ELECTRONIC STRUCTURE AND REACTIVITY OF CARBYNE BRIDGED BIMETALLIC COMPLEXES

A THESIS
SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

By

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to my beloved parents

CONTENTS

S T A T E M E N T

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the School of Chemistry, University of Hyderabad, Hyderabad, India under the supervision of **Professor E.D. Jemmis**.

In keeping with the general practice of reporting scientific observations due acknowledgements have been made wherever the work described is based on the findings of other investigators.

Bharatam V. Prasad

Hyderabad

August, 1990

C E R T I F I C A T E

Certified that the work contained in the thesis entitled : **"ELECTRONIC STRUCTURE AND REACTIVITY OF CARBYNE BRIDGED BIMETALLIC COMPLEXES"** has been carried out by Mr. Bharatam V. Prasad, under my supervision and the same has not been submitted elsewhere for any degree.

E.D. Jemmis
(Thesis Supervisor)

DEAN
School of Chemistry

A C K N O W L E D G E M E N T S

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Bharatam V Prasad

A PERSPECTIVE

The qualitative ideas of a set of philosophers, alchemists and doctors took the systematic shape of chemistry when quantitative methods are used by Lavoisier in the last quarter of 18th century. With the advancement in the mathematical applications to chemistry, and with the availability of digital computers now chemistry is becoming more and more numerical. At the same time the line of separation between fortuitously divided several branches of chemistry is gradually disappearing. This is particularly true between organic and inorganic chemistry. These two factors worked together for the development of organometallic chemistry. This is the branch of chemistry in which theory and experiment work hand in hand. This is mainly due to the fact that the theoretical results in this field are very much appealing to experimental chemist and also because the ground rules for understanding are only emerging.

Two different theoretical approaches are popular in the two arms of organometallic chemistry. Qualitative semi-empirical methods are the only practical ones in organotransition metal chemistry. Ab initio methodology is widely applied in main group organometallic chemistry. Combined efforts of these two philosophies provide dramatic results as in the case of organosilicon chemistry. Yet, the studies are mostly limited to the electronic structure analysis of individual molecules or studies on some potential energy surfaces. Even though quantitative analysis of reaction pathways in organometallic reactions are beginning to appear, the ab initio calculations on reaction paths, even today, are prohibitively expensive. An

approach advocated mainly by the Hoffmann School teaches us a way of deriving conclusions from an understanding of molecular orbitals involved in conjugation with the experimental facts. In this thesis we adopt this approach to study the chemistry of trivalent carbon in organometallic compounds. The various ways in which the fourth valency is satisfied provide interesting chemistry.

In this study, molecular orbital calculations at various levels of approximation are used depending on the problem at hand. Our arguments mainly depend on symmetry, overlap, electron count, electronegativity differences etc. Isolobal analogy is used to simplify the picture. This thesis is divided into six chapters. The first five chapters deal with the carbyne bridged transition metal compounds. The Fragment Molecular Orbital (FMO) approach where the MOs of the molecules are constructed from those of well understood smaller fragments will be used within the Extended Huckel method in these chapters. The sixth chapter deals with the compounds in which two main group atoms are bridged by carbyne group and their isomers. Semi-empirical (MNDO) and ab initio SCF MO methods are used in this chapter.

Chapter 1 deals with the electronic structure of various biscarbyne bridged bimetallic systems. $Me_2W(\mu\text{-}CH)_2WMe_2$, **1** possess a metal-metal σ bond as HOMO (d^1-d^1, W^+). The LUMO is a δ^* MO so that a d^2-d^2 system does not possess a metal-metal double bond. HOMO and LUMO of these compounds controls the reactivity towards small organic species. Only molecules with orthogonal π bonds can interact with **1**. Reaction of acetylene

with **1** is studied in detail. The electronic structures, and the reactivity of some important products is also included.

Chapter 2 explains the electronic structure of bimetallacyclopropene type of compounds. A clear double bond character between a metal and the bridging carbyne group is shown. The reactivity of these complexes arises after losing a ligand (carbonyl) from the metal which is not involved in double bond. The molecular orbital explanations for the observed reactivity are provided.

In Chapter 3, the CR^+ (and $CR^{\cdot}$) bridged bimetallic systems are studied using models. The availability of carbon based pure $p_\perp$ orbital as LUMO is responsible for the reactivity. A least motion path for the hydrocarbation reaction is studied and many more potential precursors for the hydrocarbation reaction are suggested. Theoretical studies on carbyne and heteroatom bridged bimetallic compounds are also presented in this chapter.

Molecular orbital control of the observed geometrical differences in $HM_3(CO)_{10}(\mu\text{-}CR)$ complexes is given in chapter 4. μ_2 vs μ_3 nature of bridging carbyne group in these complexes is studied. The interesting variations shown by these complexes as a change in the R group in carbyne are also discussed.

An interesting product of the reaction of carbyne bridged complexes with alkyne has the didehydroallyl bridge. The diffuse nature of the fragment molecular orbitals of metallic fragments controls the orientation of the straddling C_3R_3 ligand on a bimetallic template. This aspect is discussed in chapter 5.

A new isolobal analogy between trivalent boron and divalent silicon is pointed out in Chapter 6. Following the analogy, two novel compounds with one and two carbyne bridges are proposed. The relative energies and the stable geometries of these two compounds in comparison to their isomers is discussed using MNDO and ab initio methods.

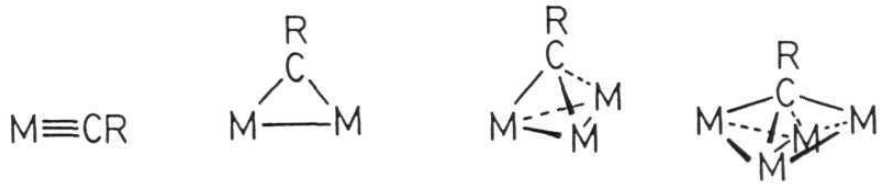
ABBREVIATIONS

Cp	: Cyclopentadienyl
Cp^*	: Pentamethylcyclopentadienyl
dmpm	: bis(dimethylphosphino)methane
dppe	: bis(diphenylphosphino)ethane
dppm	: bis(diphenylphosphino)methane
E	: Main group element
Et	: Ethyl
$HB(pz)_3$	: Tris(pyrazol-1-yl)borato
i-Pr	: Isopropyl
L	: Ligand
M	: Transitional metal
Me	: Methyl
$p_{\parallel}$	: In-plane (M-C-M) p orbital on carbynyl carbon
$p_{\perp}$	: Out-of-plane (M-C-M) p orbital on carbynyl carbon
Ph	: Phenyl
Py	: Pyridine
R	: Alkyl

Objective and Background

General Introduction

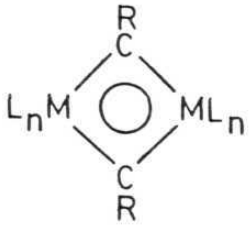
The simplest hydrocarbon ligand CH (methylidyne) is a very interesting species in organotransition metal chemistry because of its versatile coordination modes with transition metals.[1] The chemistry of carbyne complexes is also very important from the point of view of surface catalytic reactions.[2] Fischer-Tropsch synthesis[3] involves a surface bound methylidyne as an intermediate.[4] Alkyne metathesis involves the participation of alkylidyne groups.[5] The methylidyne ligand and its higher homologues (CR) form variety of organotransition metal compounds. The important structural varieties are **I-IV**[6]. All the four types



I II III IV

of compounds are shown to be very good building blocks in the cluster chemistry. Compounds of type **I** are alkylidynes where carbyne group is attached to only one transition metal.[6] The rich chemistry of these compounds is controlled by the metal carbon triple bond. In compounds of type **III** carbyne ligand bridges three metals in a μ_3-fashion. The chemistry of these compounds, which eventually are isolobal to tetrahedrane, is well documented.[7] Type **IV**[8] compounds contain a pentacoordinate carbon with a negative charge or an η^2 bridging C-R group in neutral compounds. All the three types **I**, **III** and **IV** show specific ways of satisfying the valency around carbon. Not many alternatives are available. Many experimental studies[6-8] and some theoretical studies[9] are available on compounds of type **I**, **III** and **IV**.

Our interest is specifically concentrated on compounds of type **II** where the carbyne ligand bridges the two metals in a bihapto manner. With only three valencies satisfied in two center two electron bonds, the bridging carbon is left with an electron. The multitude of the available structures show that there are a number of ways of satisfying the fourth valency. This property highlights the importance of compounds of type **II** amongst the four types **I - IV**.



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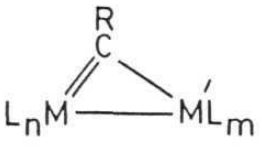

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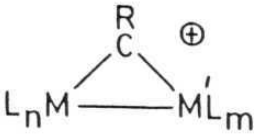

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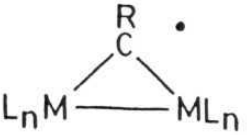

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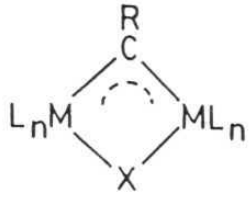

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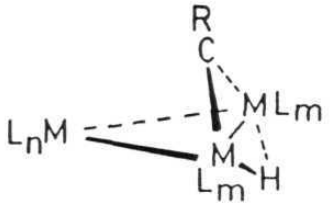

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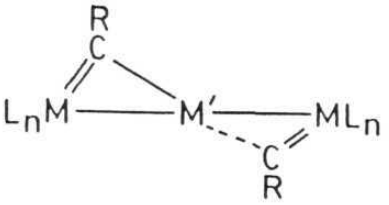


XI

Seven structural varieties **V - XI** are observed in literature for the compounds of type **II**. They are (i) 1,3-dimetallacyclobutadienes with two carbynes bridging on both sides of metallic frame work, **V**,[10] (ii) carbyne bridging heterobimetallic system, **VI**,[11] (iii) CR^+ bridging the bimetallic systems, **VII**,[12] (iv) carbyne radical bridging compounds, **VIII**,[12] (v) carbyne and heteroatom bridging a homobimetallic system **IX**,[12] (vi)carbyne group bridging two metals in trinuclear complexes **X**[13] and **XI**.[11] The bridging carbyne unit may have a more electronegative substituent like OMe, SMe or NMe_2 etc. Most of

these complexes have a metal-metal bond. But there is no paucity of complexes without metal-metal bond. Many clusters contain a unit with carbyne group bridging two metals are also known.[13]

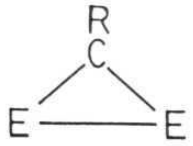
A general account is given below. 1,3-dimetallacyclobutadienes are usually obtained by treating MCl_n compounds with Grignard's reagent $ClMgCH_2SiMe_3$. Compounds of type **VI** are prepared by the reaction of alkylidynes, **I** with various lowvalent metallic species. Replacement of one ligand by alkylidyne group gives these compounds. These can grow into dimers or extended chains. Compounds of type **VII** are in general obtained from two methods. One is protonation of vinylidene bridged metal complexes and the other is dealkylation (dealkoxylation) of carbene bridged complexes. The radical bridged compounds are observed as reaction intermediates. The original precursor for compounds of type **X** is the well known $M_3(CO)_{12}$. Type **XI** compounds are actually extended from compounds of type **VI**.[14]

All the seven types of complexes are shown to be very reactive. All of them react with small organic groups to give carbon-carbon bond formation reactions. But the detailed chemistry varies from compound to compound. Compounds of the type **V** are reactive at the metal center, and the reactivity is very specific. This aspect has been explained using theoretical methods. Compounds of type **VI** are experimentally studied in detail. These compounds react with small organic molecules to give products that trigger catalytic reactions such as polymerization, oligomerization etc. Also, these complexes are shown to be the fundamental building blocks of cluster chemistry. Compounds of type **VII** react with a wide variety of small organic nucleophiles and specifically with alkenes in a reaction that is

named as hydrocarbation. This is developing into a separate branch of its own. The radicals of type **VIII**, even though unstable, are very important in catalytic processes. Compounds of type **IX** also react with alkynes and other small organic molecules to give interesting products. Compounds of type **X** show some structural changes as a function of R group on the bridging carbyne. These compounds also show specific reactivity towards organic molecules. Type **XI** compounds are used for the synthesis of larger clusters. All of these complexes, **V-XI**, react with various metal carbonyls to give large clusters.

In this thesis, we study the the electronic structure and reactivity of these complexes using qualitative molecular orbital methods. Our aim is to bring them into one frame work and to seek resemblances and differences from the point of view of both structure and reactivity. We restrict ourselves to theoretical study of reactivity of **V** to **XI** towards small organic reactants. Electronic structures of these complexes are obtained using semi-empirical molecular orbital calculations. Fragment Molecular Orbital (FMO) method[15] within the Extended Huckel approximation[16] is used to understand the interactions of bridging carbyne ligands with the remaining skeleton of the molecules. The reactivity is explained on the basis of molecular orbital patterns and Walsh diagrams constructed along appropriate reaction coordinates. Isolobal analogy[17] is used to point out the differences arising among these complexes.

An attempt is made to trace equally interesting chemistry when a carbyne group bridges two main group elements (**XII**). In the process we are able to hit at some useful analogies. These



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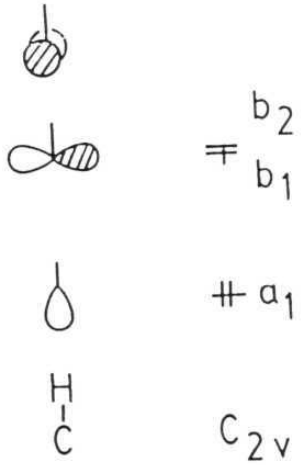
results are discussed in the last chapter of the thesis. Ab initio Quantum Chemical methods are used to get reliable results in this problem.[18]

The Carbyne Ligand

In the complexes under study, the carbon atom of the carbyne ligand has the sp^2 hybridization. One p orbital is left unhybridized. The interaction of this p orbital with other metal orbitals in the complexes is responsible for the extensive chemistry of the complexes under study. The carbyne (CR) fragment has the frontier orbitals $(a_1)^2$, $(b_1)^1$ and $(b_2)^0$ in C_{2v} symmetry, as shown in **XIII**. The a_1 and the in-plane p orbital (b_1) are responsible for the formation of metal-carbon bonds. The out-of-plane p (b_2) orbital is responsible for the reactivity of the complexes containing CR bridging the bimetallic system. In the complexes **V - XI** the bridging CR ligand may formally be treated as a three electron donor.



XIII

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(11) Details are given in Chapter 2.

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CHAPTER 1

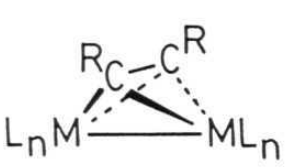
Electronic Structure and Reactivity of Biscarbyne Bridged Binuclear Transition Metal Complexes

1.1 ABSTRACT

The electronic structure and reactions of $L_4W_2(\mu\text{-}CR)_2$ are studied theoretically using the Fragment Molecular Orbital approach within the Extended Huckel method on the model $L_2W(\mu\text{-}CH)_2WL_2$, ($L=CH_3$, OCH_3, CN). $L_2W(\mu\text{-}CH)_2WL_2$ has a metal-metal single bond (d^1-d^1, W^{+5}). The LUMO is a δ^* MO (a_u) so that d^2-d^2 system does not possess a metal-metal double bond. The donation of electrons from the π MO of an incoming ligand and the back donation of the M-M bonding electrons to a π^* MO lying in a plane perpendicular to that of the donor π MO trigger the reaction of ligands with $L_2W(\mu\text{-}CR)_2WL_2$. Thus alkyne, allene, CO, CO_2, RN_3, RCN, RNC, ketenes, but not ethylene and butadiene are expected to react. The Ta and Nb analogs do not react as there is no M-M bond to donate electrons to the π^* MO of the incoming ligand. The Re analog also is not expected to react in the same fashion as the δ^* acceptor orbital is already occupied. The μ-CR in $L_2W(\mu\text{-}CR)(\mu\text{-}C_3R_3)WL_2$ does not react with another molecule of acetylene as the δ^* acceptor orbital has been pushed up by the $\mu\text{-}C_3R_3$ ligand.

1.2 Introduction

Metallacycles have been playing pivotal role in the development of organometallic chemistry.[1] Unsaturated metallacycles especially provide interesting prospects. Unsaturated metallacycles are observed in alkyne metathesis[2] and ligand replacement reactions such as those of alkynes with lowvalent metallic species.[3] Unsaturated dimetallacyclic compounds are also known.[4] Reaction between binuclear transition metal complexes with M-M multiple bonds and alkyne or two alkylidyne units in general gives rise to three types of products: a) dimetallatetrahedrane, **I**, b) 1,2-dimetallacyclobutadiene, **II**,



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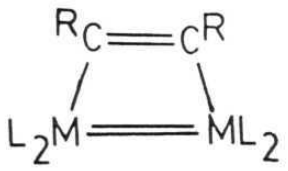

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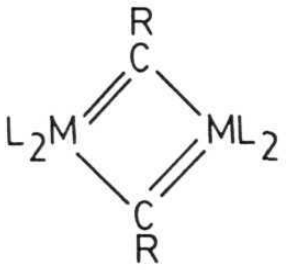
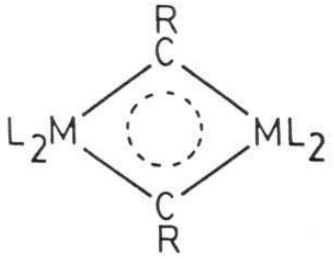


III

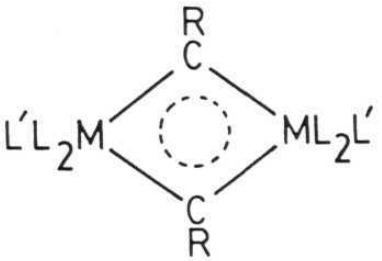
and c) 1,3-dimetallacyclobutadiene, **III**. The chemistry of perpendicular and parallel alkyne bridged bimetallic complexes **I** and **II** was discussed in detail.[5] In this Chapter we discuss the electronic structure and reactivity of 1,3-dimetallacyclobutadienes.

1,3-dimetallacyclobutadienes are an interesting structural species.[6] Even with 4n (n=1) π electrons, these compounds show exceptional stability, typical of aromatic compounds. All of them have two carbyne groups bridging the two metals. Recently many compounds with two μ_2 carbyne units bridging two metals are prepared, a few of them with a metal-metal bond. Compounds



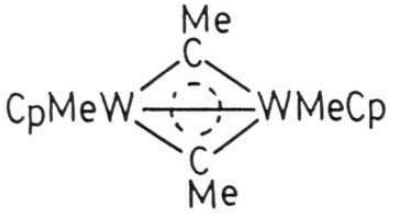
	M	R	L	Ref.
1	W	$SiMe_3$	CH_2SiMe_3	7,8
2	Ta	$SiMe_3$	CH_2SiMe_3	9
3	Nb	$SiMe_3$	CH_2SiMe_3	10
4	Re	$SiMe_3$	CH_2SiMe_3	11
5	W	Ph	O-t.Bu	12
6	W	$SiMe_3$	O-iPr	13

1-6[7-13] are isostructural. Treating CR as a 3- ligand, **2** and **3** have (d^0-d^0) metals, with no possibility for direct M-M interaction. **1, 5** and **6** are (d^1-d^1) systems indicating an M-M bond. **4** is a (d^2-d^2) system, has four electrons to be distributed between the two metals. The dependence of the M-M distance on the electron count has been described previously.[11] **7**



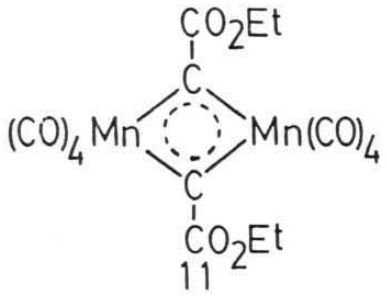
	M	R	L	Ref.
7	W	$SiMe_3$	L = CH_2SiMe_3	
			L′ = Cl	14
8	W		L=L′= $OCMe_3$	15
9	Mo,W	CMe	L=L′= CH_2CMe_3	16

is very close to **1** except that M-M σ bond in **1** is replaced by two terminal M-Cl bonds.[14] **8** and **9**, which are proposed as



10

intermediates in the alkyne metathesis reaction,[15,16] are isostructural to **7**. **10** is also a (d^1-d^1) system and has an M-M σ bond.[17] **11**[18] and **12**[19] are isoelectronic. Here, ML_n is a d^4-



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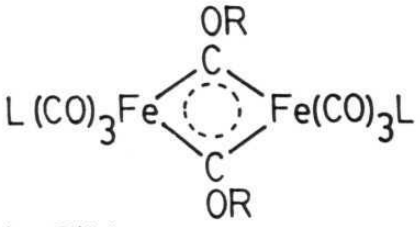
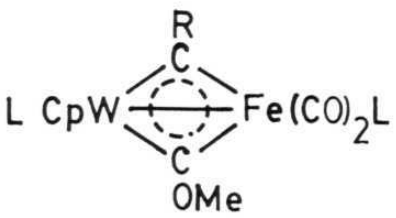
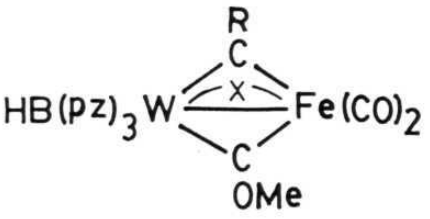


L=SiMe3 12

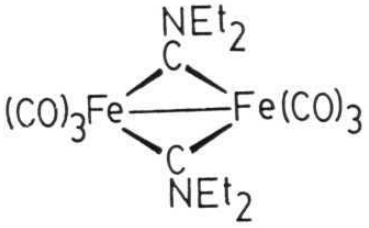
$-ML_4$ unit. **13** and **14** are isoelectronic.[20] **15** is an example of biscarbyne bridged complexes with a bent structure.[21] $CNEt_2$ group here may be treated as diethylaminocarbyne bridge because it can act as a 3 electron donor. Compounds of type **16** may also be treated as biscarbyne bridged bimetallic systems.[22]



13 L = PMe_3
R = C_6H_4Me-4



14 x = dpmp
R = C_6H_4Me-4



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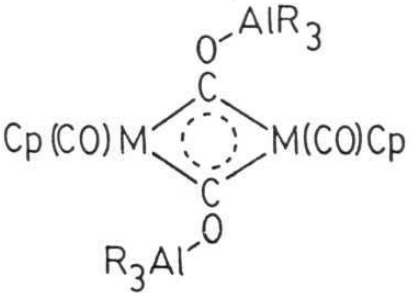
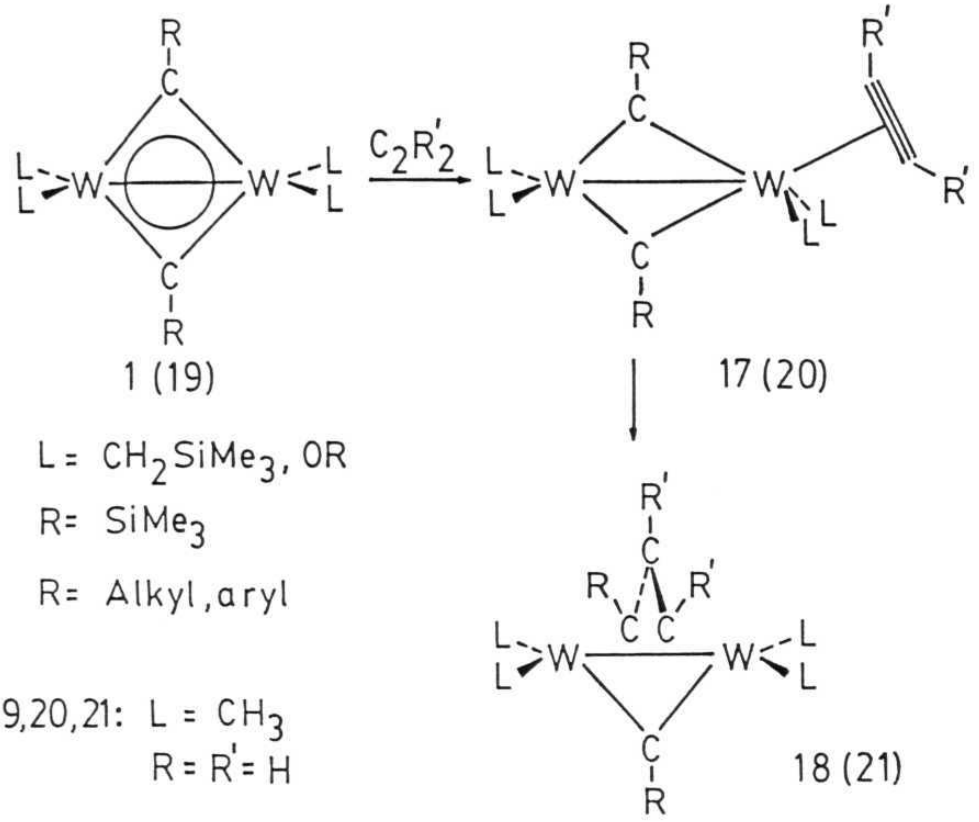


16, M=Fe,Ru

Compounds **1-7** show quasiaromatic character. Series of substitution reactions performed by Rothwell et al on **2** shows the ease of substitution on the metal.[23] The products maintain the aromatic character present in the initial starting compound. It is shown that the biscarbyne bridged bimetallic compounds may be obtained as intermediates in C-C bond formation reactions[3,24,25] and involve in some fluxional processes.[3,24] Reaction of small organic reactants towards these compounds show high selectivity. Electronic structure of these molecules gives an understanding of the interactions of CR groups with metallic template and helps us in explaining the observed reactivity.[26]

We have selected $(CH_2SiMe_3)_2W(\mu\text{-}CSiMe_3)_2W(CH_2SiMe_3)_2$, **1** for thorough analysis, from amongst these (**1-16**) for the following reasons. Reaction of $L_2W(\mu\text{-}CR)_2WL_2$, with RCCR gives $L_2W(\mu\text{-}CR)(\mu\text{-}C_3R_3)WL_2$, **18**,(L=OR, R; R=alkyl) where the C_3R_3 unit straddles the M-M axis.[6,27] The reaction proceeds through an intermediate alkyne adduct, **17** (scheme 1).[13,27] Detailed experiments of the Chisholm group have opened up a series of puzzles about this reaction.[13,27] Even though **1** has two μ-CR

Scheme 1



groups, only one mole of alkyne reacts with it; the second μ-CR is spared even when excess of alkyne is used. The reaction is facile with alkyne and allene but does not go with ethylene or butadiene. Isostructural Ta and Nb complexes which have two electrons less do not react with alkyne under similar reaction conditions.[23,27] Single crystal X-ray structures are available for representatives of **1**,[7b] **17**,[13] **18**.[13] The C_3R_3 in **18** is not symmetrical in the solid state with respect to the metals, despite the symmetric disposition of the rest of the molecule. The middle CR unit is closer to one of the metals so that the remaining metal forms an almost planar MC3 unit. However in solution the C_3R_3 group is fluxional leading to overall C_{2v} symmetry with the C_3R_3 plane bisecting the M-M bond, **18**. We analyze, explain and predict several aspects of this reaction.

Our approach is the following. The electronic structures of the stable species involved, **1, 17** and **18** are analyzed first using models **19, 20** and **21** respectively. Correlations are made between the molecular orbitals of **19-21** to understand the electronic requirements of the reaction. Reaction path for the conversion of **19** to **21** is studied next. Fluxional process and scrambling behavior of the bridging C_3R_3 unit in **18** is also studied.

