Anion,  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$  has been studied to find the relative importance of  $\sigma$ -bond and  $\pi$ -bonds in a qualitative matter based on a conventional population analysis, using an iterative extended Hückel (IEH) (88), CNDO-type methods (89), and SCF- $X\alpha$ -SW (83). The two first methods indicate an important contribution to  $\pi$ -back bonding in the olefin-metal bond. SCF- $X\alpha$ -SW based on the calculations and computation of contour plots of the individual orbitals as well as the orbital charge distribution, this gives a more important contribution to  $\sigma$ -donation than  $\pi$ -back donation. Those two first methods satisfy qualitative descriptions but the last one would be more quantitative.

The phenomenon of olefin rotation was first suggested by Cramer who demonstrated that the temperature dependent  $^1\text{H}$  n.m.r. spectrum of  $(\pi\text{-Cp})\text{Rh}(\text{C}_2\text{H}_4)_2$  could best be interpreted on the basis of such behaviour. Cramer showed (90) that the  $^1\text{H}$  n.m.r. of  $(\pi\text{-Cp})\text{Rh}(\text{C}_2\text{H}_4)_2$  has two singlets, a sharp peak at  $\delta 5.15$  and another one at  $\delta 1.93$ , the first is due to the five protons of the cyclopentadienyl group indicating fast rotation about the metal-ring axis; the second singlet is due to the olefin protons consistent with rotation about metal-olefin bond. The olefinic signal broadens at low temperature and after that more broadening agrees with two different protons in each olefin. The singlet belonging to the cyclopentadienyl group does not broaden which shows a small barrier to that rotation. The magnitude of the barrier to rotation for the olefin calculated by using the  $^1\text{H}$  n.m.r. broadening suggests a structure such as (b) rather than (a) in Figure 1.16 is involved. At  $-20^\circ\text{C}$  the resonances of the coordinated olefin splits into two, one at  $\delta 2.77$  and another at  $\delta 1.12$  (90).

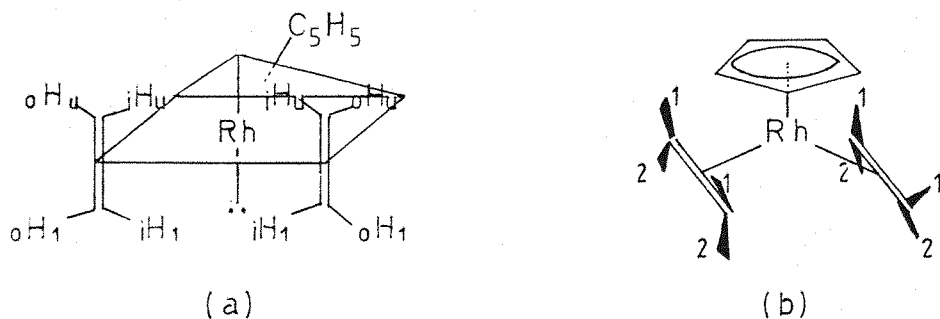


Figure 1.16. Molecular structure of  $(\eta^5\text{C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{H}_4)_2$

In a simple valence bond description, it may be assumed that the complex is a pseudo-octahedron in which cyclopentadienyl occupies three sites and each olefin one corner and a non-bonded pair<sup>of</sup> electron another side (Figure 1.16(a)). In this figure, there are two choices of two different sets, first  $H_u$ 's and  $H_i$ 's and second  $oH$ 's and  $iH$ 's which can be averaged at higher temperature. The  $^1H$  n.m.r. of  $(COCH_3CHCH_3CO) Rh(C_2H_4)$  at  $-50^\circ C$  (in which the acetylacetonate (acac) would be in the coordination plane) is similar to the  $^1H$  n.m.r. of  $(\pi-Cp) Rh(C_2H_4)_2$  suggests the sets which participate in averaging are not the upper protons with lower proton but are inner and outer protons and is consistent with indistinguishable chemical shifts between  $H_u$  and  $H_i$ . This suggests that the cyclopentadienyl group is symmetrically disposed with respect to the coordinated olefins as in (b) (Figure 1.16). In structure (b), the signal of the protons in situation 1 will average with the protons in situation 2, by rotation along the M-olefin axis. In the rotation process, both sets of  $\pi$ -back donation would participate with a right angle to each other and the barrier to rotation will be related to the energy difference of the bonding molecular orbitals formed for the in-plane and out-of-plane bonding situation (91).

The rotation could be in two different modes (a) or (b) of Figure 1.17, i.e. about an axis along metal to mid point of olefin C-C bond or about carbon-carbon bond. The former was assumed by Cramer for discussion about the rotation barrier in a series of rhodium (I) (90-95), iridium (I) (95-97) and platinum (II) (98-101) complexes, as they argued that the rotation about C-C axis would be led to cleavage of the metal-olefin  $\sigma$ - and  $\pi$ - bonds, hence causing olefin dissociation and also must expect greater barrier to rotation of olefin than 38.5 KJ/mol for complex  $[(\pi-Cp) Fe(CO)_2(C_3H_6)] BF_4$  (102,103). But now it is believed that dissociation is not necessary



Figure 1.17. Modes of rotation of an olefin about M-olefin or C-C axis.



in rotation mode (b), Figure 1.17, and a new bonding arrangement has been suggested by Jonassen and co-workers (23) for an olefin (Figure 1.18). If the olefin is in the xy plane (Figure 1.18)(b) it is possible to say that the  $\delta$ -overlap of the olefin  $\pi^*$  orbital with the  $dyz$  metal orbital is acceptable.

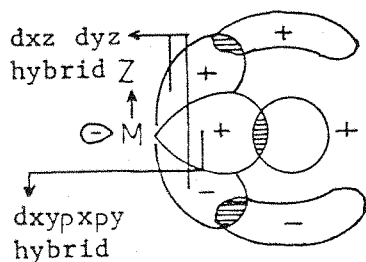
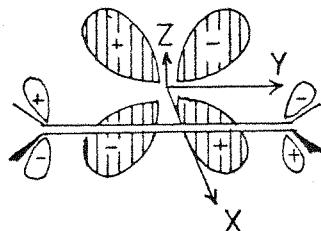
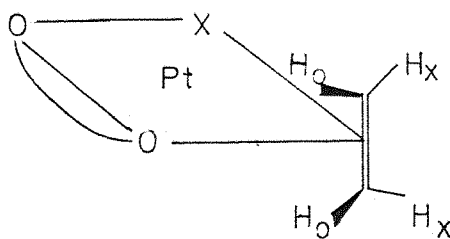


Figure 1.18 (a)

Figure 1.18 (b) olefin  $\pi^*$  orbital orientation for  $\delta$  overlap

In complexes like  $[\text{PtCl}(\text{olefin})(\text{acac})]$  (Figure 1.19) in which the olefin is perpendicular to the coordinated plane, then in this situation the four protons of olefin could have two different environments, i.e. the two  $H_o$  are adjacent to an O-atom, and the other two  $H_x$  are adjacent to halogen in the ground state. The  $^1\text{H}$  n.m.r. of this complex detected two environments for olefin protons, which averaged at high temperature to one signal.

Figure 1.19 Geometry of  $[\text{PtCl}(\text{olefin})(\text{acac})]$  at the ground state.

But this does not differentiate between the two possible rotational

modes. The mode of rotation can only be determined from n.m.r. spectral data provided that the two ends of the olefin are in the different chemical environments. The mode of rotation was found in  $[\text{Os}(\text{CO})(\text{NO})(\text{C}_2\text{H}_4)(\text{PPh}_3)_2] \text{PF}_6$  by use of  $^1\text{H}$  n.m.r. and  $^{13}\text{C}$  n.m.r. at low and high temperature. The  $^{13}\text{C}$  n.m.r. of this complex has detected two resonances at  $\delta 54.4$  and  $43.6$  at low temperature with equal intensities, which clearly indicates two different carbon of the ethylene in a rigid situation at  $-80^\circ\text{C}$ . These two peak average and give a singlet at  $\delta 49.3$ , at  $20^\circ\text{C}$ , which shows that there is a barrier to olefin rotation and confirms the rotation mode is type (a) in Figure 1.17. This result shows that the ethylene occupies the in-plane orientation in the octahedral ground state geometry, Figure 1.20. The  $^1\text{H}$  n.m.r. of this complex at  $-90^\circ\text{C}$  gives two resonances of equal intensity at  $\delta 3.49$  and  $1.23$ .

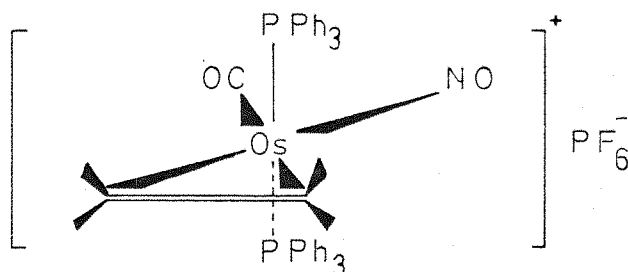


Figure 1.20. The stereochemical picture of  $[\text{Os}(\text{CO})\text{NO}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)] \text{PF}_6$

At high temperatures those two peaks average to a triplet at  $\delta 2.62$ . The barrier to rotation for this complex is  $\Delta G_{\text{Tc}}^\ddagger = 54.7 \text{ KJ/mol}$  (104) and is lower than that found for square planar platinum complexes. In this complex, if the olefin takes an out-of-plane orientation, then in the ground state there would be two different protons for olefin but only one carbon and this is not matched with  $^{13}\text{C}$  n.m.r. spectrum. The rotation mode (b) (Figure 1.17) cannot average the protons in  $^1\text{H}$  n.m.r. and carbons in  $^{13}\text{C}$  n.m.r.

The barrier is believed to represent the difference in energy between the olefin-metal bonding, when olefin is oriented horizontally and vertically. The most important factors that cause the barrier to rotation may be considered. Firstly, there is the

electronic distribution within the molecule (82), which will depend upon the  $\sigma$  and  $\pi$ -bonding properties of other ligands in the molecule, causing the nonequivalence of the d-orbitals interacting with the olefin. Thus for a complex like  $\text{Cr}(\text{CO})_5(\text{C}_2\text{H}_4)$  there would be no electronic barrier to rotation because in any case of rotation the local symmetry of  $\text{Cr}(\text{CO})_5$  remains  $C_{4v}$ . Secondly, the steric factor should be very important if a bulky group is cis to olefin (100) (87). In the complex of type  $[\text{PtXYL}(\text{C}_2\text{H}_4)]$  where X,Y are halogen or a carboxylate group and L is phosphorus or arsenic base, any change in the substituent of the bases would affect the steric factor, and at the same time affects the distribution of electrons within the molecule both of which vary the barrier to rotation.  $\Delta G^\ddagger_{\text{Tc}}$  for these Pt complexes are 52.5 KJ/mol, 61.6 KJ/mol, 56.8 KJ/mol, 64.5 KJ/mol for  $\text{L} = \text{Et}_3\text{As}, \text{Et}_3\text{P}, \text{Ph}_3\text{As}, \text{Ph}_3\text{P}$ , respectively ( $\text{CDCl}_3$  solvent, and X,Y = Cl). There is an increase in the barrier with steric bulk, also, in this case at the same time will be a decrease in it with a decrease of electron donation ability of the ligand (100). Thirdly, the barrier to rotation varies with olefin substituent, for example, in  $(\eta^5\text{C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{H}_4)(\text{C}_2\text{F}_4)$   $\Delta G^\ddagger$  is 65.5 KJ/mol and 96.3 KJ/mol for  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{F}_4$  respectively (92). The central metal is important as well as there is an increase in barrier to rotation in going down a column in the periodic table (91)(95).

Orientation preference in the most stable conformation of a complex would vary with steric factors and all the other factors mentioned above. The preferred orientation in the complex  $[(\pi\text{-Cp})\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_4)]\text{X}$  is configuration (a) Figure 1.15, which is accompanied by more stability for the complex. The  $^1\text{H}$  n.m.r. of this complex has showed two singlets are due to the  $\text{C}_5\text{H}_5$  protons and another belonging to the four ethylene protons, are averaged. The equilibration of proton in this case would occur by two mechanisms. A fast rotation of coordinated ethylene about the C-C axis and also about the metal-ethylene mid point axis could lead to a single proton signal. Furthermore, dissociative mechanisms would allow either side of the planar ethylene group to face the iron atom and average the environments.

In substituted olefins the strong steric factor between olefin and ring would maintain another preferred orientation. In the complex  $[(\pi\text{-Cp})\text{Fe}(\text{CO})_2(\eta^2\text{-C}_7\text{H}_{12})]^+$  the angle between the normal to the plane of the  $\text{C}_5\text{H}_5$  ring and C(3) - C(4) vector is  $74.0^\circ$  with the substituents oriented away from the ring (Figure 1.3) (10). This may affect a further back donation to the olefin and the complex would be much more stable. The increasing alkyl substitution destabilizes the M-olefin bond. Highly substituted olefins would be displaced easily in the  $[(\pi\text{-Cp})\text{Fe}(\text{CO})_2(\text{olefin})]^+$  cations in accord with the stability series  $\text{C}_2\text{H}_4 > \text{C}_2\text{H}_3\text{R} > \text{C}_2\text{H}_2\text{R}_2 > \text{C}_2\text{HR}_3 > \text{C}_2\text{R}_4$ . In mono, di or tri substituted olefins a deviation from the horizontal plane might be anticipated especially in trans disubstituted olefins (81). Although the  $^1\text{H}$  n.m.r. study of olefin rotation provides information about the lowest-energy pathway for a given site interchange, it could be difficult to find out whether the olefin functions as full rotation ( $360^\circ$ ) or oscillates ( $\sim 180^\circ$ ), but it is clear that the oscillation needs lower energy. In the complex  $[(\text{C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\text{propene})]^+$  the large steric interaction between the methyl and indenyl groups suggests the oscillation mechanism would take place.

The broadening observed in the ethylene complexes is attributed to proton exchange between two equally-populated non-equivalent sites in the lowest energy conformation. Substituted ethylene in the low energy conformation produces configurations which would not be expected to have identical populations (Figure 1.21) (14)(105). Then a smaller broadening would be absorbed in the case of unequal populations in the fast exchange. The configuration (b) Figure 1.21 is likely to have a much smaller population than that of the configuration (a) and so broadening of Hc of this complex (0.8 Hz) is smaller than ethylene (9 Hz) at the same temperature. Steric factors do not allow any vertical population for the olefin (like that of ethylene (b) (Figure 1.15) in the indenyl complexes. Also there are many configurations between the two extreme configurations, Figure 1.21, which allow propene to oscillate without reaching one of the extreme configurations, i.e. configuration (b), Figure 1.21.



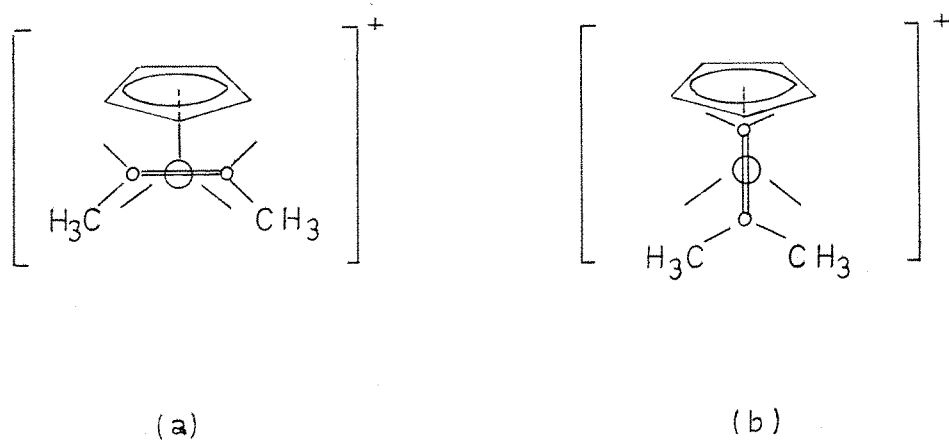


Figure 1.22 Symmetrical orientation of ligands in cis-2-butene and isobutene complexes.

Two singlets appeared for trans-2-butene protons at room temperature but they broaden at low temperatures ( $-60^{\circ}\text{C}$ ). The data agrees with an interconversion of involving 2 probable conformations (Figure 1.23). Here the predominant group is the cyclopentadienyl rather than the carbonyl groups. In those two cases there is not one exact preferred orientation.

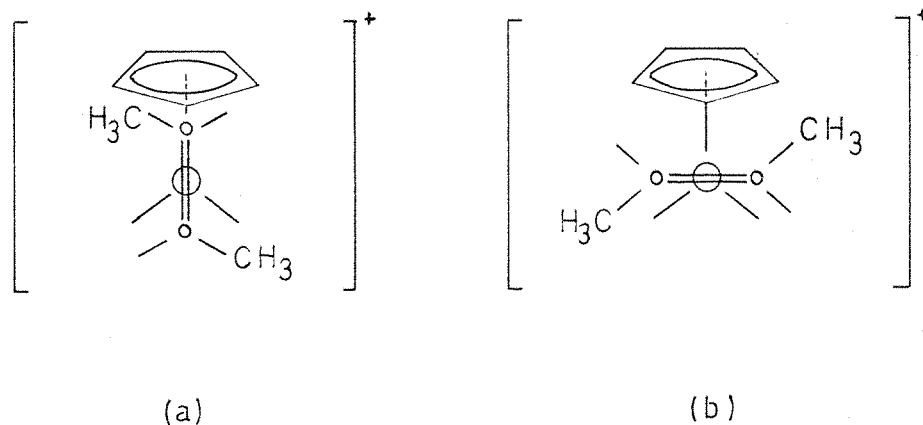


Figure 1.23 Possible orientations of the trans-butene complex.

If one of the carbonyl group is substituted with another ligand like  $\text{SnR}_3$  (81) this would affect the electron density on the central metal.

and create a chiral centre at the iron atom. In this case, low temperature  $^{13}\text{C}$  n.m.r. or  $^1\text{H}$  n.m.r. spectra show an inequivalence of the ethylene nuclei. Then in this case replacing ethylene by propene would result in two pairs of diastereoisomers (Figure 1.25). However, when two bulky groups are near each other, the configuration would be unstable and have just a transient existence prior to decomposition of the complex by loss of propene. Then in this case also there may be an oscillatory movement which does not complete the  $360^\circ$  (Figure 1.26). Then usually the rotation barriers are sufficiently higher than the cationic complex so that the complete dynamic processes, including the nonrotating orientation can be absorbed by n.m.r. Here the thermodynamically preferred orientation of olefin before the ring can be better explained (Figure 1.25).

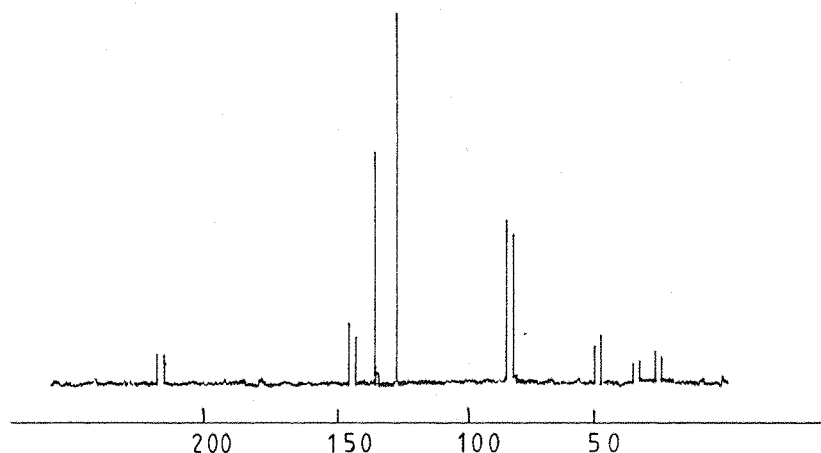


Figure 1.24  $^{13}\text{C}$  N.m.r. spectra of  $[\text{CpFe}(\text{CO})(\text{SnPh}_3)(\text{C}_3\text{H}_6)]^+$  showing resonances of each diastereoisomer.



Figure 1.25 Diastereoisomers in chiral iron propene complexes.

Also between two isomers one is more stable and the one (b) in which two bulky groups are near causes a decomposition and loss of propene. Then the more stable configuration would be (a) (Figure 1.25), based on steric requirements. With exchange of cyclopentadienyl by the larger indenyl group the configuration (b) (Figure 1.21) would be more unstable and have just a transient existence. An interesting difference in rotation barrier is seen for the propene diastereoisomers, where the more stable isomer has a barrier nearly 14.4 KJ higher than the other. The low-temperature n.m.r. spectra of diastereoisomers (Figure 1.24) showed the presence of one set of resonances for each. Although some broadening of signals results from raising the temperature, the time-averaged spectra have chemical shifts very close to those of the unaveraged case, which suggests that one orientation of the olefin predominates at low temperatures.