1.3 Results and Discussion

Electronic Structure of $(CH_3)_2W(\mu\text{-}CH)_2W(CH_3)_2$, 19

$(CH_3)_2W(\mu\text{-}CH)_2W(CH_3)_2$, **19**, has been used as a model for **1**. The molecular orbitals of **19** can be constructed from simpler fragments W_2Me_4 and $(CH)_2$. The molecular orbitals of W_2Me_4, inturn, can be obtained from two WMe_2 units (Fig. 1.1). The WMe_2 fragment has a cluster of four orbitals $1a_1$, b_1, a_2, $2a_1$ (C_{2v} point group). The d_{yz} orbital (b_2) lies above these four. In addition there is a $3a_1$, a predominantly sp^n hybrid orbital, very high in energy. When the ML_2 fragments are brought together the b_1, a_2 and b_2 orbitals of WMe_2 give the bonding combinations b_{3u} (M-M, π)^2, b_{1g} (δ)^2, b_{2u} (π)^0 and the antibonding orbitals $b_{2g}(\pi^*)^0$, $a_u(\delta^*)^0$, $b_{3g}(\pi^*)^0$ orbitals (D_{2h} symmetry).[26a] The four orbitals resulting from the $1a_1$ and $2a_1$ are $1a_g(\sigma)^2$, $2a_g(\delta)^2$, $1b_{1u}(\sigma^*)^0$ and $2b_{1u}(\delta^*)^0$. With W^{2+}, the lowest two MOs are filled in WMe_2 and lowest four MOs are occupied in the W_2Me_4. These are all bonding and can be labeled according to Mulliken symbols as to predominantly σ, π or δ. The electronic configuration of W_2Me_4 is $\pi^2(b_{3u})$, $\sigma^2(1a_{1g})$, $\delta^2(b_{1g})$, $\delta^2(2a_g)$. The $(CH)_2$ group orbitals are essentially similar to

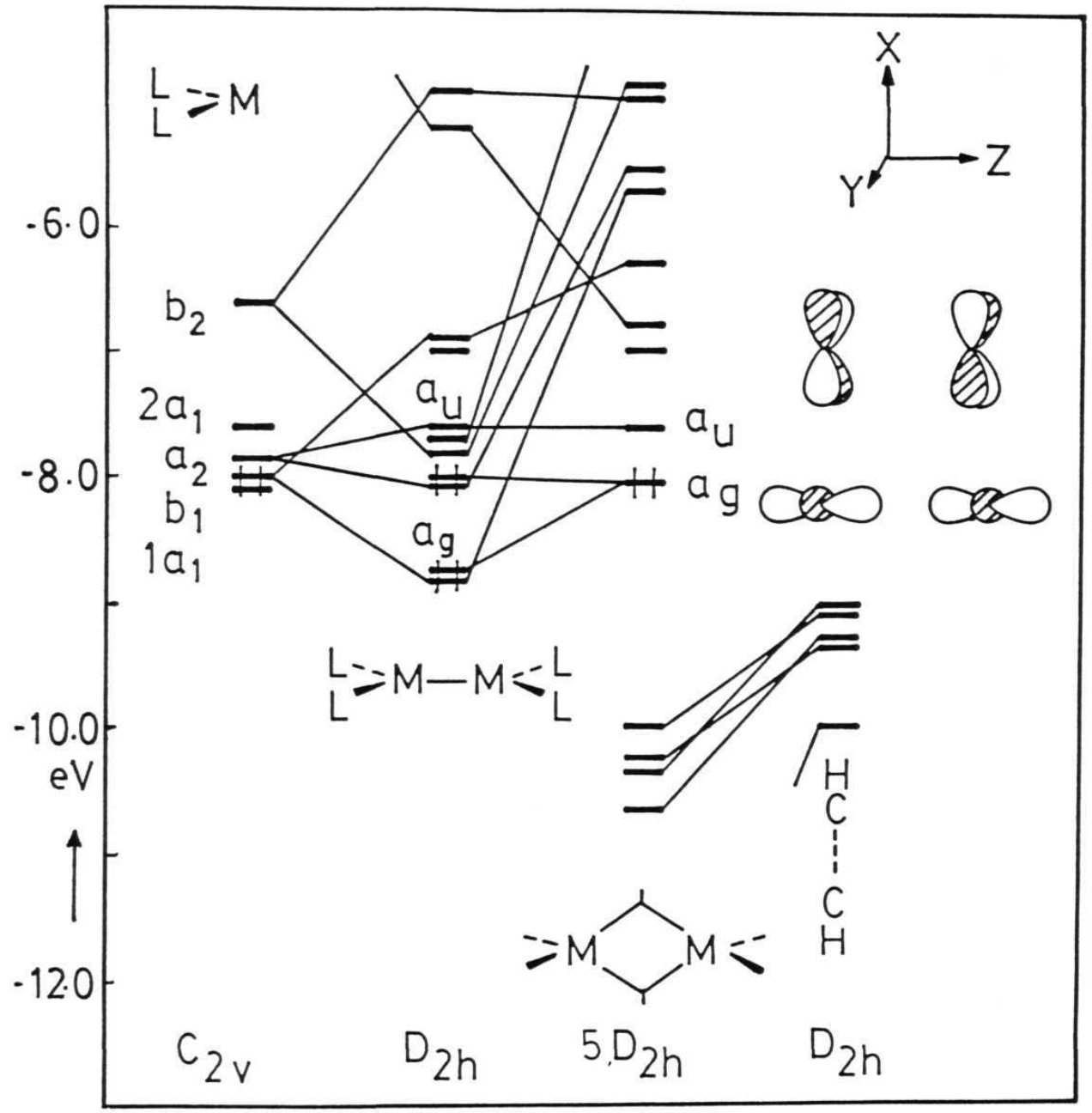


Fig. 1.1 The construction of the molecular orbitals of $(Me)_2W(\mu\text{-}CH)_2W(Me)_2$, 19 from smaller fragments. Two $(CH_3)_2W$ units are brought together (left) to give the MOs of $(Me)_2W\text{-}W(Me)_2$. This is interacted with the MOs of HC....CH leading to the MOs of **19**.

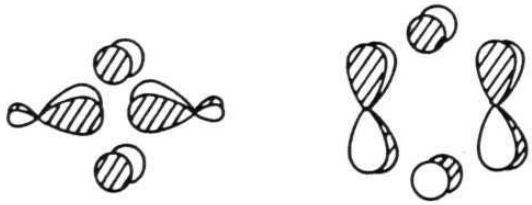
that of acetylene except for the feeble interaction between the two carbon atoms due to the large CC distance. Within D_{2h} symmetry the π (b_{2u}, b_{1u}) and the π^* (b_{1g}, b_{2g}) orbitals of HC ... CH lie close to each other but above the σ^* (b_{3u}).

The interaction of $W_2(CH_3)_4$ with HC...CH leads to **19**. Each of the frontier orbitals of $(CH)_2$ find a partner in the W_2Me_4 fragment and is stabilized so that there is a formal charge transfer of 6 electrons to the $(CH)_2$ fragment. Correspondingly some of the metal orbitals are pushed up high in energy. The a_u and b_{3g} orbitals of W_2Me_4 do not find match among the orbitals of $(CH)_2$ and remain non bonding. The metal orbitals ($1a_g$, $1b_u$ and b_{2g}) are not changed to a greater extent. The a_g (σ) orbital of (HC...CH) interacts with $1a_g$, $2a_g$ and $3a_g$ of W_2Me_4 and pushes them up in energy. $1a_g$ of W_2Me_4 becomes $1a_g$, HOMO of **19**. $2a_g$ corresponds to a δ bond, but not occupied. The transfer of six electrons from M_2L_4 to $(CH)_2$ justifies the classification of bridging CH ligand as 3-, leading to an oxidation state of W^{+5}. The two remaining 'metal electrons' go into the W-W σ bonding orbital. The LUMO is a δ^* orbital (a_u). Hence, the Ta and Nb (d^0-d^0) analogs do not have M-M bond and the Re analog (d^2-d^2) has an M-M sigma bond and a δ^* bond. So, the possibility of double bond in Re analog is ruled out. The two orbitals σ (HOMO) and δ^* (LUMO) of **19** are to be followed carefully as they turn out to be the key for the reactivity or the lack of it of the μ-CH groups in **1** with alkyne. The HOMO-LUMO gap in **19** is rather small. This can be increased by varying the metal parameters, but optimum metal parameters do not change our arguments and hence were not sought. Fig. 1.1 shows that the carbyne (CR) based orbitals are very low in energy and are not

readily available for reaction. The metal based orbitals are in the frontier range. So, the reactivity of the species **1-6** should originate at the metal center. The observed substitution reactions support this idea.[23]

Quasiaromatic nature

Often the M_2C_2 unit in **1-16** is represented as metallacyclobutadiene with two MC double bonds. Occasionally a circle is drawn inside the M_2C_2 rhombus. What is the extent of the π-delocalization in these 1,3-dimetallacyclobutadiene compounds? This is an unusual example of a four membered ring with four π-electrons and yet 'aromatic', if this term is taken to mean extra stabilization. Fig. 1.2 shows the origin of the extra stabilization in comparison to cyclobutadiene. The $(CH)_2$ unit (along X axis) has b_{2u} (π) and b_{1g} (π^*) orbitals within D_{2h} point group. The $(CH)_2$ unit (along Z axis) has b_{2u} (π) and b_{3g} (π^*) orbitals. On the other hand, W_2Me_4 has a b_{1g}, b_{2u}, a_u and b_{3g} orbitals. So, the fragment $(CH)_2$ can find one stabilizing interaction and a degenerate pair in cyclobutadiene. But there are two stabilizing out-of-plane interactions in the formation of **19**. Both the bonding combinations b_{2u} (**22**) and b_{1g} (**23**) are occupied imparting extra stablility to the compound. Six π type orbitals are present in **19** in comparison to four in C_4H_4. The



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four π electrons in compounds **1-6** may be considered to be delocalized in the ring. Unlike in the organic counter part, a

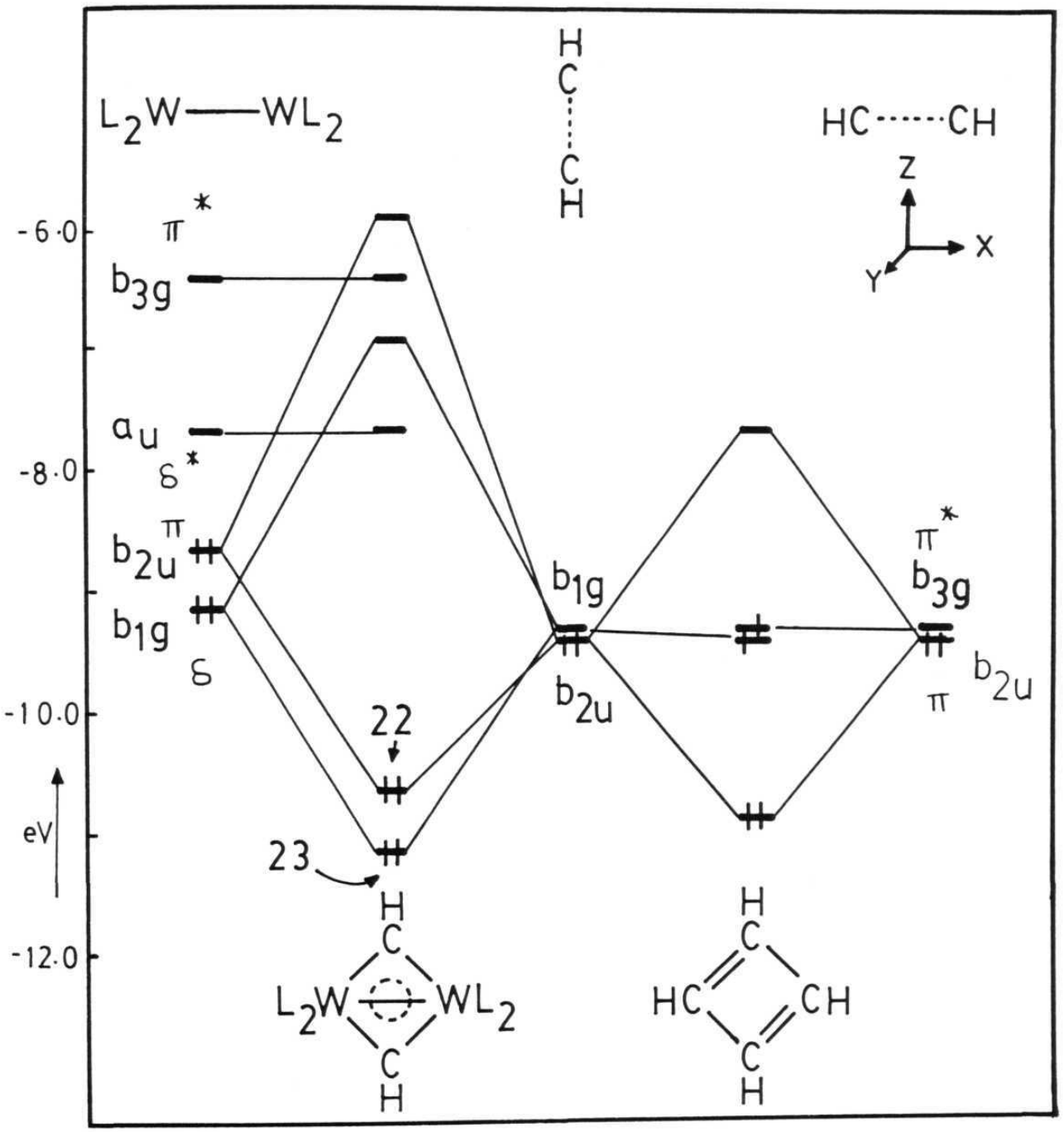
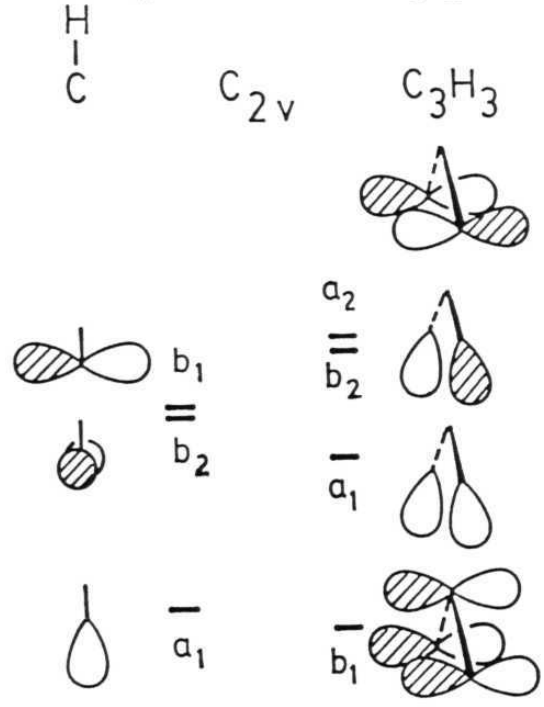


Fig. 1.2 Schematic interaction diagrams showing the correlation between the out-of-plane orbitals of **19** and cyclobutadiene.

1,3- σ bond between the two metals in **1,4-6** does not detract much from the π delocalization. Such, d orbital participation in π delocalization was pointed out earlier.[28,29]

A comparison of CH and C_3H_3 fragments. The Electronic Structure of $(CH_3)_2W(\mu\text{-}CH)(\mu\text{-}C_3H_3)W(CH_3)_2$, 21.

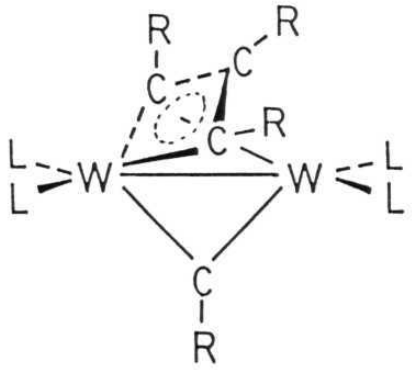
Replacement of one of the CR groups in **1** by C_3R_3 gives **18**. The electronic structure of the corresponding model, $(CH_3)_2W(\mu\text{-}CH)(\mu\text{-}C_3H_3)W(CH_3)_2$, **21** may be analyzed from the fragments using an interaction diagram. However, it is not necessary. The difference between **18** and **21** is that of μ-CH and $\mu\text{-}C_3H_3$. The frontier molecular orbitals of C_3H_3 and CH are similar, with the exception of the extra a_2 orbital of C_3H_3, **24**. Thus the MOs of



24

21 should be very much similar to that of **19** except for the changes in the a_2 (a_u and b_{3g} in D_{2h}) orbitals. The correlation of the MOs of **19** and **21** shows that the a_u orbital (LUMO in **19**)

forms bonding and antibonding combinations with the a_u orbital of C_3H_3 Fig. 1.3 (a,b). Consequently the vacant metal based δ^* MO is now rather high in energy. This, as will be seen below, decides the reactivity of **19** over **21**. In these calculations, **21** was assumed to have c_{2v} symmetry where the C_3H_3 plane bisects the W-W bond. However, in the solid state, **18** is found to have less symmetrical disposition of the C_3R_3 group, with the middle carbon atom closer to one of the metals, **25**.[13] C_3R_3 group shows a dynamic behavior at room temperature giving an effective symmetry



25, C_s (26, R=H, L=CH_3)

of **21** (C_{2v}). Extended Huckel calculations gave nearly the same energy for **21** and **26** ($Me_4W_2(\mu\text{-CH})(\mu\text{-}C_3H_3)$, a model of **25**). The major changes in energy occur to HOMO and HOMO-1 Fig. 1.3 (b,e). HOMO comes down in energy by 0.5 eV while HOMO-1 goes up in energy by 0.35 eV. Since the variations are in opposite directions, the only conclusion to be drawn is that the energy difference between **21** and **26** will be small. The reasons for the tilting of **18** to **25** are explained in Chapter 5.

Despite similarities between CH and C_3H_3 MOs they differ in detail. One factor is the greater extension in space of the orbitals of C_3H_3 in relation to the MOs of CH. The immediate consequence of this is seen in the LWL angle in **1** and **18**. To

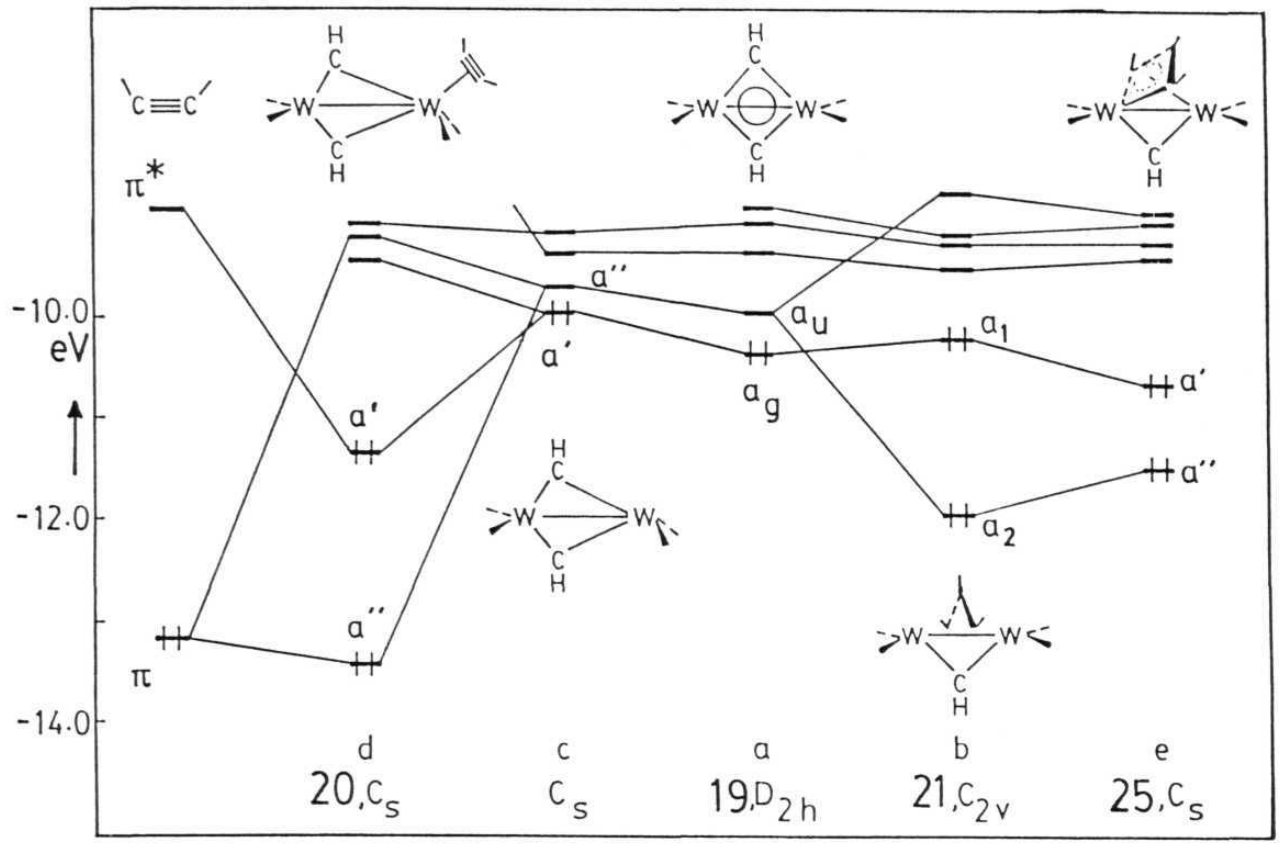


Fig. 1.3 This forms the central part of our arguments. (a) The lower lying metal orbitals of **19** are from Figure 1. (b) A correlation is made here from part 'a' since the difference between the two stems from the a_u (a_2 in C_{2v}) orbital of C_3H_3 which is absent in CH. (c) This part represents a distortion of **19** to a geometry found in the intermediate complex, **20**. (d) together with part 'c' and the MOs of acetylene, extreme left, we have the interaction of HCCH with distorted **19** leading to the MOs of the intermediate, **20** . Only the two stabilizing donor-acceptor interactions are shown. This indicates that the M-M bond donation to π^* is probably stronger than the π donation to M-M δ^* (LUMO). (e) (b ---> e) shows the correlation diagram for the distortion of **21** (C_{2v}) to **25** (C_s) which is the geometry observed in the solid state.

orient the $W(CH_3)_2$ fragment orbitals for better overlap with the μ-C_3R_3 ligand, the LWL angle in **18** should be smaller than that in **1**. This is indeed found to be true (the average values are 114.9° in $W_2(\mu\text{-}CSiMe_3)_2(O\text{-}i\text{-}Pr)_4$ and 102.4° in $W_2[\mu\text{-}CHCHC(SiMe_3)](\mu\text{-}CSiMe_3)(O\text{-}i\text{-}Pr)_4$.[27b] Such correlations exist between the cone angle and n in the $C_nH_nM(CO)_3$ complexes.[30]

Electronic Structure of the Intermediate, $Me_2W(\mu\text{-}CH)_2W(\eta^2\text{-}HCCH)Me_2$, 20 and the requirements for its formation.

The intermediate **17** formed during the reaction **1** ----> **18** is modeled by $Me_2W(\mu\text{-}CH)_2W(\eta^2\text{-}HCCH)Me_2$, **17**. The molecular orbitals of **17** are constructed from those of **19** and of acetylene. **19** is distorted first to a geometry close to that found in **17**. The two bridging groups are closer to one of the metals and the methyl ligands on the other metal are tilted to give way for incoming acetylene. Fig. 1.3 (a,c) shows the variation in the MOs during this distortion. Consequently the metal-metal bond is broken, the symmetry is reduced, and the metal based MOs are polarized on one or the other metal. The important interactions involved in the complexation with alkyne are the following. What was originally the M-M σ bond is now localized on one metal and donates electrons to the inplane π^* MO of acetylene, **27**, (Fig. 1.4). The δ^* LUMO in the new geometry is an ideal acceptor from the π bond of alkyne perpendicular to the C_2H_2 plane, **28**, (Fig. 1.4). The in-plane π bond (a') of acetylene is involved in destabilizing four electron two orbital interactions while the perpendicular π^* of acetylene (a'') interacts only with the empty orbitals of the metal fragment (these are not shown in the

diagram). Thus the requirements on the π ligands for the formation of the intermediate complex is the availability of one acceptor and one donor π orbitals in orthogonal planes. The metal requires corresponding donor and acceptor orbitals. The Ta or Nb analogs of **1** (**2** and **3**) do not have the two electrons of the M-M bond for donation to the π^* of alkyne to trigger the reaction. The Re analog of **1** (**4**) (d^2-d^2) should also not favour the initial complex formation as the acceptor orbital δ^* is already filled. Fully knowing the limitations of the Extended Huckel method, we have plotted the total energy as a function of the reaction coordinate designed to get the intermediate complex **20** from **19** for W and for two electrons less and two electrons more (Fig. 1.5). The energy goes down after initial increase of the d^1-d^1 system (W2) while it goes up for d^0-d^0 or d^2-d^2 electron count without any minima corresponding to the intermediate complex.

The absence of reactivity of **17** with further alkynes can also be explained based on Fig. 1.3. The δ^* orbital of **19** which accepts electrons from the π orbitals of alkyne is not the LUMO in **21**; this has been pushed away by the a_2 orbital of C_3H_3 (Fig. 1.3b). Thus a second acetylene does not have the same advantage along the reaction coordinate to form the intermediate complex. This protects the second μ-CR group from reacting. Ethylene, butadiene and other ligands with π MOs in one plane alone are not expected to react with **1** under similar conditions. These are supported by experimental observations.[6] In addition to acetylene, CO, CO_2, allene, ketene, HCN, HNC, RN2 and to a certain extent ketones should react with **1**. Some of these are already known,[6,31,32] others are worth trying.

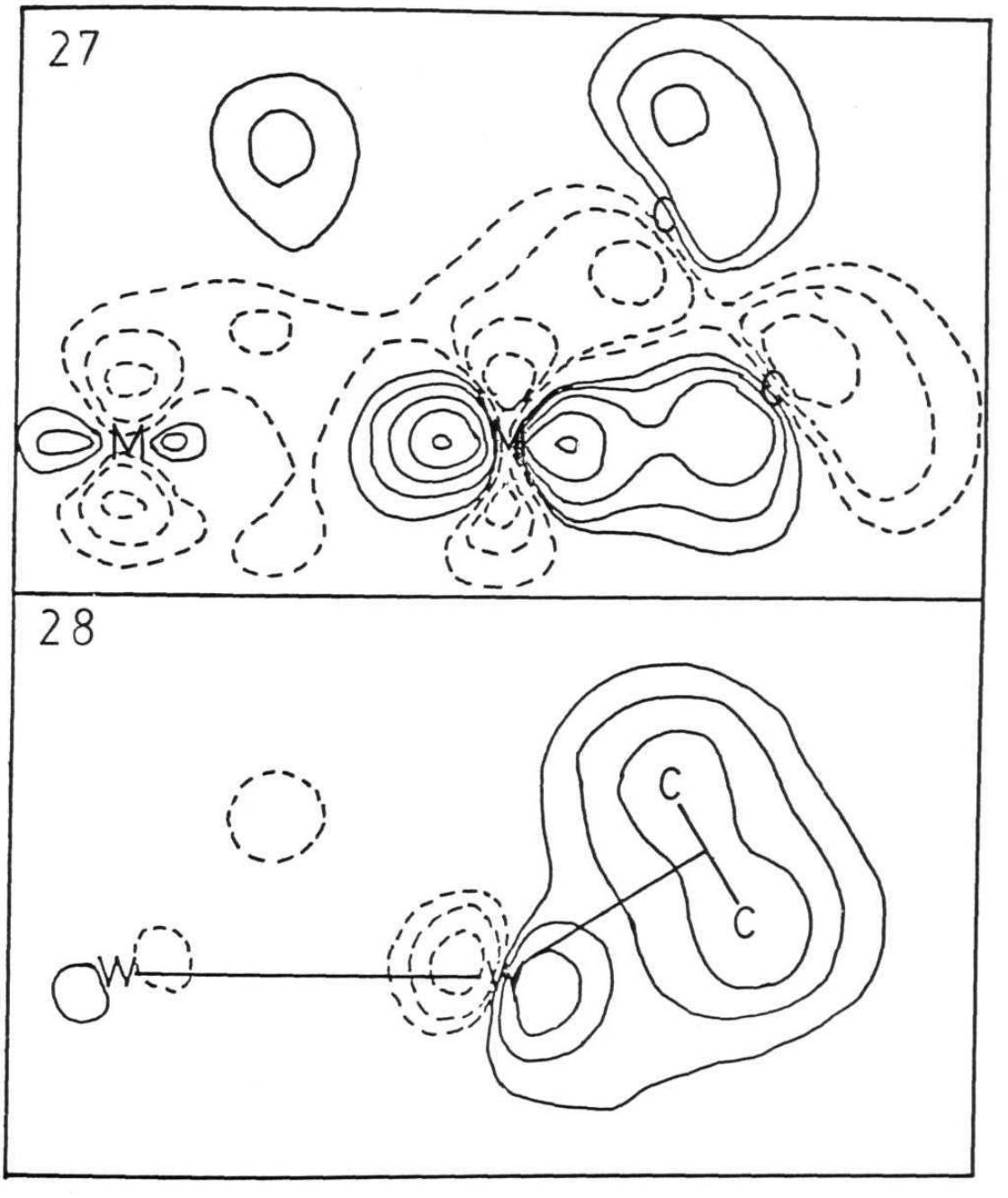


Fig. 1.4 Cross section of the MO corresponding to π(alkyne) to metal δ^* donation (**28**) and the metal σ to π^* (alkyne) donation **27**. **28** was plotted in a plane 0.5 Å above the plane of the drawing in **27**. The contours used are $\pm$0.4, $\pm$0.2, $\pm$0.1, $\pm$0.05 and $\pm$0.025.