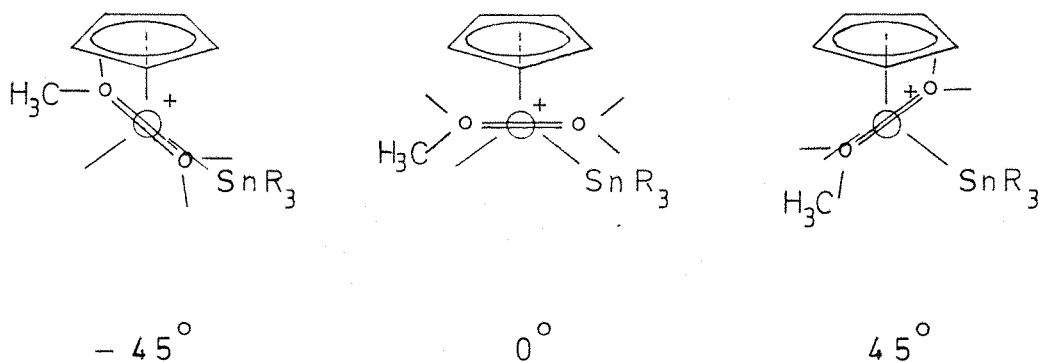


Figure 1.26. Oscillation of propene in cyclopentadienyl iron trialkyl tin complex.

Although the olefin (107-110) and acetylene (111-115) complexes are characterized as having similar bonding mechanisms, it is not necessary that they have similar stability (87)(115-120).

The acetylene orbitals involved in bonding with the metal are two  $\pi$  and two  $\pi^*$  and the local metal-acetylene symmetry is  $C_{2v}$ . This symmetry would be reduced to  $C_s$  in a complex like  $(\pi\text{-Cp})M(\text{CO})_2$  -



(acetylene), (Figure 1.27). The two configurations (a) and (b) (Figure 1.27), would cause different symmetries for these four orbitals (Figure 1.28).

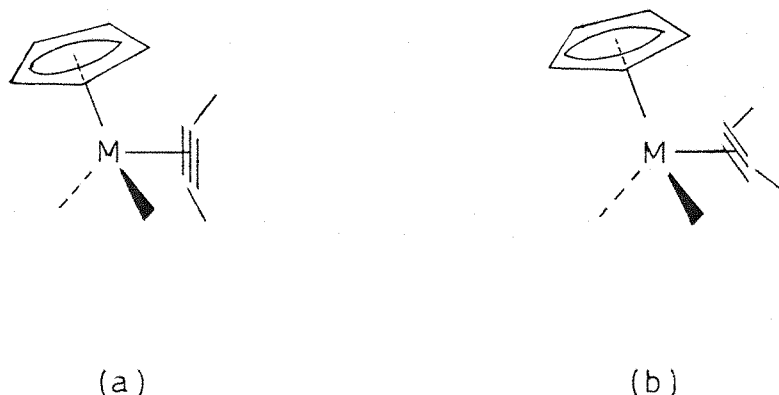


Figure 1.27. The two configurations for acetylene complex

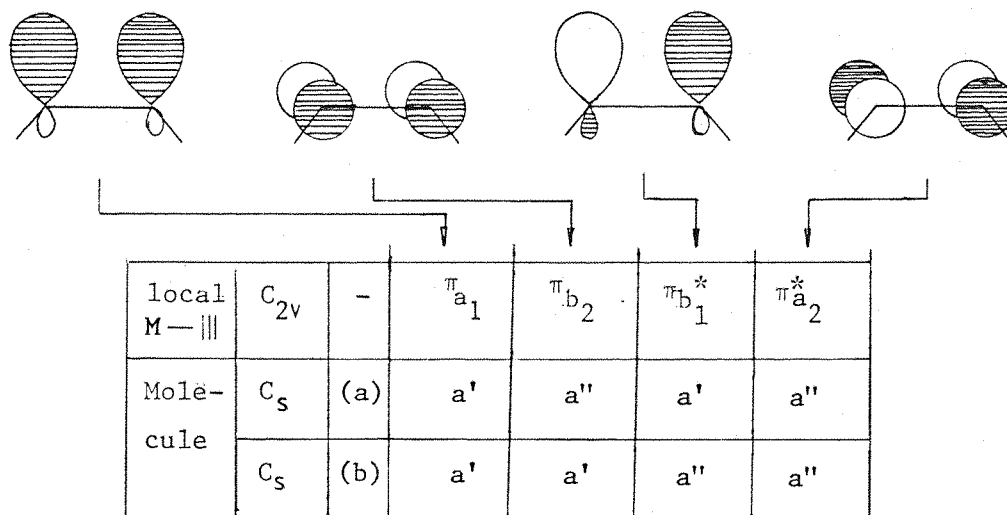


Figure 1.28 The acetylene orbital in M-Acetylene local and in  $C_p M(CO)_2$  (acetylene)

The  $\pi^*$  orbital which has  $a_2$  (local  $C_{2v}$  group) becomes  $a''$  in the both configurations (a) and (b), but the pseudosymmetry  $a_2$  prevents it from having significant interaction.

Another acetylene orbital  $\pi_{a_1}$  which has approximately similar interaction in the two geometries. So geometry preference depends on two other orbital of acetylene, i.e.  $\pi_{b_2}$  and  $\pi_{b_1}^*$ . The series of

complexes of  $(\pi\text{-Cp})\text{M}(\text{CO})_2$  (acetylene), ( $\text{M}=\text{Fe}, \text{Mo}, \text{W}, \text{Cr}$ ), are derived from  $(\pi\text{-Cp})\text{M}(\text{CO})_3$  after loss of one (CO) group and addition of acetylene. In  $(\pi\text{-Cp})\text{M}(\text{CO})_3$  the z axis is along five fold axis of the  $(\pi\text{-Cp})$  ring (Figure 1.29). The symmetry around the metal is pseudo-octahedral and  $(\text{OC})\text{M}-(\text{CO})$  angle is near  $90^\circ$ . The d orbitals are divided into low and high energy levels. The low levels contain an  $a_1$  orbital which is  $z^2$  for configuration in Figure 1.29, but would reform to  $yz$  when the complex takes the configuration in Figure 1.30, and two others ( $1e$ ) are mainly  $x^2-y^2$  and  $xy$  for configuration in Figure 1.29, which become  $x^2-y^2$  and  $xz$  for configuration in Figure 1.30. The two higher orbitals,  $2e$  are mainly  $xz$  and  $yz$  and they also convert

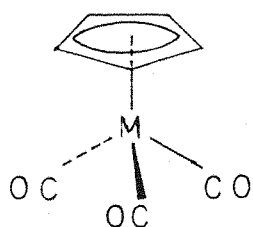


Figure 1.29

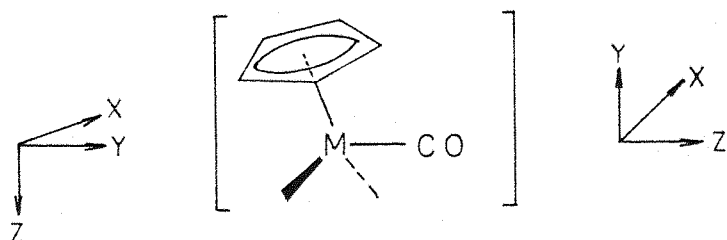


Figure 1.30

to  $z^2$  and  $xy$ . Removing a CO along the z axis from the configuration in Figure 1.30, causes a slight difference; it generates another low-lying acceptor orbital,  $3a'$ , which mainly  $z^2$ , Figure 1.31. Also removal of CO from  $\text{Cp Fe}(\text{CO})_3$  lowers the symmetry around the metal  $a_1$  and  $1e$  mix as shown in Figure 1.31, and two orbitals of  $1e$  split into  $a'$  and  $a''$ , symmetric and antisymmetric orbitals with respect to the  $yz$  plane.

It is important to know which orbitals are more favoured for the  $\pi$  interactions necessary in acetylene bonding. The  $a''$  orbital has higher energy than  $1a'$  and  $2a'$  and is hybridized around the vacant coordination site (Figure 1.32). As shown in Figure 1.31 the energy of the  $1e$  orbitals is altered by removing a CO group (the M-CO bond is stabilized  $\pi$  interaction from the cationic tri-carbonyl complex). The  $a''$  is the destabilized orbital, which makes it suitable for  $\pi$  interaction, but the  $2a'$  has slightly decreased energy than the correlated  $1e$  orbital, and has much less  $\pi$  interaction.

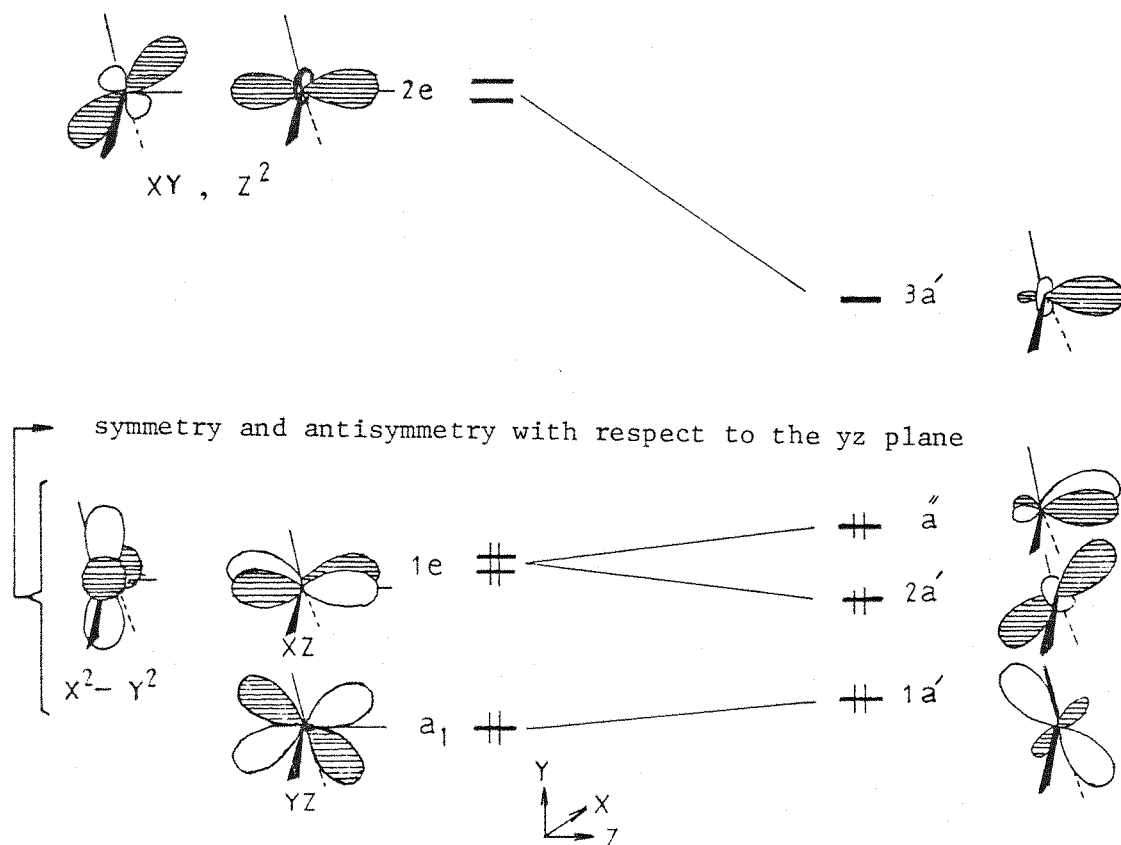


Figure 1.31 The valence orbitals of  $[\text{Cp Fe}(\text{CO})_2]^+$  and  $[\text{Cp Fe}(\text{CO})_3]^+$

The  $a_1$  orbital energy has increased in the  $1a'$  orbital by that removal. This orbital is slightly destabilized by having less  $\pi$  interaction in the yz plane.

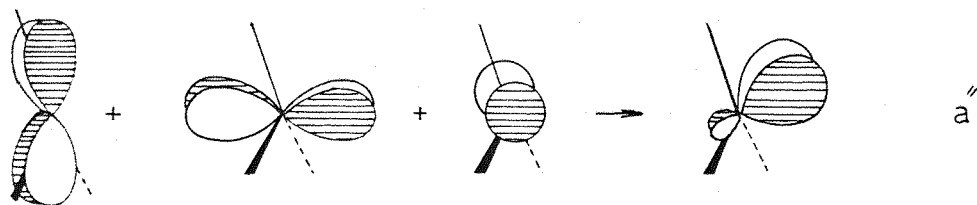


Figure 1.32 The hybridization toward the vacant coordination site to make  $a''$ . The orientational preferences of the acetylene would be governed by the better ability of the  $a''$  for  $\pi$  interaction, than the  $a'$ . The interaction of  $[\text{Cp M}(\text{CO})_2]^+$  orbitals with acetylene is shown in Figure 1.33.

The maximum stabilizing interaction is achieved in the configuration (b) (Figure 1.27). The  $\pi$  donor interaction is minimized as well in this geometry.

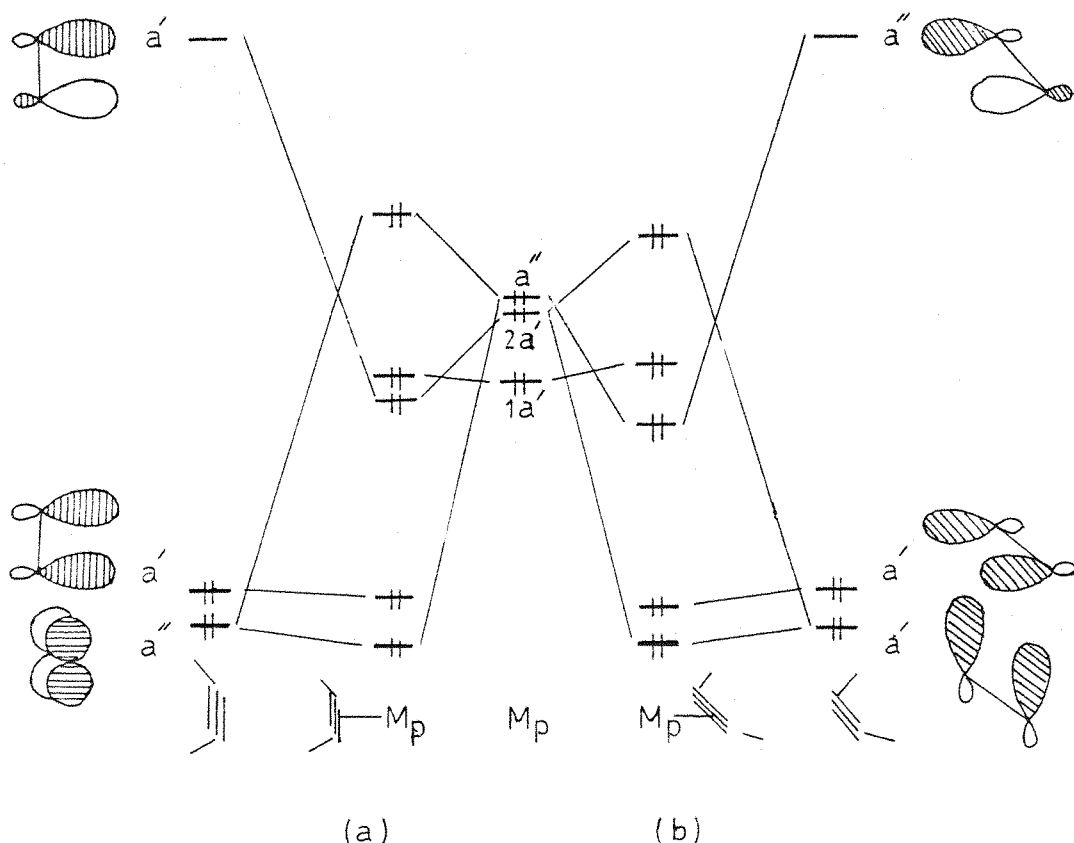


Figure 1.33. The orbital interaction of acetylene and  $[(\pi\text{-Cp})\text{M}(\text{CO})_2]^+$  with two different orientations of acetylene in complex conformation (a) and (b).

The barrier to rotation which depends on an orientation preference in the complex, would be governed mostly by electronic factor.

The electronic factor arises from the nonequivalence of the metal orbitals in the molecular environment causing the strength of the  $\pi$ -back-bonding component of the bond to vary from one configuration to another.

In the orbital diagram (Figure 1.33) if the higher MO be vacant for a complex like  $[\text{CpMo}^0(\text{CO})_2(\text{acetylene})]^+$ , with a  $d^4$  configuration, the barrier to rotation is 62.6 KJ/mol. In  $d^6$  complexes  $[\text{Cp Mo}(\text{CO})_2(\text{acetylene})]^-$  or  $[\text{Cp Fe}(\text{CO})_2(\text{acetylene})]^+$  in which the higher MO was occupied by two electrons causing repulsion

with the molecule and geometry (b) (Figure 1.27) would be more preferred. The calculated barrier in this case would be higher, 110.7 KJ/mol for  $[(\pi\text{-Cp})\text{MoL}_2\text{un}]^-$  and 91.5 KJ/mol for  $[(\pi\text{-Cp})\text{FeL}_2\text{un}]^+$ , (un = acetylene) (121).

Substitution of auxiliary ligands in the molecule or differences of acetylene substituents would vary the electronic nonequivalence of the metal orbitals. If we look at complexes like  $[\text{Cp Mo}(\text{CO})(\text{SC}_6\text{F}_5)(\text{CF}_3\text{C}_2\text{CF}_3)]$  and  $[\text{Cp Mo}(\text{O})(\text{SC}_6\text{F}_5)(\text{CF}_3\text{C}_2\text{CF}_3)]$ , here with the change of one ligand (CO) to (O), the orientation preference would vary (Figure 1.34). In both complexes, the molybdenum atom has approximately octahedral coordination, one site occupied by M-bonded acetylene, one by  $\text{SC}_6\text{F}_5$ , three by  $\text{C}_5\text{H}_5$  and the last by a carbonyl in (a) and an oxygen in (b) (Figure 1.34). In complex (a) acetylene C-C axis is approximately parallel to M-C-O bond axis, but in complex (b) it has turned about  $90^\circ$  to be parallel to M-S bond. The reason for the

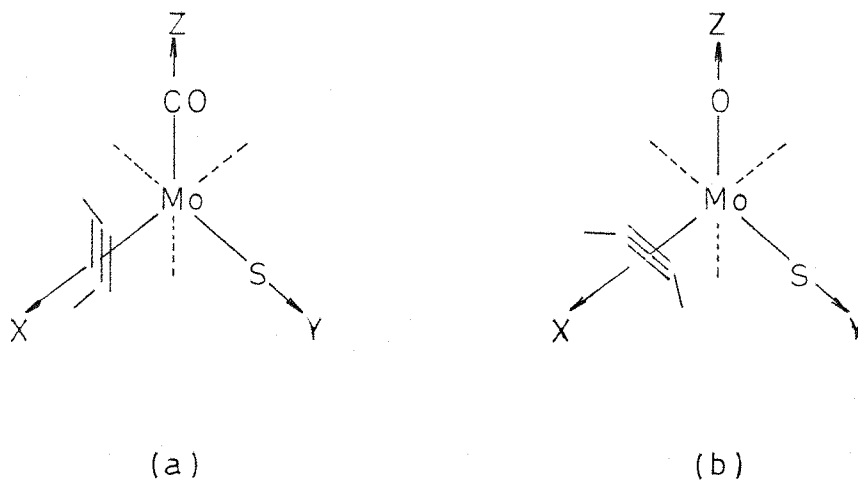


Figure 1.34

different orientation of acetylene is that in first compound the back-donation can occur through  $dxz$  and in the second one through  $dxy$ . In this case, the very short M-O suggests a triple bond. If oxo-ligand donated two electrons into the orbitals hybrid  $d^2sp^3$  in the z direction, then the  $dxz$  and  $dyz$  orbitals can have one electron to make  $\pi$  bond with oxygen leaving two electrons of Mo

in the  $d_{xy}$  which would give a good back donation to acetylene. On the other hand, acetylene can reinforce the M-O bond by donation into  $dx_z$ .

In the first compound, the  $d_{xy}$  would be mostly empty because the four electrons in the  $dx_z$  and  $dy_z$  would give most back donation to CO, so acetylene changes its orientation to donate to an octahedral orbital and use the  $d_{xy}$ . For back donation using the  $dx_z$  would weaken the M-CO bond. In both series, rotation of the acetylene would cause loss of all the metal-acetylene  $\pi$ -bonding and it is not surprising that such rotation is not shown on the n.m.r. time-scale. The  $^{19}\text{F}$  variable-temperature n.m.r. spectrum of  $[\text{CpM}(\text{CO})(\text{CF}_3\text{-C}_2\text{CF}_3)\text{SCF}_3]$ , (M = Mo, W), (117) shows the two signals for the  $\text{CF}_3\text{C}$  groups at high temperature, and an unchanged signal at low temperature, showing non-equivalent  $\text{CF}_3\text{C}$  groups.

The substituent group in the acetylene also would affect the orientation preference of acetylene within the molecule, as expected from a consideration of the relative electron-withdrawing properties of acetylenes.  $\text{C}_2(\text{CO}_2\text{Me})_2$  generally forms particularly stable derivative. In comparing the stabilities of the acetylene complexes, the following order is found:  $\text{PhC}_2\text{Ph} > \text{MeC}_2\text{Me} > \text{CF}_3\text{-C}_2\text{CF}_3 \approx \text{CF}_2\text{C}_2\text{H}$  in the complexes  $[(\eta^5\text{C}_5\text{H}_5)\text{M}(\text{CO})(\text{acetylene})\text{SR}_F]$  (117), the electronic effect of substituents in acetylene would be similar to olefin complexes which was explained above.

The steric factor arises when the ligand sweeps from its lowest energy position. This would happen with bulky acetylene substituents or in the presence of a bulky ligand. In the complexes with a bulky group like Cp, orientation of acetylene is mostly approximately parallel to the  $\eta^5\text{C}_5\text{H}_5$  ring. The variable temperature n.m.r. studies of  $[\text{Cp MoO}(\text{CF}_3\text{C}_2\text{CF}_3)\text{SC}_6\text{F}_5]$  at low temperature showed five non-equivalent fluorines for pentafluorophenyl group which would be associated with a fixed orientation of this group at this temperature; this shows a strong steric interaction of the group with the  $\text{CF}_3$  group, which would affect the rotation of the acetylene in the complex. The steric factor would increase the barrier to rotation.

CHAPTER TWO

EXPERIMENTAL

## 2.1 Introduction

Acetylene iron complexes were prepared in order to measure the barrier to rotation of the acetylene group in the complex. The barrier must neither be very small nor very large since it could not be detected by n.m.r. spectroscopy. The acetylene activation energy or so called barrier to rotation which here has been investigated was in complexes of iron like  $[(\pi\text{-Cp})\text{Fe}(\text{CO})_2(\text{R}_2\text{C}_2)]^+$  when one or two carbonyl groups are replaced by phosphine group. In the dicarbonyl complex there is expected to be a small barrier to rotation when the C-C axis is vertical to the cyclopentadienyl plane; as the only contribution to the barrier is due to the electronic difference between the two acetylene directions and as mostly the rigid position of acetylene is parallel to  $\text{C}_5\text{H}_5$  plane. To observe this one or two small carbonyl groups were replaced by one or two phosphine groups to make two different ends for the acetylene carbons, which could be detected by n.m.r. spectroscopy. In the complex of  $(\pi\text{-Cp})\text{Fe}(\text{CO})_2\text{I}$  one of carbonyl groups was replaced by  $\text{P}(\text{OPh})_3$ ,  $\text{PPh}_3$ ,  $\text{P}(\text{OCH}_3)_3$  or  $\text{P}(\text{OC}_2\text{H}_5)_3$ . Two carbonyl groups were replaced by (P-P), (P'-P') or  $[\text{P}(\text{OPh})_3]_2$ .

In this work acetylenes with different substituents were used with the aim of considering how they affect the barrier to rotation and stability of the complex.

Preparation of the acetylene complexes from irradiation of  $(\eta^4\text{CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{L}$  (L = CO,  $\text{PPh}_3$ ) with  $\text{Ph}_2\text{C}_2$  was attempted. But replacement of carbonyl group by  $\text{Ph}_2\text{C}_2$  by using U.V. light was not very satisfactory because purification of the compounds was difficult. Another way which proved unsatisfactory was the replacement of an olefin by an acetylene in complexes like  $[(\pi\text{-Cp})\text{M}(\text{CO})_2(\text{CH}_2\text{CH}=\text{CH}_2)]^+ \text{X}^-$  (M = Fe, X = Cl,  $\text{BF}_4$ ,  $\text{PF}_6$ ).

## 2.2 Experimental:

The I.R. spectra were recorded on a Perkin-Elmer 580B,  $^1\text{H}$  n.m.r. spectra were recorded on a Perkin-Elmer R12 and Varian XL-100, and the  $^{13}\text{C}$  and  $^{19}\text{F}$  n.m.r. were recorded on a Varian XL-100. TMS was added as



internal reference for  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r.,  $\text{C}_6\text{F}_6$  was added to the sample as a reference in the case of  $^{19}\text{F}$  n.m.r. spectra. The complex  $\text{Cr}(\text{acac})_3$  was used as a relaxation agent in  $^{13}\text{C}$  n.m.r.

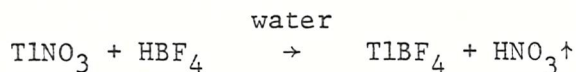
All the solvents were purified, dried and in most cases degassed before being used. The reactions were carried out under an atmosphere of nitrogen.

All the complexes were dried under vacuum.

The U.V. irradiation used a 125 Watt mercury lamp.

$\text{CH}_2\text{Cl}_2$  was dried over  $\text{CaH}_2$ , refluxed under nitrogen and stored for not more than one hour over sodium wire before it was used.

$\text{TlBF}_4$  prepared from reaction between  $\text{TlNO}_3$  and  $\text{HBF}_4$  and  $\text{HNO}_3$  was evaporated away.



2.2.1 Preparation of  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OPh})_3(\text{Ph}_2\text{C}_2)]\text{BF}_4$  (122) from  $\text{Ph}_2\text{C}_2$  and  $(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OPh})_3\text{I}$  (123)

$(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OPh})_3\text{I}$  (0.4g, 0.68 m.mol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (12 ml) and  $\text{AgBF}_4$  (0.152 g, 0.78 m. mol) was added. This mixture was stirred for 30 minutes (the red compound was very air sensitive) before being filtered to remove the  $\text{AgI}\cdot\text{Ph}_2\text{C}_2$  (0.39 g, 2.20 m. mol) was added to the filtrate, this mixture was stirred for 30 minutes and then  $\text{Et}_2\text{O}$  (40 ml) was added. The solvent was reduced in volume by removing it by means of a stream of nitrogen. The remainder was decanted off from the product as red crystals which were washed with  $\text{Et}_2\text{O}$  (10 ml) and dried, yield 0.4037 g (81%). The crystals were air stable and could be stored in closed container in a cool place for months. I.R. ( $\text{CH}_2\text{Cl}_2$ )  $2002.5\text{ cm}^{-1}$  ( $\nu\text{CO}$ ). The  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ )  $\delta$  5.22 (5H, S,  $\text{C}_5\text{H}_5$ ),  $\delta$  6.89 (10H, S,  $\text{Ph}_2\text{C}_2$ ) and  $\delta$  7.23 (15H, M,  $\text{P}(\text{OPh})_3$ ). The  $^{13}\text{C}$  n.m.r. ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  62.2

(C  $\equiv$  C),  $\delta$  82.3 (C<sub>5</sub>H<sub>5</sub>),  $\delta$  88,  $\delta$  121.5, 126.4, 130.7 (Ph's),  $\delta$  150.3 (Ph) and series of solvent peaks at  $\delta$  52.1-56.5. Found: C, 61.4; H, 4.3. Calc.: C, 61.87; H, 4.07%.

2.2.2 Preparation of  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OPh})_3\{(\text{CH}_3)_2\text{C}_2\}]\text{BF}_4$  from  $(\text{CH}_3)_2\text{C}_2$  and  $(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OPh})_3\text{I}$  (123).

$(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OPh})_3\text{I}$  (0.264 g, 0.45 m.mol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (7.92 ml) and AgBF<sub>4</sub> (0.1004 g, 0.67 m.mol) was added. This mixture was stirred for 30 minutes before silver iodide (AgI) was filtered off from the red (air sensitive) solution. To the filtrate (CH<sub>3</sub>)<sub>2</sub>C<sub>2</sub> (0.184 ml, d = 0.691, m = 0.127 g, 2.35 m. mol) was added, the mixture cooled, and then allowed to warm up to 10-15°C, then stirred for one hour. It was filtered and then the filtrate reduced in volume to approximately 7 ml. To the latter Et<sub>2</sub>O (85 ml) was added, or until the solution became cloudy. After two days in the refrigerator the volume of solution was reduced until orange crystals precipitated, recrystallization was from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O, and subsequently dried. The yield was 0.102 g (49%). The orange crystals were air stable and very soluble in polar organic solvents; the complex decomposed in solution. The solid compound was stored for months. I.R. (CH<sub>2</sub>Cl<sub>2</sub>) 2016 cm<sup>-1</sup> (νCO). The <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>)  $\delta$  4.85 (5H, S, C<sub>5</sub>H<sub>5</sub>),  $\delta$  2.25 (6H, S, Me<sub>2</sub>C<sub>2</sub>) and  $\delta$  7.2 [15H, M, P(OPh)<sub>3</sub>]. Found: C, 55.6; H, 4.4. Calc: C, 56.00; H, 4.33%.

2.2.3 Preparation of  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OPh})_3\{(\text{CH}_3\text{OOC})_2\text{C}_2\}]\text{BF}_4$  from  $(\text{CH}_3\text{OOC})_2\text{C}_2$  and  $(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OPh})_3\text{I}$  (123)

$(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OPh})_3\text{I}$  (1.0 g, 1.7 m. mol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (30 ml) and then AgBF<sub>4</sub> (0.39 g, 1.9 m. mol) was added. The mixture was stirred for thirty minutes before silver iodide filtered off. Then (CH<sub>3</sub>OOC)<sub>2</sub>C<sub>2</sub> (0.8 ml, d = 0.992, m = 0.72 g, 5.07 m.mol) was added to the filtrate. The mixture was stirred for two hours, then Et<sub>2</sub>O (ca. 300 ml) was added. The latter was cooled in the refrigerator for two days then solution removed to another flask. After one - two days the yellow-orange crystals were collected and dried. Yield 0.2374 g (20%). The complex was more stable in solution than previous complexes

but far less stable in the solid state. The I.R. ( $\text{CH}_2\text{Cl}_2$ )  $2050.9 \text{ vs cm}^{-1}$  ( $\nu\text{CO}$ ). The  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ )  $\delta$  5.38 (5H, S,  $\text{C}_5\text{H}_5$ ),  $\delta$  3.9 [6H, S,  $(\text{CH}_3\text{OOC})_2\text{C}_2$ ] and  $\delta$  7.3 [15H, M,  $\text{P}(\text{OPh})_3$ ].

2.2.4 Preparation of  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OPh})_3\{(\text{CF}_3)_2\text{C}_2\}] \text{BF}_4$  from  $(\text{CF}_3)_2\text{C}_2$  and  $(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OPh})_3\text{I}$  (123)

$(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OPh})_3\text{I}$  (1.0 g, 1.7 m.mol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (60 ml) and  $\text{AgBF}_4$  (0.38 g, 1.95 m.mol) was added. The mixture was stirred for thirty minutes before being filtered to remove the silver iodide.  $(\text{CF}_3)_2\text{C}_2$  was bubbled through the filtrate for an hour, the solvent was then reduced to 10 ml and then  $\text{Et}_2\text{O}$  (100 ml) added. After two days of being cooled, the deep red crystals were precipitated by solvent volume being reduced, yield 0.2937 g (24%). The I.R. ( $\text{CH}_2\text{Cl}_2$ )  $2002.2 \text{ cm}^{-1}$  ( $\nu\text{CO}$ ). The  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ )  $\delta$  4.38 (5H, S,  $\text{C}_5\text{H}_5$ ),  $\delta$  7.2 (15 H, S,  $\text{P}(\text{OPh})_3$ ). The  $^{19}\text{F}$  n.m.r. ( $\text{CD}_2\text{Cl}_2$ ) 12.25 PPM (ref. to  $\text{C}_6\text{F}_6$ ).

2.2.5 Preparation of  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OPh})_3\{\text{PhC}_2\text{H}\}] \text{BF}_4$  from  $\text{PhC}_2\text{H}$  and  $(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OPh})_3\text{I}$  (123)

$(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OPh})_3\text{I}$  (0.241 g, 0.412 m.mol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (20 ml), then  $\text{AgBF}_4$  (0.092 g, 0.472 m.mol) was added. The mixture was stirred for thirty minutes, then silver iodide was separated by filtration.  $\text{PhC}_2\text{H}$  (0.24 ml,  $d = 0.923$ ,  $m = 0.222 \text{ g}$ , 2.17 m. mol) was added to the filtrate. The mixture was stirred for thirty minutes and left aside for an hour before it was filtered again. The mixture volume was then reduced to 10-15 ml.  $\text{Et}_2\text{O}$  (ca. 60 ml) was added. An oily compound resulted which was recrystallized by  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  (1/8) and deep red compound produced from that was dried. Yield 0.1037 g (39%). I.R. ( $\text{CH}_2\text{Cl}_2$ ) 2020, 2080  $\text{cm}^{-1}$  ( $\nu\text{CO}$ ). The  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ )  $\delta$  5.05 (5H, S,  $\text{C}_5\text{H}_5$ ),  $\delta$  7.25 [20 H, M,  $\text{P}(\text{OPh})_3$  and  $\text{PhC}_2\text{H}$ ].

2.2.6 Preparation of  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{PPh}_3(\text{Ph}_2\text{C}_2)]\text{BF}_4$  from  $\text{Ph}_2\text{C}_2$  and  $(\pi\text{-Cp})\text{Fe}(\text{CO})\text{PPh}_3\text{I}$  (124)

$(\pi\text{-Cp})\text{Fe}(\text{CO})\text{PPh}_3\text{I}$  (0.6 g , 1.115 m.mol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (30 ml), then  $\text{AgBF}_4$  (0.3 g , 1.54 m.mol) and  $\text{Ph}_2\text{C}_2$  (0.6 g , 3.37 m. mol) were added. This reaction was carried out at  $-15$  to  $-20^\circ\text{C}$ . The mixture was stirred for fifteen minutes before silver iodide was filtered off from the solvent. The solvent volume was reduced to 25 ml by removing it by a stream of nitrogen.  $\text{Et}_2\text{O}$  (60 ml) was added. The red-violet crystals were dried. The temperature was very important, the red compound would decompose if the temperature went higher than  $-15^\circ\text{C}$ . These red crystals decomposed to a green compound, while being dried. Yield 0.3347 g, I.R. ( $\text{CH}_2\text{Cl}_2$ )  $1976_{\text{vs}}\text{ cm}^{-1}$  ( $\nu\text{CO}$ ) and  $1550_{\text{m}}\text{ cm}^{-1}$ . The  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ )  $\delta$  5.2 (5H, S,  $\text{C}_5\text{H}_5$ ).  $\delta$  7.22 (25H, M,  $\text{PPh}_3$  and  $\text{Ph}_2\text{C}_2$ ).

2.2.7 Preparation of  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{PPh}_3\{(\text{CH}_3)_2\text{C}_2\}]\text{BF}_4$  from  $(\text{CH}_3)_2\text{C}_2$  and  $(\pi\text{-Cp})\text{Fe}(\text{CO})\text{PPh}_3\text{I}$  (124)

$(\pi\text{-Cp})\text{Fe}(\text{CO})\text{PPh}_3\text{I}$  (0.6 g , 1.115 m.mol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (30 ml).  $\text{AgBF}_4$  (0.3 g , 1.54 m. mol) and  $(\text{CH}_3)_2\text{C}_2$  (0.4 ml,  $d = 0.691$ ,  $m = 0.276$  g , 5.1 m. mol) were added. The reaction was carried out at  $-15^\circ\text{C}$ . The mixture was stirred for fifteen minutes before silver iodide was removed by means of filtration. The filtrate volume was reduced to 25 ml by a stream of nitrogen.  $\text{Et}_2\text{O}$  (60 ml, or until the solution became cloudy) was added. The remainder was decanted off leaving deep red (violet-red) crystals as the product. These were subsequently dried. Yield 0.4441 g (72%), I.R. ( $\text{CH}_2\text{Cl}_2$ )  $1995.5_{\text{vs}}\text{ cm}^{-1}$  ( $\nu\text{CO}$ ). The  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ )  $\delta$  5.12 (5H, S,  $\text{C}_5\text{H}_5$ ),  $\delta$  7.54 (15H, M,  $\text{PPh}_3$ ) and  $\delta$  1.78, 2.45 {6H, S,  $(\text{CH}_3)_2\text{C}_2$ }. Found: C, 60.4; H, 4.6. Calc.: C, 60.8; H, 4.71%.

This complex was very air stable and could be stored in a closed container in a cool place for months. Also, the pure solution was stable up to  $55^\circ\text{C}$ .

2.2.8 Preparation of  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{PPh}_3\{(\text{CH}_3\text{OOC})_2\text{C}_2\}] \text{BF}_4$  from  $(\text{CH}_3\text{OOC})_2\text{C}_2$   
and  $(\pi\text{-Cp})\text{Fe}(\text{CO})\text{PPh}_3\text{I}$  (124)

$(\pi\text{-Cp})\text{Fe}(\text{CO})\text{PPh}_3\text{I}$  (1.0 g , 1.858 m. mol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (40 ml).  $\text{AgBF}_4$  (0.4 g , 2.054 m. mol) and  $(\text{CH}_3\text{OOC})_2\text{C}_2$  (1.0 ml,  $d = 0.992$ ,  $m = 0.992$ , 6.985 m. mol) were added. The mixture was stirred for two hours (the reaction was carried out at  $-15^\circ\text{C}$ ) before it was filtered to remove silver iodide. The filtrate volume was reduced to 20 ml under reduced pressure. Toluene (60 ml) was added to the mixture. The solvent volume was reduced by removing it very slowly by a stream of nitrogen until red crystals precipitated. The crystals were dried. Yield 0.7759 (65%). I.R. ( $\text{CH}_2\text{Cl}_2$ )  $2035.5_{\text{vs}} \text{cm}^{-1}$  ( $\nu\text{CO}$ ),  $1723_{\text{vs}} \text{cm}^{-1}$  ( $\nu\text{C} \equiv \text{C}$ ). The  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ )  $\delta$  5.55 (5H, S,  $\text{C}_5\text{H}_5$ ),  $\delta$  3.36 and 4.05 [6H, S,  $(\text{CH}_3\text{OOC})_2\text{C}_2$ ] and  $\delta$  5.3 (5H, S,  $\text{C}_5\text{H}_5$ ),  $\delta$  3.84 & 4.56 [6H, M,  $(\text{CH}_3\text{OOC})_2\text{C}_2$ ] (The intensity of latter series of peaks was one third of those of the former) and  $\delta$  7.55 (15H, M,  $\text{PPh}_3$ ). The  $^{13}\text{C}$  n.m.r. has resonances at  $\delta$  64 PPM ( $\text{C} \equiv \text{C}$ ),  $\delta$  91.6 ( $\text{C}_5\text{H}_5$ ),  $\delta$  130.2 and 132.6 (Ph's),  $\delta$  149.6 (CO) and series of peaks  $\delta$  51.5 - 56 ( $\text{CD}_2\text{Cl}_2$ ).

The crystals were air stable in the solid state and could be stored in a closed container (in the cold) for months, and it was stable in solution up to  $52^\circ\text{C}$ . It is more soluble and less stable in methylene chloride than in chloroform. Found: C, 54.5; H, 4.2. Calc.: C, 56.25; H, 4.02%.

2.2.9 Attempted preparation of  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{PPh}_3\{(\text{CF}_3)_2\text{C}_2\}] \text{BF}_4$   
from  $(\text{CF}_3)_2\text{C}_2$  and  $(\pi\text{-Cp})\text{Fe}(\text{CO})\text{PPh}_3\text{I}$  (124)

$(\pi\text{-Cp})\text{Fe}(\text{CO})\text{PPh}_3\text{I}$  (0.2143 g , 0.398 m. mol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (20 ml) and  $\text{AgBF}_4$  (0.15 g , 0.76 m. mol) was added. The mixture was stirred for ten minutes before being treated with a stream of  $(\text{CF}_3)_2\text{C}_2$  for an hour. The reaction was carried out at  $-15^\circ\text{C}$  and the intermediate was a red compound. The mixture was left in the refrigerator for two days before silver iodide was removed by filtration.

Et<sub>2</sub>O (60 ml) was added to the filtrate. A dark red compound precipitated as the product which was subsequently dried. Yield 0.045 g (17%). The purification of the product was very difficult. Several recrystallizations from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O resulted in a red-brown compound which had a very broad <sup>1</sup>H n.m.r. spectrum. This compound was not stable and decomposed to a brown compound.

2.2.10 Preparation of (π-Cp)Fe(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>) I (123) from dppe and (π-Cp)Fe(CO)<sub>2</sub>I (125)

(π-Cp)Fe(CO)<sub>2</sub>I (1.2 g, 3.94 m. mol) was dissolved in C<sub>6</sub>H<sub>6</sub> (40 ml) and dppe (1.46 g, 3.67 m. mol) was added. The mixture was refluxed for twenty four hours (temperature 78°C) before it was filtered hot. The filtrate was dried and then dissolved in methylene chloride (minimum volume) and heptane was added until the solution was rather cloudy. The dark grey (or black) crystals were dried. Yield 0.8851 g (36%). I.R. (CH<sub>2</sub>Cl<sub>2</sub>) 1603<sub>m</sub> cm<sup>-1</sup>, 1570<sub>w</sub> cm<sup>-1</sup>, 1481<sub>s</sub> cm<sup>-1</sup>. The <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>) δ 2.5 {4H, Br, (CH<sub>2</sub>CH<sub>2</sub>) of dppe}, δ 4.15 (5H, S, C<sub>5</sub>H<sub>5</sub>) and δ 7.3, 7.9 (20 H, M, Ph's of dppe). Found: C, 54.6; H, 4.5. Calc.: C, 57.58; H, 4.489%.