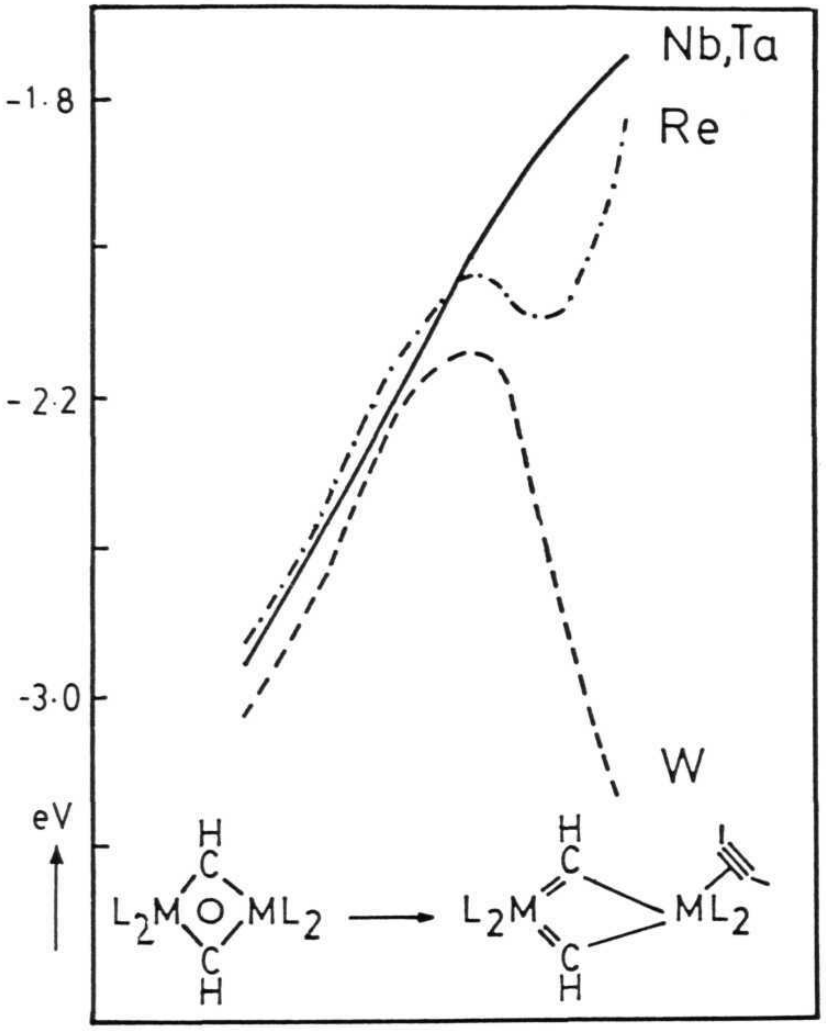


Fig. 1.5 The variation of sum of one-electron energies along the reaction coordinate leading to intermediate complex **20**, Nb, Ta and Re curves are approximated by adding and subtracting two electrons from that of $(CH_3)_2W(\mu\text{-}CH)_2W(CH_3)_2W(\eta^2\text{-}HCCH)$.

Effect of ligand substitution

Experimentally the stability of the intermediate complex **17** is found to be less for L=OR than for L=R.[13,27b] At the same time **17** with L=OR reacts faster to give the final product **18**. Any contribution from direct electronic effects to these observations were searched by calculations on **1** and **17** (L=OMe and CN, R=H). The replacement of CH_3 by CN or any π acceptor ligand lowers the energy of metal orbitals of π symmetry in ML_2 fragment. Similarly OCH_3 ligand pushes the d orbitals up in energy. These are reflected in the energies of the MOs of **1** for L=CN, CH_3 and OCH_3 (Fig. 1.6). The acceptor orbitals (LUMO) in **1** is higher for L=OCH_3 leading to decreased interaction between the π donor MOs of acetylene and the δ^*. The MO corresponding to the metal-metal bond also goes up with L=OCH_3. This helps in increasing the back donation to the π^* of the incoming acetylene. Since these are opposing each other we hesitate to draw any conclusions in the absence of more quantitative study.

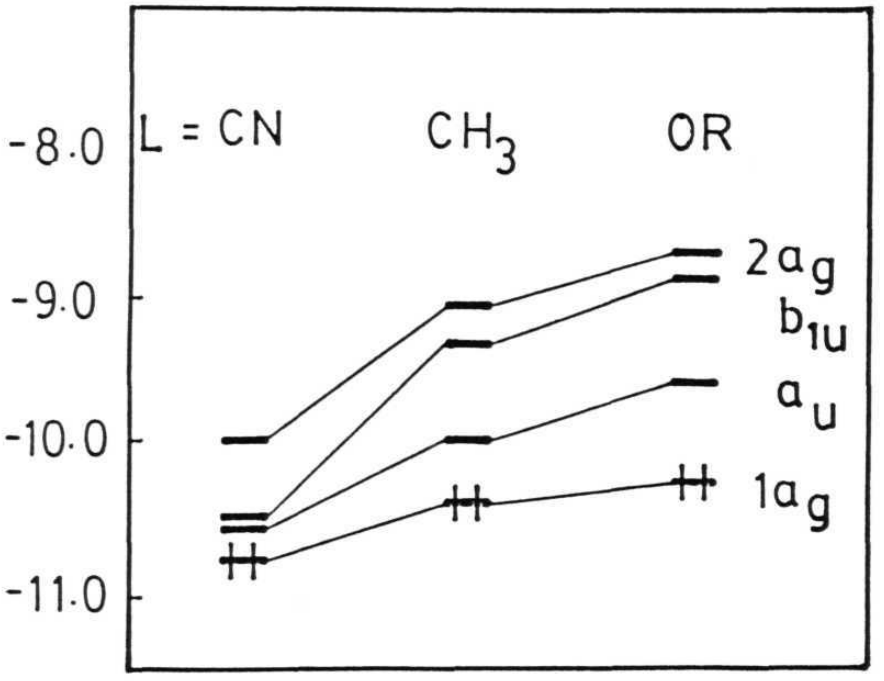


Fig. 1.6 The variation of frontier orbital energies of **19** with terminal ligands.

1.4 Conclusions

Electronic structure of complexes with a 1,3-dimetallacyclobutadiene unit is studied theoretically using Extended Huckel calculations on model compounds. The reaction of $L_2W(\mu\text{-}CR)_2WL_2$ with C_2R_2 is also studied. The donation of π electrons of an alkyne to the δ^* orbital of the metals and the back donation of the metal-metal bonding electrons to the π^* orbital in alkyne in a plane perpendicular to that of the donating π bond trigger the formation of the intermediate complex, $(Me_2W(\mu\text{-}CH)WMe_2(\eta^2\text{-}C_2H_2)$. This explains the lack of reactivity of ethylene and butadiene which do not have π MOs in perpendicular planes and of the Nb and Ta analogs which do not have the metal-metal bonding electrons for back donation. The Re analog is also not expected to react as δ^* MO is already occupied and hence cannot act as an acceptor orbital. The δ^* MO is pushed up in energy in the final product $Me_2W(\mu\text{-}CH)(\mu\text{-}C_3H_3)WMe_2$ so that the remaining μ-CH group does not react with acetylene.

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CHAPTER 2

Electronic Structure and Reactivity of Dimetallacyclopropenes

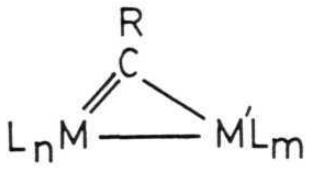
2.1 Abstract

Electronic structure studies of the compounds $Cp(CO)_2W[\mu\text{-}C(C_6H_4Me\text{-}4)]Fe(CO)_4$, **2** and $Cp(CO)_2W[\mu\text{-}C(C_6H_4Me\text{-}4)]Fe(CO)_3$, **3** by Extended Huckel method shows that their reactivity is controlled by the LUMO. In **3**, two π electrons are delocalized in the Fe-W-C ring. **2** is reactive towards carbene and fragments isolobal to carbene at the W-C axis. In **3** incoming carbene finds perfect match at Fe-C and Fe-W centres. Possible mechanistic paths are suggested for the reaction of carbenes and alkynes with **2** and **3**.

2.2 Introduction

Compounds of type **1** where the carbyne group bridges heterobimetallic template provide interesting chemistry. These compounds are shown to be the building blocks for the synthesis of larger cluster compounds.[1] These compounds can be used as very good catalytic reagents in their reaction with small organic molecules.[2] Polymerization and oligomerization are also triggered by these complexes.[3]

Bridging carbyne complexes represented by the general formula $L_nM(\mu\text{-}CR)M'L_m$, **1**, are prepared in a systematic way by



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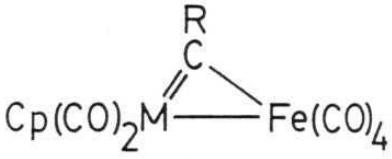
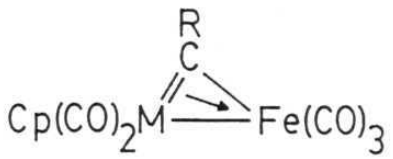
the reaction of alkylidynes ($L_nM{\equiv}CR$) with various low valent metallic species by replacing one or two of their ligands.[4] Stone and coworkers have synthesised a large set of such complexes with the general formula $Cp(CO)_2W[\mu\text{-}CR]M'L_m$, where $M'L_m$ ranges as $TiCp_2$, $ZrCp_2$, VCp_2, $Cr(CO)_2(C_6R_6)$, $W(CO)_5$, $Mn(CO)_2Cp$, $Re(CO)_2Cp$, $Fe(CO)_3$, $Fe(CO)_4$, $Co(CO)Cp$, $Rh(CO)(C_9H_7)$, $Ir(CO)(C_9H_7)$, $Pt(PR_3)_2$, etc.[5,6] More complexes are known where the $Cp(CO)_2W$ fragment is replaced by electronically equivalent metallic fragments such as $Cp(CO)_2Mo$.[7-11] In all of these complexes, a π bond is invoked between the carbynyl carbon and one of the metals to satisfy the valency at carbon and 18 electron count around the metal. Dimers or polymers of these dimetallacyclopropene type of molecules can be synthesized with spiro linkage.[12]

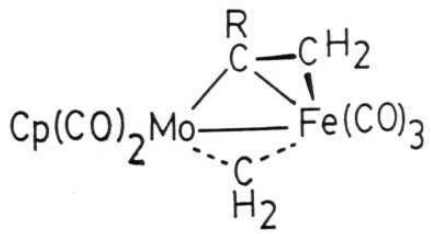
Among the many representative examples of type **1**, compounds with iron carbonyl fragments as $M'L_m$ provide wide ranging chemistry.[6-10] Both $Cp(CO)_2W(\mu\text{-}CR)Fe(CO)_4$, **2**[2d] and $Cp(CO)_2W(\mu\text{-}CR)Fe(CO)_3$, **3**[2d] are prepared. Crystal structures of compounds isoelectronic to them are known. In **2**, regular Fe-C and Fe-W

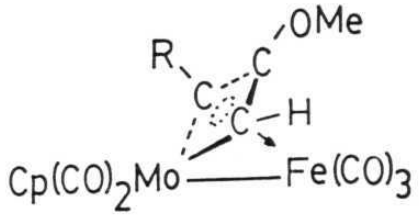




	M	R	
2	W	p-tol	3
4	Mo	p-tol	
5	W	H	12

single bonds and W-C double bond are indicated. In **3**, 4 π electron interaction of alkylidyne unit with $Fe(CO)_3$ is suggested. How is the electronic distribution in these compounds different? Reaction of $Cp(CO)_2Mo(\mu\text{-}CR)Fe(CO)_4$, **4** with small organic molecules give different products depending on the reaction conditions.[1] At room temperature **4** reacts with diazomethane to give $Cp(CO)_2Mo(\mu\text{-}CH_2)[\mu,\sigma : \eta^2\text{-}CR{=}CH_2]Fe(CO)_3$, (R=p-Tol, **6a** ; R=H, **6b**), and at low temperatures the reaction gives $Cp(CO)_2Mo[\mu\text{-}C(R)C(OMe)C(H)]Fe(CO)_3$, (R=p-Tol, **7a**; R=H,





6a R = C_6H_4Me-4
6b R = H

7a R = C_6H_4Me-4
7b R = H

7b).[13] Reaction of diphenyl acetylene with **2** gives $Cp(CO)_2W[\mu\text{-}C(R)C(Ph)C(Ph)]Fe(CO)_3$.[14] Reaction of **2** with various alkynes gives several products in which C_nR_n or C_nR_nCO groups bridge the two metals.[15] What is the electronic origin of this reactivity? Several other compounds of type 1 also show similar reactivity. Is the electronic origin of all these reactions same?

Electronic structure of **2** and **3** is studied to understand and to explain the reactivity. Fragment molecular orbital approach within the Extended Huckel formalism is used in this study. The reactivity of **2** and **3** towards carbene and alkynes is also pursued.

2.3 RESULTS AND DISCUSSION

Electronic Structure of $(CO)_2CpW[\mu\text{-}C(C_6H_4Me\text{-}4)]Fe(CO)_4$, 2.[2d]

$(CO)_2CpW[\mu\text{-}CH]Fe(CO)_4$, **5**, is taken as a model for **2**. The molecular orbitals of **5** can be constructed in two different ways: 1) From the interaction of CR with the remaining fragment. But this fragmentation did not provide any useful insights and is not discussed further. 2) Recognising the analogy between $Cp(CO)_2W{\equiv}CR$ and alkyne,[16] **5** may be fragmented as $Cp(CO)_2W{\equiv}CR$ and the $Fe(CO)_4$. Coordination around tungsten is adjusted to maintain C_s symmetry in the molecule. Even though this is slightly different from the coordination of ligands around Mo in **4**,[7] this simplification does not affect the electronic structure description.[17]

Fig. 2.1 shows the construction of the molecular orbitals of $Cp(CO)_2W(\mu\text{-}CH)Fe(CO)_4$, **5** from the interaction between $Cp(CO)_2W{\equiv}CH$ (**8**) and $Fe(CO)_4$ (**9**) fragments. The orbitals of the

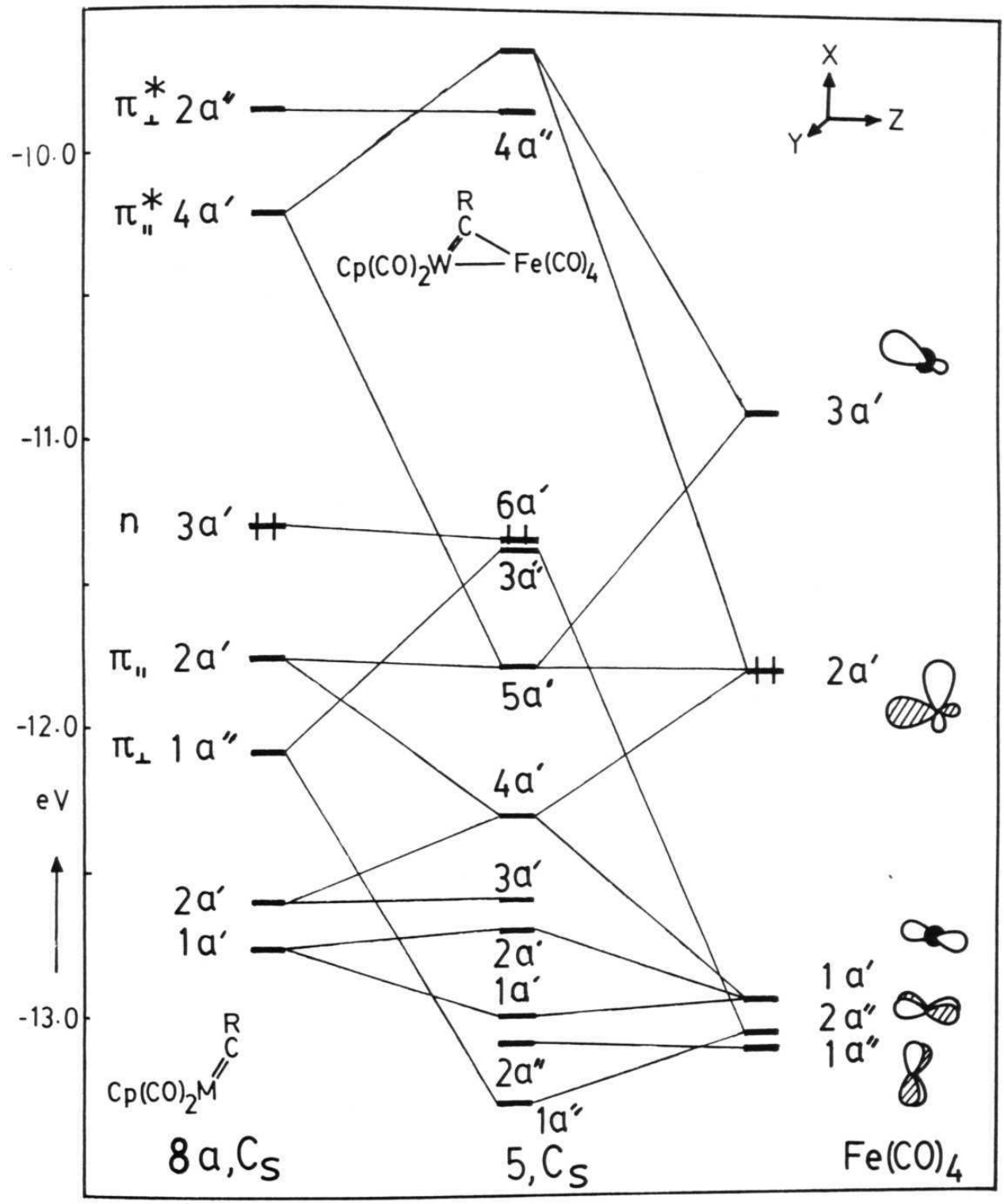
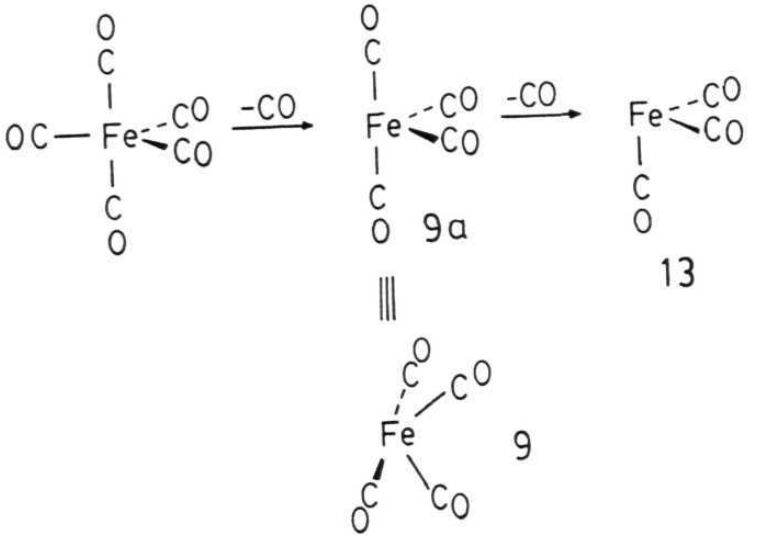


Fig. 2.1 Interaction diagram showing the construction of the MOs of $Cp(CO)_2W(\mu\text{-}CH)Fe(CO)_4$, **5** from $Cp(CO)_2W{\equiv}CH$, **8a** and $Fe(CO)_4$, **9**.

$Fe(CO)_4$ fragment are well documented.[18] This can be viewed as obtained from $Fe(CO)_5$ by removing one equitorial carbonyl (Scheme 1).[19] The fragment present in our complex, **9** is slightly distorted **9a**. This is a d^8-ML_4 fragment and four of the metal orbitals are filled. These are 1a" (d_{xz}), 2a" (d_{yz}), 1a' (mainly originating from d_z2), and the HOMO (2a') d_{xy} which has lobes directed towards the missing carbonyl. LUMO (3a') is a σ orbital with its lobe directed towards the missing carbonyl.

Scheme 1



Electronic structure of alkylidynes in general was studied in detail.[20] The geometry in the fragment **8** is different from the structure **10** where W-C-H is linear (Fig. 2.2).[21] The analogy between **10** and alkyne is earlier pointed out using isolobal arguments.[16] **10** has an M-C σ bond, two M-C π bonds and correspondingly two unoccupied π* orbitals.[16a] Non-bonding d_x2_-y2 orbital based on tungsten is the HOMO of **10**, (3a'). The differences between **8** and **10** are those between linear and bent acetylenes.[22] The crystal structures of compounds of type **1** shows two types of geometry around tungsten-carbon bond, represented by **8a** and **8b** (Fig. 2.2).[5,6] In **8a**, the centre of the Cp ring lies in the W-C-H plane and in **8b** one of the carbonyls is

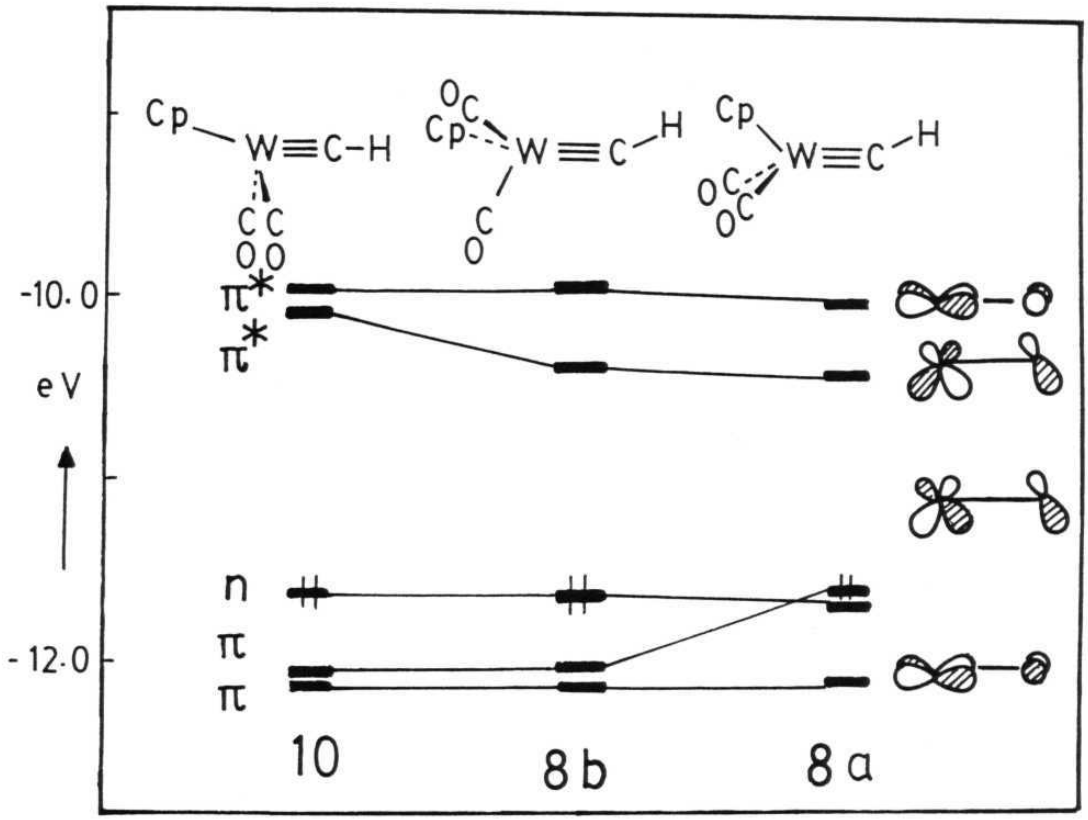
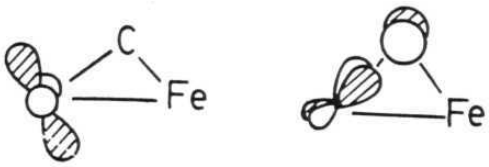


Fig. 2.2 Correlation diagram showing the orbital of **8a**, **8b** and **10**.

in the W-C-H plane. There are only minor differences in the energy levels of **8a** and **8b**. The correlation is shown in Fig. 2.2. Many of the complexes of type **1** have **8b** as the fragment.[5-6] Since the differences between the two are small, we use **8a** for the construction of the interaction diagram Fig. 2.1 (so as to maintain atleast C_s symmetry). The change of geometry from **10** to **8a** directs the in-plane π orbitals towards the $Fe(CO)_4$ ligand. The out-of-plane π orbitals do not show major change. The bent fragment **8a** has the following MO order: 1a" $(\pi)^2$, 1a' $(\pi)^2$, 2a' $(n)^2$, 3a' $(\pi^*)^0$ and 2a" $(\pi^*)^0$ (Fig. 2.2).

In **2**, the alkylidyne occupies an equitorial coordination site, where W≡C takes the place of a carbonyl of $Fe(CO)_5$. An interaction diagram to obtain the MOs of $Cp(CO)_2Mo(\mu\text{-}CH)Fe(CO)_4$ was given earlier by Stone and coworkers.[23] Only the important interactions involved in the formation of **5** are given here. There is a strong interaction between 1a" of **8a** and 2a" of **9**. The bonding combination 1a" corresponds to the delocalized π MO. The antibonding combination 3a" has Fe-C π^* character. Both of them are occupied. Net effect is slight destabilization of W-C π combination. The in-plane π (2a') and π^*(4a') orbitals of **8a** interact with 2a' and 3a' of **9** leading to Fe-W and Fe-C bond formation. These interactions are similar to Dewar-Chatt-Duncanson model.[24] The non-bonding W orbital (3a') of **8a** remains unchanged to become HOMO 6a' in **5** (**11a**). The out-of-plane π^* orbital of the W-C axis does not find any match and becomes LUMO in the complex **5**, **11b**. **2** is isolobal to cyclopropene.



11a 11b

Calculations made on **5** using the geometry given in crystal structure of **4**[7] shows that the electronic structure is very much similar to that shown in Fig. 2.1 (specifically a non-bonding W based orbital remains as HOMO and a W-C π^* orbital as LUMO). Slight differences are observed only in energies of the MOs and coefficient sizes. No interaction between the in-plane carbonyl and the Fe atom is found. The reduced overlap population between the in-plane C(O) and Fe is negligible (0.018). No partial bond between the in-plane C(O) and Fe atoms should be invoked. Probably minor differences in the steric factors might have led to the low symmetry, observed geometry.

Electronic Structure of $(CO)_2CpW[\mu\text{-}C(C_6H_4Me\text{-}4)]Fe(CO)_3$, 3.[2d]

The electronic structure of $(CO)_2CpW(\mu\text{-}CH)Fe(CO)_3$, **12**, (a model for $HB(pz)_3(CO)_2W[\mu\text{-}C(C_6H_4Me\text{-}4)]Fe(CO)_3$[12] is obtained from the interaction of **8a** with $Fe(CO)_3$, **13** (Fig. 2.3). The fragment $Fe(CO)_3$[25] can be conceptually obtained from $Fe(CO)_4$ by removing one axial carbonyl ligand (Scheme 1). With a local C_{3v} symmetry, the $Fe(CO)_3$ fragment has a typical three below two orbital pattern. **13** has pseudo C_{3v} symmetry. The orbitals are shown in Fig. 2.3. HOMO of **13** is a 2a" (d_{yz}) orbital which has lobes directed towards the missing ligand. These are all occupied in the d^8 electron count. LUMO is 3a' (d_{xz}) orbital,

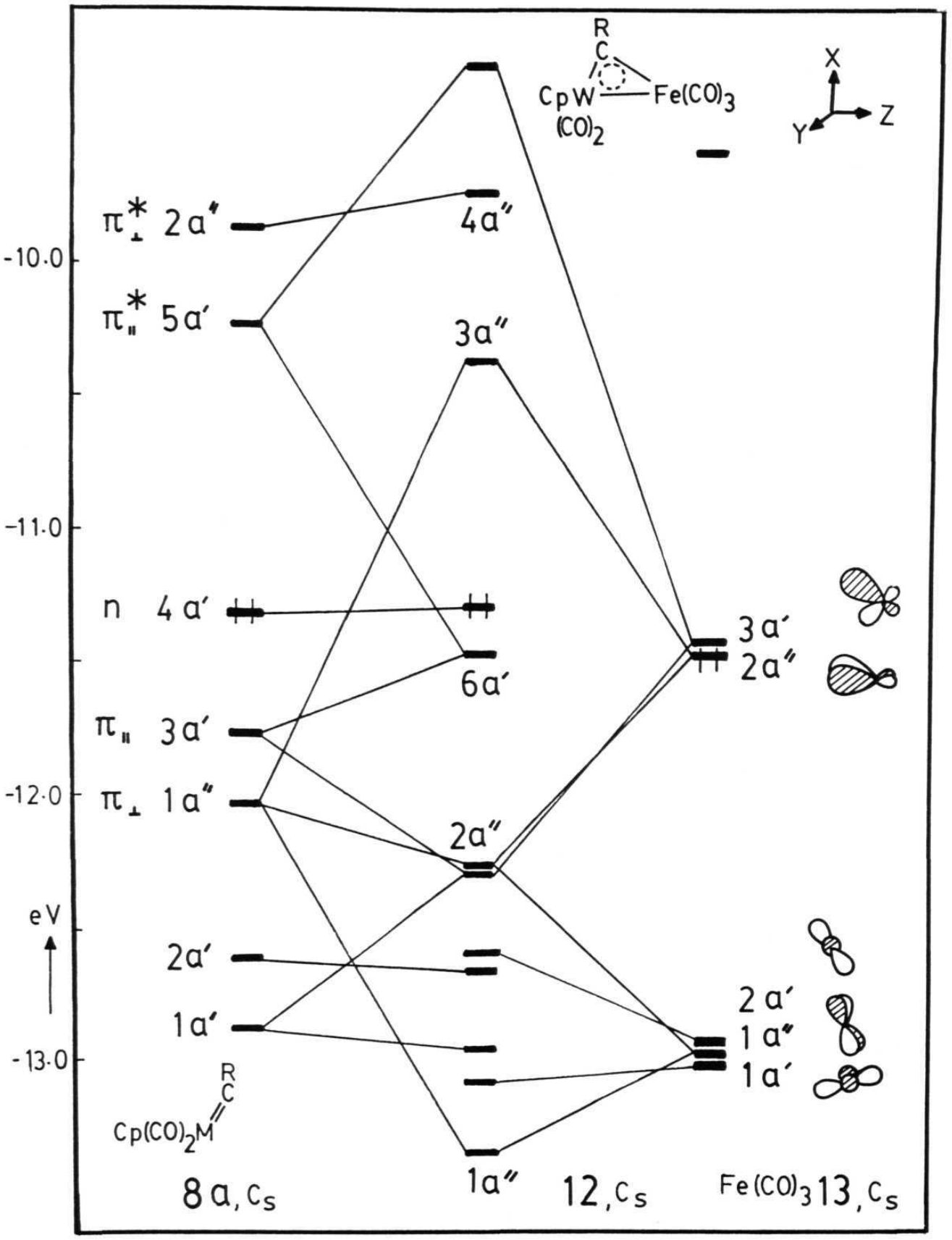
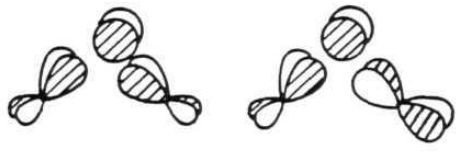


Fig. 2.3 Interaction diagram showing the construction of the MOs of $Cp(CO)_2W(\mu\text{-}CH)Fe(CO)_3$, **12** from smaller fragments **8a** and $Fe(CO)_3$, **13**.

which also has lobes directed towards the missing ligand. In **3**, the alkylidyne occupies two coordination sites, one axial and one equitorial, of $Fe(CO)_5$ replacing two carbonyls whereas in **2** the alkylidyne occupies only one axial site of $Fe(CO)_5$.

The out-of-plane π orbital of **8a** strongly interacts with 1a" and 3a" of $Fe(CO)_3$ in a three orbital four electron interaction. The resulting stable combination is a delocalized 1a" (**14a**) Fe-W-C π orbital. 3a" of **13** gets destabilized to become LUMO 3a" (**14b**), which is mostly based on Fe atom . The



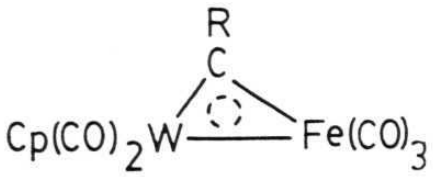
14a 14b

in-plane π pair of **8a** interacts with 1a' and 2a' orbitals of **13** to give metal-metal and metal-carbon bonds. W-C π^* is LUMO+1 here. Consequent to the observed π delocalization, in **3**, the Fe-C, and W-Fe bond lengths are short and the W-C bond length is long in comparison to **2**.[7,9] Table 1 shows the observed bond

Table 1 : Reduced overlap population values along important bonds in compounds **2**, **3**, **25** and **21**.

Reduced overlap population	**2**	**3**	**25**	**21**
Fe-W	0.0811	0.2203	0.0656	0.0450
W-C	0.8757	0.6731	0.8009	0.9045
Fe-C	0.3597	0.7444	-0.1058	0.3501
Fe-C(O)	0.7400		0.5067	
C-C	0.0217		0.9209	0.0308

lengths and reduced overlap populations for the two compounds **2** and **3**. The extra electron donation from W≡C bond to $Fe(CO)_3$, **3** (analogous to the participation of second π orbital of acetylene in coordination with transition metal[26]) actually corresponds to π delocalization, **15**. **3** is isolobal to cyclopropenyl cation.



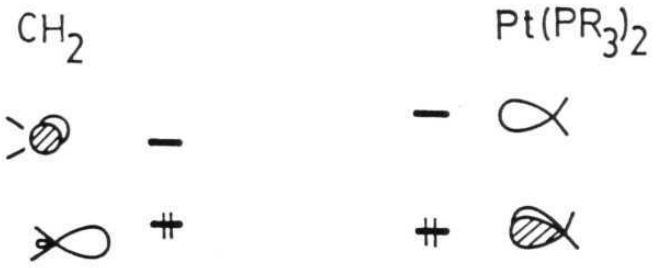
15

Reaction with carbene

The presence of a tungsten based non-bonding orbital as HOMO and W-C π^* orbital as LUMO in **2** indicates that in principle the compounds of type **2** can be reactive either at tungsten or at carbon. The electrons in the non-bonding ($d_{x^2-y^2}$) tungsten atom can be donated to an incoming electrophile. This favours reaction at tungsten centre. But steric factors do not favour such a reaction. A nucleophile can attack at the carbon centre. Carbynyl cation bridged heterobimetallic compounds show such reaction.[27]

Since there is a double bond between tungsten and carbon in **2**, a reaction with carbene can be envisaged at the W-C axis as in the reaction of carbene with alkene.[28] (MOs of carbene are shown in scheme 2). The HOMO in carbene finds perfect match with the W-C π^* LUMO of compound **2** as shown in scheme 3. Correspondingly a stabilizing interaction exists between the LUMO of carbene and W-C π orbital of **2**. A similar attack at the Fe-C centre would have only one stabilizing interaction corresponding to the HOMO-1 of **2** (Fe-C π^*) and the LUMO of carbene. The HOMO of carbene will

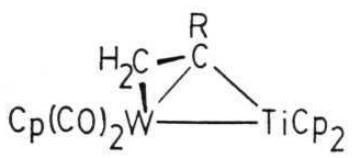
Scheme 2



Scheme 3

not find a matching MO along the Fe-C axis. An attack of carbene at W-C centre leads to two stabilizing HOMO-LUMO interactions whereas an attack at Fe-C axis gives only one stabilizing interaction. Therefore a reaction of carbene with **2** should lead to an attack of carbene at the W-C double bond rather than at the Fe-C centre.

Stability of compounds $Cp(CO)_2W[\mu-\sigma:\eta^2-C(C_6H_4Me-4)=CH_2]TiCp_2$, **16**[29], $(CO)_2CpW[\mu-\sigma:\eta^2-C(C_6H_4Me-4)=CH_2]Pt(PR_3)_2$, **17**[30] and $(dppe)(CO)_2W(\mu-\sigma:\eta^2-CH=CH_2)PtL_2^+$, **18**[31] support that



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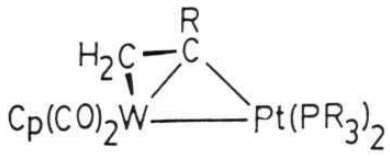

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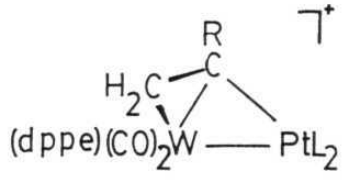


18

carbene unit can find a perfect match on the W-C bond. The fact

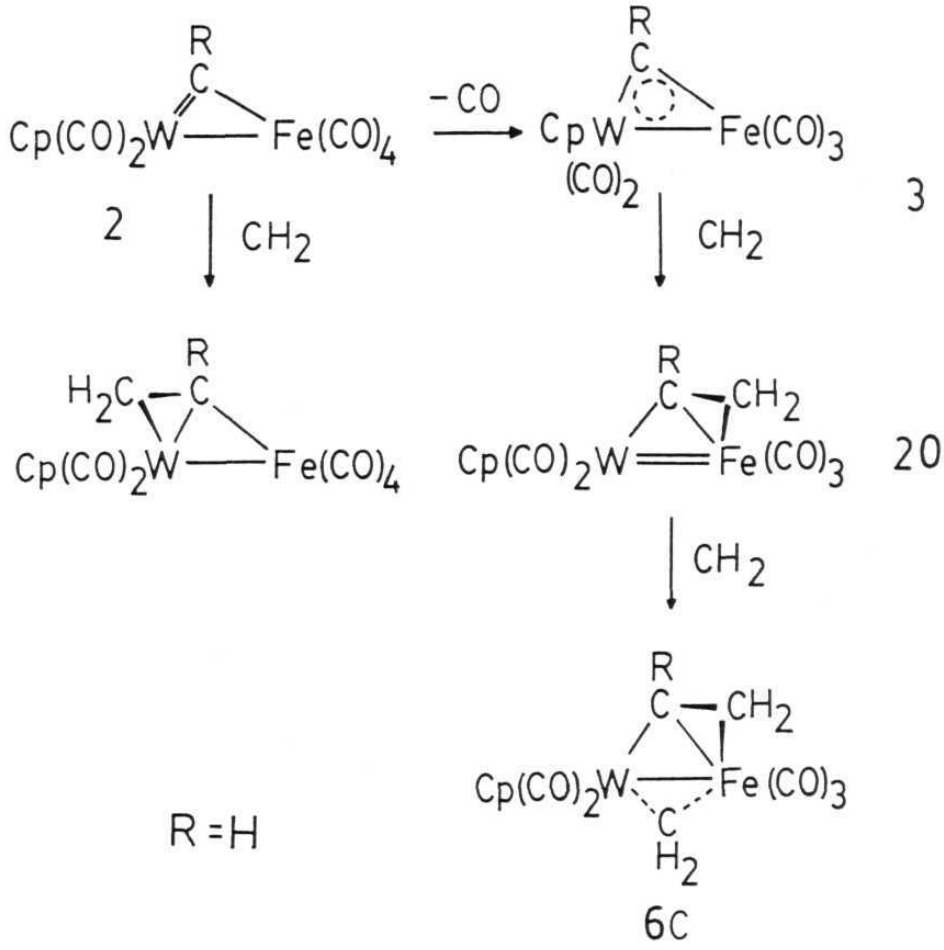
that Pt(cod) ligand (which is isolobal to methylene)[32] attacks on either side of the W≡C bond in $Cp(CO)_2W[\mu\text{-}CR]Pt(M')Pt(cod)$ (where (M') is a unit of the type $Cp(CO)_2M{\equiv}CR$) supports the reactivity at the W-C π^* LUMO.[33] Such a reaction should be responsible for the formation of the extended chains of bismetallacyclopropene (eg. $[Cp(CO)_2WPt]_4$).[4] The directional property of π^* LUMO in **2** dictates that the incoming nucleophile should approach the molecule in a plane perpendicular to the molecular plane. The crystal structures of **6**, and **16 to 18** clearly show the out-of-plane bridging of CH_2.[13, 29-31]

HOMO of carbene might be expected to interact with the LUMO (W-C, π) of **3** but it is not possible because of the lack of out-of-plane W-C π^* combination among the filled levels. The LUMO of **3**, is antibonding (π^*) between Fe and both carbon and W. This could interact with the HOMO of carbene. The Fe-C or Fe-W bonding (π) combinations can interact with the LUMO of carbene. This indicates that carbene can attack both at Fe-C and Fe-W axes in **3**. This is supported by the reaction of $Cp^*(CO)_2W[\mu\text{-}C(C_6H_4Me\text{-}4)]Fe(CO)_3(PR_3)$, **19**, with diazomethane to give $Cp^*(CO)_2W(\mu\text{-}CH_2)[\mu\text{-}\sigma:\eta^2\text{-}C(C_6H_4Me\text{-}4){=}CH_2]Fe(CO)_2(PR_3)$.[10b] In **6**, the two CH_2 groups are on either side of the Mo-C-Fe ring. This is exactly what one expects from the LUMO of **3**. A carbene attack at W-C axis and then reorganization to give **20** is not possible and it is not necessary to invoke such a scheme.[13b]

From the above observations we propose the following mechanistic paths for the carbene attack at **2** and **3** (Scheme 4 and 5). In scheme 4, removal of a carbonyl from **2** gives **3**. **3** has Fe-C π^* combination as LUMO, a carbene can attack at the Fe-C axis. The resultant $Cp(CO)_2W[\mu\text{-}\sigma:\eta^2\text{-}CR{=}CR_2]Fe(CO)_3$, **20** losses

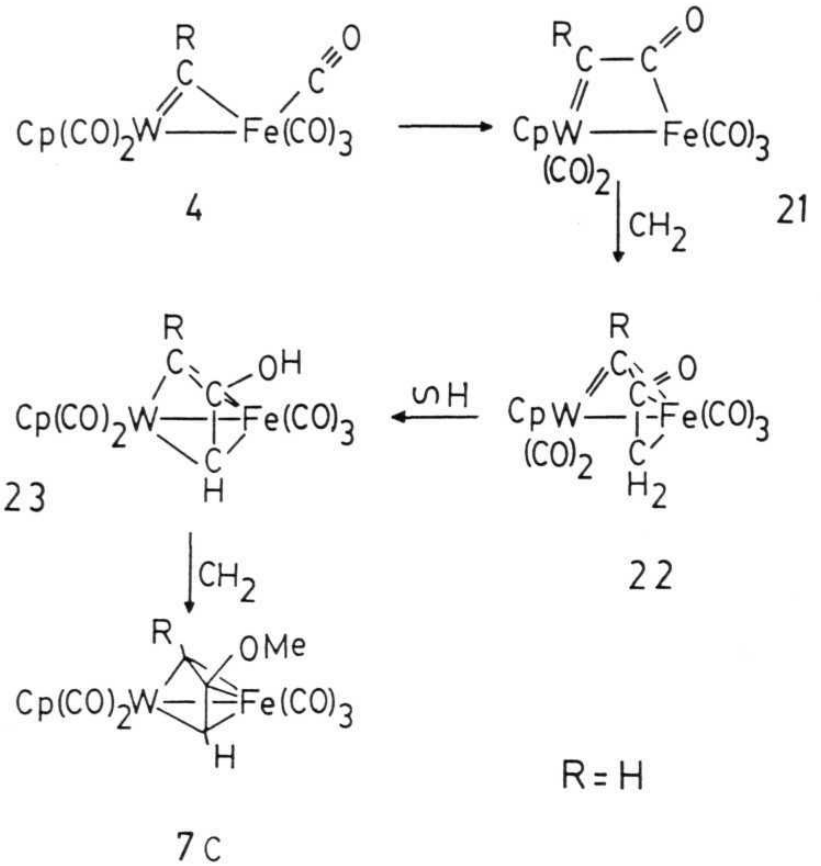
the delocalized nature of the 2 π electrons. The unsaturation at the two metals in **20** gives rise to localized M-M π bond, which eventually takes up another carbene unit to give $Cp(CO)_2W(\mu\text{-}CH_2)[\mu\text{-}\sigma : \eta^2\text{-}CR{=}CH_2]Fe(CO)_3$, **6c**. An attack of carbene to **2** is more favourable at the W-C axis.

Scheme 4



Scheme 5 suggests a mechanistic path for the formation of $Cp(CO)_2W[\mu\text{-}CRC(OMe)CH]Fe(CO)_3$, **7c** from a reaction of **2** with diazomethane. Earlier it was suggested that transfer of a carbonyl from Fe atom to M-C π bond as the first step in the reaction.[13b] We suggest a different route in which the first step indicates the carbonyl insertion into Fe-C bond. The carbonyl insertion into M-C bond is a well known process.[34,35]

Scheme 5



Even though the question of alkyl migration vs. carbonyl insertion is not yet resolved,[36] the abundance of such reactions prompts us to think about the insertion process of one of the carbonyls in **4**. Fig. 2.4 describes the Walsh diagram for the step 1 of scheme 5. The process is symmetry allowed. Several avoided crossings between 1a' and 4a' lead to the formation of carbon-carbon bond between the bridging carbyne and the carbonyl carbon. 1a" decreases in energy because of the development of π interaction between bridging carbon and incoming carbon. The reduced overlap population between the two carbons in **21** is 0.984 indicating a strong C-C bond. The electronic structure of **21** shows the delocalized nature of π electrons in the W-C(H)-C(O) unit. An attack of carbene at **21** leads to **22** which on keto-enol tautomerism gives **23**. **23** has a C_3R_3 unit bridging the W-Fe axis. Insertion of another carbene into O-H bond leads to the formation

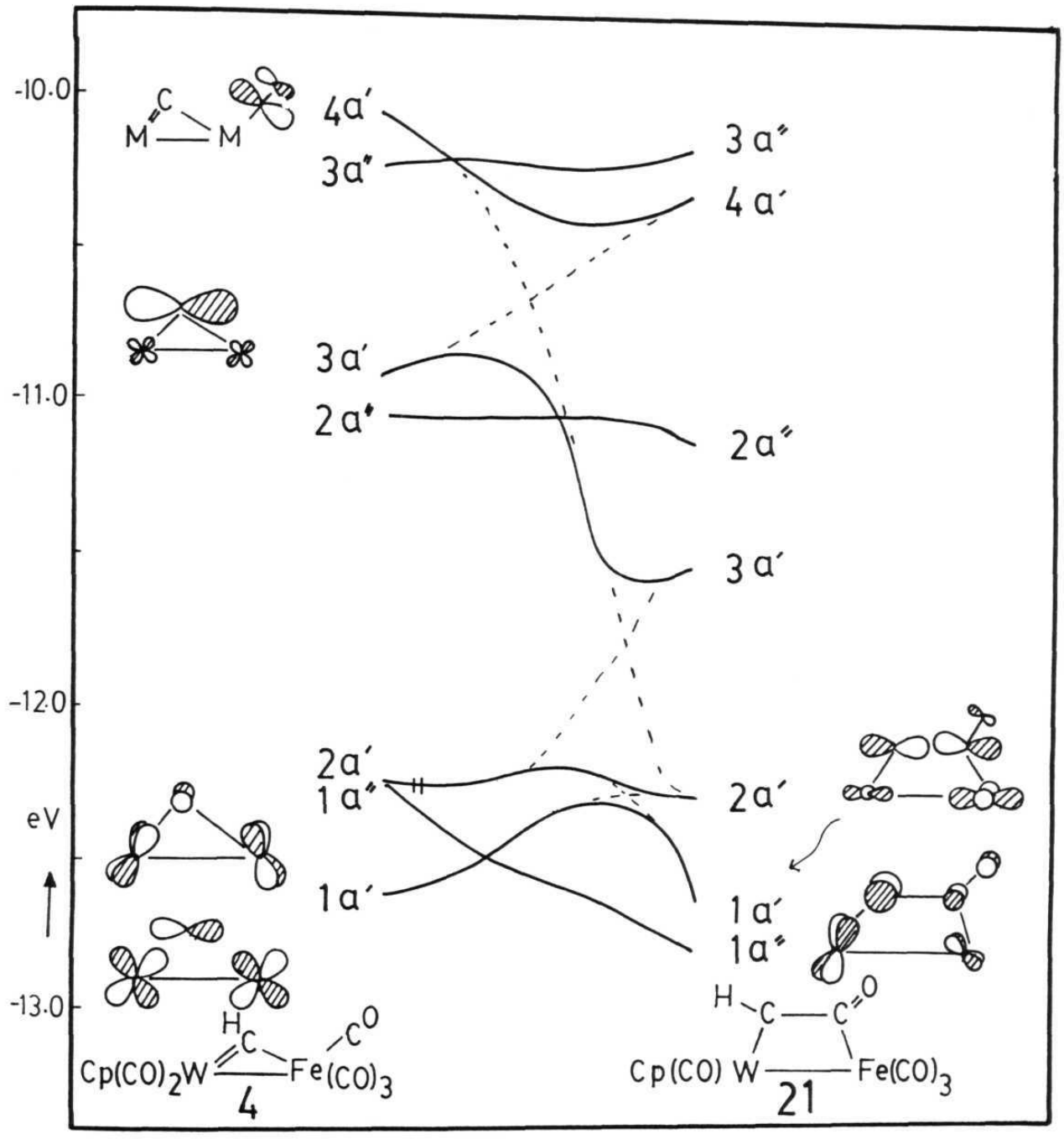


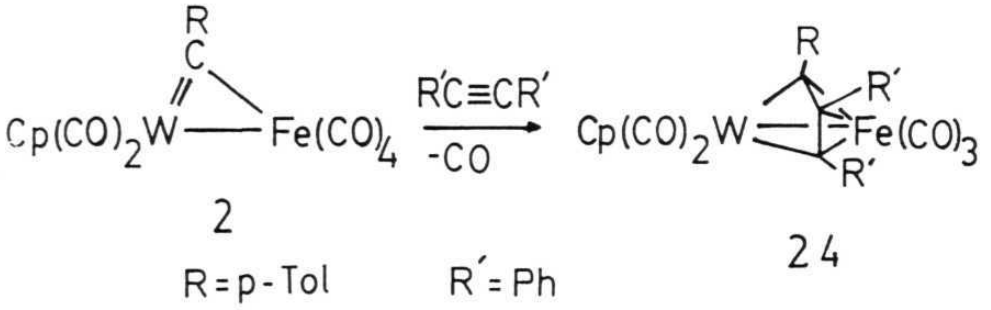
Fig. 2.4 Walsh diagram for the carbonyl insertion into Fe-C bond in **2** to give **21**.

of $Cp(CO)_2W[\ \mu\text{-}C(H)C(OMe)C(H)\ ]Fe(CO)_3$, **7b**.

Reaction with alkyne

Reaction of $Cp(CO)_2W[\ \mu\text{-}C(C_6H_4Me\text{-}4)\ ]Fe(CO)_4$, **2** with alkynes gives several products where C_nR_n or C_nR_nCO ligands bridge W-Fe bimetallic template, losing a carbonyl from the Fe centre.[14,15] Formation of a series of new carbon-carbon bonds lead to the observed products. Reaction of **2** with diphenylacetylene gives $(CO)_2CpW[\ \mu\text{-}C(C_6H_4Me\text{-}4)CPhCPh\ ]Fe(CO)_3$, **24** (scheme 6) losing a

Scheme 6



carbonyl from the iron centre.[14] Similarly isoelectronic $(CO)_2CpW[\ \mu\text{-}CR\ ]Rh(C_9H_7)(CO)$ on reaction with diphenylacetylene gives $(CO)_2CpW[\ \mu\text{-}CRCPhCPh\ ]Rh(C_9H_7)$, losing a carbonyl at the Rh centre.[14] Corresponding cobalt complex also shows such reaction.[14] Carbonyl elimination initiate the reaction. Even though the reaction seem to be controlled by the substituent in alkyne,[15] the origin of the reactivity can be traced to the electronic structure of the bimetallic systems **2** and **3**.

None of the frontier orbitals of **2** or **3** has proper symmetry to interact with the frontier orbitals of the alkyne in a stabilizing interaction. If we replace one of the carbonyls in **2** by alkyne, a stabilizing interaction is possible. Fig. 2.5 shows

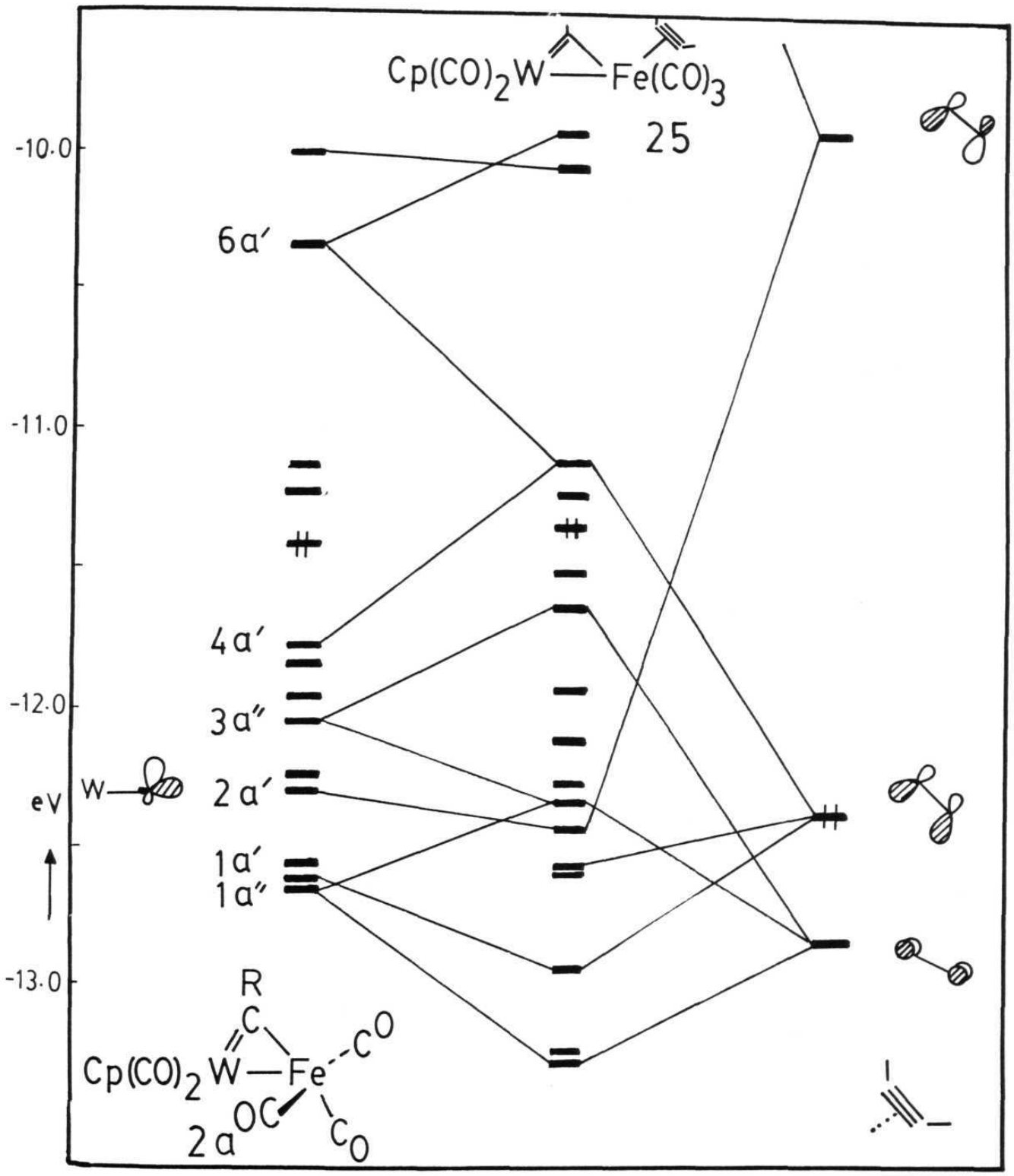
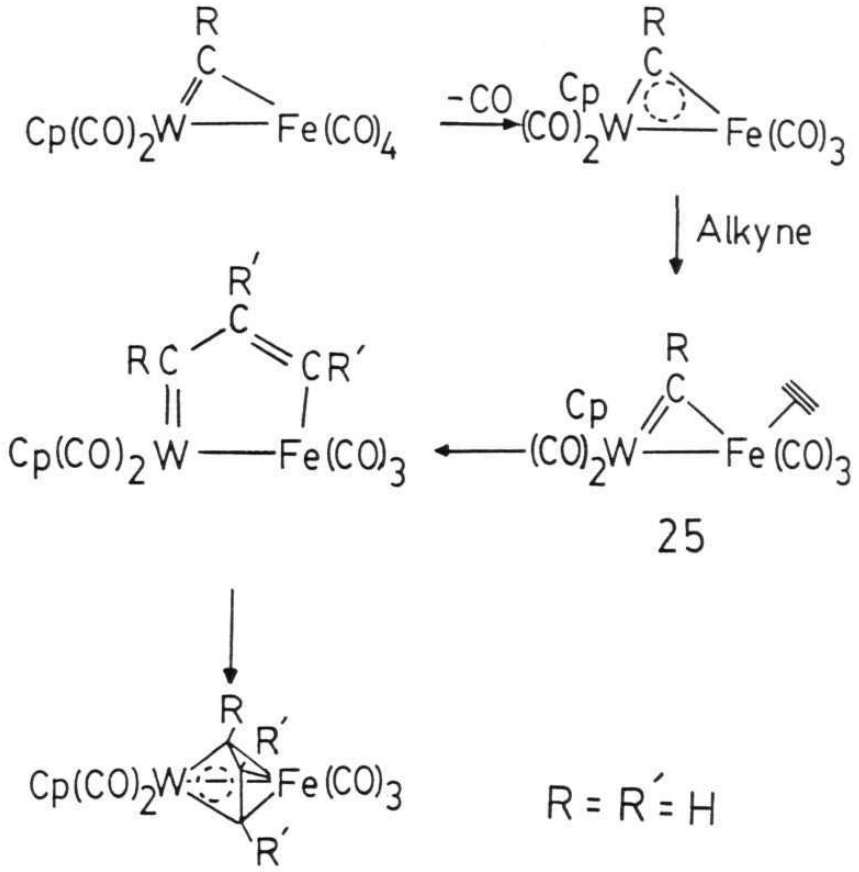


Fig. 2.5 Interaction diagram for the construction of the MOs of the alkyne adduct $Cp(CO)_2W(\mu\text{-}CH)Fe(CO)_3(\eta^2\text{-}C_2H_2)$, **25**.