Two other compounds were prepared from the experiment. Firstly a yellow compound which collected on the filter and secondly a green-yellow compound which was collected from the cold filtrate as the solution was decanted off and left the green compound behind. The latter was recrystallized from chloroform/heptane. I.R. (CH<sub>2</sub>Cl<sub>2</sub>) 1976<sub>vs</sub> cm<sup>-1</sup> (νCO).

The yellow compound was recrystallized from CHCl<sub>3</sub>/Et<sub>2</sub>O. The crystals were dried. Yield 1.2444 g (49%). I.R. (CH<sub>2</sub>Cl<sub>2</sub>) 2056<sub>s</sub> cm<sup>-1</sup> and 2009<sub>s</sub> cm<sup>-1</sup> (νCO). The <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>) δ 2.8 (4H, Br, CH<sub>2</sub>CH<sub>2</sub> of dppe), δ 4.8 (5H, S, C<sub>5</sub>H<sub>5</sub>) and δ 7.4 (20 H, M, Phs of dppe). The compound was air stable.

The black crystals were air stable and could be stored in a closed container for a year.

The compound  $(\pi\text{-Cp})\text{Fe}(\text{P}'\text{-P}')\text{I}$  was attempted to make this way. A dark red compound was resulted as the product. The  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ )  $\delta$  1.54,  $\delta$  1.73 {16H, Br, protons of (P'-P') group},  $\delta$  4.43 (5H, Br,  $\text{C}_5\text{H}_5$ ). This preparation was also tried from the reaction between  $(\pi\text{-Cp})\text{Fe}[\text{P}(\text{OPh})_3]_2\text{I}$  (2.2.16) and (P'-P'). The  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ )  $\delta$  1.55,  $\delta$  17.6 {16H, Br, protons of (P'-P') group},  $\delta$  4.3 (5H, v. Br,  $\text{C}_5\text{H}_5$ ) and also  $\delta$  7.2 { 30H, M,  $[\text{P}(\text{OPh})_3]_2$  } which must be from impurity.

2.2.11 Preparation of  $(\pi\text{-Cp})\text{Fe}(\text{P-P})\text{Br}$  (126) from dppe and  $(\pi\text{-Cp})$   
 $\text{Fe}(\text{CO})_2\text{Br}$  (125)

$(\pi\text{-Cp})\text{Fe}(\text{CO})_2\text{Br}$  (0.5 g , 1.945 m. mol) was dissolved in  $\text{C}_6\text{H}_6$  (80 ml) and dppe (0.5 g , 1.256 m. mol) added. The solution was irradiated with U.V. light for six hours before it was filtered leaving a yellow residue. I.R. ( $\text{CH}_2\text{Cl}_2$ )  $2050_{\text{vs}}$ ,  $2003.9_{\text{s}}\text{ cm}^{-1}$  ( $\nu\text{CO}$ ). The filtrate was dried. The mixture was dissolved in methylene chloride (minimum volume) and then heptane or hexane (7 ml) added. The solvent volume was reduced by removing it by a stream of nitrogen until the solution became cloudy. A dark green compound was precipitated. The solution was dried, dissolved in chloroform and heptane then added, and green crystals precipitated which were subsequently dried. I.R. ( $\text{CH}_2\text{Cl}_2$ )  $1950\text{ cm}^{-1}$  ( $\nu\text{CO}$ ). The  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ )  $\delta$  2.4 (4H, Br,  $\text{CH}_2\text{CH}_2$ ),  $\delta$  4.17 (5H, Br,  $\text{C}_5\text{H}_5$ ) and  $\delta$  8.2 (20H, M,  $\text{Ph}_4$ ). The remainder was dried and the black crystals were crystalized using methylene chloride/hexane. The complex was dried. Yield 0.6532 g (56%). I.R. ( $\text{CH}_2\text{Cl}_2$ )  $1600_{\text{m}}$ ,  $1575_{\text{w}}$ ,  $1479_{\text{s}}\text{ cm}^{-1}$ . The  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ )  $\delta$  2.4 (4H, Br,  $\text{CH}_2\text{CH}_2$ ),  $\delta$  4.35 (5H, S,  $\text{C}_5\text{H}_5$ ) and  $\delta$  7.35,  $\delta$  7.23 (20H, M,  $\text{Ph}_4$ ).

Preparation of the complexes  $(\pi\text{-Cp})\text{Fe}(\text{P-P})\text{X}$  (X=Cl, I) in this way was unsuccessful.

2.2.12 Preparation of  $[(\pi\text{-Cp})\text{Fe}(\text{P-P})\{(\text{CH}_3)_2\text{C}_2\}] \text{BF}_4$  from  $(\text{CH}_3)_2\text{C}_2$  and  
 $(\pi\text{-Cp})\text{Fe}(\text{P-P})\text{I}$  (2.2.10)

$(\pi\text{-Cp})\text{Fe}(\text{P-P})\text{I}$  (1.0 g, 1.547 m. mol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (60 ml).

AgBF<sub>4</sub> (0.4133 g , 2.12 m.mol) and (CH<sub>3</sub>)<sub>2</sub>C<sub>2</sub> (0.5 ml, 0.345 g , 6.39 m. mol) were added. The reaction was carried out at -15°C. The mixture was stirred for thirty minutes. After one and a half hours silver iodide was filtered off. The solvent volume was reduced to 25 ml and toluene (22 ml) added. The mixture was left for two days in a refrigerator and for another two days at room temperature before being transferred to another container. Toluene was added dropwise until the solution became cloudy. Red crystals precipitated upon cooling. These crystals were then dried. Yield 0.1569 (15%). I.R. (CH<sub>2</sub>Cl<sub>2</sub>) 1712<sub>m</sub> (νC≡C), 1602<sub>m</sub> , 1480<sub>m</sub> , 1056.4<sub>vs</sub> cm<sup>-1</sup> (νBF<sub>4</sub>). The <sup>1</sup>H n.m.r. of the compound was very broad.

Another orange compound was precipitated here which has an I.R. (CH<sub>2</sub>Cl<sub>2</sub>) 1976.4<sub>s</sub> (νCO), 1056.6<sub>vs</sub> cm<sup>-1</sup> (νBF<sub>4</sub>).

2.2.13 Preparation of [(π-Cp)Fe(P-P){(CH<sub>3</sub>)<sub>2</sub>C<sub>2</sub>}] BF<sub>4</sub> from (CH<sub>3</sub>)<sub>2</sub>C<sub>2</sub> and (π-Cp)Fe(P-P)I (2.2.10), using TlBF<sub>4</sub>.

(π-Cp)Fe(P-P)I (0.15 g , 0.232 m.mol) was dissolved in acetone (20 ml) and TlBF<sub>4</sub> (0.187 g , 0.63 m.mol) and (CH<sub>3</sub>)<sub>2</sub>C<sub>2</sub> (0.3 ml, 0.2073 g , 3.83 m.mol) added. The same method as that used in (2.2.12) was followed. The red crystals were dried. Yield 0.2932 g (29%). I.R. (CH<sub>2</sub>Cl<sub>2</sub>) 1710.7<sub>m</sub> (νC≡C), 1600<sub>w</sub> , 1483<sub>m</sub> , 1057.3<sub>vs</sub> cm<sup>-1</sup> (νBF<sub>4</sub>). The <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>) δ 2.25 {δH,S,(CH<sub>3</sub>)<sub>2</sub>C<sub>2</sub>} , δ 2.98, 3.32 (4H,v.Br, CH<sub>2</sub>CH<sub>2</sub>), δ 4.56 (5H,v.Br,C<sub>5</sub>H<sub>5</sub>) and δ 7.2 (20H,M,Ph<sub>4</sub> of dppe). Found: C, 63.2; H, 5.3. Calc.: C, 63.63; H, 5.3%.

The red(blood-red) complex was very air stable and could be stored in the solid state for several months and was easily recrystallized from methylene chloride.

2.2.14 Preparation of [(π-Cp)Fe (P-P){(CH<sub>3</sub>OOC)<sub>2</sub>C<sub>2</sub>}] BF<sub>4</sub> from (CH<sub>3</sub>OOC)<sub>2</sub>C<sub>2</sub> and (π-Cp) Fe(P-P)I (2.2.10)

(π-Cp)Fe(P-P)I (0.634 g , 0.98 m.mol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (40 ml). AgBF<sub>4</sub> (0.2 g , 1.027 m.mol) or TlBF<sub>4</sub> (0.72 g , 2.3 m.mol)



and  $(\text{MeOOC})_2\text{C}_2$  (0.5 ml, 0.496 g, 3.497 m.mol) were added. The mixture was stirred for fifteen minutes and left for two hours before it was filtered to separate silver iodide. The reaction was carried out at  $-15^\circ\text{C}$ . Methylene chloride/toluene was used to crystallize the complex (the same procedure as that used in (2.2.10) was followed). The red crystals were dried. When  $\text{TlBF}_4$  was used the yield was 0.1692 g (23%). In the case of using silver tetrafluoroborate the yield was very small. I.R. ( $\text{CH}_2\text{Cl}_2$ )  $1724_{\text{s}}$  ( $\nu\text{C}\equiv\text{C}$ ),  $1605_{\text{w}}$ ,  $1484_{\text{m}}$ ,  $1059.5_{\text{vs}}\text{cm}^{-1}$  ( $\nu\text{BF}_4$ ). The  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ )  $\delta$  2.25 [6H, S,  $(\text{CH}_3\text{OOC})_2\text{C}_2$ ],  $\delta$  2.7 (4H, M,  $\text{CH}_2\text{CH}_2$ ),  $\delta$  4.3 (5H, Br,  $\text{C}_5\text{H}_5$ ) and  $\delta$  7.15 (20H, M,  $\text{Ph}_4$ ). Found: C, 59.7; H, 4.7. Calc.: C, 59.35; H, 4.68%. The red complex was very air stable.

An orange compound which also precipitated from this reaction had I.R. bands at ( $\text{CH}_2\text{Cl}_2$ )  $1976.5_{\text{s}}$  ( $\nu\text{CO}$ ),  $1605_{\text{w}}$ ,  $1484_{\text{m}}$ ,  $1059_{\text{vs}}\text{cm}^{-1}$  ( $\nu\text{BF}_4$ ) and was air stable.

2.2.15 Preparation of  $[(\pi\text{-Cp})\text{Fe}(\text{P-P})(\text{CF}_3)_2\text{C}_2]\text{BF}_4$  from  $(\text{CF}_3)_2\text{C}_2$  and  $(\pi\text{-Cp})\text{Fe}(\text{P-P})\text{I}$  (2.2.10)

$(\pi\text{-Cp})\text{Fe}(\text{P-P})\text{I}$  (0.5 g, 0.773 m.mol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (30 ml) and  $\text{AgBF}_4$  (0.16 g, 0.82 m.mol) added. The mixture was stirred while the stream of  $(\text{CF}_3)_2\text{C}_2$  was passed through for ten minutes. After an hour the silver iodide was filtered off. The solution volume was reduced to 20 ml and  $\text{Et}_2\text{O}$  added until a red-orange compound precipitated as the product. The crystals were dried. Yield 0.0788 g (13%). I.R. ( $\text{CH}_2\text{Cl}_2$ )  $1756_{\text{s}}$  ( $\nu\text{C}\equiv\text{C}$ )  $1602_{\text{m}}$ ,  $1486_{\text{s}}$ ,  $1058.9_{\text{vs}}\text{cm}^{-1}$  ( $\nu\text{BF}_4$ ). The  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ )  $\delta$  2.9 (4H, Br,  $\text{CH}_2\text{CH}_2$ ),  $\delta$  4.55 (5H, v.Br,  $\text{C}_5\text{H}_5$ ) and  $\delta$  7.32 (20H, M,  $\text{Ph}_4$ ). Found: C, 54.8; H, 3.9. Calc: C, 54.68; H, 3.77%. The complex was air stable and could be stored for several months.

An orange compound was also produced which had I.R. bands at ( $\text{CH}_2\text{Cl}_2$ )  $1973.73_{\text{s}}$  ( $\nu\text{CO}$ ),  $1604_{\text{m}}$ ,  $1486_{\text{m}}$ ,  $1058_{\text{vs}}\text{cm}^{-1}$  ( $\text{BF}_4$ ).

2.2.16 Preparation of  $(\pi\text{-Cp})\text{Fe}[\text{P}(\text{OPh})_3]_2\text{I}$  (127) from  $\text{P}(\text{OPh})_3$  and  $(\pi\text{-Cp})\text{Fe}(\text{CO})_2\text{I}$  (125)

$(\pi\text{-Cp})\text{Fe}(\text{CO})_2\text{I}$  (2.0 g , 6.58 m.mol) was dissolved in  $\text{C}_6\text{H}_6$  (25 ml) and  $\text{P}(\text{OPh})_3$  (5.12 ml,  $d = 1.84$ , 6.06 g , 19.36m.mol) added. The mixture was stirred while being irradiated by U.V. light for ten hours before it was dried. The latter was eluted by  $\text{C}_6\text{H}_6/\text{P.E.}$  (80-100°C) (7:3) on an alumina chromatography column. The deep red solution was dried and the compound crystallized using methylene chloride/heptane (1:1). I.R. ( $\text{CH}_2\text{Cl}_2$ ) 1590<sub>s</sub>, 1490<sub>s</sub>, 1420<sub>vs</sub>, 1270<sub>vs</sub>, 1200<sub>vs</sub>, 910<sub>vs</sub>. The  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ )  $\delta$  3.93 (5H, s,  $\text{C}_5\text{H}_5$ ) and  $\delta$  7.2 [30H, m,  $\text{P}(\text{OPh})_3$ ]. The complex was very air stable and could be stored for more than a year. Found: C, 57.4; H, 4.0. Calc.: C, 56.68; H, 4.0%.

The green compound which precipitated from a methylene chloride solution of the red crystals after two days had I.R. bands at ( $\text{CH}_2\text{Cl}_2$ ) 1590<sub>s</sub>, 1490<sub>s</sub>, 1200<sub>vs</sub>, 912<sub>vs</sub>.

2.2.17 Attempted preparation of  $\{(\pi\text{-Cp})\text{Fe}[\text{P}(\text{OPh})_3]_2[(\text{CH}_3)_2\text{C}_2]\}\text{BF}_4$  from  $(\text{CH}_3)_2\text{C}_2$  and  $(\pi\text{-Cp})\text{Fe}[\text{P}(\text{OPh})_3]_2\text{I}$  (2.2.16)

$(\pi\text{-Cp})\text{Fe}[\text{P}(\text{OPh})_3]_2\text{I}$  (0.3056 g , 0.538 m.mol) was dissolved in acetone (20 ml) .  $\text{TlBF}_4$  (0.2389 g , 0.8168 m.mol) and  $(\text{CH}_3)_2\text{C}_2$  (0.2 ml, 2.55 m.mol) were added. The mixture was stirred for twenty minutes before being filtered to remove thallium iodide. The red solution volume was reduced by a stream of nitrogen until a green compound precipitated as the result of decomposition of the compound. The solvent was removed under reduced pressure and methylenechloride/toluene used for recrystallisation. The crystallisation of the compound proved very difficult and this resulted in a green compound precipitating. I.R. ( $\text{CH}_2\text{Cl}_2$ ) 1589<sub>s</sub>, 1498<sub>s</sub>, 1050.5<sub>vs</sub> ( $\nu\text{BF}_4$ ). The  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ ) spectrum was very broad.

2.2.18 Preparation of  $(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OCH}_3)_3\text{I}$  from  $\text{P}(\text{OCH}_3)_3$  and  $(\pi\text{-Cp})\text{Fe}(\text{CO})_2\text{I}$  (125).

$(\pi\text{-Cp})\text{Fe}(\text{CO})_2\text{I}$  (1.0 g, 3.289 m.mol) was dissolved in  $\text{C}_6\text{H}_6$  (20 ml) and  $\text{P}(\text{OCH}_3)_3$  (0.39 ml,  $d = 1.052$ , 3.211 m.mol) added. The mixture was stirred while being refluxed for twenty one hours ( $79^\circ\text{C}$ ) before being filtered hot. The solution was removed and  $\text{CHCl}_3/\text{P.E.}$  ( $80\text{-}100^\circ\text{C}$ ) used for the crystallisation. The green compound was washed by P.E. and then dried. For recrystallisation of the compound  $\text{CH}_2\text{Cl}_2/\text{P.E.}$  ( $80\text{-}100^\circ\text{C}$ ) was used. I.R. ( $\text{CH}_2\text{Cl}_2$ )  $1977.9_{\text{s}}$  ( $\nu\text{CO}$ )  $1422_{\text{vs}}$   $\text{cm}^{-1}$ . The  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ )  $\delta$  3.53,  $\delta$  3.72 {9H,S, protons of  $\text{P}(\text{OCH}_3)_3$ },  $\delta$  4.62 (5H,S,  $\text{C}_5\text{H}_5$ ).

The crystals were air stable and very soluble in polar organic solvents and were stable in  $\text{CDCl}_3$  for several days.

2.2.19 Attempted preparation of  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OCH}_3)_3\{(\text{CH}_3)_2\text{C}_2\}]\text{BF}_4$  from  $(\text{CH}_3)_2\text{C}_2$  and  $(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OCH}_3)_3\text{I}$  (2.2.18).

$(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OCH}_3)_3\text{I}$  (0.3 g 0.75 m.mol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (15 ml) and  $\text{AgBF}_4$  (0.2 g, 1.02 m.mol) and  $(\text{CH}_3)_2\text{C}_2$  (0.2 ml, 2.55 m.mol) added. The mixture was stirred for forty-five minutes before being filtered to remove silver iodide. The filtrate was concentrated to 10 ml and the orange crystals precipitated by dropwise addition of diethyl ether. The crystals were dried. Yield 0.072 (21%). I.R. ( $\text{CH}_2\text{Cl}_2$ )  $2003.3$  ( $\nu\text{CO}$ )  $\text{cm}^{-1}$ . The  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ )  $\delta$  1.26 [6H, slightly Br,  $(\text{CH}_3)_2\text{C}_2$ ],  $\delta$  3.8 [9H,Br,  $\text{P}(\text{OCH}_3)_3$ ],  $\delta$  5.3 (5H,Br,  $\text{C}_5\text{H}_5$ ) and  $\delta$  0.88.

2.2.20 Attempted preparation of  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OMe})_3\{(\text{MeOOC})_2\text{C}_2\}]\text{BF}_4$  from  $(\text{MeOOC})_2\text{C}_2$  and  $(\pi\text{-Cp})\text{Fe}(\text{O})\text{P}(\text{OMe})_3\text{I}$  (2.2.18)

$(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OMe})_3\text{I}$  (0.3g, 0.75 m.mol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (15 ml) and  $\text{AgBF}_4$  (0.2 g, 1.02 m.mol) and  $(\text{MeOOC})_2\text{C}_2$  (0.37 ml, 2.58 m.mol) added (method as in (2.2.19)). The yellow crystals were

dried. Yield 0.802 g (20%). I.R. ( $\text{CH}_2\text{Cl}_2$ )  $2052.8_{\text{m}} \text{cm}^{-1}$  ( $\nu\text{CO}$ ),  $17.27_{\text{m}} \text{cm}^{-1}$  ( $\nu\text{C}\equiv\text{C}$ ). The  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ )  $\delta$  2.4 [6H, Br,  $\{(\text{MeOOC})_2\text{C}_2\}$ ],  $\delta$  3.65 [9H, Br,  $\{\text{P}(\text{OMe})_3\}$ ] and the  $\text{C}_5\text{H}_5$  peak was very broad.

### 2.3 Chemistry of the Synthesised Acetylene Complexes

The synthesis and characterization of acetylene iron complexes in Figure 2.1 are reported.