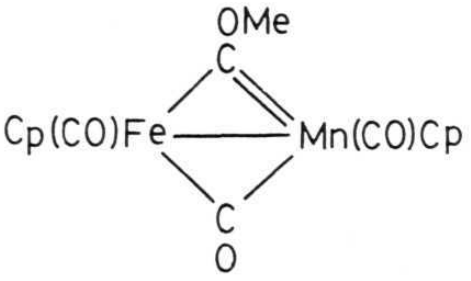
the interaction diagram for the formation of alkyne adduct $Cp(CO)_2W(\mu\text{-}CH)Fe(CO)_3(\eta^2\text{-}C_2H_2)$, **25** from fragments **2a** (**2** with a loss of an equitorial carbonyl) and alkyne. The in-plane π^* of alkyne finds proper match with 2a' orbital of **2a**. The in-plane π orbital of alkyne interact with 1a', 4a' and 6a' and stabilizes the adduct **25**. The out-of-plane π orbital of alkyne is involved in a 3 orbital 6 electron interaction with 1a" and 3a" of **2a** resulting in no net bonding. **25** appears to have one alkyne and one alkylidyne in the equitorial sites of $Fe(CO)_5$ and is highly congested. The HOMO-LUMO gap in **25** is small indicating the instability of alkyne adduct. A positive overlap population of 0.183 between the carbynyl carbon and one of the carbons of alkyne close to it is observed in **25**. A C-C bond formation can take place to give a five membered ring. Walsh diagram for the formation of five membered ring is a smooth process. Orbitals corresponding to C-C bond formation are well below in energy. The details of the MO variation in the Walsh diagram do not give any further insight and is not reproduced here. The sum of one-electron energy curve shows monotonous decrease in energy. The HOMO-LUMO gap in the five membered ring is also small. Its conversion to $Cp(CO)_2W(\mu\text{-}C_3H_3)Fe(CO)_3$ is a C_1 process. On the basis of the above results, we propose scheme 7 as a plausible pathway for the reaction of compounds of type 2 with alkyne. The fact that only in-plane π orbitals of alkyne are involved in stabilizing interaction indicates that ethylene also may react with **2**. The product may not be as dramatic as that in the case of alkyne but the reaction might give a five membered metallocycle. This is in sharp contrast to the reactivity of $W_2(\mu\text{-}CR)_2L_4$[37] (Chapter 1).

Scheme 7



We have also performed Extended Huckel calculations on various other Stone's compounds containing CR bridging heterobimetallic systems $Cp(CO)_2W(\mu\text{-}CR)Cr(CO)_2(C_6R_6)$,[5k] $Cp(CO)_2W(\mu\text{-}CR)Pt(PR_3)_2$[5k], $Cp(CO)_2W(\mu\text{-}CR)Rh(CO)(C_9H_7)$,[5k] $Cp(CO)_2W(\mu\text{-}CR)W(CO)_5$,[10b] $Cp(CO)_2W(\mu\text{-}CR)TiCp_2$,[5h,5l,30] $Cp(CO)_2W(\mu\text{-}CR)VCp_2$[5h,5l] $Cp(CO)_2W(\mu\text{-}CR)Cr(CO)(NO)Cp$[5u] etc. Most of the compounds has W-C π^* as LUMO and W based nonbonding orbital as HOMO. This supports the general electronic picture described for compound **2**.

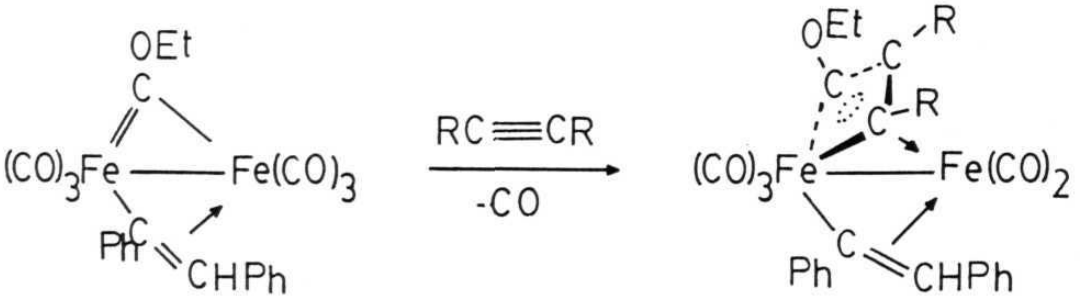
$Cp(CO)Fe(\mu\text{-}CO)(\mu\text{-}COMe)MnCp(CO)$, **26**[38a] is isoelectronic to **2**, an Mn-C double bond is proposed. **26** is isolobal to cyclopropene. Incorporation of a μ-methylene into **26** is via a reaction with diazomethane proved to be slower than its thermal decomposition.[38b] Electronic structure of **26** shows the presence



26

of an Mn-C σ and π orbitals. The Mn-C π^* orbital is LUMO + 1 and is not readily available for attack. This is responsible for the observed behaviour of **26** with diazomethane.

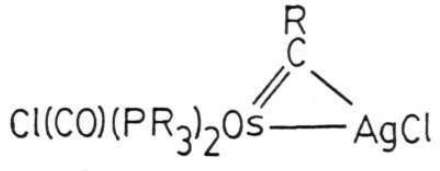
$(CO)_3Fe[\mu\text{-}\sigma\text{-}\eta^2\text{-}C(Ph)=C(Ph)(H)](\mu\text{-}COEt)Fe(CO)_3$, **27**[39] is a compound containing a carbyne bridge on two Fe atoms with different ligand environments. This compound is isolobal to cyclopropene and can be treated as a dimetallacyclopropene. Extended Huckel calculations on **27** suggests the presence of Fe(1)-C double bond. Reaction of **27** with alkynes give compound containing $(\mu\text{-}C_3R_3)$ bridging unit after losing a carbonyl from



27

Fe(2). This reaction is very much similar to the reaction of alkyne with **2**. A reaction of **27** with carbene may not readily occur because the Fe(1)-C π^* orbital is LUMO+1 in **27**.

$Cl(PPh_3)_2(CO)Os(\mu\text{-}C(C_6H_4Me\text{-}4))AgCl$, **28**[40a] contains a carbyne bridge on the Os-Ag template. Some isoelectronic compounds with a μ_2-CR bridge on the W-Au bimetallic template are also known.[40] Extended Huckel calculations on the model $(PH_3)_2(CO)(Cl)Os(\mu\text{-}CH)AgCl$, **29** suggest no significant Ag-C or Ag-W bond. Interaction diagram for the construction of MOs of **29** do not show any strong interaction between AgCl fragment and the remaining fragment. The interaction diagram is very much similar to the interaction diagram constructed for $Cp(CO)_2W(\mu\text{-}CH)Au(PH_3)^+$ (Chapter 3) and is not reproduced here. The energies of the frontier orbitals of two fragments AgCl and $(PH_3)_2(CO)ClOs{\equiv}CH$ are very different. The in-plane p orbital of Os≡C slightly get stabilized by the LUMO of AgCl. This indicates that only partial Ag-C and Ag-W can be expected. This analysis supports the representation **30** as the correct representation for $Cl(PPh_3)_2(CO)Os(\mu\text{-}C(C_6H_4Me\text{-}4))AgCl$.



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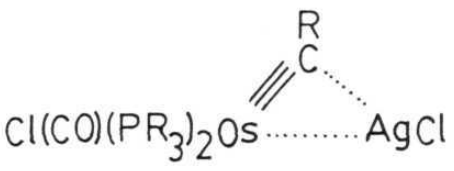

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2.4 Conclusions

The electronic structure of compounds **2** and **3** are studied. A careful assessment of the molecular orbitals present in **2** and **3** leads to the understanding of reaction of **2** and **3** with carbene and alkyne. The presence of W-C π^* orbital as LUMO in **2** indicates the reactivity with carbene or fragments isolobal to it. Removal of a ligand from Fe centre in **2** is shown to initiate the reaction with carbene to give **6a**. Carbonyl insertion into Fe-C bond and consequent addition of two carbene units give **7a** . In **3**, the two π electrons are delocalized in the Fe-W-C ring.

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CHAPTER 3

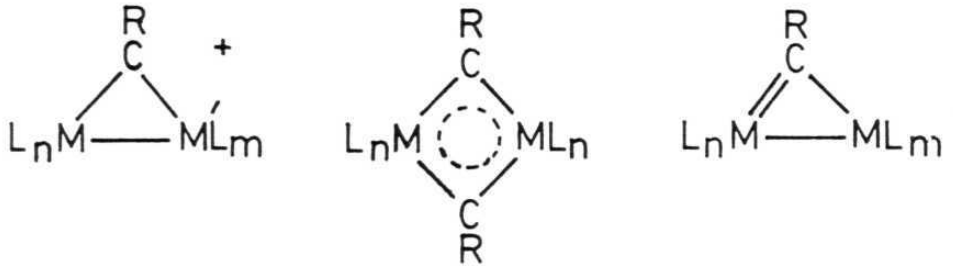
Electronic Structure and Reactivity of Carbynyl Cation Bridged Binuclear Transition Metal Complexes

3.1 Abstract

Extended Huckel method is used to study the molecular orbital pattern of carbynyl cation bridged bimetallic templates **1**. Some of the compounds of type **1** are isolobal to cyclopropyl cation. LUMO of these compounds is largely based on the out-of-plane p orbital of the bridging carbon. Electrophilicity of these compounds is due to this LUMO. A least motion path for the hydrocarbation reaction is studied. The electronic structure of doubly bridged compounds with a carbyne and a hetero atom as bridges are also reported. Many potential precursors for the hydrocarbation reaction are suggested.

3.2 Introduction

The cationic carbyne $(CR)^+$ bridged binuclear transition metal complexes of type **1** are different from the two varieties **2** and **3** discussed in chapters 1 and 2. In **1**, the active centre is found to be the carbynyl carbon, whereas in **2** and **3** the active centres are found to be either the metal or the M-C bond. In **2** and **3** the carbyne is considered as a three electron donor. But a CR^+ bridge, as in **1** can contribute only two electrons to the complex formation. These two participate in regular M-C σ bonds. The unsaturation at the carbon centre remains in the form of the +ve charge.



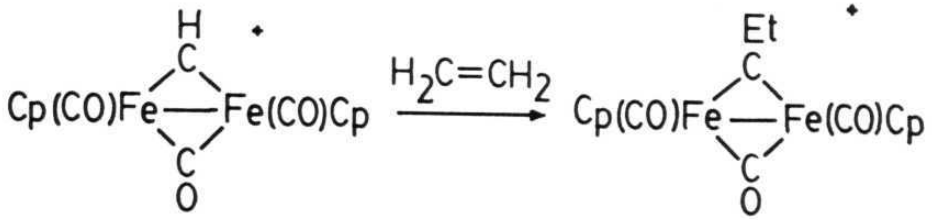
1 2 3

In general the compounds of type **1** are prepared in five different routes. (1) Protonating vinylidene bridged bimetallic compounds,[1] (2) dealkylating (or dealkoxylating) carbene bridged binuclear transition metal complexes,[2] (3) reaction of alkylidyne cations $L_nM{\equiv}CR^+$ with low valent metallic species,[3] (4) reaction of metallaallene with cationic metallic fragments,[4] and (5) protonation of 1,1-didehydrocyclopropane bridges.[5] Some compounds in which the R group (NHMe) of the bridging CR^+ unit is electron donating are also known.[6]

Almost all these compounds are shown to be reactive towards nucleophiles.[2a,8] The reactive centre is always the carbon,[8-13] the product is a carbene bridged binuclear transition metal

complex. Deprotonation at the R group in **1** yields vinylidene bridged bimetallic compounds.[1a,1d,9] Hydrogen migration from the R group to bridging carbon gives alkenyl bridged complexes.[10] Apart from these three, another interesting reaction is also observed. The reaction of $Cp(CO)Fe(\mu\text{-}CH)(\mu\text{-}CO)Fe(CO)Cp^+$, **4** with ethylene gives an adduct $Cp(CO)Fe(\mu\text{-}CC_2H_5)(\mu\text{-}CO)Fe(CO)Cp^+$, **5** (Scheme 1).[3] When the hydrogen on the carbyne bridge in **4** is

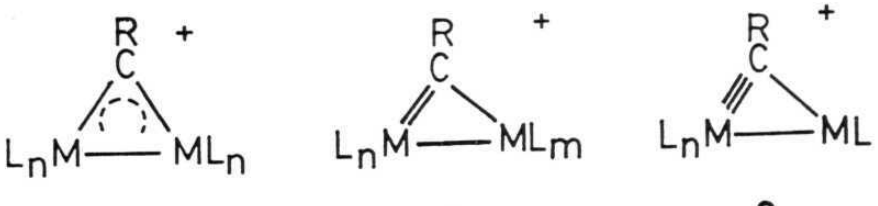
Scheme 1



4 5

replaced by any R group, such an adduct is not formed.[11,12] This reaction is very much similar to the well known hydroboration reaction[14] where $R_2B\text{-}H$ reacts with ethylene to give an adduct and hence the name hydrocarbation.[11a]

Formal electron count suggests that most of the metallic fragments are 16 electron units. An electron from M-C bond makes it 17 electron and a metal-metal bond satisfies the 18 electron count. In some examples a π delocalization in the M-C-M framework, **6**, is indicated.[1c,1d] In some other complexes, an



6 7 8

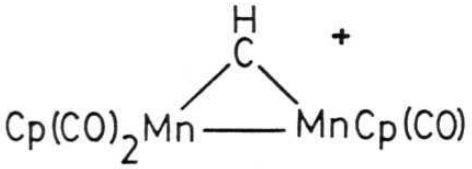
M-C double bond is suggested, **7**.[3a,15] The metal electron count do not demand a delocalized picture in **6** and an M-C double bond in **7**. Triple bond nature between M and carbon is pointed out in a few examples **8**.[7] Charge distribution is not equivocally established. Is there any π delocalization? How is the reactivity of these compounds can be accounted for?

The hydrogen migration reaction was explained by Hoffmann et al using theoretical methods.[16] The electronic structure studies on the CH^+ bridged piano-stool dimers is reported previously by Bursten et al.[17] In this chapter, we discuss our results on the electronic structure studies on compounds of type **1**. Fragment Molecular Orbital (FMO) approach within Extended Huckel Theory is used to understand the molecular orbital patterns and to explain the reactivity.

3.3 Results and Discussion

Electronic Structure of $(CO)_2CpMn(\mu\text{-}CH)MnCp(CO)_2^+$, 9.

$(CO)_2CpMn(\mu\text{-}CH)Mn(CO)_2Cp^+$, **9** is taken as the representative example of the bimetallic complexes with a carbynyl cation bridge, **1**. Figure 3.1 shows the interaction diagram for the construction of the molecular orbitals of **9** from smaller



9, C_2

fragments CH^+ and $[Mn(CO)_2Cp]_2$, **10** (C_2 symmetry maintained). Details of the geometric and atomic parameters are given in

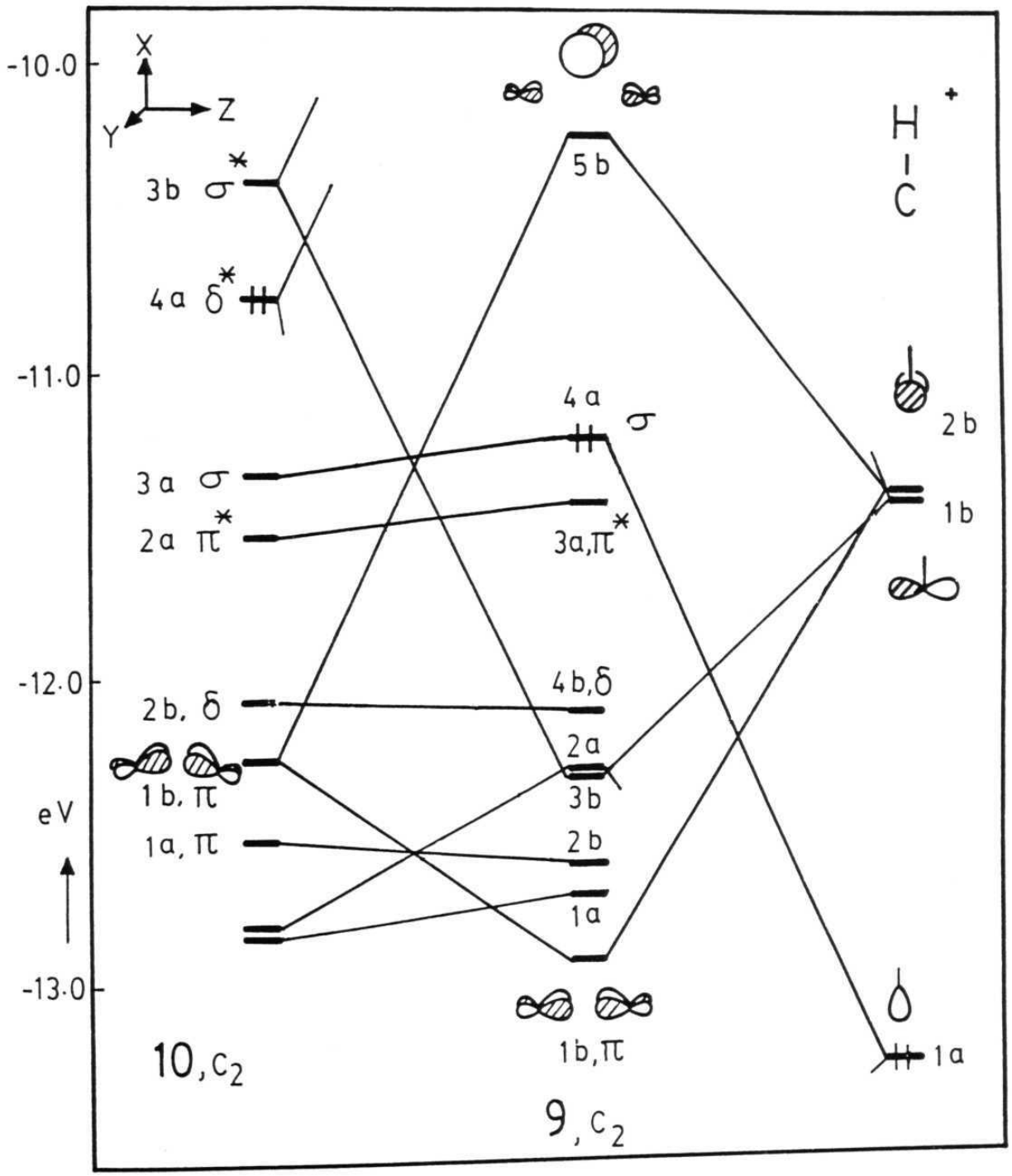


Fig. 3.1 Interaction diagram for the construction of molecular orbitals of $[Mn(CO)_2Cp]_2(\mu\text{-}CO)(\mu\text{-}CH)^+$ **9** (C_2) from smaller fragments $(CH)^+$ and $[Mn(CO)_2Cp]_2$ **10**, (C_2).

appendix. With a d^6-d^6 electron count, the metallic fragment **10** has 6 of the metal d orbitals occupied. HOMO-1 is 3a (σ) orbital. LUMO is 3b (σ^*) orbital with lobes directed towards the missing ligand (CH^+). Another orbital with directed lobes is 1b (π). The fragment further has 1a (π), 2b (δ), 2a(π^*), and 4a (δ^*) metal based occupied orbitals. The availability of σ and π orbitals makes, the fragment **10** equivalent to a distorted ethylene. Isolobal analogy[18] also supports this idea. 1b (π) orbital of **10** destabilizes the $p_\perp$ orbital of carbynyl cation to give LUMO. The interaction diagram (Fig 3.1) shows strong interaction between the 1b orbital of fragment **10** and the 2b orbital of CH^+. 1a orbital of CH^+ slightly destabilized the 3a (σ) orbital of fragment **10**. 1a orbital of CH^+ destabilizes the orbitals of **10** with (a) symmetry, 4a (δ^*) of **10** is pushed high up in energy into the unoccupied region. The metal-carbon σ bond formation is due the interaction of 3b (LUMO) of **10** with the in-plane p orbital of the carbyne group.

4a orbital corresponds to the M-M σ bond in **9**. 1b orbital of **9** is the bonding combination of the π orbital of **10** and $p_\perp$ of carbon, leading to a proposal of cyclic π system in the molecule.[1c,1d] But 1b orbital of **9** is mostly based on the two metals. Interesting aspect of this interaction diagram is the

11

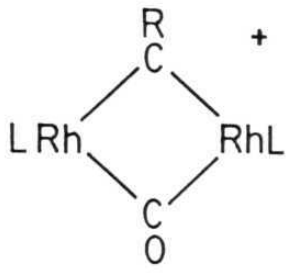
presence of an almost pure carbon $p_\perp$ (5b) orbital as LUMO, **11** (Fig. 3.1). **9** is isolobal to cyclopropyl cation, $C_3H_5^+$. The

charge matrix of **9** shows that the positive charge in the molecule is concentrated at the carbon centre.

The reactivity of the complexes of type **1** should arise from this easily accessible $p_\perp$ orbital as LUMO. The electronic structure and reactivity of piano-stool dimers bridged by CH^+ have been reported previously.[17] It was pointed out that the presence of carbon $p_\perp$ orbital as LUMO in $Cp(CO)Fe(\mu\text{-}CO)(\mu\text{-}CH)Fe(CO)Cp^+$, **4** is responsible for its electrophilicity. Non availability of carbon based $p_\perp$ orbital as LUMO is shown to be responsible for the unreactivity of $CpFe(\mu\text{-}NO)(\mu\text{-}CH)FeCp^+$ towards nucleophiles.[17] In tune with this, $[Mn(CO)_2Cp]_2(\mu\text{-}CH)^+$, **9** should also be highly reactive at the carbon centre towards nucleophiles. $[Mn(CO)_2Cp]_2(\mu\text{-}CR)^+$ is found in solution as an intermediate in vinylidene interconversion on metallic template,[1a] indicating the high reactivity at the carbon centre in these complexes.

Electronic Structure of $(C_5Me_5)Rh(\mu\text{-}C(C_6H_4Me\text{-}4))(\mu\text{-}CO)Rh(C_5Me_5)$,$^+$ 12.[2i]

$CpRh(\mu\text{-}CH)(\mu\text{-}CO)RhCp^+$, **13** is taken as a model for **12**. Fig. 3.2 shows the interaction diagram for the construction of the molecular orbitals of **13**, from smaller fragments, CH^+ and



12 $L = C_5Me_5$ $R = C_6H_4Me$

13 $L = C_5H_5$ $R = H$

CpRh(μ-CO)RhCp, **14**. In **14** apart from the ligand based orbitals (not labeled), the following metal based orbitals are occupied. $1b_1(\delta)$, $1a_1(\delta)$, $1b_2(\delta^*)$, $1a_2(\delta^*)$, $2a_1(\sigma)$, $2b_2(\sigma^*)$, $2b_1(\pi)$, $3a_1(\pi)$. The HOMO is the $3a_1$ (in-plane π orbital) between the two metals. LUMO is the $3b_2$ (in-plane π^* orbital). $2a_2$ (out-of-plane π^* orbital) is the LUMO+1. In **14**, both $2a_1(\sigma)$ and $2b_2(\sigma^*)$ are occupied indicating the absence of M-M σ interaction. Two M-M π^* orbitals $2b_1$ and $3a_1$ are occupied. Interaction of fragment **14** with CH^+ leads to **13** (Fig. 3.2). The major interactions are between $3b_2$ (π^*) of **14** and b_2 orbital of CH^+ leading to M-C bond formation. The resultant $3b_2$ of **13** is slightly pushed up by the interaction with the $1b_2$ and $2b_2$ orbitals of **14**. The a_1 orbital of CH^+ pushes the a_1 orbitals of **14**, $3a_1$ orbital of **14** is pushed up into the unoccupied region of **13**. Instead the $3b_2$ of **13** is occupied. The a_2 orbitals do not find a match among the orbitals of CH^+ and remain untouched. $2a_2$ of **14** becomes LUMO $2a_2$ of **13**. The $p_\perp$ orbital of CH^+ stabilizes the $2b_1$ of **14**. The corresponding antibonding combination $3b_1$ is LUMO+1 in **13**, mainly concentrated on the $p_\perp$ orbital of carbon. All the bonding and antibonding interactions of metal-metal axis are occupied. $1b_2(\delta^*)$, $1b_1(\delta)$, $1a_1(\delta)$, $2a_2(\delta^*)$, $2a_1(\sigma)$, $2b_2(\sigma^*)$, $3b_1(\pi)$ and $3b_2(\pi^*)$. This precludes any possibility of Rh-Rh bond in **13** and the proposed bond order of 2 for **13** cannot be true.[19] The M-M Mulliken overlap population in **13** is calculated to be 0.064 HOMO-LUMO gap is large (1.72 eV) which accounts for the high stability of the compound.[2i] The $1b_1$ orbital of **13** is the bonding combination of the π orbital of **14** and the $p_\perp$ orbital leading to a proposal of cyclic π delocalization. But $1b_1$ is mostly based on metals. It was suggested that compound **12** can react with various nucleophiles to

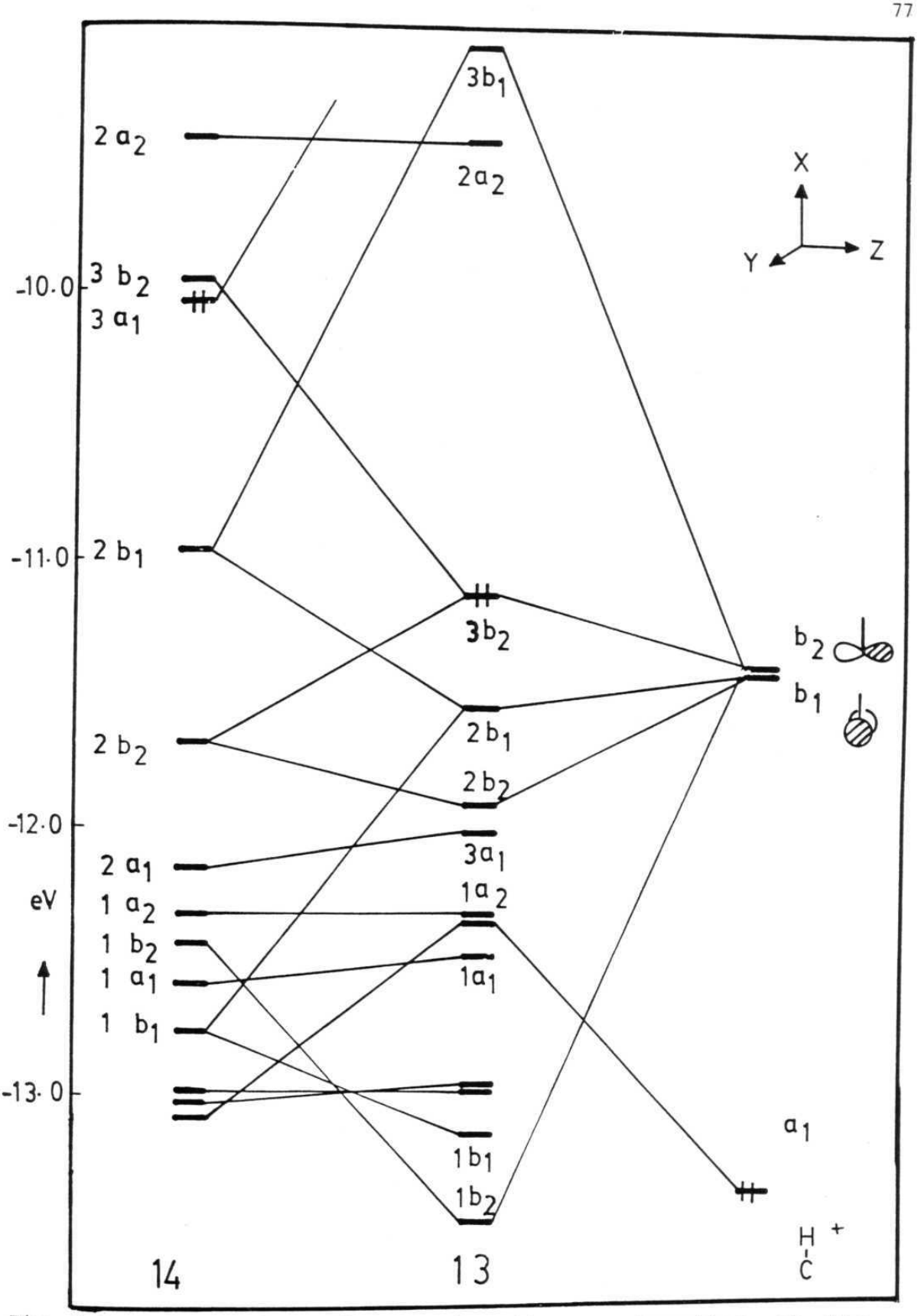


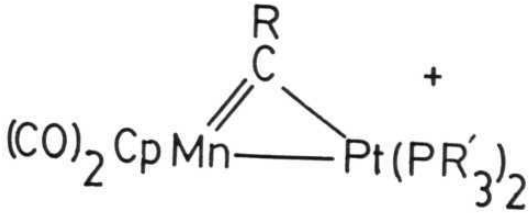
Fig. 3.2 Interaction diagram for the construction of the molecular orbitals of CpRh(μ-CO)(μ-CH)RhCp$^+$, **13**(C_{2v} from the smaller fragments CH^+ and CpRh(μ-CO)RhCp, **14**(C_{2v}).

give carbene bridged bimetallic system.[2i] Our analysis shows that the carbon based $p_\perp$ orbital is LUMO+1 in **13**. This indicates that the reactivity of **12** with nucleophiles may not be very high. **12** is isolobal to cyclopropenyl cation, $C_3H_3^+$.[18]

Extended Huckel calculations are performed on various other carbynyl cation bridged bimetallic systems. They include $[Fe(CO)Cp]_2(\mu\text{-}CO)(\mu\text{-}CH)^+$,[2b] $[Fe(CO)Cp]_2(\mu\text{-}CO)(\mu\text{-}CCH_3)^+$,[1g] $[Fe(CO)_4]_2(\mu\text{-}CCH_3)^+$,[2d] $[RuCp(CO)]_2(\mu\text{-}CO)(\mu\text{-}CMe)^+$,[1n,1z] $[FeCp]_2(\mu\text{-}dmpm)(\mu\text{-}CO)(\mu\text{-}COMe)^+$,[2g] $[(CO)CpCo]_2(\mu\text{-}CMe)^+$.[2f] All of them are isolobal to cyclopropyl cation and show similar electronic structure as that of **9**. Most of them are reported to be reactive towards the incoming nucleophiles.[1] The LUMO of these compounds is in favour of this observation.