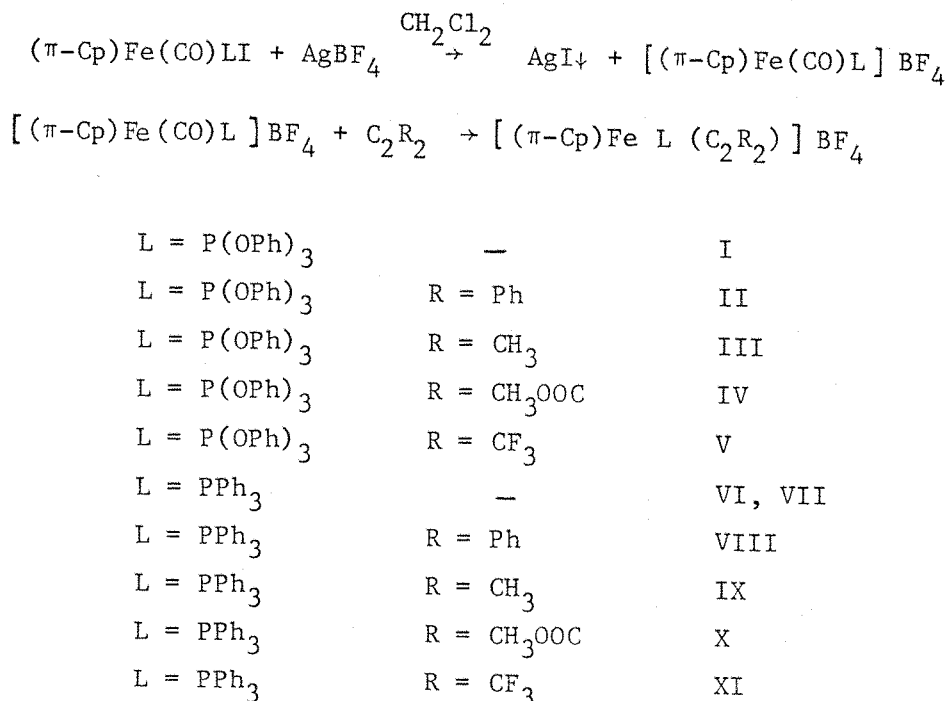


Figure 2.1

A green CH<sub>2</sub>Cl<sub>2</sub> solution of (π-Cp)Fe(CO)P(OPh)<sub>3</sub> I was reacted for 30 minutes with AgBF<sub>4</sub> (about equimolar), and the solution slowly turned red, due to the preparation of the cationic 16-electron species [(π-Cp)Fe(CO)P(OPh)<sub>3</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup> (I). This intermediate is air sensitive and the solution rapidly turned brown when exposed to air. However, it was quite stable in the absence of oxygen. This intermediate could react with incoming acetylene ligands. The red CH<sub>2</sub>Cl<sub>2</sub> solution of (I) was separated from AgI by filtration. This solution reacted with Ph<sub>2</sub>C<sub>2</sub> to give red crystals of (II). This new complex with 18-electrons is an air stable complex in the solid, but in solution it decomposed and a brown compound precipitated. [(π-Cp)Fe(CO)P(OPh)<sub>3</sub>(Ph<sub>2</sub>C<sub>2</sub>)]<sup>+</sup> (II) has a carbonyl stretching frequency at 2024<sub>s</sub> cm<sup>-1</sup>, ν(C≡C) at 1715 cm<sup>-1</sup> and BF<sub>4</sub> group at 1050<sub>vs</sub> cm<sup>-1</sup>. Its <sup>1</sup>H n.m.r. spectrum has a resonance at δ5.22 (5H, s, C<sub>5</sub>H<sub>5</sub>) and a multiplet at δ6.89 - 7.23 due to the phenyl protons. The CH<sub>2</sub>Cl<sub>2</sub>

solution of (II) after being heated to 50°C gave a yellow solution with I.R. bands at 2076.6, 2035.6 and 1985.5  $\text{cm}^{-1}$ . The reaction of the red  $\text{CH}_2\text{Cl}_2$  solution of (I) and  $(\text{CH}_3)_2\text{C}_2$  and  $(\text{MeOOC})_2\text{C}_2$  is slower than its reaction with  $\text{Ph}_2\text{C}_2$ , the reaction was completed after stirring for one hour for  $(\text{CH}_3)_2\text{C}_2$  and for  $(\text{CH}_3\text{COO})_2\text{C}_2$  after one hour stirring the solution was left for two or three days until yellow crystals appeared. The orange crystals (III) are stable in the solid and decomposition occurred after one year, but the dried yellow complex (IV) decomposed after one month in a closed container, but this complex is stable in solution for days. Light accelerated the decomposition. The I.R. spectrum contained one CO peak for each at 2016 (III) and 2050.9 (IV)  $\text{cm}^{-1}$ . The  $^1\text{H}$  n.m.r. of (III) contains a singlet at  $\delta$  2.25 due to the acetylene methyl protons indicating free rotation for the acetylene at room temperature (Figure 2.2) and also a singlet for  $\text{C}_5\text{H}_5$  and a multiplet for the  $\text{P}(\text{OPh})_3$ . The structure of these complexes may be described as (Figure 2.2) pseudo-octahedral, with three sites occupied by  $\text{C}_5\text{H}_5$  and one by CO group and one by  $\text{P}(\text{OPh})_3$  and the last one by acetylene group as it is parallel to  $\text{C}_5\text{H}_5$  plane; this would require rapid rotation of the acetylene at room temperature. The I.R. spectrum of the yellow complex (IV) showed a CO stretching frequency at 2050.9 which shows a clear increase in the CO bond strength compared with complexes of III and II (2016 III < 2024 II < 2050.9 IV).

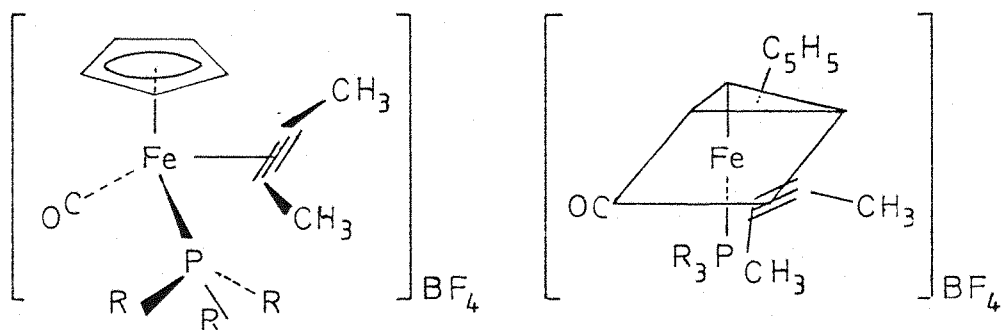


Figure 2.2 The structure of acetylene complexes of  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{L}(\text{acetylene})]^+\text{BF}_4^-$   
 $\text{L} = \text{P}(\text{OPh})_3, \text{PPh}_3$

The chemical shift changes of the  $C_5H_5$  proton resonance for different acetylenes are in the order  $\delta$  4.85 III <  $\delta$  5.22 II <  $\delta$  5.38 IV which suggests the  $(MeOOC)_2C_2$  affects the central atom more than the other acetylenes and changes its electron density. The  $^1H$  n.m.r. of the brown-red complex V which was prepared in this way showed resonances for  $C_5H_5$  at  $\delta$  4.38 and for  $P(OPh)_3$  at  $\delta$  7.2 and a (CO) stretching frequency at  $2002.3\text{ cm}^{-1}$  showed weakest C-O bond of this series. This would not be accountable by the withdrawing of electron from the central atom by the highly electronegative group in the acetylene substituent, which would reduce the back donation from the central atom to the CO group. This may suggest the dissociation of acetylene from the compound in the solution. But in the literature a weaker CO bond was mentioned for complex of  $(\pi-Cp)Ru(CO)PPh_3 [C(CF_3) = CMe(CF_3)]$  at  $1896\text{ (}\nu CO\text{)}$  in comparison with the CO stretching frequency in the complex  $(\pi-Cp)Ru(CO)PPh_3 [C(CO_2Me) = CH(CO_2Me)]$  at  $1951\text{ cm}^{-1}$ . However a  $(\nu CO)$  band at  $1970\text{ cm}^{-1}$  is reported for  $(\pi-Cp)Ru(CO)PPh_3 [C(CF_3) = CH(CF_3)]$  (128).  $^{19}F$  n.m.r. spectrum of the complex V showed a resonance at 12.25 PPM which belongs to the  $BF_4$  group. It is not exactly clear if the  $(CF_3)_2C_2$  peak was missed or there was not any acetylene group in the complex in solution. The preparations of the triphenylphosphite iron complexes were easier than those of  $PPh_3$  and  $Ph_2PCH_2CH_2PPh_2$ , because as the intermediate is sufficiently stable to separate AgI from the reaction before addition of the acetylene, avoiding unwanted side reactions.

The green  $CH_2Cl_2$  solution of compound VI (Figure 2.1) immediately turned bright green, when reacted with  $AgBF_4$ , but this 16-electron intermediate compound is very unstable. To make the acetylene complexes of this intermediate there must be acetylene available as it is formed. Then the acetylene must be added the same time or before the  $AgBF_4$ . Then at the same time as  $[(\pi-Cp)Fe(CO)PPh_3]BF_4$  is formed, it reacts with the acetylene, otherwise this compound would react quickly with a CO group and make  $[(\pi-Cp)Fe(CO)_2PPh_3]BF_4$ . The reactions were carried at  $-15^\circ C$  or below to prevent decomposition of the intermediate until after 20 minutes reaction time. But the red compound VIII was very unstable itself and decomposed when the temperature rose above  $-10^\circ C$  during drying. The

red-purple complex IX and red complex X were prepared in good yield and are stable in the solid. The reaction with  $(CF_3)_2C_2$  failed as the red product decomposed to a brown-red compound. In complex IX, the I.R. showed one stretching frequency at  $1995.5\text{ cm}^{-1}$  for the (CO) group and the  $^1H$  n.m.r. at room temperature showed a multiplet at  $\delta$  7.54 for the  $PPh_3$ , a peak at  $\delta$  5.12 for the  $C_5H_5$  and two peaks at  $\delta$  1.78 and 2.45 for the  $CH_3$  group of acetylene. This suggests no rotation of the acetylene at room temperature, a higher temperature than that required by the similar complex of the  $P(OPh)_3$  ligand. But for the complex X there is a higher stretching frequency for the CO group at  $2035.4\text{ cm}^{-1}$  and there are two peaks for the  $C_5H_5$  at  $\delta$  5.55 and 5.3 (the  $^1H$  n.m.r. at room temperature) two peaks for the  $(MeOOC)_2$  protons at  $\delta$  3.36 and 4.05 and another two peaks with intensity 1/5 to two previous peaks at  $\delta$  3.84, 4.56. This may suggest two different structures for complex, with the acetylene in vertical and horizontal position with respect to the cyclopentadienyl plane (Figure 2.3). As the  $^1H$  n.m.r spectra may suggest, they exist along side each

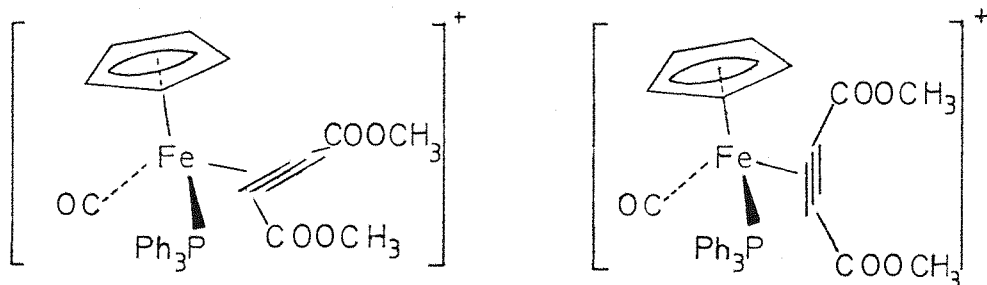


Figure 2.3 Two different configurations of the  $[(\pi-Cp)Fe(CO)PPh_3-((CH_3COO)_2C_2)]^+ BF_4^-$ .

other from below  $-50^\circ C$  to about  $50^\circ C$ . This behaviour of this complex may depend to magnitude of the acetylene substituent group.

Preparation of acetylene complexes of  $(\pi-Cp) Fe(Ph_2PCH_2CH_2PPh_2)X$

XII X = I

XIII X = Br

X = Cl



The complex  $(\pi\text{-Cp})\text{Fe dppe X}$  was prepared by heating of the  $(\pi\text{-Cp})\text{Fe}(\text{CO})_2 \text{X}$  and dppe when  $\text{X} = \text{I}$  (Figure 2.4). The dark brown  $\text{C}_6\text{H}_6$  solution of  $(\pi\text{-Cp})\text{Fe}(\text{CO})_2\text{I}$  turned to a black reaction mixture after being refluxed for 24 hours with dppe. The yellow (B) compound was

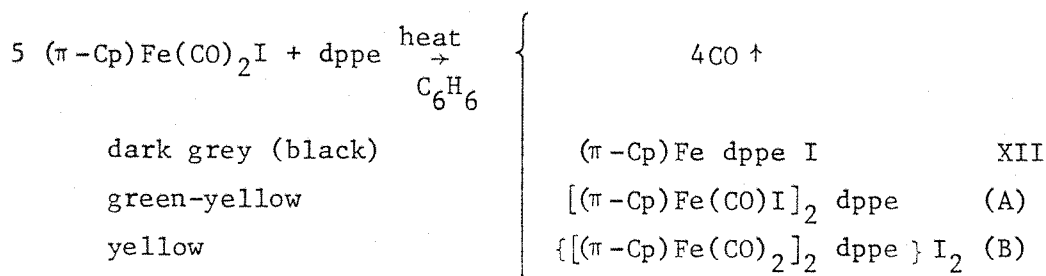
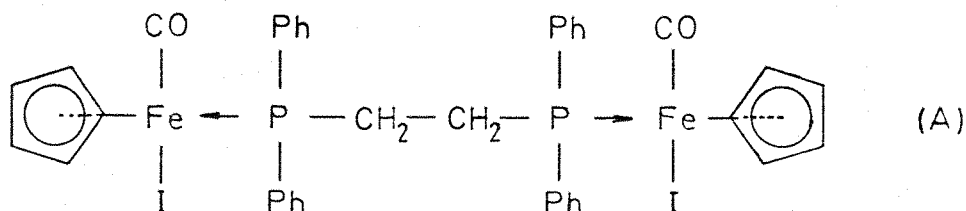


Figure 2.4

collected on the filter. The I.R. of this compound showed two stretching frequencies at  $2056_{\text{s}}$  and  $2009_{\text{s}}\text{cm}^{-1}$ , which would agree with formula mentioned. The  $^1\text{H}$  n.m.r. contained a resonance at  $\delta 2.8$  ( $4\text{H}, \text{S}, \text{CH}_2$ ), one peak due to the ten protons of  $\text{C}_5\text{H}_5$  at  $\delta 4.8$  and at  $7.4$  due to twenty protons of the phenyl groups. The compound(B) is most insoluble in non polar organic solvents such as  $\text{C}_6\text{H}_6$  because it is ionic. The yellow colour of (B) would agree with the absence of an iron-iodine covalent bond (129). This compound with a yield of 49%, accounts for most of the isolated products of this route. From the very dark green filtrate a green compound precipitates which could be identified as (A) having a Fe-I covalent bond. It showed a CO stretching frequency at  $1976_{\text{vs}}\text{cm}^{-1}$  but was obtained in very small yield.



The dark grey (black) complex which made up 36% of all products appears to have an iron-halogen covalent bond. It showed no CO stretching frequency. This complex probably has a structure XII similar to that shown in (Figure 2.5). Its  $^1\text{H}$  n.m.r. spectrum showed two phenyl peaks at  $\delta 7.3$  and  $7.9$ , equivalent protons for the  $\text{C}_5\text{H}_5$  at  $\delta 4.15$  and a broad peak at  $\delta 2.5$  for the methylene protons, consistent

with that structure, as two phenyls are near to the cyclopentadienyl group and two others are near the iodine. This compound is very

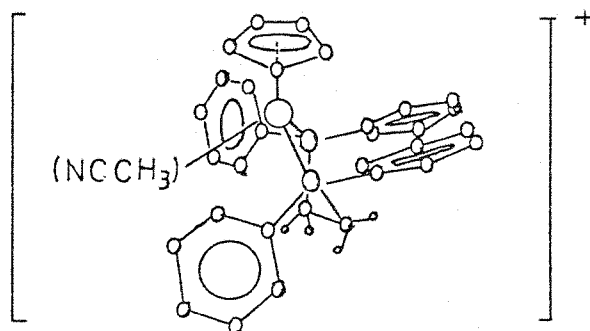
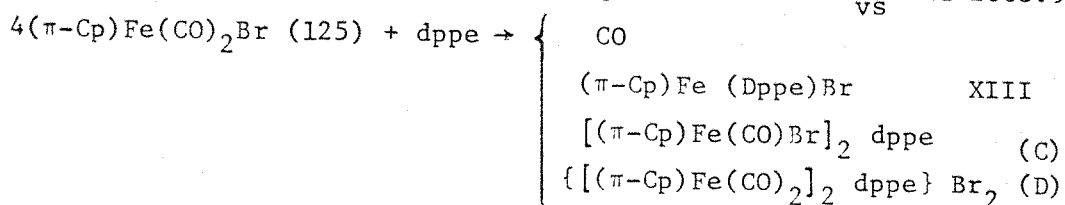


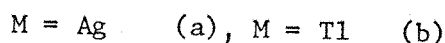
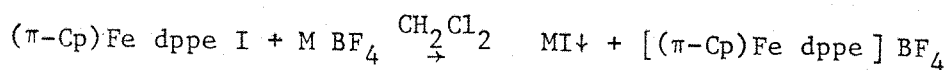
Figure 2.5. The structure of  $[(\pi\text{Cp})\text{Fe}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{NCCH}_3]^+$  (130)

soluble in  $\text{C}_6\text{H}_6$  (126)(129). A brown  $\text{C}_6\text{H}_6$  solution of  $(\pi\text{-Cp})\text{Fe}(\text{CO})_2\text{Br}$  turned to a black reaction mixture after six hours stirring before U.V. irradiation. The yellow (129) compound(D), which was collected on a filter, has an I.R. stretching frequencies of  $2050_{\text{vs}}$  and  $2003.9_{\text{s}}$ .



The yellow colour would suggest the absence of an Fe-Br covalent bond. The green compound which has a CO stretching frequency at  $1950_{\text{vs}} \text{ cm}^{-1}$  probably has the formula (C) its green colour indicating as Fe-Br covalent bond. The  $^1\text{H}$  n.m.r. [ $\delta$  2.4 ( $\text{CH}_2$ ),  $\delta$  4.17 ( $\text{C}_5\text{H}_5$ ) and  $\delta$  8.2 ( $\text{Ph}_4$ )] suggest a similar structure to (A). The black (or dark grey) crystals which showed no stretching frequency for a CO group and  $^1\text{H}$  n.m.r. resonances at  $\delta$  2.4 (4H, Br,  $\text{CH}_2\text{CH}_2$ ),  $\delta$  4.35 (5, Br,  $\text{C}_5\text{H}_5$ ) and  $\delta$  7.35 & 7.23 (20H, M,  $\text{Ph}_4$ ) is compound XIII with a covalent bond between Fe and Br. There is a difference in yield between photochemical and thermal preparations. For the former route the main product is  $(\pi\text{-Cp})\text{Fe dppe}$  X and for the latter  $\{[(\pi\text{-Cp})\text{Fe}(\text{CO})_2]_2 \text{ dppe}\} \text{X}_2$ .

A black  $\text{CH}_2\text{Cl}_2$  solution of XIII and  $\text{AgBF}_4$  with more than three molar equivalents of  $(\text{CH}_3)_2\text{C}_2$  turned to a brighter colour



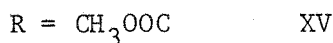
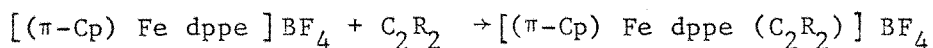
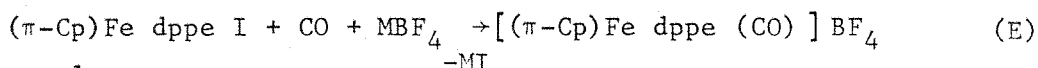


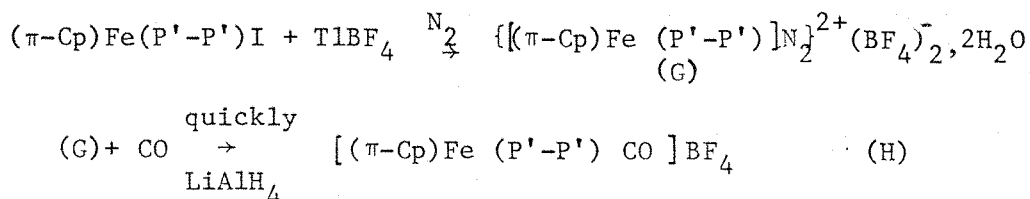
Figure 2.6. The preparation of  $[(\pi\text{-Cp})\text{Fe dppe} (\text{C}_2\text{R}_2)] \text{BF}_4$

after two hours (Figure 2.6). The solid compound was filtered off. After four days, the red crystals yielded 15%. The I.R. of this complex has no CO-stretching frequency but bands at  $1712_{\text{m}}$  ( $\text{C}\equiv\text{C}$ ),  $1602_{\text{m}}$ ,  $1480_{\text{m}}$  ( $\text{H-C-C}$ ),  $1056.4_{\text{vs}} (\text{BF}_4) \text{ cm}^{-1}$ , this compound is indicated to be XIV (Figure 2.6). An orange compound which precipitated with good yield after the first filtration by adding toluene to the filtrate has a  $\nu(\text{CO})$  peak at  $1976.4_{\text{s}} \text{ cm}^{-1}$  and another at  $1056.6_{\text{vs}} \text{ cm}^{-1}$  ( $\nu\text{BF}_4$ ). This compound may be  $[(\pi\text{-Cp})\text{Fe}(\text{dppe})(\text{CO})] \text{BF}_4$  (E), which may be formed from the reaction between  $(\pi\text{-Cp})\text{Fe dppe}$  I and a CO group from carbonyl compound as an impurity and  $\text{MBF}_4$ .



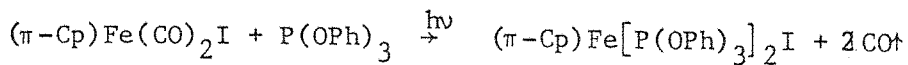
The  $^1\text{H}$  n.m.r. spectrum of XIV was very broad which may be due to presence of the paramagnetic cation  $[(\pi\text{-Cp})\text{Fe}(\text{dppm})\text{I}] \text{BF}_4$  (F) which has been recently reported (131); it would be produced from the reaction of  $\text{Ag}^+$  and complex XII. For preparation of XIV in higher yield and better purity  $\text{TlBF}_4$  was used instead of  $\text{AgBF}_4$ . The  $\text{Tl}^+$  cation is rather less oxidising than  $\text{Ag}^+$ , so the compound (F) would not be expected as a product from the reaction of  $\text{Tl}^+$  and XII. The yield of complex XIV in this case is 29%. Its  $^1\text{H}$  n.m.r. showed a resonance at  $\delta$  2.25 [6H, s,  $(\text{CH}_3)_2$ ], and there are very broad peaks for  $\text{C}_5\text{H}_5$  and  $\text{CH}_2\text{CH}_2$  at  $\delta$  4.56 ( $\text{C}_5\text{H}_5$ ) and  $\delta$  2.98 & 3.32 ( $\text{CH}_2\text{CH}_2$ ), and a singlet for 20 phenyl protons which would be required for compound XIV; the analysis result also fits. In this case, an orange compound was also precipitated after the first filtration from the solution. It showed a CO stretching frequency at  $1975 \text{ cm}^{-1}$ . Silverthorn has mentioned a possibility for a carbonyl compound, which has been prepared by the following route (132), as the reaction carried out under nitrogen in both cases this carbonyl compound may have been produced.

But as there was no  $\text{LiAlH}_4$  in the area then preparation of a carbonyl complex like (H) is not very likely and compound like (E) is more likely to be present here.  $\nu(\text{CO})$  ( $\text{CHCl}_3$ ) for (H) is at  $1960 \text{ cm}^{-1}$ . It is also possible that the 18-electron compound (E) is also a product, and after all, the purification of final product was not completed.

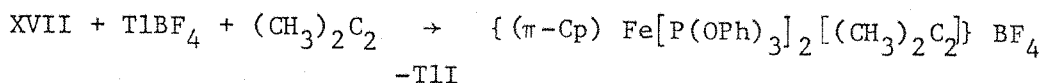


The compound XV was prepared in a similar yield as XIV from  $\text{TiBF}_4$  and XII. The blood red compound which was crystallized after four days has I.R. frequencies at  $1724 \text{ cm}^{-1}$  ( $\nu\text{C}\equiv\text{C}$ ),  $1605 \text{ cm}^{-1}$ ,  $1484 \text{ cm}^{-1}$  ( $\nu\text{C-C-H}$ ) and  $1059.5 \text{ cm}^{-1}$  ( $\nu\text{BF}_4$ ) and  $^1\text{H}$  n.m.r. signals at  $\delta$  2.25, a single peak which may be due to  $(\text{CH}_3\text{OOC})$  protons, a multiplet at  $\delta$  2.7 from methylene protons of the  $(\text{Ph}_2\text{PCH}_2)_2$  group, a broad peak at  $\delta$  4.3 due to  $\text{C}_5\text{H}_5$  and a multiplet from phenyl protons at  $\delta$  7.15. Hence this red complex is identified as XV which was confirmed by the elemental analysis result. It is possible that the presence of a little paramagnetic cation similar to (F) makes the  $^1\text{H}$  n.m.r. spectrum broad. Here also an orange carbonyl compound (possibly (H)) was precipitated, which has I.R. stretching frequencies at  $1976.5 \text{ cm}^{-1}$  and  $1059 \text{ cm}^{-1}$ . The deep-red complexes of XIV and XV are very air stable and could be crystallized in air. The  $\text{CH}_2\text{Cl}_2$  solution of XII and  $\text{AgBF}_4$  turned to red-brown after ten minutes as  $(\text{CF}_3)_2\text{C}_2$  was bubbled through. Two compounds were precipitated. One has I.R. bands at  $1756 \text{ cm}^{-1}$  (possibly  $\text{C}\equiv\text{C}$  stretching frequency),  $1602 \text{ cm}^{-1}$ ,  $1486 \text{ cm}^{-1}$ ,  $1058 \text{ cm}^{-1}$  and this red compound is identified as XVI, which is supported by analysis results. Another compound which has I.R. stretching frequencies at  $1973.7 \text{ cm}^{-1}$  ( $\nu\text{CO}$ ),  $1604 \text{ cm}^{-1}$ ,  $1486 \text{ cm}^{-1}$ ,  $1058 \text{ cm}^{-1}$ , may be the carbonyl compound similar to (H). The  $^1\text{H}$  n.m.r. of XVI was very broad and no peak was recognisable; this may depend upon the presence of a paramagnetic compound (F) in the product.

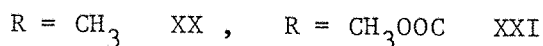
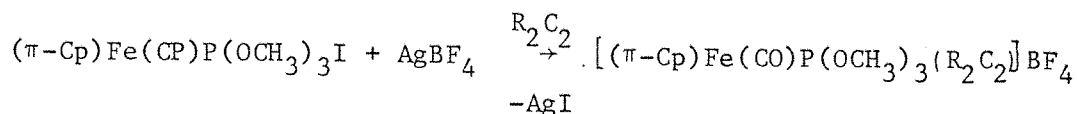
The preparation of acetylene complexes of  $\{(\pi\text{-Cp})\text{Fe}[\text{P}(\text{OPh})_3]_2(\text{acetylene})\} \text{BF}_4$  is shown as following route. The brown  $\text{C}_6\text{H}_6$  solution



XVII



of  $(\pi\text{-Cp})\text{Fe}(\text{CO})_2\text{I}$  turned deep-red after ten hours before U.V. light (127). The red solution which gave a dark reddish complex that has no C-O stretching frequency in its I.R. spectrum and its  $^1\text{H}$  n.m.r. contained a singlet at  $\delta 3.93$  and it is supposed that in this isomer the  $\text{C}_5\text{v}$  symmetry of the  $(\eta^5\text{C}_5\text{H}_5)\text{Fe}$  fragment exists. Another so-called isomer for this complex (133) was found to have a bond between cyclopentadienyl group and one of the phenyl groups. The preparation of the acetylene complexes of this compound was very difficult, because most of the complexes decomposed during crystallization to green compounds. The green compound product obtained after twenty-one hours refluxing of  $\text{P}(\text{OCH}_3)_3$  and  $(\pi\text{-Cp})\text{Fe}(\text{CO})_2\text{I}$  has an I.R. frequency at  $1977.9\text{ cm}^{-1}$  ( $\nu\text{CO}$ ) and its  $^1\text{H}$  n.m.r. showed a doublet centered at  $\delta 3.62$  ( $J = 19\text{ Hz}$ ) which belongs to the  $\text{P}(\text{OCH}_3)_3$  and a singlet at  $\delta 4.62$  due to the  $\text{C}_5\text{H}_5$  group, and was identified as  $(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OCH}_3)_3\text{I}$  (XIX). The orange crystals which were produced from treating  $(\text{CH}_3)_2\text{C}_2$  and XIX



have an I.R. stretching frequency  $2003.3\text{ cm}^{-1}$  ( $\nu\text{CO}$ ) and the  $^1\text{H}$  n.m.r. spectrum has peaks at  $\delta 0.88$ ,  $\delta 1.26$ ,  $\delta 3.8$  [ $\text{Br}, \{\text{P}(\text{OCH}_3)_3\}$ ] and  $\delta 5.3$  ( $\text{Br}, \text{C}_5\text{H}_5$ ). The yellow compound which was prepared from  $(\text{CH}_3\text{OOC})_2\text{C}_2$  and XIX has I.R. with ( $\nu\text{CO}$ ) at  $2052.8\text{ cm}^{-1}$  and ( $\nu\text{C}=\text{C}$ ) frequency at  $1727\text{ cm}^{-1}$  and its  $^1\text{H}$  n.m.r. spectrum was very broad, it has peaks at  $\delta 2.4$  due to  $(\text{CH}_3\text{OOC})_2\text{C}_2$  protons,  $\delta 3.65$  due to  $\text{P}(\text{OCH}_3)_3$  protons. These two compounds could not be purified completely and may be accompanied by a paramagnetic compound like  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OCH}_3)_3\text{I}]\text{BF}_4$ , which made the  $^1\text{H}$  n.m.r. spectra so broad.

The complexes with general formula  $[(\pi\text{-Cp})\text{Fe}(\text{CO})(\text{PR}_3)\text{acetylene}]^+$  or  $[(\pi\text{-Cp})\text{Fe}(\text{Ph}_2\text{PCH}_2)_2\text{acetylene}]^+$  which were made by this work are

not an exception to general law which organometallic transition metal complexes are thermodynamically unstable to oxidation (134), but most of those complexes are kinetically stable enough to crystallize at room temperature and in presence of oxygen, because the valance orbitals are saturated by 18 electrons. But most of them are unstable to oxidation in solution which may show that the valance orbitals are saturated but the energy gap between filled nonbonding and empty antibonding (molecular orbitals) is not very large. In some complexes like  $\{(\pi\text{-Cp})\text{Fe}(\text{CO})\text{PPh}_3 [(\text{CH}_3)_2\text{C}_2]\}^+$  the crystallization must be carried out under room temperature and for the complex  $\{(\pi\text{-Cp})\text{Fe}(\text{CO})\text{PPh}_3 [\text{Ph}_2\text{C}_2]\}^+$  crystallization must be carried out below  $0^\circ\text{C}$  and the reason may be a smaller HOMO-LUMO gap.

CHAPTER THREE

ACETYLENE ROTATION

### 3.1 Calculation of the Barrier to Rotation

The only convenient technique available to measure the rate of rotation of acetylene in complexes with transition metals - which also are of low thermal stability - is variable temperature n.m.r. The calculated simulated spectra can be prepared by computer techniques. In many organic or inorganic molecules, the groups are not rigid. If nuclei are moving between different environments A and B they have an average residence time of  $\tau_A$  and  $\tau_B$  at each site. These are given by:

$$\tau_A = 1/k_A \quad \text{and} \quad \tau_B = 1/k_B$$

where  $k_A$  and  $k_B$  are the rate constants for exchange. If the residence times in each site are short, only a single resonance is observed. When the population of both sites are equal  $\tau_A = \tau_B$  the resonance is observed as an average in the middle of the resonant frequencies of both environments. When residence times are longer, separate resonance lines will be observed.



### 3.2 Exchange between Two Different Chemical Environments

The intensity at any angular frequency  $\omega$  ( $\omega = 2\pi\nu$  in Radian/s) given by  $\nu$ , for two sites A and B, each of which is a singlet (135).

$$\nu = \frac{\gamma B_1 [(1 + \tau T_2^{-1}) P + QR]}{P^2} \quad 3.1$$

$$\text{where } P = \tau \{ T_2^{-2} - [\frac{1}{2} (\omega_A - \omega_B) - \omega]^2 + \frac{1}{4} (\omega_A - \omega_B)^2 \} + T_2^{-1}$$

$$Q = \tau [\frac{1}{2} (\omega_A + \omega_B) - \omega - \frac{1}{2} (P_A - P_B) (\omega_A - \omega_B)]$$

$$R = [\frac{1}{2} (\omega_A - \omega_B) - \omega] (1 + 2\tau T_2^{-1}) + \frac{1}{2} (P_A - P_B) (\omega_A - \omega_B)$$

$$\tau = \frac{\tau_A \tau_B}{(\tau_A + \tau_B)}$$

$$P_A = \frac{\tau_A}{\tau_A + \tau_B} \quad \text{and} \quad P_B = \frac{\tau_B}{(\tau_A + \tau_B)} \quad 3.2$$

$\nu$  (Equation 3.1) was evaluated for 200 points for a given frequency range using computer programs written in BASIC which give screen graphic or hard copy plotted displays.

The parameters used are chemical shifts in Hz relative to an arbitrary reference, the effective transverse relaxation time  $T_2$ , the proportions,  $P_A$  and  $P_B$  and the residence times  $\tau_A$  and  $\tau_B$ . The energy of activation can be obtained from rate constants using equation 3.3.

$$\log k = \log_{10} A - \frac{E_a}{2.303RT} \quad 3.3$$

where A is a frequency factor, and  $E_a$  is the empirical activation energy. This frequency factor can be related to the entropy of activation,  $\Delta S^\ddagger$ , by expression 3.4.

$$A = (C.K.T \exp \Delta S^\ddagger / R) h \quad 3.4$$

where K and h have their normal physical magnitude. Here  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values calculated from a computer program which determines the

result of the Eyring plot of  $\ln k/T$  vs  $1/T$ . The plot was used from the following equation.

$$\ln \left( \frac{k}{T} \right) = \left( \ln \frac{K}{h} + \Delta S^\ddagger / R \right) - \frac{\Delta H^\ddagger}{RT} \quad 3.5$$

The error of the results is calculated from the equation 3.6

$$\text{Error} = \pm \frac{tQ \times \sigma}{N} \quad 3.6$$

where  $N$  = NO. of observation,  $Q = N - \text{NO. of results}$ ,  $t$  is a statistical factor which has been calculated for  $Q$ , and  $\sigma$  is standard deviation of the result.

### 3.2.1 Initial Line Broadening

In n.m.r. spectra of exchange systems there are three different parts. When the life time  $\tau$  of each site is long and the spectra is hardly altered, when the life time is very short and the spectra show a single resonance and the two different environments are not distinguishable, at intermediate life times a broadened line could be seen. As the line width of the spectra in each stage changes with temperature, it is possible to estimate the rate constant  $k$  for each part and estimate  $\Delta G^\ddagger$ . As  $k$  and  $\Delta G^\ddagger$  relate together by a logarithmic equation then an error in  $k$  gives a much smaller error for  $\Delta G^\ddagger$ . At slow exchange two sites A and B have apparent relaxation times  $T_2'$ , which are related to  $\tau$  and  $T_2$  as is shown in equation 3.7.

$$\frac{1}{T_{2A}'} = \frac{1}{T_{2A}} + \frac{1}{\tau_A}$$

and

$$\frac{1}{T_{2B}'} = \frac{1}{T_{2A}} + \frac{1}{\tau_A} \quad 3.7$$

where relaxation time is  $T_2'$  in the case of slow exchange and is  $T_2$  when there is no exchange. When limiting low temperature spectra can be obtained for a compound, the rate constant for exchange can be estimated from the slow exchange limiting equation 3.8.

$$k = \pi(\Delta\nu_{\frac{1}{2}}' - \Delta\nu_{\frac{1}{2}}) \quad 3.8$$

The error in  $\Delta G^\ddagger$  from using slow exchange equation is not more than  $\pm 1.4$  kJ/mol and depends on the determination of the temperature and broadening measurements (81). When rotation has a low barrier, the limiting low-temperature spectrum cannot be obtained.

### 3.2.2 Fast Exchange Regime

Approximate equations of line broadening after coalescence can be used to calculate rate constants and to estimate free energy of activation for exchange.

In single spectra of the fast exchange of two uncoupled sites A and B, the line width can be obtained from

$$\frac{1}{T_2'} = \frac{P_A}{T_{2A}} + \frac{P_B}{T_{2B}} + P_A^2 P_B^2 (2\pi\Delta\nu)^2 (\tau_A + \tau_B) \quad 3.9$$

where  $\Delta\nu$  is chemical shift difference between the resonances in Hz when there is no exchange.  $P_A$  and  $P_B$  are obtained from equation 3.2. The single resonant frequency as a broad end signal is obtained by  $\nu' = P_A\nu_A + P_B\nu_B$

The equation 3.9 holds for very fast exchange when  $1/\tau \gg 2\pi\delta\nu$ . To find the error for  $\Delta G^\ddagger$  using this equation, estimates of maximum and minimum possible values of  $\Delta\nu$  (taken from the spectra of similar compound) can be used.

### 3.2.3 Coalescence Point

The approximate equation at coalescence is used when the rate constants cannot be obtained from line shape fits, for example when  $\Delta\nu$  is very small. Then the rate constant at the coalescence point  $k_c$  can be calculated by using equation 3.10, which is appropriate for singlets with no coupling constant between A and B sites.

$$k_c = (\pi/\sqrt{2}) \Delta\nu \quad 3.10$$

When there is a coalescence of a coupled AB spin system (with coupling constant J) to a singlet equation 3.11 is used.

$$k_c = (\pi/\sqrt{2})(\Delta\nu^2 + 6J^2)^{\frac{1}{2}} \quad 3.11$$

when  $\Delta\nu$  is difference of chemical shift in Hz. Errors of 10, 25, 100% in the rate constant calculation by using equation 3.10 and 3.11 would result in an error of 0.3, 0.5 and 1.9 KJ/mol for  $\Delta G^\ddagger$  respectively. Then an error of 25% for  $k$  would be acceptable because an acceptable experimental error for  $\pm 2^\circ\text{C}$  in temperature gives the same error of 0.5 - 1.0 KJ/mol (104) for  $\Delta G^\ddagger$  by comparing with complete line shape analysis. By using equation 3.10 for equally intense coalescing singlets or doublets the error would increase when  $\Delta\nu$  is smaller than 3 Hz. There is a 20 and 80% error in calculation of  $k_c$  for  $\Delta\nu$  equal to 3 and 1 Hz respectively. For  $\Delta\nu$  larger than that the error would be very small. For coupled systems equation 3.11 is acceptable when  $\Delta\nu > J$  and equation 3.10 when  $\Delta\nu/J > 3$ .

The value of the free energy of activation was calculated by using the following formula.

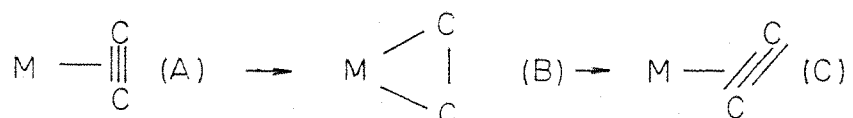
$$\Delta G_{T_c}^\ddagger = -RT \ln \frac{\pi\Delta\nu h}{\sqrt{2}kT_c}$$

where  $\Delta\nu$  is the chemical shift of the coalesced peaks, and  $T_c$  is the coalescence temperature. The approximation in the magnitude of  $\Delta G^\ddagger$  resulting from the above equation is estimated by Reger and Coleman (136) to be within  $\pm 2.41$  KJ/mol.  $T_c$  was obtained from computer simulated and experimental spectra, as they were matched by usual comparison of the spectra.

### 3.3 Results and Discussion

Variable temperature proton n.m.r. studies were carried out on  $[(\pi\text{-Cp})\text{Fe}(\text{CO})(\text{PR}_3)(\text{R}'_2\text{C}_2)]\text{BF}_4$  {  $\text{R} = (\text{OPh})$ ,  $\text{R}' = \text{CH}_3$  and  $\text{R} = \text{Ph}$ ,  $\text{R}' = \text{CH}_3$  or  $\text{CH}_3\text{OOC}$  } and exchange rate were calculated for the acetylene rotation by line shape simulations, limiting low temperature spectra and experimental and calculated partial spectra of the exchanging methyl groups are given in Figures 3.1 - 3.6. These results are collected in Table 1, which also included  $\Delta G^\ddagger$  estimation for  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OPh})_3\{(\text{CH}_3\text{OOC})_2\text{C}_2\}]$ .

The kinetic data may provide information about the mechanism of rotation of acetylene. In vibrational and rotational motion, the degree of order of the system depends in the degree of rigidity of the molecular configuration, then  $\Delta S^\ddagger$  relates to degree of order of molecule in different stages of the mechanism of rotation of the acetylene. If acetylene dissociates, then this mechanism would give a positive value for  $\Delta S^\ddagger$ . But calculated entropies for the complexes mentioned here showed negative values. There is therefore a higher degree of order for acetylene group in the molecule in the transition state, which could be more like metallacyclopropene



The other factor which may influence the energy of the system is order due to translational motion which depends on the number of particles in solution and the solvent freedom. The solvents are chosen to be unreacted with the complex.