Electronic structure of $Cp(CO)_2Mn(\mu\text{-}C(C_6H_4Me\text{-}4))Pt(PH_3)_2^+$, 15[3a]

A Few examples are known where the CH^+ bridges a heterobimetallic template.[3] Two different electron distributions are proposed. One with metal carbon double bond, **7** where the charge is suggested to be localized on ML_n unit. The other is with a metal carbon triple bond where the charge is suggested to be localized on $M'L_m$, **8**. In analogy to compounds of type **3** (chapter 2), complexes of type **7** should be reactive towards carbene to give an adduct (because of the M-C double bond). But no report of such a reaction is available in literature. Instead these compounds show exceptional reactivity towards the nucleophiles at the carbon centre,[8d] very much similar to compounds of type **6**. To clearly understand the bonding and reactivity of these compounds, Extended Huckel calculations are performed on $Cp(CO)_2Mn(\mu\text{-}CH)Pt(PH_3)_2^+$, **16**, a representative of compounds of



15 $R=C_6H_4Me\text{-}4$ $R'=Ph$

16 $R=R'=H$

type **7**. Both the fragments $MnCp(CO)_2$ and $Pt(PH_3)_2$ are isolobal to CH_2, compound **15** is isolobal to cyclopropyl cation (Scheme 2).

Scheme 2

$Cp(CO)_2Mn \longleftrightarrow d^6ML_5 \longleftrightarrow CH_2$

$(PR_3)_2Pt \longleftrightarrow d^6ML_2 \longleftrightarrow CH_2$

$Cp(CO)Co \longleftrightarrow d^8ML_4 \longleftrightarrow CH_2$

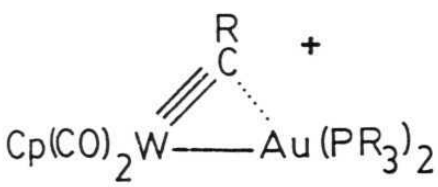
$(PH_3)Au \longleftrightarrow d^{10}s^1ML \longleftrightarrow H$

Extended Huckel calculations suggest that the electronic structure of compound **15** is very much similar to that of **9** in the frontier range. Small differences appear due to the hetero nature of the metallic template. LUMO is purely carbon based p orbital which has antibonding interaction with the δ orbital of the M-M axis, **11**. The interaction diagram between $Cp(CO)_2Mn{\equiv}CR^+$ and PtL_2 is not reproduced because it gives no further clues other than the standard M-C and M-M bonding interactions. From the nature of the LUMO, the observed reactivity towards nucleophiles can be supported. Since no orbital corresponding to the out-of-plane Mn-C π bond is occupied, an Mn-C double bond should not be expected. The charge matrix shows that the carbon

is positively charged. This indicates that structure **7** is not a correct representation of these compounds instead structure **1** is best suited to represent these examples. MO pattern of $(CO)_5W(\mu\text{-}CR)Pt(PH_3)_2^{+}$[3a] also is similar to that of **15**. In $Cp(CO)_2Mn(\mu\text{-}C(C_6H_5Me\text{-}4))Pt(PMe_3)_2^{+}$,[3b] a partial bridging interaction between one of the carbonyls on Mn and the metal Pt is reported.[3a,3b] The overlap population between Pt and the C(O) close to it is positive (0.024) indicating a very weak semi bridging Pt-C bond.

Electronic structure of $Cp(CO)_2W(\mu\text{-}CH)Au(PH_3)^{+}$, 17.

$Cp(CO)_2W(\mu\text{-}C(C_6H_4Me\text{-}4))Au(PPh_3)^{+}$,[7] is an example of compounds of type **8**. Two different representations,[7b] one with a partial Au-C bond **18** and the other in which the Au atom donates electrons to the W atom, with a regular Au-C bond **19** are



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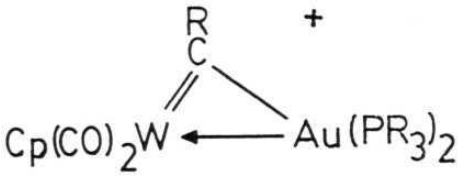

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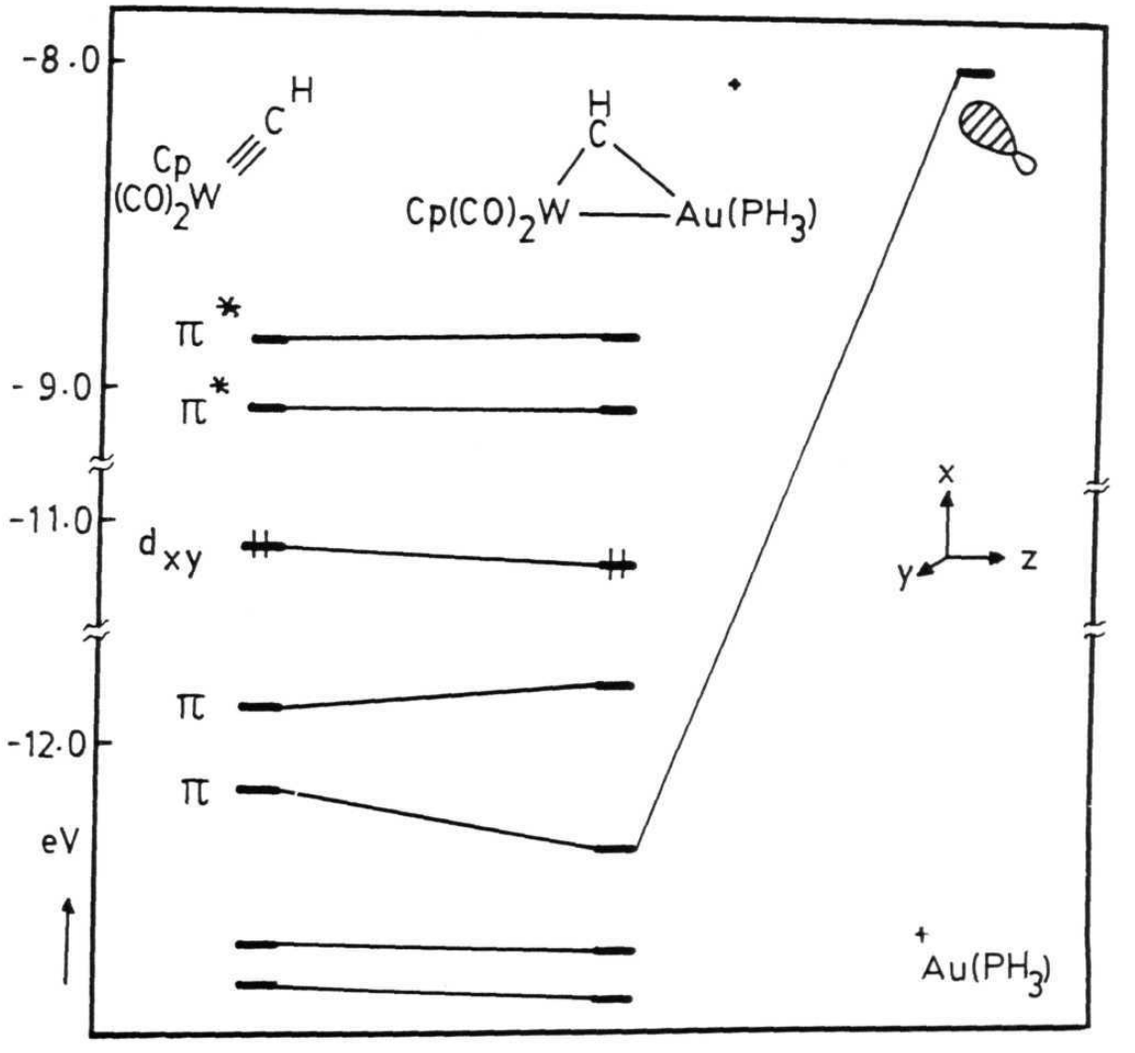
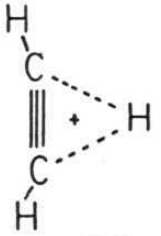
suggested for **8**.[7b] The molecular orbitals of **17** are constructed from those of the fragments $(CO)_2CpW{\equiv}CH$ and $Au(PH_3)$ (Fig. 3.3). The energies of HOMO and LUMO of $Au(PH_3)$ are not close to the energies of the frontier orbitals of $Cp(CO)_2W{\equiv}CH$. The fragment $(CO)_2CpW{\equiv}CH$ has a σ and two π occupied orbitals along the W-C axis (Chapter 2). LUMO is a W-C π^* orbital. The interaction diagram clearly shows that there is no significant interaction between the two fragments. The in plane π orbital of



3.3 Interaction diagram for the construction of molecular orbitals of $Cp(CO)_2W(\mu\text{-}CH)Au(PH_3)$ **17** from smaller fragments $Cp(CO)_2W{\equiv}CH$ and $Au(PH_3)$. The occupied orbitals of $Au(PH_3)$ are very low in energy (HOMO is at -14.28 eV.)

$Cp(CO)_2W{\equiv}CH$ is only slightly stabilized because of its interaction with the σ (LUMO) of fragment $Au(PH_3)$. The in-plane W-C π^* orbital is not affected because of the absence of the corresponding metal based orbital on $Au(PH_3)$. The large W-C-R angle (164^o) in **17** suggest the absence of significant hybridization at carbon centre. The W-Au and Au-C overlap populations 0.084 and 0.343 indicate some bonding interaction. The situation here is reminiscent of the bonding pattern in vinyl cations, $C_2H_3^+$, **20**.[20] The Au-C overlap population of 0.343 is



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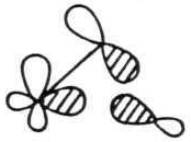

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arising mostly from the MO shown in **21**.$Cp(CO)_2W$ is isolobal to CH and $Au(PH_3)$ is isolobal to H. Hence, **17** is isolobal to the vinyl cation, **20**. Compound **17** should not be considered as a part of the CH^+ bridged bimetallic complexes, because the charge in this molecule is more concentrated on Au rather than the Carbon.

The above discussion suggests that carbynyl cation bridged compounds which are isolobal to cyclopropyl cation have their LUMO on the $p_\perp$ orbital of the bridging carbon. These compounds are reactive towards the nucleophilic attack at the carbon centre. The carbynyl cation bridged compounds which are not isolobal to cyclopropyl cation are not reactive towards nucleophilic attack because of the absence of $p_\perp$ orbital as LUMO. Hence, $[Fe(CO)Cp]_2(\mu\text{-}CO)(\mu\text{-}CH)^+$, $[Fe(CO)_4]_2(\mu\text{-}CMe)^+$, $[Co(CO)Cp]_2(\mu\text{-}CMe)^+$, $Cp(CO)_2Mn(\mu\text{-}CR)PtL_2^+$ etc. but not $CpRh(\mu$ -

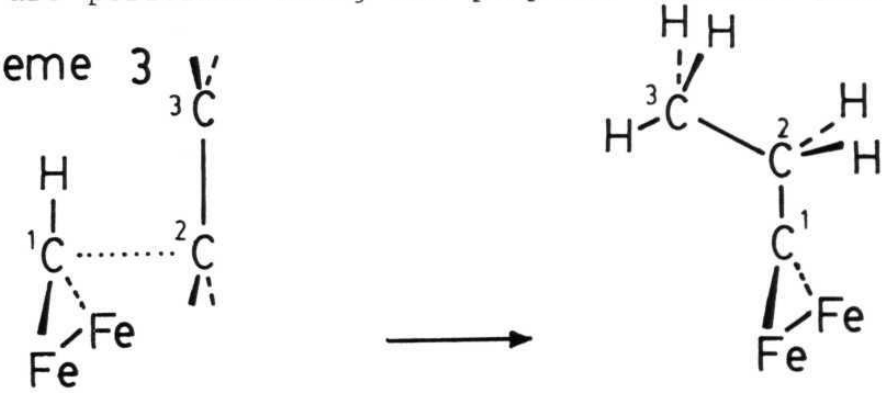
CR)(μ-CO)RhCp$^+$, $Cp(CO)_2W(\mu\text{-}CR)AuL^+$, $CpFe(\mu\text{-}CH)(\mu\text{-}NO)_2FeCp^+$ etc. are expected to be electrophilic.

Hydrocarbation Reaction

Reaction of $Cp(CO)Fe(\mu\text{-}CH)(\mu\text{-}CO)Fe(CO)Cp^+$, **4** with ethylene gives $Cp(CO)_2Fe(\mu\text{-}CCH_2CH_3)(\mu\text{-}CO)Fe(CO)Cp^+$, **5** (Scheme 1).[11] This reaction is found to be very general and found to takeplace with every possible alkene. $Cp(CO)Fe(\mu\text{-}CO)(\mu\text{-}CEt)Fe(CO)Cp^+$, **5** does not react with alkenes. Hence, it was proposed that a 1,2-C-H addition to ethylene is responsible for the reaction. One expects that the C-H bond cleavage can be possible only when ethylene (or alkene) donates electrons to the C-H σ^* orbital of the methylidynyl cation bridge. But the LUMO of **4** is only a carbon based $p_\perp$ orbital, there is no interaction between carbon and hydrogen in this orbital. What is the electronic origin for the hydrocarbation reaction?

A least motion path for the hydrocarbation reaction where one carbon of the ethylene attacks the bridging carbon of **4** is given in Scheme 3 (C_S symmetry is maintained). Extended Huckel calculations are performed along the proposed reaction path to

Scheme 3



construct an orbital correlation diagram (Fig. 3.4). The variation in the sum of one-electron energy shows a barrier of 1.9 eV. Fig. 3.4 do not show any crossing between the occupied

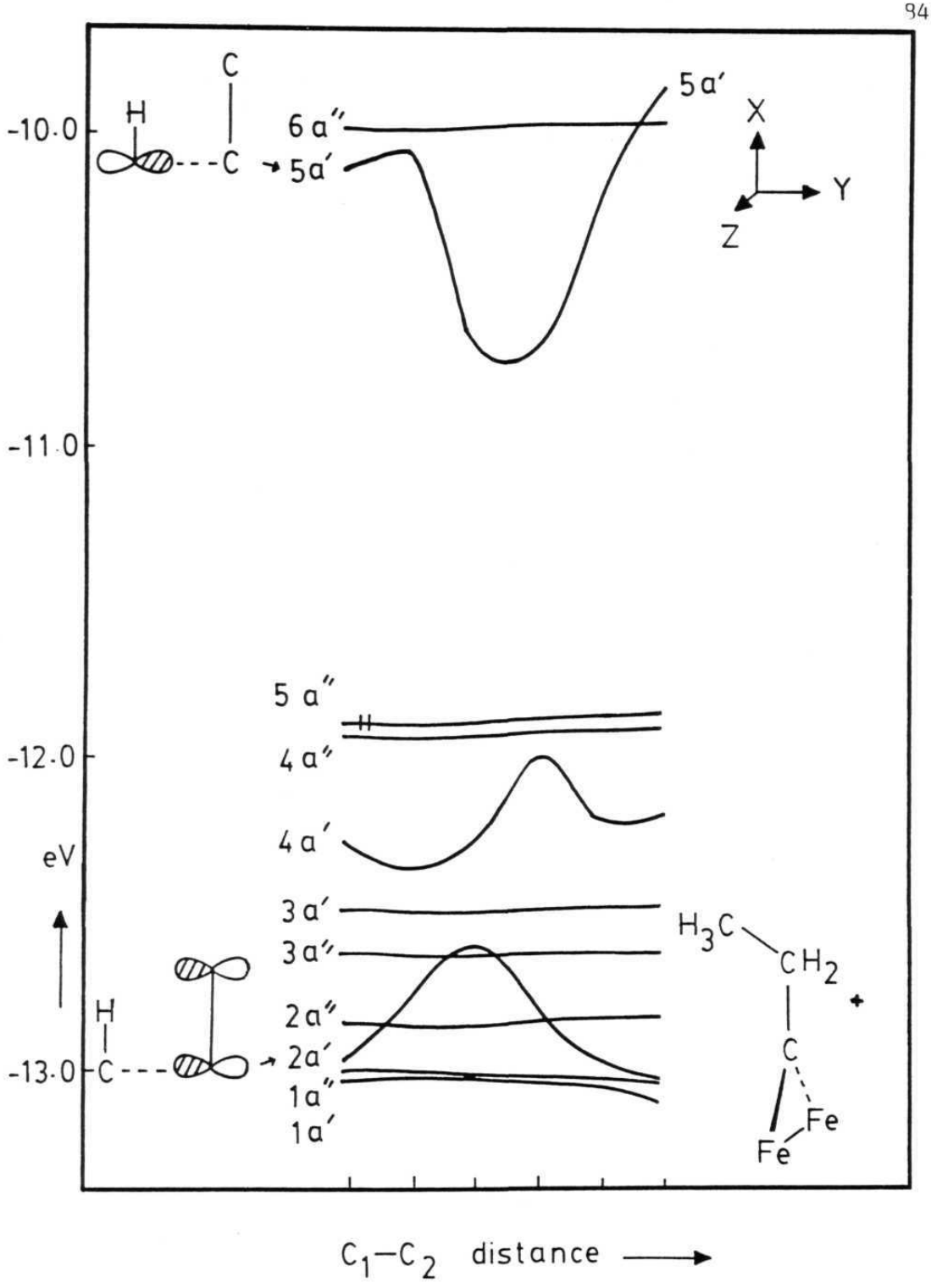
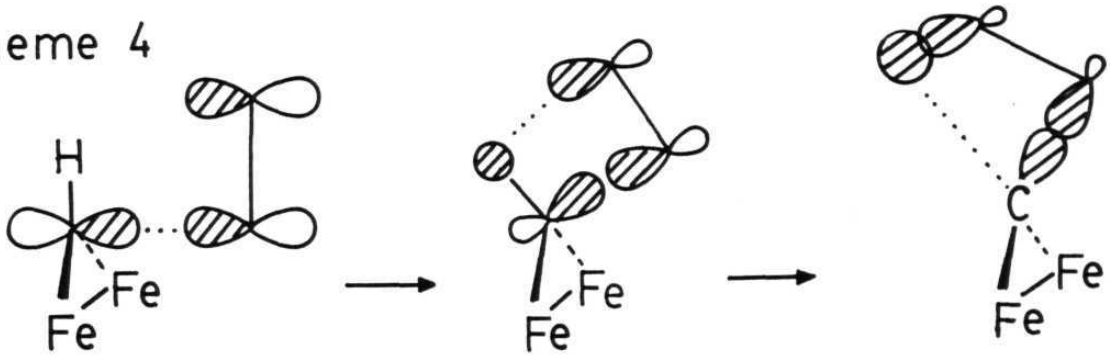


Fig. 3.4 Walsh diagram showing the least motion pathway for the hydrocarbation reaction between (CO)CpFe(μ-CO)(μ-CH)Fe(CO)Cp^+ and ethylene. (C_s symmetry maintained).

and unoccupied levels, this reaction path is symmetry allowed. Major changes are observed only in the symmetric a' orbitals. There are a series of avoided crossing between 2a', 4a' and 5a'. Detailed analysis shows that these avoided crossings are due to the donation of ethylene π electrons to the C-H σ^* orbital as (Scheme 4), finally leading to the formation of C_1-C_2, and C_3-H bonds and C_1-H bond cleavage. The ethylene π orbital in 2a' goes up in energy due to the decrease in the π interaction. The 5a' initially increases in energy due to the development of C-H antibonding interaction, later decreases due to the decrease in

Scheme 4



C-H σ^* interaction as the distance between C and H increases. The avoided crossing gives rise to the observed energy barrier (1.9 eV). Thus our calculations support the concerted reaction path proposed by Casey et al.[11d]

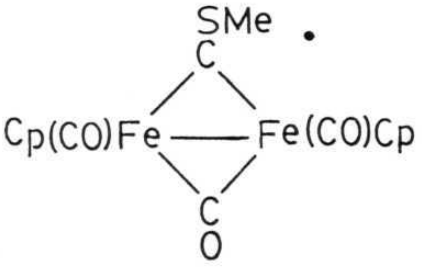
A similar reaction is not possible when hydrogen is replaced by an alkyl group.[11,12] This is because of the following reason. The LUMO in (CO)CpFe(μ-CO)(μ-CCH_3)Fe(CO)Cp^+, **22** is also carbon based $p_\perp$ orbital. But it has a π^* interaction with a psuedo **p** orbital of the CH_3 group. As the ethylene approaches the carbynyl carbon this C-Me π^* interaction in **22** is increased and no trace of a C-Me σ^* interaction is observed in the frontier range. Hence, donation of π electrons from the ethylene to the

C-Me σ^* orbital of **22** is not possible, which denies the adduct formation necessary for this reaction of **22** with ethylene.

Above discussion suggests that ethylene can react at the carbyne carbon only if the R group on the carbynyl carbon is hydrogen. Hence compounds $(CO)_2CpMn(\mu\text{-}CH)PtL_2^+$, $(CO)_5W(\mu\text{-}CH)PtL_2^+$, $[Ru(CO)Cp]_2(\mu\text{-}CO)(\mu\text{-}CH)^+$ and similar compounds which are isolobal to cyclopropyl cation should show hydrocarbation reaction. Since the hydrocarbation reaction is shown to be catalytically useful,[11] we suggest that the preparation of all the CH^+ bridged compounds which are isolobal to cyclopropyl cation should be attempted, and tested for their hydrocarbation reaction.

Carbyne Radical Bridges on Bimetallic Templates

Some radical species are identified with the help of ESR spectra in compounds where a carbyne group bridges two metals.[1r,21,22] The well characterized examples are $[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CSMe)^{\bullet}$, **23**,[21] and $[Cp(CO)Co]_2(\mu\text{-}CMe)^{\bullet}$, **24**.[2f,22] The Fe system, **23** is very close to **4** except for H is replaced by SMe group and for the extra electron. The electronic structure is very much similar to **4**. The extra electron in **23**



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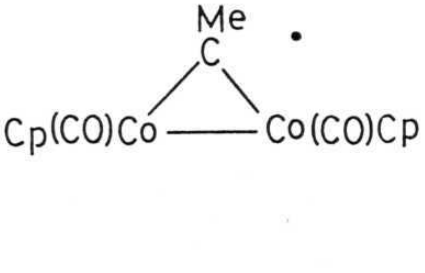

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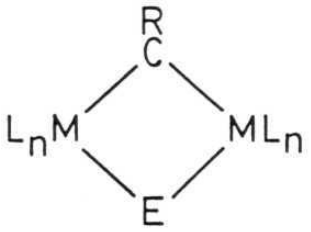
goes into the LUMO of **4** i.e. **11** . Since **11** is antibonding between $p_{\perp}$ orbital of carbon and δ orbital of the metallic template, no delocalization of this extra electron should be expected. The chemical reactivity of these radicals is not studied in detail. Reaction of **23** with another radical (•SePh) gives a carbene-like bridging unit.[21] This supports the idea that the odd electron in **23** is localized on carbon only. Co(CO)Cp is isolobal to CH_2. Thus **24** is supposed to have similar electronic structure as that of **23**. Both **23** and **24** are isolobal to cyclopropyl radical. However the sharp pyramidalization observed in cyclopropyl radical may not be necessary here because the more diffuse orbitals of the metals allows an MCM angle much larger than 60^{o}.

Carbyne and hetero atom bridges on the M-M axis.

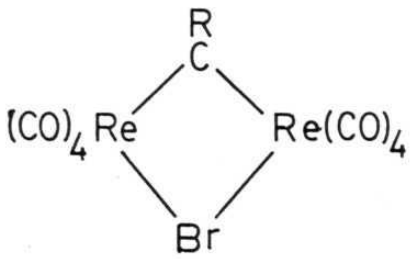
A few compounds with a carbyne and hetero atom bridges on the bimetallic system **25** are reported in literature. The



25

reactivity of these species **26-32** is not yet studied in detail. There seem to be little in common among these and so these are studied individually.

In $(CO)_4Re(\mu\text{-}Br)(\mu\text{-}C(C_6H_5))Re(CO)_4$, **26**,[23] the fragment $Re(CO)_4$ is a $d^7\text{-}ML_4$ unit and is isolobal to CH_2. The metal environment is of 18 electron and no M-M bond should be expected. **26** may formally be considered as equivalent to Br^- and CR^+

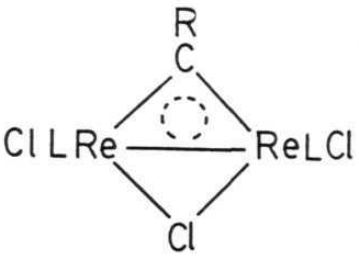


26 R = Ph

33 R = H

bridged species. That makes the compound isoelectronic to **4**. Thus **26** may be treated as a part of the CH^+ bridged bimetallic systems. Extended Huckel calculations on $[Re(CO)_4]_2(\mu\text{-}Br)(\mu\text{-}CH)$, **33** shows that σ, σ^*, π, π^* and δ, δ^* orbitals of M...M axis are occupied. The π and δ combinations of M...M are stabilized by the participation of the π and π^* combinations of HC...Br unit respectively, but the MOs are mostly on metal and Br. The carbon based $p_\perp$ orbital is destabilized to become the LUMO. It is antibonding with the M-M δ MO. The coefficient on Br is very small here. This is very much similar to the LUMO observed in **4** and **9**, **11**. The charge matrix also supports consideration of **26** as Br^- and CR^+ bridged species. As in the earlier cases we expect hydrocarbation reaction of **26** with ethylene when the phenyl group is replaced by H. Electrophilic nature of this compound has not been studied and is worth pursuing.

$[ReCp^*Cl]_2(\mu\text{-}Cl)(\mu\text{-}CPh)$, **27**[24] is an example with a Cl and CR bridges on the bimetallic template. This is a 16 electron species and a double bond is predicted on the basis of electron count.[22] Extended Huckel calculations of $[ReCpCl]_2(\mu\text{-}Cl)(\mu\text{-}CH)$, **34** shows that the σ and $p_\perp$ orbitals of carbyne are involved in M-C bond formation. The $p_\perp$ orbital of carbyne is stabilized by the δ orbital of the metallic template, leading to the Re-C-Re π delocalization. In a d^3-d^3 metal electron count, three of

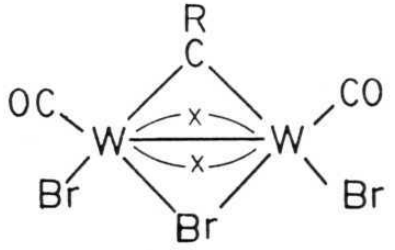


27 R = Ph L = Cp

34 R = H L = Cp

the metal based orbitals are occupied. They are δ^*, σ and π^*. LUMO is an M-M π orbital. This indicates that only an M-M single bond is present in **27**, along with Re-C-Re π delocalization. The charge matrix shows a large concentration of charge in the carbynyl carbon.

$Br(CO)W(\mu\text{-}PF_2NMePF_2)_2(\mu\text{-}Br)(\mu\text{-}C(C_6H_4\text{-}Me))W(CO)Br$, **28**[25] also has a Br and CR groups bridging two transition metals. The metal and ligand environment is very much different. There are two more bridges (PF_2NRPF_2). Formally the (PF_2NRPF_2) fragment may be replaced by two PH_3 groups one each on the two metals. The metallic fragment becomes $d^5\text{-}ML_4$ which is isolobal to BH^+. This clearly shows that the metallic environments in **26** and **28** are quite different. Extended Huckel calculations on $[W(CO)Br(PH_3)_2]_2(\mu\text{-}Br)(\mu\text{-}CH)$, **35**, shows only two of the metal



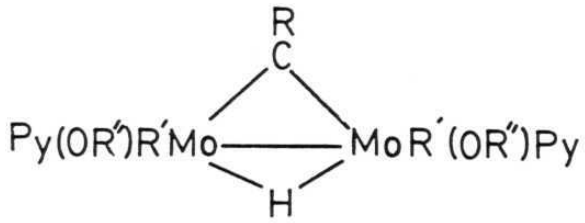
X = $PF_2CH_2PF_2$

28 R = C_6H_4Me-4

35 R = H

based orbitals σ and π* are to be occupied (d^2-d^2). The $p_\perp$ orbital of carbon is stabilized because of its interaction with the π orbital of metallic template. This orbital account for the 2 π electron delocalization in the M-C-M unit. The small W-C distances (1.86 Å) supports this idea. This compound show aromatic character to certain extent.