A large value of  $\Delta H^\ddagger$  is dominating factor in the  $\Delta G^\ddagger$ .

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

One of the contributory causes to increase  $\Delta H^\ddagger$  for rotation of the acetylene is ability of the central metal to back donate electrons to the acetylene orbitals. This ability could be altered by a change in the electronegativity of ligands in the complex. As the  $\Delta H^\ddagger$  values which are calculated here show that alteration for two different phosphorus groups,  $\Delta H^\ddagger$  of rotation differ in this order  $\text{PPh}_3 > \text{P(OPh)}_3$ . As  $\text{PPh}_3$  is a bulkier group and a stronger electron donor ligand than  $\text{P(OPh)}_3$ , this shows steric and electronic factors in those examples play a role together and one cannot separate them from each other. Also from this data one can suggest that the steric factor does not dominate the energy barrier by comparing the data of the dimethylacetylene with dimethylacetylene carboxylate complexes in the phosphine system. This barrier  $\Delta H^\ddagger$  is only 1.0 KJ/mol larger for the dimethylacetylene

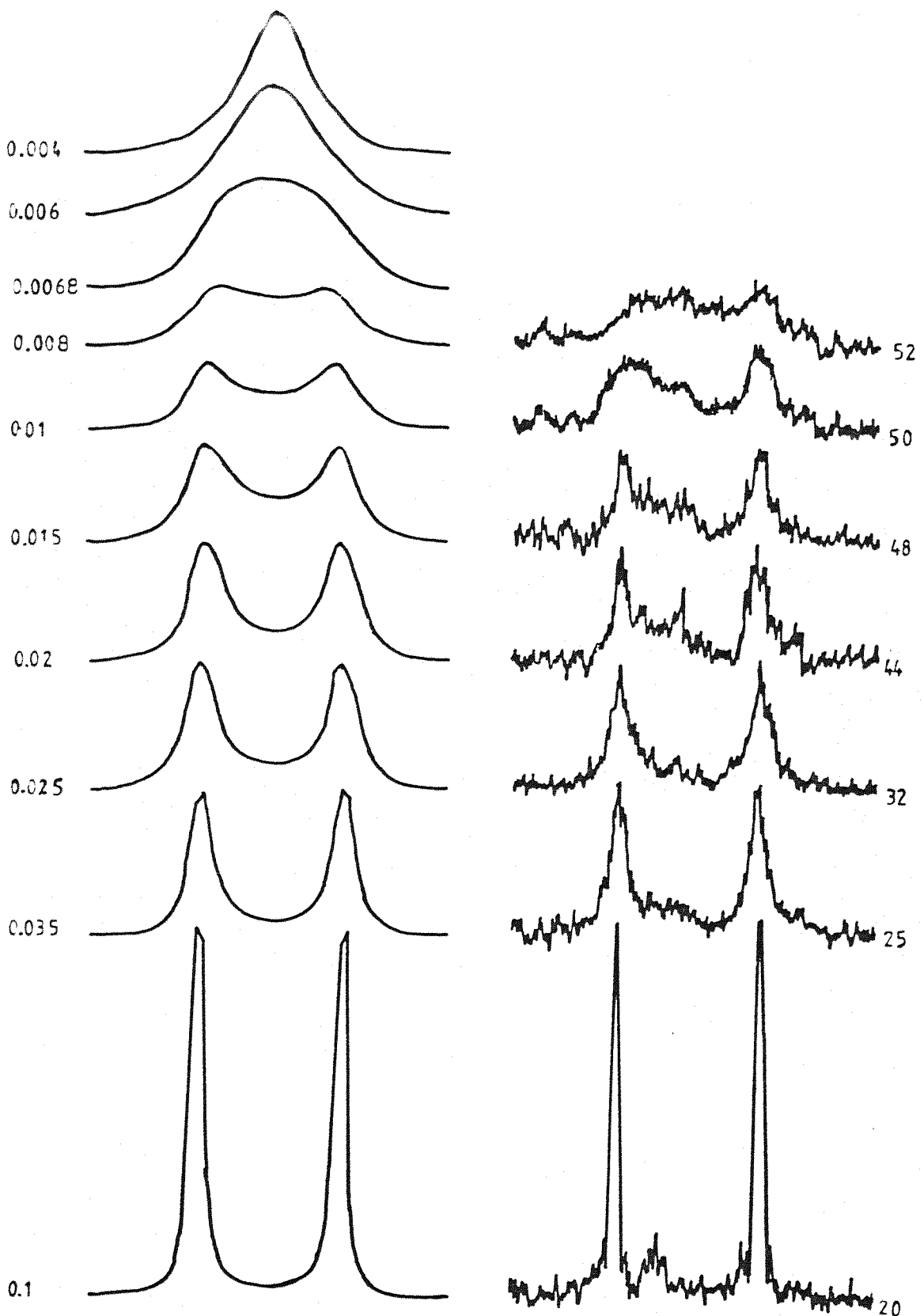


Figure 3.1  $^1\text{H}$  n.m.r. spectra of the methyl resonances of  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{PPh}_3(\text{CH}_3\text{OOC})_2\text{C}_2]\text{BF}_4$  in the temperatures range  $+20$  to  $+52^\circ\text{C}$  and lifetimes  $0.1$  to  $0.004\text{s}$  respectively, observed spectra on the right and calculated on the left.

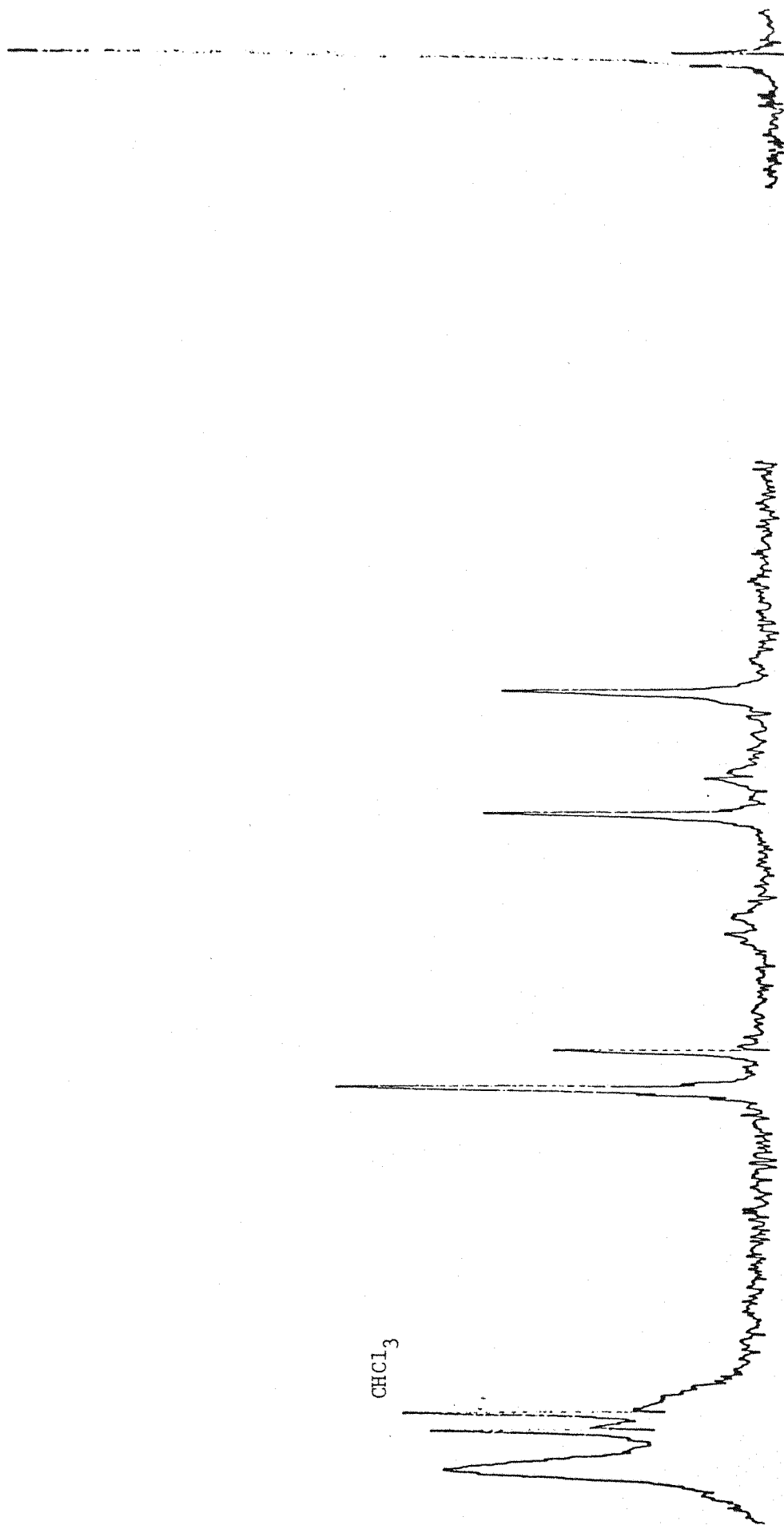


Figure 3.2.  $^1\text{H}$  n.m.r. of  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{PPh}_3(\text{CH}_3\text{OOC})_2\text{C}_2]\text{BF}_4$  in  $\text{CDCl}_3$  at  $20^\circ\text{C}$ .

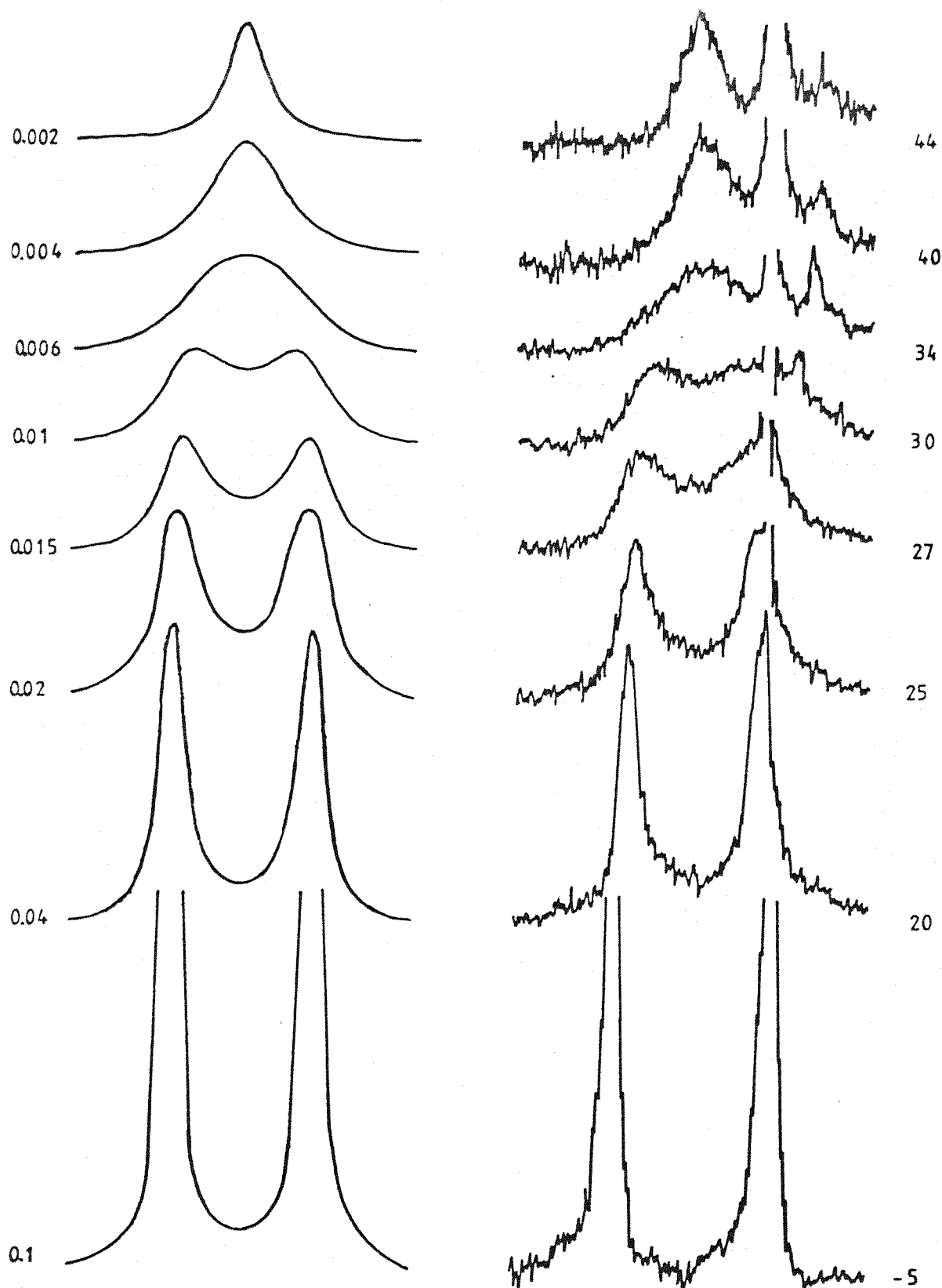


Figure 3.3  $^1\text{H}$  n.m.r. spectra of the methyl resonances of  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{PPh}_3(\text{CH}_3)_2\text{C}_2]\text{BF}_4$  in the temperatures range  $-5$  to  $+44^\circ\text{C}$  and lifetimes  $0.1$  to  $0.002\text{S}$  respectively, observed spectra on the right and calculated on the left.



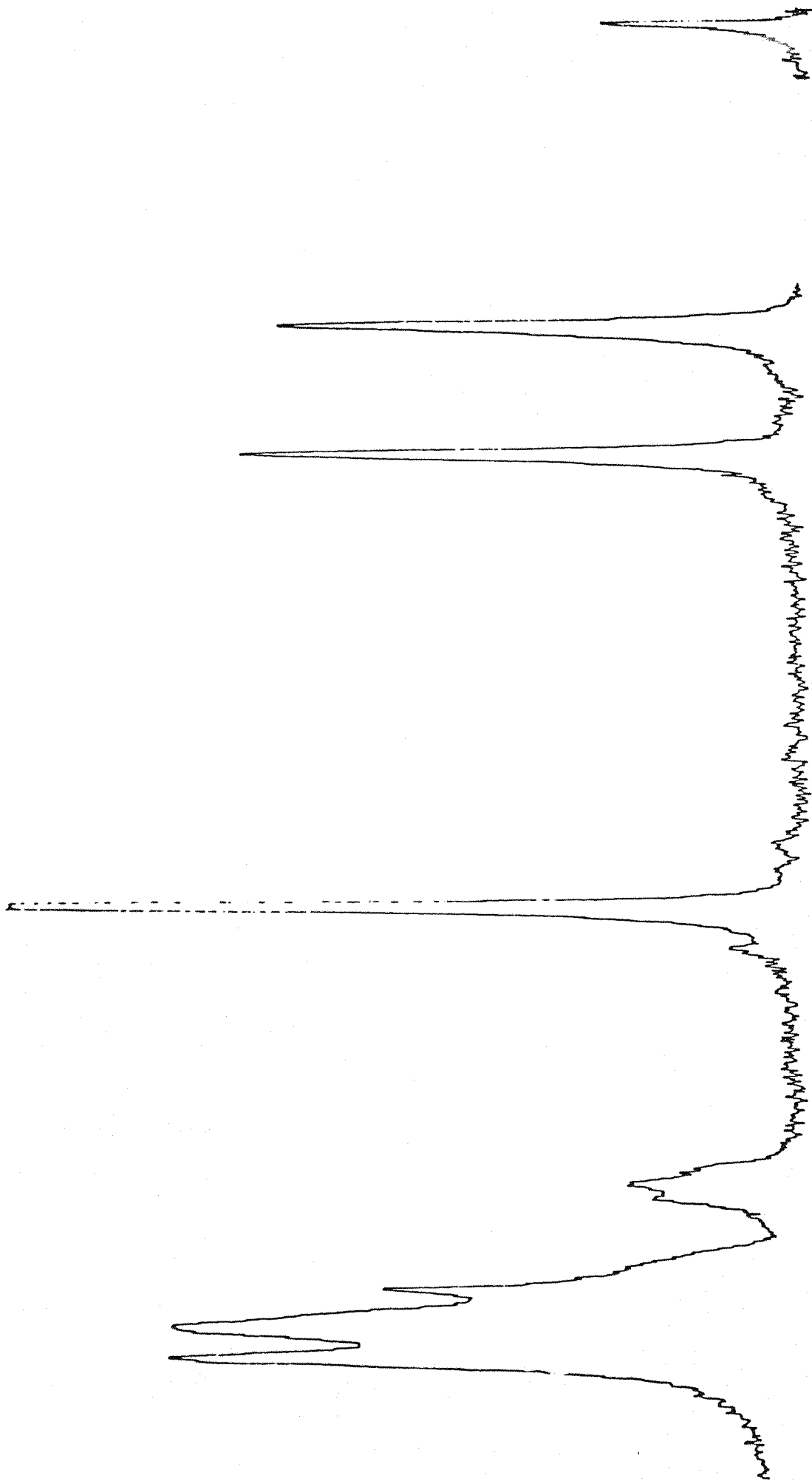


Figure 3.4  $^1\text{H}$  n.m.r. of  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{PPh}_3(\text{CH}_3)_2\text{C}_2]\text{BF}_4$  in  $\text{CDCl}_3$  at  $-5^\circ\text{C}$ .

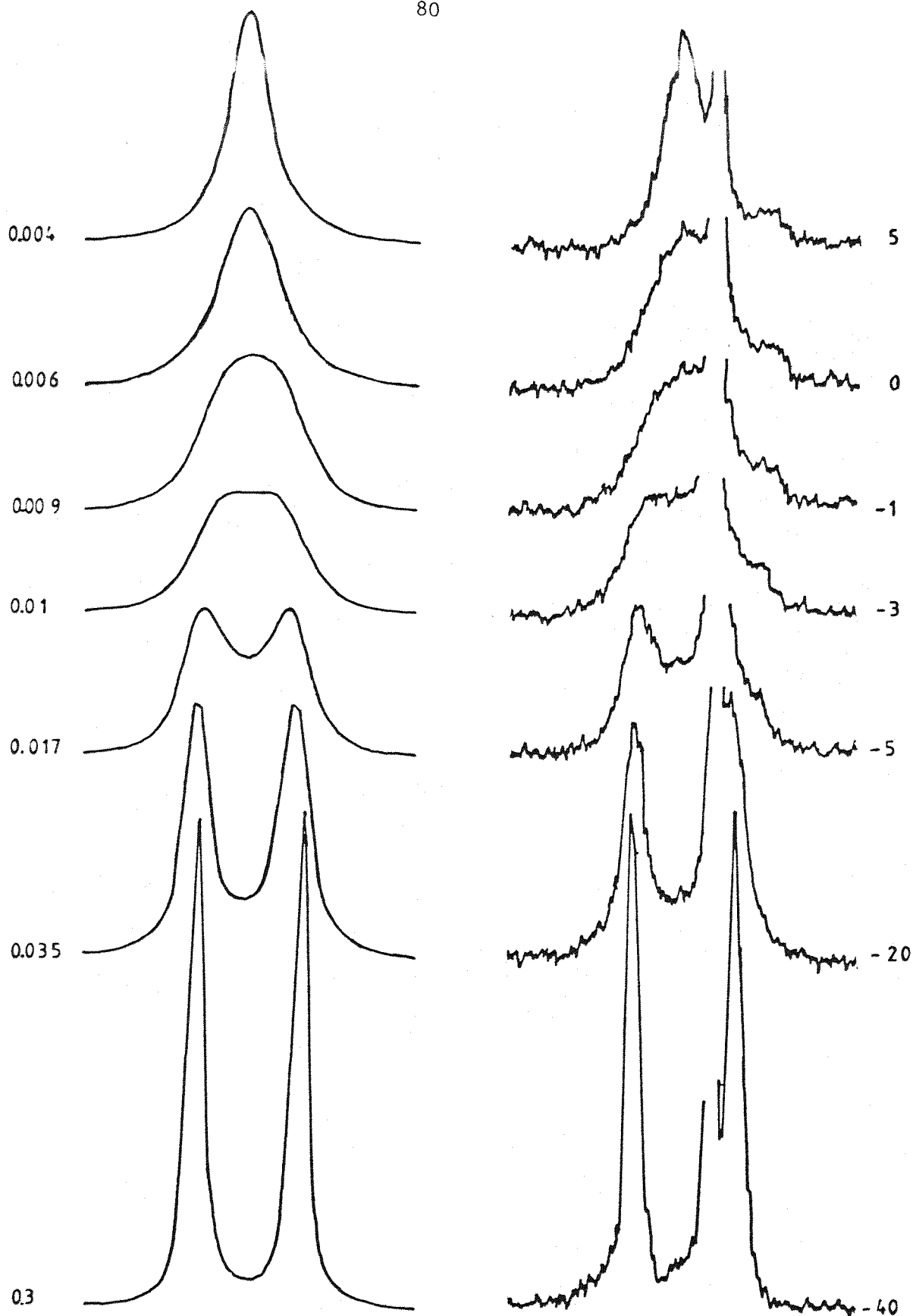


Figure 3.5  $^1\text{H}$  n.m.r. spectra of the methyl resonances of  $[(\pi\text{-Cp})\text{Fe CO P(OPh)}_3(\text{CH}_3)_2\text{C}_2] \text{BF}_4$  in the temperatures range  $-40$  to  $+5^\circ\text{C}$  and lifetimes  $0.3$  to  $0.004$  S respectively, observed spectra on the right and calculated on the left.

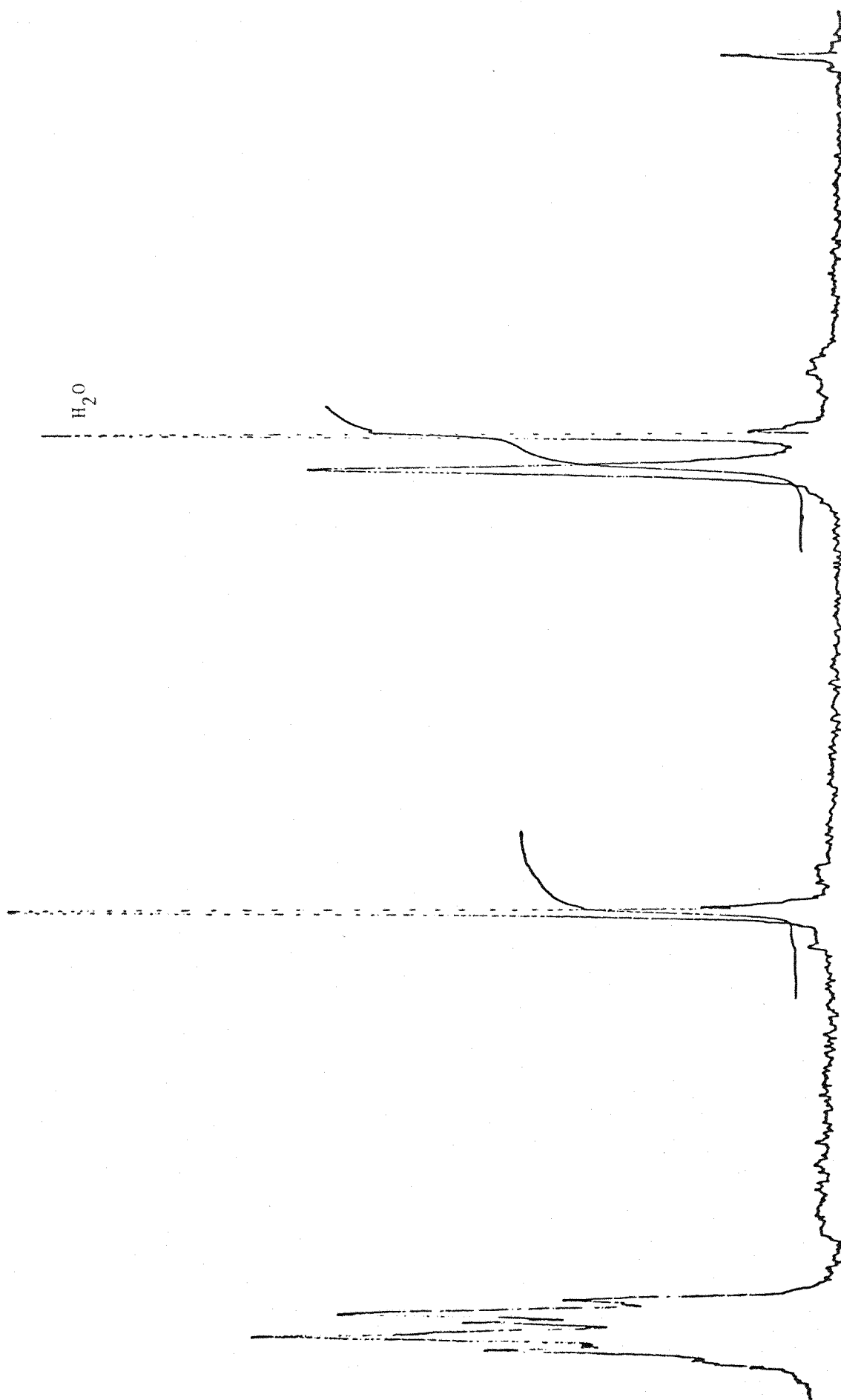


Figure 3.6  $^1\text{H}$  n.m.r. of  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OPh})_3(\text{CH}_3)_2]\text{BF}_4$  in  $\text{CDCl}_3$  at  $30^\circ\text{C}$ .

Table 1

Kinetic data of four $\pi$ -cyclopentadienyl carbonyl phosphine acetylene complexes									
Complexes	$\Delta G^\ddagger$ KJ/mol	error of $\Delta G$	$\Delta H^\ddagger$ KJ/mol	error of $\Delta H^\ddagger$	$\Delta S^\ddagger$ J/deg/mol	error of $\Delta S^\ddagger$	error of $\Delta S^\ddagger$	confidence limit	T °K
$[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{PPh}_3(\text{CH}_3\text{OOC})_2\text{C}_2]^+\text{BF}_4^-$	75.3 <sup>a</sup> +		47.0	$\pm 2.0$	-63.5	$\pm 7.0$	$\pm 7.0$	93.79%	325
$[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{PPh}_3(\text{CH}_3)_2\text{C}_2]^+\text{BF}_4^-$	69.2 <sup>a</sup> ++		53.0	$\pm 2.0$	-32	$\pm 7.0$	$\pm 7.0$	93.32%	305
$[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OPh})_3(\text{CH}_3\text{OOC})_2\text{C}_2]^+\text{BF}_4^-$	74.0 <sup>b</sup>	$\pm 0.4$							283
$[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OPh})_3(\text{CH}_3)_2\text{C}_2]^+\text{BF}_4^-$	63.8 <sup>a</sup>		47.0	$\pm 1.0$	-32	$\pm 4.0$	$\pm 4.0$	98.60%	270

a - Computer simulation (using comparison of calculated  $^1\text{H}$  n.m.r. spectra with observed)

b - k is calculated by using approximation equation at coalescence,  $\Delta\nu = 3.4 \text{ Hz}$ ,  $k_c = \frac{\pi(\Delta\nu)}{\sqrt{2}}$

+ - The temperature  $\Delta G^\ddagger$  was calculated was T = 325, and coalescence temperature has not reached

++- The temperature  $\Delta G^\ddagger$  was calculated was T = 268

carboxylate. Since the energy barrier  $\Delta H^\ddagger$  is the best factor to compare complexes, but as there is not enough data in the literature, further comparison is done by using free energy of activation,  $\Delta G^\ddagger$  data.

In a general formula of  $[(\pi\text{Cp})\text{MXY}(\text{acetylene})]$  when  $(\text{M}=\text{W}, \text{X}=\text{CO}, \text{Y}=\text{CH}_3)$  for  $\text{C}_2\text{H}_2$   $\Delta G^\ddagger$  is 87.6 KJ/mol, if the  $\text{CH}_3$  group is changed to another bulkier and a more electronegative group like  $\text{C}_6\text{H}_5$  the free energy of activation is decreased to 84.3 KJ/mol. Now if an electropositive group like  $\text{CH}_3$  is substituted in the acetylene for the former complex  $\Delta G^\ddagger$  decreases to 81.4 and if this substituent group is changed with a bulkier and more electronegative group like  $\text{C}_6\text{H}_5$ ,  $\Delta G^\ddagger$  increases to 82.8 KJ/mol (error of  $\Delta G^\ddagger = \pm 1.0$  KJ/mol). By looking at acetylene complexes of transition metals in the same column as W like Cr we see some reduction in  $\Delta G^\ddagger$  of rotation as in complexes of  $(\text{C}_5\text{H}_5)\text{Cr}(\text{CO})(\text{NO})(\text{Acetylene})$  (137) for  $\text{C}_2\text{H}_2$   $\Delta G^\ddagger$  varies between 58.3 - 66.4 KJ/mol in different solvents. The dipole moment of the solvent alters the magnitude of  $\Delta G^\ddagger$ . Here a very big reduction in  $\Delta G^\ddagger$  has been seen from the replacement of W by Cr, but also a nucleophilic group of  $\text{CH}_3$  changes to an electronegative group like NO. This may depend largely on a change of ligand and on the potential of 5d for providing more electron density in back bonding with acetylene. In cationic species a lower barrier has been seen, and it is suggested by Faller and his coworkers(81) that there is a decrease in backbonding in the case. Acetylene rotation barriers have been calculated by Hoffmann et al (121). In the Mo complex of  $[(\pi\text{-Cp})\text{Mo}(\text{CO})\text{L}(\text{acetylene})]^+$  when  $\text{L} = \text{CO}$ ,  $\Delta G^\ddagger$  is 62.6 KJ/mol but when the central metal with  $d^4$  is replaced by one with  $d^6$  as molecular orbital  $a''$  which is a better electron donor to the acetylene is full the calculated  $\Delta G^\ddagger$  increases to 110.7 KJ/mol (for example, in the complex  $[(\pi\text{-Cp})\text{Mo}(\text{CO})_2(\text{acetylene})]^-$ . In the former case when  $\text{L} = \text{CH}_3$  or  $\text{PH}_3$  (121)  $\Delta G^\ddagger$  is 81.8 KJ/mol by comparing it with the W complexes it has a smaller magnitude and when  $\text{L} = \text{NO}^+$ ,  $\text{NO}^-$ ,  $\Delta G^\ddagger$  is 19.3 and 105.9 KJ/mol respectively. In the case of  $\text{NO}^+$ ,  $\Delta G^\ddagger$  of the complex is smaller than that in the similar complex when  $\text{M} = \text{Cr}$  that may suggest more electronegativity of the group and cationic species for Mo complex. The transition metal complexes of  $d^6$  which have a filled  $a''$  and a better potential to back donate electron to

the acetylene have a higher  $\Delta G^\ddagger$  than that for the complexes of  $[(\pi\text{-Cp})\text{Fe}(\text{CO})_2 \text{ acetylene}]^+$  (91.5 KJ/mol). These calculated barriers are much larger than the experimental values reported here and this is probably due to the inaccuracy of EHT calculations. In this series of iron complexes if R substitutes for acetylene hydrogen then the barrier would be decreased. By replacing one of the carbonyl groups for  $\text{PPh}_3$  it decreases the stability of the complex as it is presented in this report, but the EHT calculations suggest an increase in  $\Delta G^\ddagger$  of acetylene rotation, as is shown above for Mo, when one of CO groups substituent by  $\text{PH}_3$ . Substitution of a CO group by  $\text{P}(\text{OPh})_3$  makes more stable complexes than  $\text{PPh}_3$  substituent complexes.

The n.m.r. spectra of  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OPh})_3(\text{H PhC}_2)]^+$  is very complicated, which may be due to the instability of the complex in solution.

It was not possible here to measure the kinetic data from  $^1\text{H}$  n.m.r. spectra for the iron complexes when acetylene is  $\text{Ph}_2\text{C}_2$  because the  $^1\text{H}$  resonance belonging to Ph part of the acetylene are masked by complicated resonances of  $\text{PPh}_3$  or  $\text{P}(\text{OPh})_3$  groups.  $^{13}\text{C}$  n.m.r. spectra of complex in the case of  $\text{P}(\text{OPh})_3$  ligand showed a resonance at 62.9 PPM for acetylene carbon and another peak may be masked by up field resonances of  $\text{CD}_2\text{Cl}_2$  (a series of peaks centred at 54.3 PPM, 52.1 - 56.4) this peak did not change from  $-80^\circ\text{C}$  to room temperature.  $\Delta G^\ddagger$  of this complex was calculated from the similar  $^{13}\text{C}$  n.m.r. spectra (136), 66.9 KJ/mol.  $\Delta G^\ddagger$  was determined by the method of initial line broadening of the static low-temperature spectra. Barrier to rotation increases for acetylene substituent as follows  $\text{CH}_3 < \text{Ph} < \text{CH}_3\text{OOC}$ . In the complex  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OPh})_3\{(\text{CH}_3\text{COO})_2\text{C}_2\}]^+$  the difference in proton chemical shift of the methyl group was very small ( $\Delta\nu = 3.4$  Hz). The  $\Delta\nu$  value looks unusual if one compares it with a comparatively large  $\Delta\nu = 68.0$  Hz for the similar complex when ligand is  $\text{PPh}_3$  instead of  $\text{P}(\text{OPh})_3$ . But this large difference could not be seen in the case of dimethylacetylene by comparing phenyl phosphite and phenylphosphinesystems. This suggests an unusual configuration for acetylene group in the complex  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OPh})_3\{(\text{CH}_3\text{OOC})_2\text{C}_2\}]^+$ . Then it is possible that the  $(\text{CH}_3\text{OOC})_2\text{C}_2$  ligand is in

a vertical situation to the ( $\pi$ -Cp) group and population of acetylene parallel to the ( $\pi$ -Cp) is not large, so as to say the steric factor here is very important. In this complex P-H coupling was observed at room temperature  $^1\text{H}$  n.m.r. spectra, that it agrees with nondissociative mechanism in it. It is also possible that the bulky substituent group of ( $\text{CH}_3\text{OOC}$ ) in acetylene is bent very much away from other groups in the complex.

### 3.4 Conclusion

The barrier to rotation in these complexes of acetylene consists of both steric and electronic factors. The steric factors here usually arise when ligands move from lowest energy configuration which is approximately parallel to bulky group of cyclopentadienyl, and an electronic factor is important when central metal has a different donation to the ligand with different configuration which is governed by non-equivalents of metal orbitals in the molecular environment. There, two factors function together. The molecular energy would be different in different symmetry whereas overlap of orbitals would vary. It is not possible to estimate contributions to  $\Delta G^\ddagger$  for each of them separately, but by comparison of similar complexes with just a different ligand, we can find which one is more important. Looking closer at these matters, it is difficult to separate the effects from one another, as the electronic effects can have important steric consequences and vice versa. For example, the percentage of s characters will decrease in the lone pair of phosphorus when a substituent causes an increase of the angle between substituents. Also distances and angles would vary by altering the electronegativity of atoms. In any pure way, it is not possible to separate those two



Figure 3.7 A schematic definition of electronic and steric effects.

effects, but a practical separation can be made through the parameters  $\nu$  and  $\theta$  (138) (where  $\nu$  is the electronic parameter and  $\theta$  is the steric parameter, e.g. the phosphorus ligands can be ranked in an electronic series - based on CO stretching frequencies - which is generally valid for a wide variety of monosubstituted transition metal carbonyls.  $\theta$  is the ligand cone angle (Figure 3.3)). Comparison of the two groups of triphenylphosphine with triphenyl phosphite is made for steric and electronic point of view. Sterically triphenylphosphine is obviously a bulkier group, and electronically it has more ability to donate electrons to metal than to accept from it, then it leaves metal with more opportunity to donate electrons to an alkyne or an alkene



ligand than triphenyl phosphite does. In another way, because electron density is greater in the former acceptance to a bulky substituted acetylene is more difficult, like  $\text{Ph}_2\text{C}_2$  which is not a very electronegative group to unload the electron density around the metal. Then the barrier to rotation for acetylene complexes should be greater for complexes containing <sup>en</sup>triphylphosphine than other complexes which has triphenyl phosphite with the same alkyne, because the  $\pi$ -bond of M-acetylene link is stronger in the former than in the latter. Finding the dominating factor (steric or electronic) for creating the barrier works practically if the comparison of barrier is made between complexes of same ligands when substituent of the acetylene differs. For example, in two complexes of  $[(\pi\text{-Cp})\text{Fe}(\text{CO})\text{P}(\text{OPh})_3 (\eta^2 \text{ acetylene})]^+$  where acetylene is diphenylacetylene or 3-hexyne, whereas former acetylene which has the bulkier group is expected to have a much greater barrier to rotate than the latter if steric factor is a dominating factor, but this difference is only 3.8 KJ/mol, which suggests that the steric factor does not dominate the barrier in the phosphite complexes.

In the complexes of  $[(\pi\text{-Cp})\text{Fe} \text{ dppe} (\eta^2 \text{ acetylene})]^+$  the steric factor possibly has an important effect as  $(\text{Ph}_2\text{PCH}_2)_2$  is a very bulky group which cannot move as fast as two separate groups and in other complexes one of the ligands was a (CO) group. This is a small and an electronic withdrawing group. Replacing it with a group which gives electron to the central atom has two effects: first increased ability of the metal to donate electron to the acetylene and make a strong bond and second not to allow an acetylene with bulky substituent to come too close to the central metal. This restricts back donation to a acetylene leaving it electrophilic. There are not two different sites for the acetylene protons or carbons when it lies parallel to the cyclopentadienyl group, and this is why a broad singlet resonance was observed for the acetylene protons of each complex in this system.

After all comparison of phosphine and phosphite complexes shows that  $\sigma$  donation of acetylene is more important to make more stable complexes which is improved in phosphite complexes. But the higher barrier to rotation mostly depends on more  $\pi$ -back donation from the metal to the acetylene antibonding orbital which is demonstrated by

bigger values of  $\Delta H^\ddagger$  and  $\Delta G^\ddagger$  to rotating of the acetylene in the phosphine complexes. As shown in table 1, as the electron back donation ability of the metal is decreased for the reasons mentioned above the barrier to rotation of those complexes also decreased in the same way.

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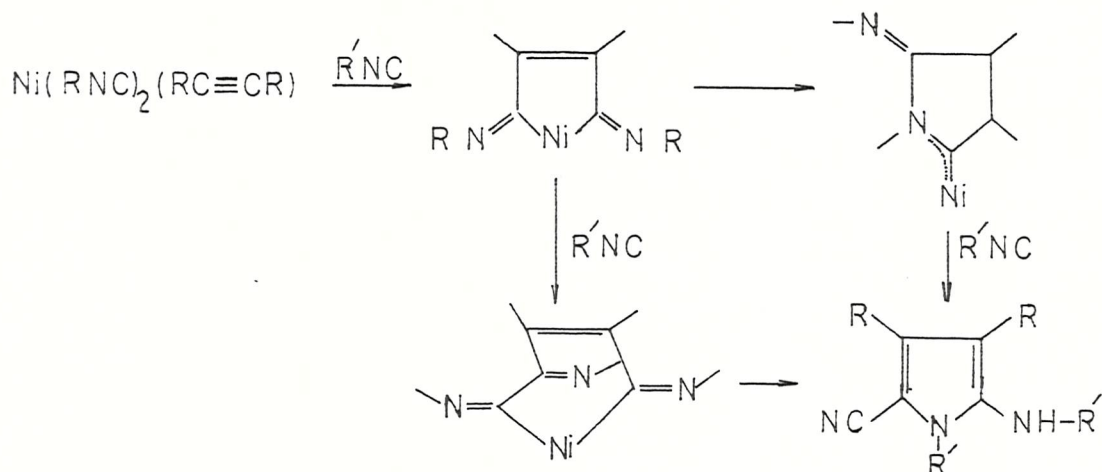
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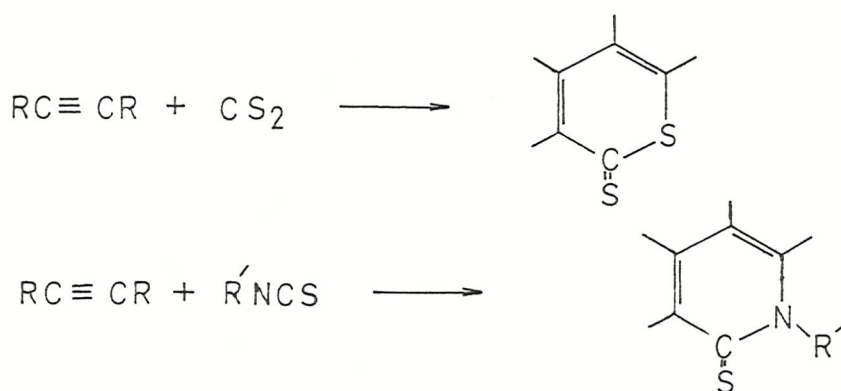
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D - Catalytic Cocyclization with Heterounsaturation

Various cobalt complexes reported by Yamazaki et al. (62) (77) and Bonnemann et al. (78) catalysed the syntheses of substituted pyridines from acetylenes and nitriles. Similar reaction is presented in Scheme 1.11 where a Ni complex plays the role.



The reaction with  $\text{CS}_2$  and  $\text{RNCR}$  act also in the similar way with acetylene (62) to give new heterocycles.  $\text{CpCo}(\text{PPh}_3)_2$  catalyzed those



reactions. An ionic intermediate  $\text{Cp}(\text{PPh}_3)\text{Co}^+ - \text{C}(\text{R}) = \bar{\text{C}}\text{R}$  has been suggested. The presence of this intermediate is supported by isolation of an intermediate complex (E) (79) from a similar reaction where Rh complex is the catalyst.