$[(CH_2SiMe_3)(OC_6H_3Me_2)(Py)Mo]_2(\mu\text{-}H)(\mu\text{-}CSiMe_3)$, **29** [26] is a unique example in which a carbyne and a hydrogen bridge two metals.[27] Considering CR as a three electron donor and hydrogen contributing one electron, the metals have d^2 electron count. EH calculations on the model $[Mo(CH_3)(OCH_3)(NH_3)]_2(\mu\text{-}H)(\mu\text{-}CH)$, **36**

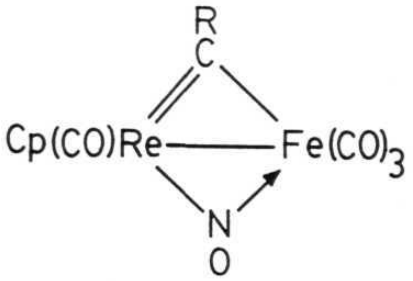


29 $R = SiMe_3$ $R' = CH_2SiMe_3$ $R'' = C_6H_3Me_2$

36 $R = R' = R'' = H$

show that the M-M σ and π* orbitals are occupied. The M-M π orbital stabilizes the carbyne $p_\perp$ orbital to give π delocalization to this compound. The corresponding antibonding combination is LUMO+3 and is mostly metal based. LUMO is a Mo-Mo π* orbital. So, the nucleophilic attack at carbon centre should not be expected. The shorter Mo-C and Mo-Mo distances[26] are suggestive of two π electron delocalization.

Another interesting compound is $Cp(CO)Re(\mu\text{-}NO)(\mu\text{-}C(C_6H_4Me\text{-}4))Fe(CO)_3$, **30**.[3d] Both the bridging groups CR and NO are three electron donors as neutral ligands, but in general NO is treated

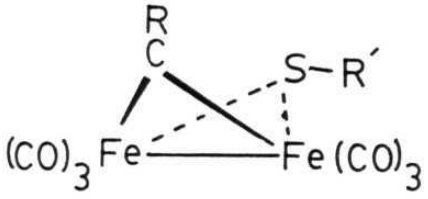


30 R = C_6H_4Me-4

37 R = H

as NO^+. The Extended Huckel calculations on the model $Cp(CO)Re(\mu\text{-}NO)(\mu\text{-}CH)Fe(CO)_3$, **37** show orbitals corresponding to Re-C π bond. LUMO is based on the bridging nitrogen with some π^* interaction with Re. An orbital corresponding to Re-Fe bond is also present. The reaction of carbene with **30** will be difficult even though there is an Re-C double bond because the Re-C π^* orbital is very high in energy.

An SR bridging group is present in $(CO)_3Fe(\mu\text{-}COMe)(\mu\text{-}SCMe_3)Fe(CO)_3$, **31**[28] in addition to a carbyne bridge. The four



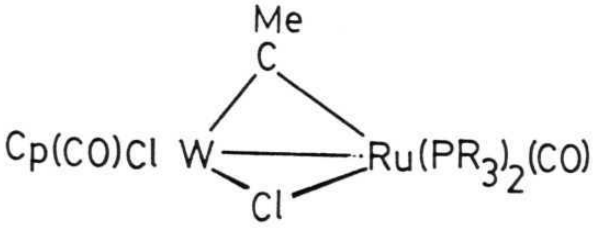
31 R = OMe R´ = CMe_3

38 R = R´ = H

membered ring Fe-C-Fe-S adopts a butterfly arrangement. In this compound both the bridging units are three electron donors as neutral bridges. The molecule may also be considered to have SR^- and CR^+ bridges. EH calculations on $(CO)_3Fe(\mu\text{-}CH)(\mu\text{-}SH)Fe(CO)_3$, **38** suggest that the carbyne bridge may be considered as a CR^+ bridge. No MO corresponding to the Fe-C double bond is

observed. LUMO is mostly based on $p_\perp$ orbital of bridging carbon. This indicates that the compound may be reactive towards nucleophiles at the carbon centre.

$Cp(CO)ClW(\mu\text{-}CR)(\mu\text{-}Cl)Ru(PR_3)_2(CO)$, **32**[29] is isolobal and isostructural to **31**. EH calculations show that in **32** also the



32

LUMO is based on $p_\perp$ orbital of the bridging carbon. No orbital corresponding to the W-C double bond is observed. Our results suggest that **32** should be electrophilic at the carbon centre.

According to the above discussion the compounds **26, 31** and **32** are similar to carbynyl cation bridged bimetallic compounds and is isolobal to cyclopropyl cation, should be electrophilic. Preparation of the compounds $[Re(CO)_4]_2(\mu\text{-}Br)(\mu\text{-}CH)$, $(CO)_3Fe(\mu\text{-}CH)(\mu\text{-}SR)Fe(CO)_3$, $Cp(CO)ClW(\mu\text{-}CH)(\mu\text{-}Cl)Ru(PR_3)_2(CO)$ is worth trying because they can act as potential reagents for the hydrocarbation reaction. 2 π electron delocalization can be expected in M-C-M ring of **27, 28, 29** and **30**.

3.4 Conclusions

LUMO of the compounds with carbynyl cation bridged bimetallic systems controls the reactivity of these compounds. Nucleophilic attack at carbon centre is triggered by this LUMO in those compounds which are isolobal to cyclopropyl cation. Hydrocarbation reaction in $(CO)CpFe(\mu\text{-}CO)(\mu\text{-}CH)Fe(CO)Cp^+$ with ethylene occur in a least motion path which allows the donation of ethylene π electrons to the C-H σ^* orbital. **17** should not be considered as a carbynyl cation bridged complex. **26, 31** and **32** have electronic structures similar to that of CR^+ compounds. If the R group on the carbynyl cation bridges in compounds isolobal to cyclopropyl cation is replaced by hydrogen, hydrocarbation reaction can be expected.

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CHAPTER 4

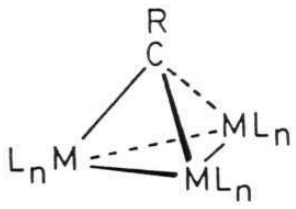
Electronic Origin for the Geometric Preferences of Carbyne Bridges in $HM_3(CO)_{10}(\mu\text{-}CR)$ Complexes

4.1 Abstract:

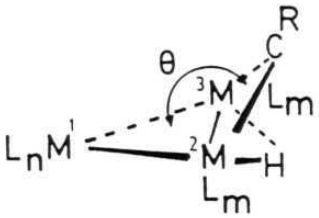
The electronic factors that control the variation of the bridging carbyne unit in $HM_3(CO)_{10}(\mu\text{-}CR)$ from μ_2- to μ_3- have been studied by Extended Huckel calculations on the model $HFe_3(CO)_{10}(\mu\text{-}CH)$, **3a**. HOMO-1 of **3a** has antibonding character between the $p_\perp$ orbital of carbyne and all the three metals. Substituents on the carbynyl carbon influence this metal-carbon antibonding interaction, but not equally with all metals. This leads to a variation in the dihedral angle θ between the M-M-M plane and M-C-M plane as a function of R. Molecular orbital patterns indicate only μ_2 arrangement for carbyne in all $HM_3(CO)_{10}(\mu\text{-}CR)$ compounds. The μ_3 arrangement of carbyne in $HRhFe_2(CO)_7Cp(\mu\text{-}COMe)$ is due to the directionality of the MOs of Rh(CO)Cp unit.

4.2 Introduction

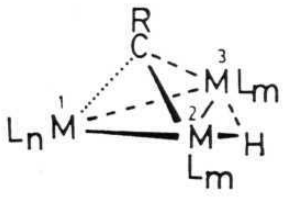
Carbyne (CR) ligands appear in organometallic chemistry with metal attachments ranging from one to four, (μ_1- μ_4).[1] μ_1, μ_2 and μ_3 bridging carbyne arrangements are in principle possible with a trinuclear carbyne complex. There has been no characterised example of a monohapto (μ_1) carbyne ligand attached to a trinuclear cluster. μ_3 carbyne bridging mode is well known in the trinuclear complexes, **1**[1c], isolobal to tetrahedrane. μ_2 -CR on trimetallic templates presents a different story.[2-19] A perusal of available structures, (Table 1) indicates that the μ_2-CR attachment is a very delicate one. With changes in the substituent R, the CR group could shift gradually from a μ_2 to a μ_3 position. The electronic factors that control such a gradation are discussed in this chapter.



1



2a



2b

All structures of type **2** (listed in Table 1) have 48 valence electrons, same as that in **1**. However, their geometries are very different. At one extreme these could be described as the bicyclobutane-like structure **2a** where the angle **θ** between the M(1)-M(2)-M(3) plane and the M(2)-C-M(3) plane is much larger than 90^{o}, (**VI**, Table 1).[6] This leaves no possibility for M(1)-CR bonding. If one assumes that the four electrons (3 from CR and 1

Table 1 : The structures of trinuclear carbyne complexes (**I-XXIII**) along with the M(1)-C distance dihedral angle θ. Distances in angstrom units and angles in degrees.

Compound		M(1)-C	θ	Ref.
$HFe_3(CO)_{10}(\mu\text{-}CO)^-$	**I**	3.00	102.0	2a
$HFe_3(CO)_{10}(\mu\text{-}CNMe_2)$	**II**	2.89	96.8	3e
$HFe_3(CO)_{10}(\mu\text{-}COMe)$	**III**	2.70	91.0	2a
$HFe_3(CO)_{10}(\mu\text{-}COH)$	**IV**	--	--	4
$HRu_3(CO)_{10}(\mu\text{-}CO)^-$	**V**	3.17	102.4	5
$HRu_3(CO)_{10}(\mu\text{-}CNMe_2)$	**VI**	3.08	100.4	6
$HRu_3(CO)_{10}(\mu\text{-}COMe)$	**VII**	2.90	94.4	7
$HRu_3(CO)_9Py(\mu\text{-}CNBz_2)$	**VIII**	--	--	8b
$HRu_3(CO)_9PPh_3(\mu\text{-}CNBz_2)$	**IX**	--	--	8b
$HOs_3(CO)_{10}(\mu\text{-}COMe)$	**X**	--	--	9
$HOs_3(CO)_{10}(\mu\text{-}CNMe_2)$	**XI**	--	--	10
$HOs_3(CO)_{10}(\mu\text{-}CPh)$	**XII**	2.59	78.2	11
$HOs_3(CO)_{10}(\mu\text{-}CCH{=}CH_2)$	**XIII**	--	--	12
$HOs_3(CO)_{10}(\mu\text{-}CCH_3)$	**XIV**	--	--	13
$HOs_3(CO)_{10}(\mu\text{-}CC_2H_5)$	**XV**	2.64	82.1	12
$HOs_3(CO)_{10}(\mu\text{-}CH)$	**XVI**	2.35	69.7	14
$HRhFe_2Cp(CO)_7(\mu\text{-}COMe)$	**XVII**	2.21	69.2	15
$HCoFe_2Cp(CO)_7(\mu\text{-}COMe)$	**XVIII**	2.00	64.7	16
$NiFe_2Cp(CO)_7(\mu\text{-}COMe)$	**XIX**	1.96		16
$(AuPPh_3)M_3(CO)_{10}(\mu\text{-}COMe)$[a]	**XX**			17
$(AuPPh_3)Fe_2CoCp(CO)_7(\mu\text{-}COMe)$	**XXI**	1.93		16
$HOs_3(\mu\text{-}CPh)(CO)_9(=COMe_2)$	**XXII**	2.29	66.6	9b
$HOs_3(CO)_{10}(\mu\text{-}C(PhC{=}C{=}C(Ph)\text{-}Re(CO)_4PMe_2Ph)$	**XXIII**	3.09	99.1	18

[a] M=Fe,Ru

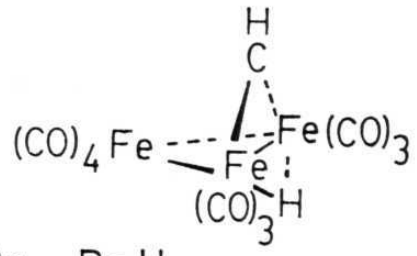
from H) donated to the bridge are equally shared by M(2) and M(3) all the three metals in **2a** would satisfy the 18 electron rule. At the other extreme we have the compound, **XVIII** (Table 1) where θ is as small as 64.7^{o} (**2b**).[16] This leads to an M(1)-CR distance of about 2.0 Å which is clearly within the bonding range. A conventional electron count that demands the carbyne to be three electron donor (one electron to each metal) leads to the electron counts M(1) = 19, M(2) = M(3) = 17.5 in **2b**. A charge-separated structure where M(1) holds +1, M(2) and M(3) -1/2 each brings back the 18 electron count. This does not provide any better understanding of the electronic structure of the system especially when one considers the fact that the structure is controlled by the substituent R on the carbynyl carbon.

With electron donating substituents on the carbynyl carbon, the angle θ is large (as large as 102^{o} when $R=O^{-}$, **V**, table 1). As the electron donating capacity of the R group decreases, θ and M(1)-C distance decrease. This can be clearly observed in table 1 (**I** to **III** Fe complexes; **V** to **VII** Ru complexes; **XII**, **XV** and **XVI** Os complexes). It appears that the Os complexes can accommodate smaller dihedral angles. When R is replaced by hydrogen (in **XVI**, Table 1), θ is less than 70^{o} and a semi-triply bridging nature of the CH group is suggested on the basis of distances.[14] What is the electronic origin for this change of θ as a function of R? What is the actual bridging nature of the carbyne (CR) group in these series of complexes? At small values of θ (70^{o}) can the CR group be described as μ_3? Is there any π delocalization in the M(2)-C-M(3) plane? How do the electron withdrawing substituents dictate the redistribution of charge implied in the electron count ? The bulkiness of the R group

does not appear to control the angle, θ . It has been suggested that the metal M(1) donates electrons to the π^* orbital of C-OMe or C-NMe_2 bridging groups.[3d] But a conventional electron count demands localization of extra charge on M(2) and M(3) and not on CR.

Replacement of $M(1)(CO)_4$ unit in **2** by isoelectronic Cp(CO)Rh or Cp(CO)Co units (**XVII** or **XVIII**, Table 1) leads to μ_3 arrangement for the carbyne ligand , with short M(1)-C distance, even with an electron donating R.[15,16] Is it possible that the origin of the short M(1)-C distance in the $HM_3(CO)_{10}(\mu\text{-CR})$ and in $HM_2M'Cp(CO)_7(\mu\text{-CR})$ are different? There are several examples in literature where short interatomic distances donot represent bonding interactions.[20] Are the compounds under discussion further examples to this?[21]

In this chapter, we have tried to understand the electronic origin for the variation of θ as a function of substituent (R) on the bridging carbyne (CR) in **2**. The electronic structure of the model compound $HFe_3(CO)_{10}(\mu\text{-CH})$, **3a** is studied first to understand the various molecular orbital interactions present in this series of molecules. Walsh diagrams are constructed to delineate the variation in the MOs as a function of θ. Electronic structure of $HOs_3(CO)_{10}(\mu\text{-CH})$, **XVI** is studied to explain its special properties. The MO pattern of $HRhFe_2Cp(CO)_7(\mu\text{-CH})$ is also studied to explain the μ_3 arrangement of CR bridge in **XVII** and **XVIII**. Fragment Molecular Orbital approach[22] within the Extended Huckel method [23] is used in these studies.



3a R = H

3b R = NH_2

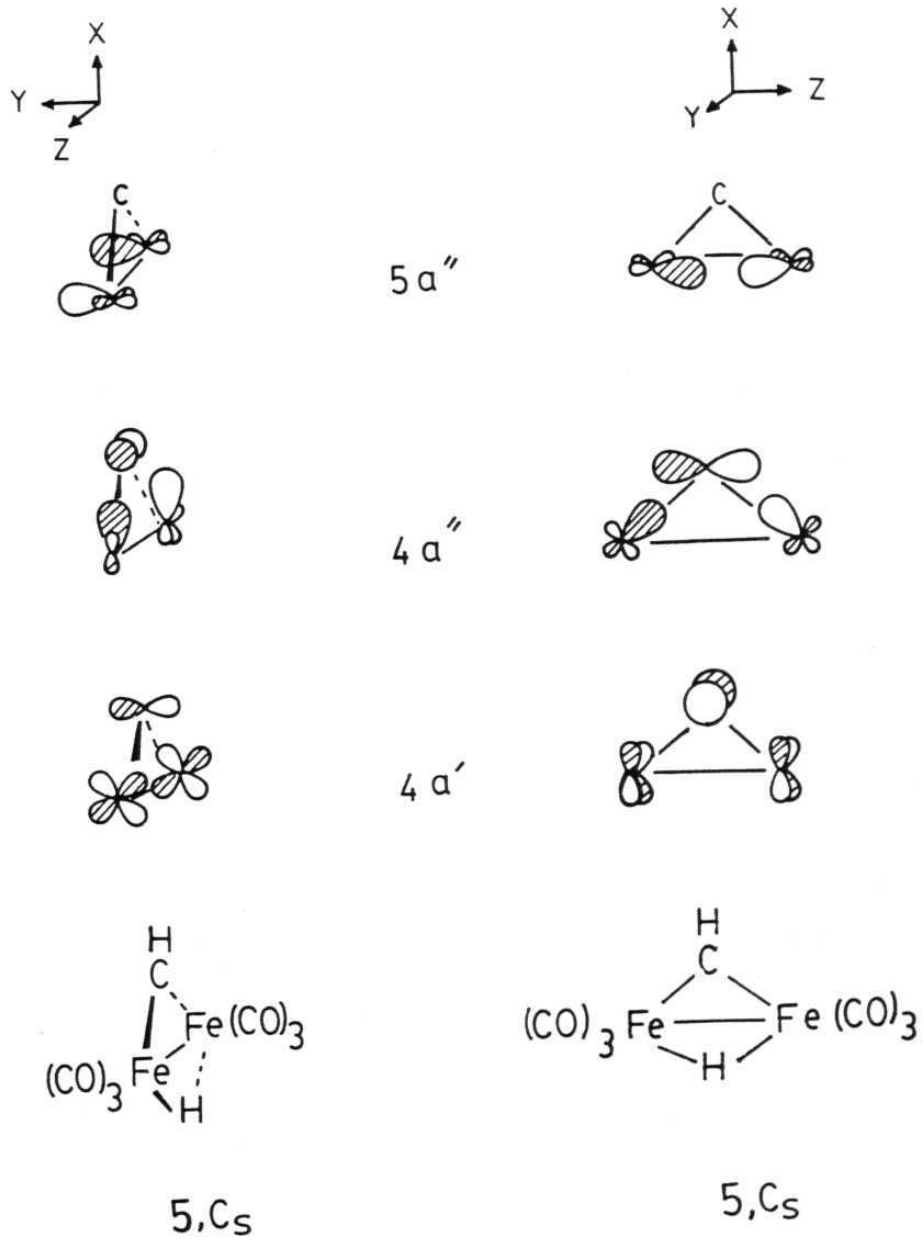
4.3 Results and Discussion

Electronic Structure of $HFe_3(CO)_{10}(\mu\text{-}CH)$, 3a.

$HFe_3(CO)_{10}(\mu\text{-}CH)$, **3a**, in which the dihedral angle θ formed by the two planes, Fe(1)-Fe(2)-Fe(3) and Fe(2)-C-Fe(3) is kept at 90^{o} is taken as a model to understand the molecular orbital pattern of the complexes of type **2**. The details of atomic and geometric parameters used in the calculations are given in the appendix. Molecular orbitals of **3a** are constructed from the MOs of smaller fragments $Fe(CO)_4$, **4**, and $HFe_2(CO)_6(\mu\text{-}CH)$, **5**. The MOs of fragment **5**, in turn are constructed from those of the carbyne group, **6**, and of the remaining fragment $HFe_2(CO)_6$, **7** (Fig. 4.1). The carbyne group has a σ orbital and two unhybridized p orbitals one in the plane of the fragment ($p_{\parallel}$) and the other out of the plane ($p_{\perp}$). The important orbitals 3a'(δ), 4a'(δ), 5a'(π), 5a''(π^*) of fragment **7** are shown in Fig. 4.1. Mulliken symbols σ, π and δ, should not be taken literally here as the low symmetry of the system results in considerable mixing amongst them. Fig.4.1 shows that major interactions between fragments **6** and **7** leads to HOMO and HOMO-1 of **5**. 5a'' (π^*) of fragment **7** does not find any match in the orbitals of **6** and becomes LUMO (5a'') of **5**. 4a'' of **7** interacts with $p_{\parallel}$ of **6** to give 4a'' of **5**, corresponding to an M-C σ bond. 1a' of **5** is a π MO delocalized over Fe(2)-C-Fe(3). 4a' (HOMO) is the corresponding antibonding combination, obtained from a

three centre four electron interaction between 3a' (δ), 4a'(δ) of **7** and $p_\perp$ of carbyne. In 4a' of **5**, $p_\perp$ of carbyne has bonding interaction with one of the M(2)-M(3) δ bonds and antibonding interaction with another (Fig.4.1). M(2)-C-M(3) π delocalisation should not be expected in fragment **5** because both 1a' and 4a' are occupied. The presence of 4 π electrons prompts

Scheme 1



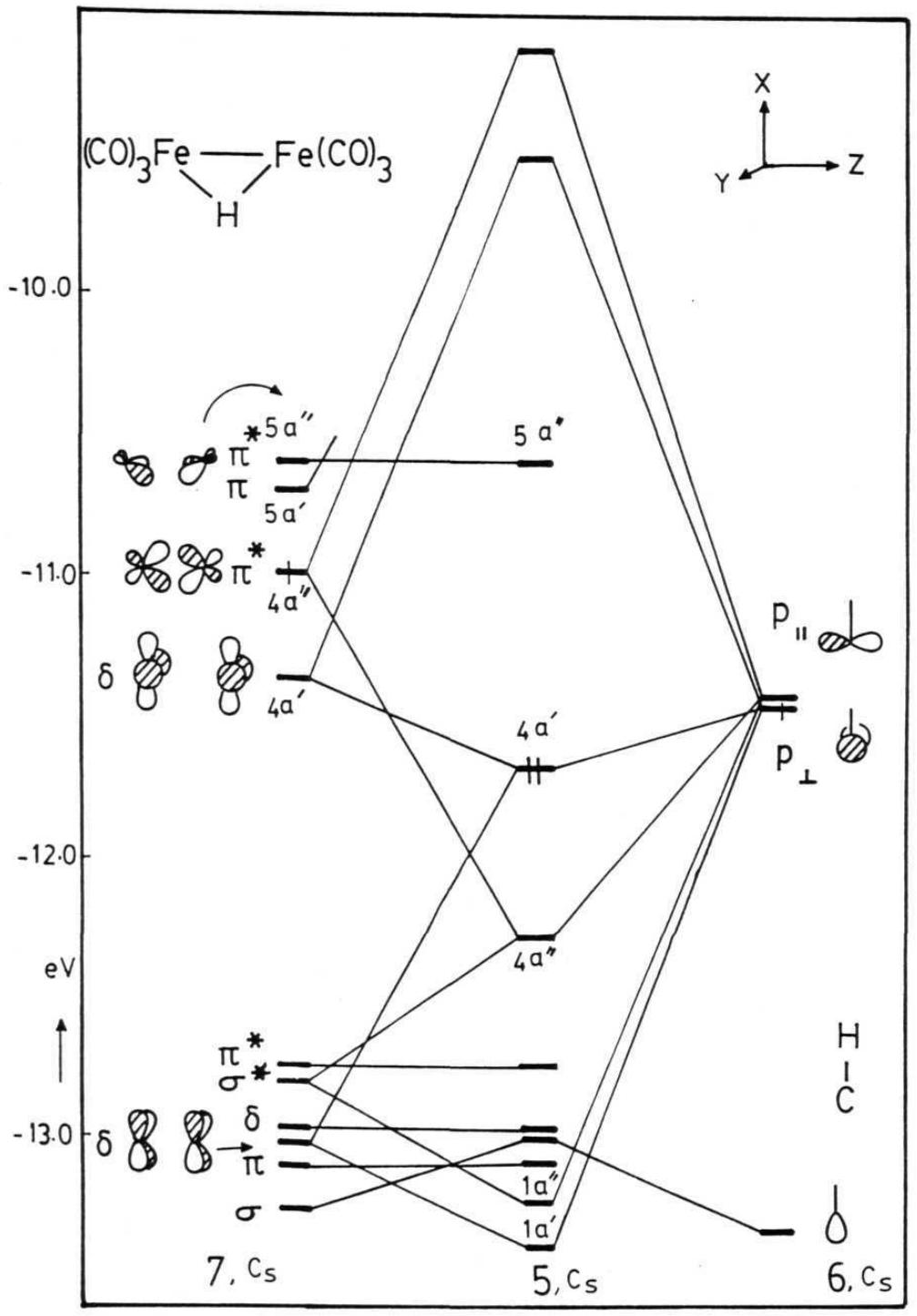
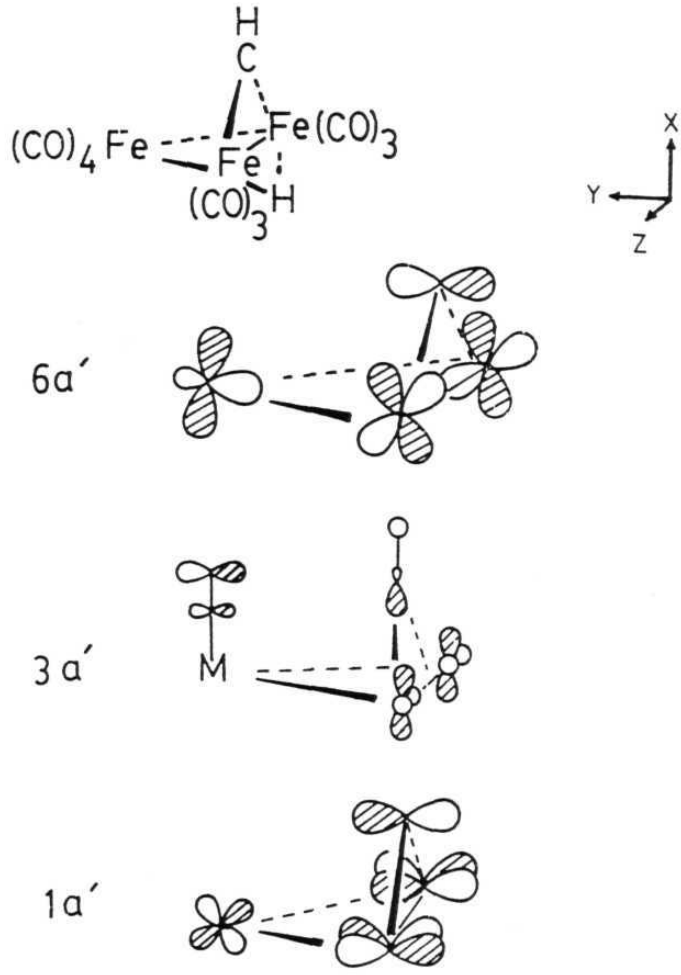


Fig. 4.1 Interaction diagram for the construction of the MOs of the fragment $Fe_2(CO)_6(\mu\text{-}H)(\mu\text{-}CH)$, **5** from smaller fragments CH, **6** and $Fe_2(CO)_6(\mu\text{-}H)$.

us to consider the fragment **5** to be analogous to the cyclopropenyl anion.[24] The three orbitals 4a', 4a'' and 5a'' of **5** are important for further discussion and are drawn in Scheme 1.

Scheme 2



Interaction of fragment $HFe_2(CO)_6(\mu\text{-}CH)$, **5** with the familiar $Fe(CO)_4$ group[25] gives **3a**. Interaction diagram (Fig. 4.2 left) shows that HOMO-LUMO interactions lead to metal-metal bonds, 6a' and 6a''. 4a'' of fragment **5** becomes HOMO-2 (5a'') of **3a**. The remaining interactions are 2c-4e kind and do not contribute to the bonding. The important molecular orbitals (1a', 3a' and 6a') of **3a** are shown in Scheme 2. 1a' orbital of **3a** corresponds to Fe(2)-C-Fe(3) π delocalization. In addition

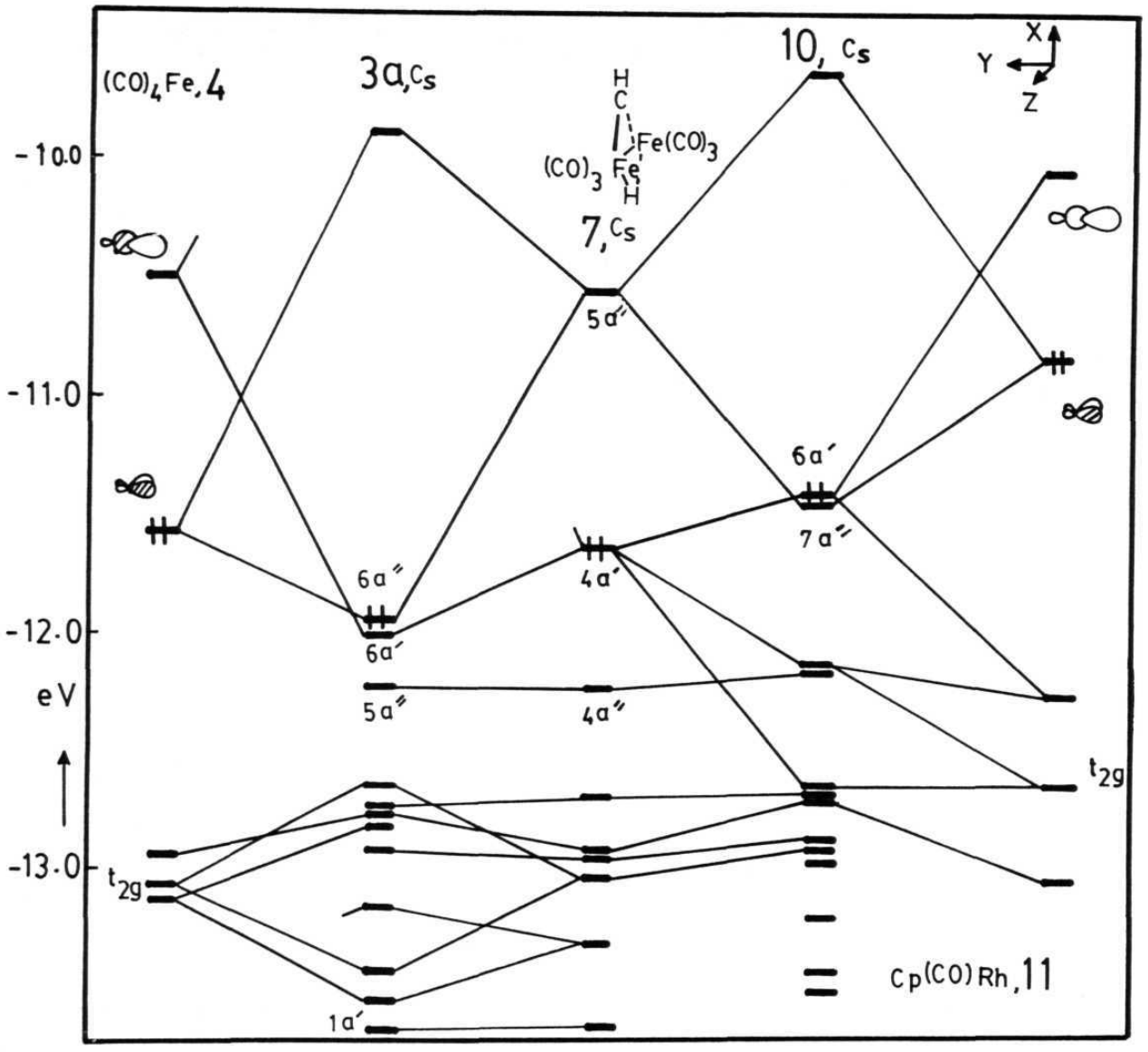


Fig. 4.2 Diagram showing the interaction of fragment $HFe_2(CO)_6(\mu\text{-}CH)$, **5** (left) with $Fe(CO)_4$ to give $HFe_3(CO)_{10}(\mu\text{-}CH)$, **3** and (right) with $Rh(CO)Cp$ to give $HRhFe_2(CO)_7Cp(\mu\text{-}CH)$, **10** (at $\theta = 90^{o}$).

to this interaction, carbynyl carbon has bonding interaction with Fe(1) in 1a' MO. 6a' (HOMO-1) has antibonding interaction between the $p_{\perp}$ orbital of carbyne and all the three metals, but these are not equal. The interaction of the CR group with the Fe(2)-Fe(3) fragment is through an Fe(2)-Fe(3) δ orbital while the interaction with Fe(1) may be described as σ^*. In 3a' there is an antibonding interaction between one of the carbonyls on Fe(1) and C-H of the bridging group. 6a'' is an M-M bonding orbital.

The Fe(1)-Fe(2) and Fe(1)-Fe(3) overlap populations are 0.14 each and Fe(2)-Fe(3) overlap population is 0.04 in **3a**. This indicates that there is no σ bond between Fe(2) and Fe(3). A thorough analysis of MOs suggest that there is a three centre two electron bond in the Fe(2)-H-Fe(3) framework. In this context the bridging hydrogen may be treated as H^+ and a -ve charge in the Fe(2)-C-Fe(3) ring.[3d] The Fe(2)-C and Fe(3)-C bonds are regular two centre two electron bonds which leaves 4 π electrons (one each from CR, Fe(2) and Fe(3)[26] and one because of negative charge in the Fe(2)-C-Fe(3) ring), to be distributed in Fe(2)-C-Fe(3) framework. They are found in the 1a' (π) and 6a' (π^*) orbitals.

To understand the nature of MOs of **3a** in detail, the interaction diagram between $HFe_3(CO)_{10}$ and CH is also studied (Fig. 4.3 left). The $p_{\perp}$ orbital finds antibonding interaction with d_{xy}-d_{xy} δ (δ_1) and bonding interaction with $d_{x^2-y^2}$-$d_{x^2-y^2}$ δ (δ_2) in a 3c-4e interaction. This causes a delicate balance between bonding and antibonding interactions in 6a' of **3a**. Even though the 6a' of **3a** is a result of bonding interaction of 6a' of $HFe_3(CO)_{10}$ with $p_{\perp}$ of CH, the MO diagram shows only antibonding

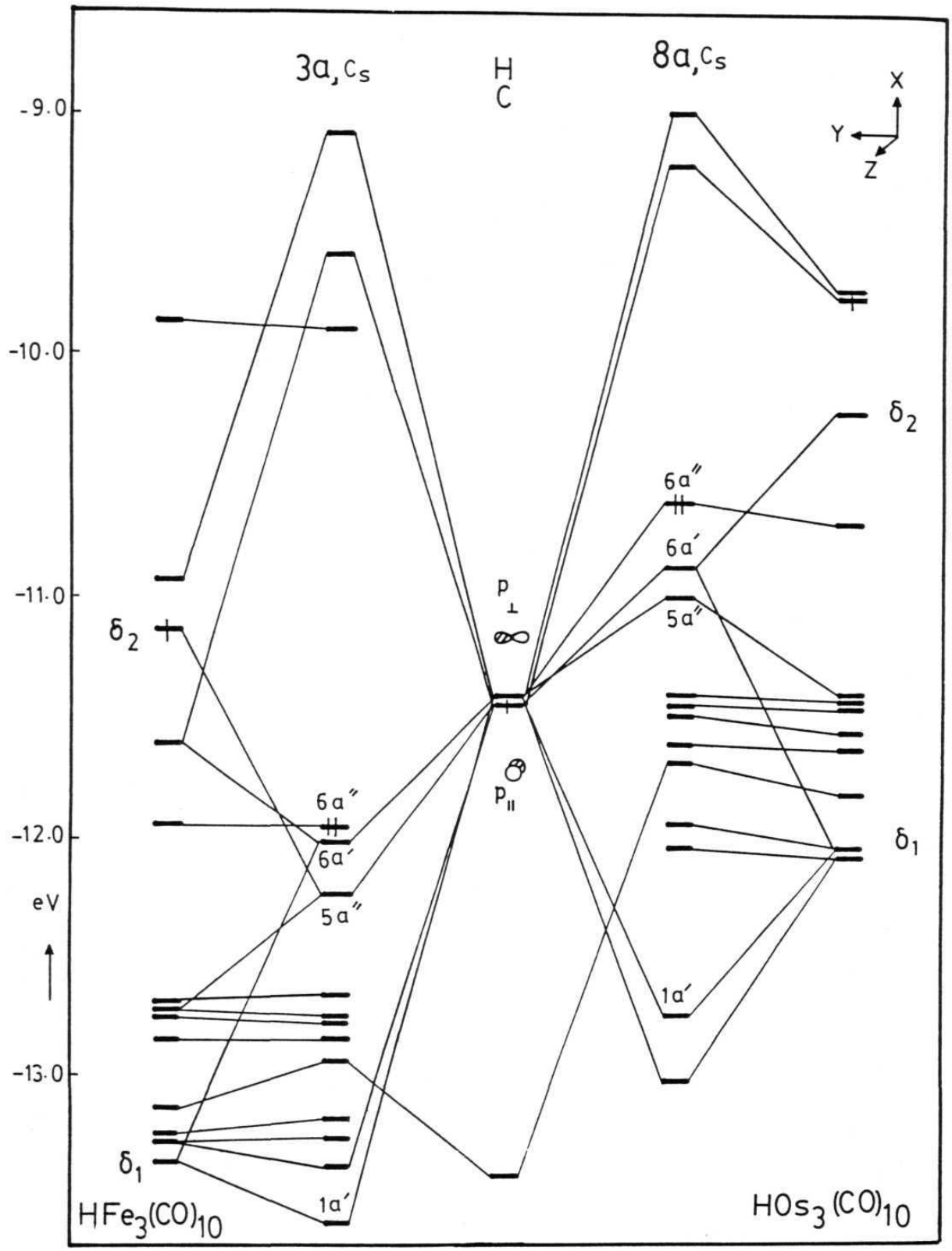


Fig. 4.3 Interaction diagram showing the interaction of bridging CH with the remaining fragment (left) leading to $HFe_3(CO)_{10}(\mu\text{-CH})$, **3a** and (right) leading to $HOs_3(CO)_{10}(\mu\text{-CH})$, **8a**.

interaction with all the three metals (Fig. 4.4a shows the contour plot for 6a' in the Fe(1)-C(H) plane). Both bonding and antibonding combinations 1a' (σ), 1a'' (π), 2a''(π^*), 6a' (σ^*) between Fe(1) and C are occupied. There is no net effective π delocalization in Fe(2)-C-Fe(3) as both the π (1a') and π^* (6a') MOs are occupied. HOMO has insignificant contribution from the CR bridge.

A Walsh diagram (Fig. 4.5a) is constructed to understand the variations in the MO pattern as a function of dihedral angle θ for the molecule **3a**. The geometric details are given in the appendix. Sum of one-electron energy curve shows a minimum at 77^{o}. Major contribution comes from the 6a' orbital which steeply decreases in energy. This is mainly due to the decrease in the Fe(2)-C-Fe(3) π^* interaction. With a decrease in θ, the antibonding interaction (σ^*) between the $p_{\perp}$ orbital of carbon and the d_{xy} of Fe(1) increases. As a result the slope of 6a' decreases at low dihedral angles. Variation in the sum of one-electron energies directly follows the variation of 6a' except for the increase in the energy due to steric factors (as shown by the 3a' orbital). 3a' increases in energy at small dihedral angles because of the development of antibonding interactions between the carbonyl group on Fe(1) and hydrogen on carbynyl group (Scheme 2). The variation in the remaining MOs contribute minimally to the variation in the sum of one-electron energies. As the dihedral angle decreases from 105^{o} to 65^{o} some bonding interactions (1a', 1a'') are developed between Fe(1) and carbynyl carbon but these are at the cost of bonding interactions already existing between Fe(2)-C and Fe(3)-C as in 1a'. The newly developing bonding interactions between Fe(1)-C are offset by the

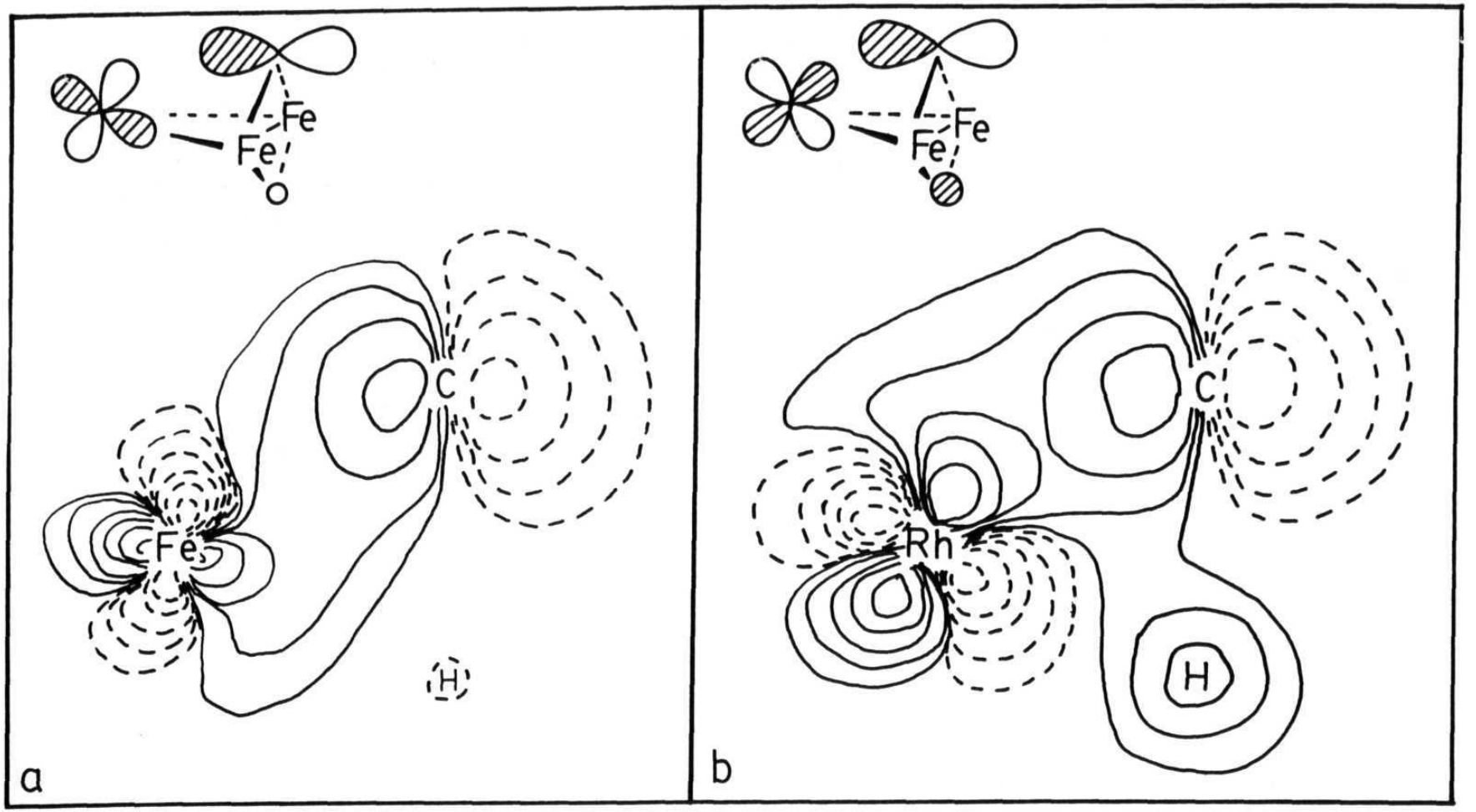


Fig. 4.4 Contour plots showing the M(1) and C(H) interaction in HOMO-1 (a) in $HFe_3(CO)_{10}(\mu\text{-}CH)$, **3a** and (b) in $HRhFe_2Cp(CO)_7(\mu\text{-}CH)$, **9**, both at $\theta = 90^{o}$.

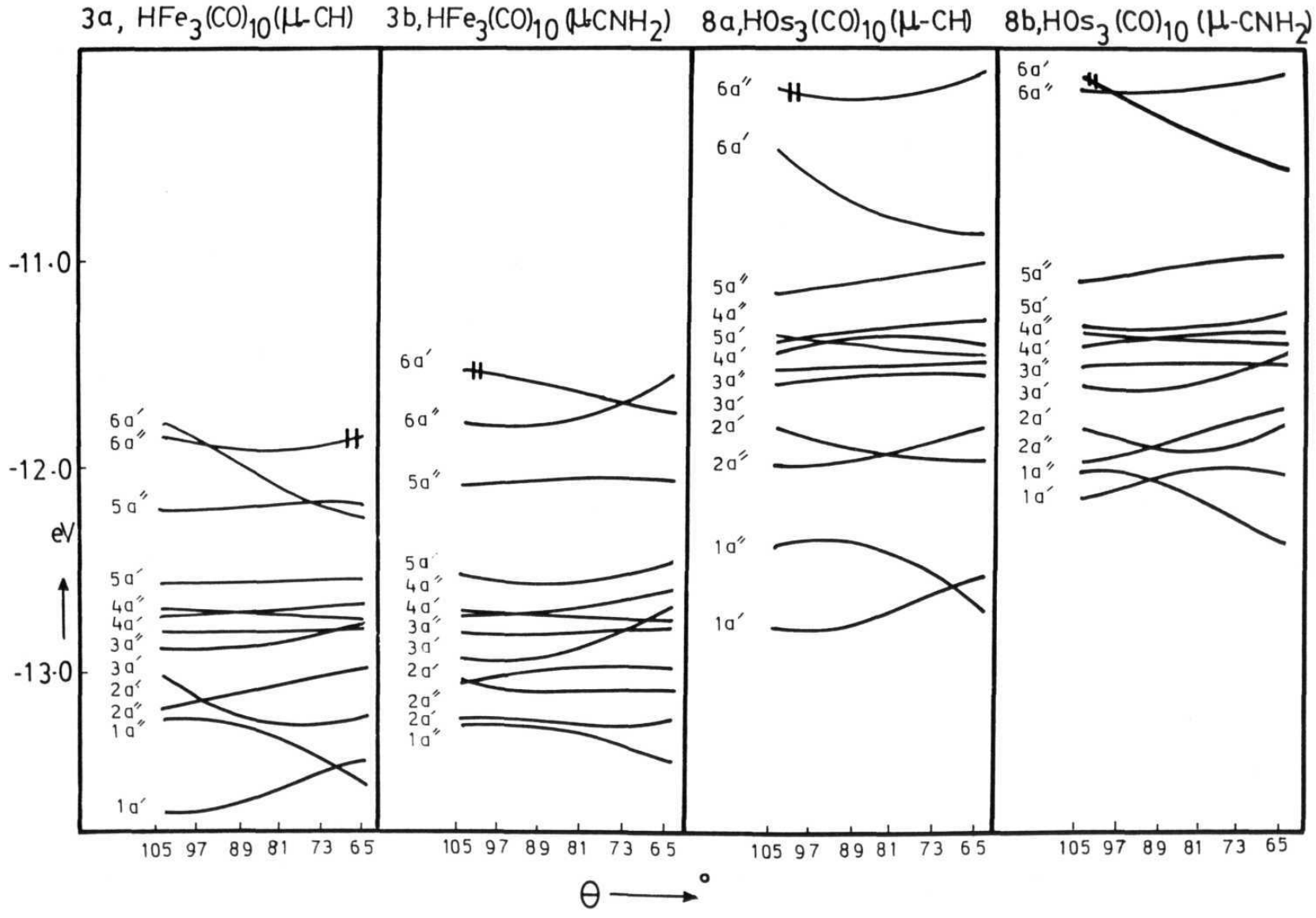


Fig. 4.5 Walsh diagrams showing the variation in the MO pattern of (a) $HFe_3(CO)_{10}(\mu\text{-}CH)$ (b) $HFe_3(CO)_{10}(\mu\text{-}CNH_2)$ (c) $HOs_3(CO)_{10}(\mu\text{-}CH)$ and (d) $HOs_3(CO)_{10}(\mu\text{-}CNH_2)$ as a function of a variation in the M(1)-M(2)-M(3) and M(2)-C-M(3) dihedral angle θ.

developing antibonding interactions (as in 1a', 6a' pair) and (1a'', 6a'' pair). The overlap population between Fe(1) and C is only slightly increased (0.053 at $\theta = 90^{o}$ and 0.061 at $\theta = 77^{o}$) and this cannot be taken as an evidence for increased Fe(1)-CR bonding interaction. The σ^{*} interaction between Fe(1) and C(H) in 6a' increases with decreasing θ. Therefore Fe(1)-C bond should not be expected at small θ. Even though the Fe(1)-C distance 2.42 Å indicates a μ_3 bridge (at $\theta = 77^{o}$), on the basis of MO pattern and overlap population analysis we should consider the carbyne as only a μ_2 rather than a μ_3 bridge in **3a**. From the Walsh diagram Fig. 4.5a it is clear that the antibonding interaction between carbon $p_{\perp}$ orbital and the δ orbital on Fe(2)-Fe(3) (6a', Scheme 2) is responsible for the preference of the structure with low dihedral angle.

Effect of the substituent on the carbynyl carbon.

The angle θ is found to increase with the electron donating capacity of the substituent R (Table 1). What is the electronic origin of this behaviour? Fig. 4.6 shows the energy level pattern of the $p_{\perp}$ orbitals of carbon in H_2CR as a function of R. The $p_{\perp}$ orbital is pushed up in energy as we go along the range of R = H, $CH{=}CH_2$, CH_3, Ph, OH, O^{-}, and NH_2. At the same time the $p_{\perp}$ orbital coefficient on carbon decreases in the same order. These effects are mainly due to the participation of pseudo $p_{\perp}$ orbital of R group in an antibonding interaction. The stronger the participation, the more the destabilization.

In the HOMO-1 (6a') of **3a**, the $p_{\perp}$ orbital of carbyne has antibonding interaction with all the three metals. The Walsh diagram (Fig. 4.5a) has shown that 6a' controls the sum of one-

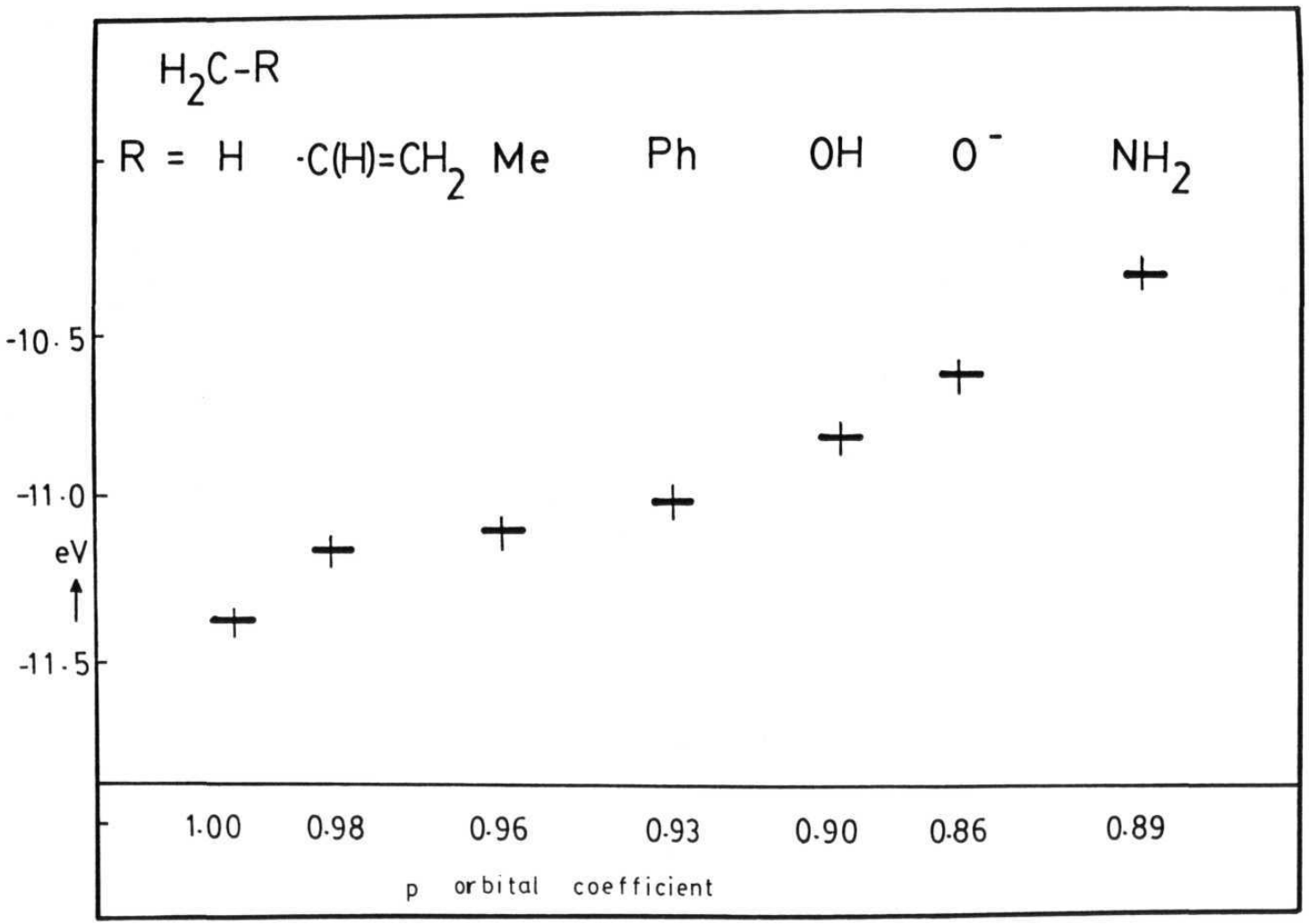
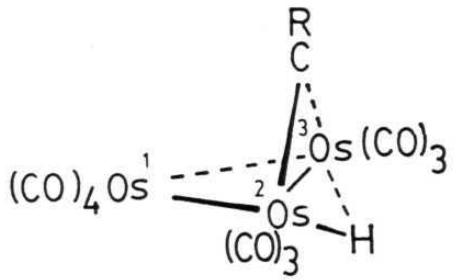


Fig. 4.6 Correlation diagram showing the variation of the energy of $p_{\perp}$ orbital as a function of R in H_2CR.

electron energies. The decrease in θ decreases the M(2)-C-M(3) π^* interaction. This antibonding interaction is considerably less with electron donating R groups because of the smaller coefficient size and higher energy of the $p_\perp$ orbital of C(R). Since the antibonding interaction is low to start with, it is not necessary to have smaller values of θ. As a result, the compounds with electron donating R can accommodate larger dihedral angle. This idea is supported by the calculations on $HFe_3(CO)_{10}(\mu\text{-}CNH_2)$, **3b**. In **3b**, the energy minimum is found at θ =93°. This is very close to the experimentally observed θ =96.8° for $HFe_3(CO)_{10}(\mu\text{-}CNMe_2)$.[3e] The Walsh diagram for a change in θ in **3b** (Fig. 4.5b) is very much similar to Fig. 4.5a except for a diminished slope of 6a'. Consequently the sum of one-electron energy curve shows a minimum at 93° in comparison to the θ =77° observed for **3a**.

ELECTRONIC STRUCTURE AND REACTIVITY OF $HOs_3(CO)_{10}(\mu\text{-}CH)$, XVI.[14]

The construction of the MOs of $HOs_3(CO)_{10}(\mu\text{-}CH)$, **8a** from smaller fragments $HOs_3(CO)_{10}$ and CH at θ =90° is shown in Fig.



8a R = H

8b R = NH_2

4.3 (right). The MOs of $HOs_3(CO)_{10}$ are comparatively at higher energy than that of $HFe_3(CO)_{10}$. As a result some stronger interactions between CH and $HOs_3(CO)_{10}$ are observed. The striking difference between Fig. 4.3 (left) and Fig. 4.3 (right) is the three center two electron interaction leading to 6a'. The antibonding interaction of the $p_\perp$ orbital of carbyne with the δ orbital of M(2)-M(3) are more strong in **8a** than in **3a** (Fig. 4.3). This should lead to smaller θ in **8a** than in **3a**. The Walsh diagram Fig. 4.5c for $HOs_3(CO)_{10}(\mu\text{-CH})$ is qualitatively similar to Fig. 4.5a except for the changes arising due to the higher energy of the Osmimum d orbitals. The variation in the sum of one-electron energy as a function of θ in **8a** shows a minimum at 70°. This is very close to the experimentally observed $\theta = 69.7^\circ$ for $HOs_3(CO)_{10}(\mu\text{-CH})$, **XVI**. Fig. 4.5c shows that in **8a** also the variation in the θ is largely controlled by 6a' orbital only. In **8a** at $\theta = 70^\circ$ also both MOs corresponding to σ (1a') and σ^* (6a') interactions between Os(1) and C are occupied. This suggests that in **XVI** the bridging carbyne should be treated as a μ_2 bridge even though the Os(1)-C distance is in the bonding range. This prompts us to consider **XVI** as a member of the group of compounds which exhibit short interatomic distances without any bonding.[20]

The effect of substituent on the carbynyl carbon is clearly observed in the case of Os compounds also (Table 1). The Walsh diagram (Fig. 4.5d) for the variation of θ in $HOs_3(CO)_{10}(\mu\text{-}NH_2)$, **8b**, is very much similar to that of Fig. 4.5c, the only difference being the slope of 6a' orbital. The sum of one-electron energy curve shows a minimum at $\theta = 91^\circ$ for **8b** in contrast to the minimum at $\theta = 70^\circ$ for **8a**. This is because of the

decrease in the antibonding interaction between $p_\perp$ orbital of carbynyl carbon and the δ orbital of M(2) and M(3) as a function of R.

In the case of regular μ_3 systems, **1**, the R group is bent away from M(1). The crystal structure of **XVI** shows that the hydrogen atom on the carbyne bridge is bent towards the Os(1).[14] This originates from the antibonding Os(1)-C interaction in HOMO-1 (6a'). To decrease this antibonding interaction the molecule pushes the hydrogen atom of the bridging carbyne away from the Os(2)-C-Os(3) plane and towards the Os(1) (Scheme 3). A weak bonding interaction between Os(1) and hydrogen of carbyne is developed. **3a** is also expected to have an M-H interaction.

The above discussion on **3a** and **8a** suggests that the dihedral angle θ is dictated by the extent of antibonding interaction observed between M(2)-M(3) θ orbitals and the carbynyl carbon. Stronger antibonding interactions in 6a' orbital leads to smaller dihedral angles because smaller value of the dihedral angles helps in decreasing the antibonding interaction. However this is tempered by the M(1)-C antibonding interaction. This delicate balance between the M(2)-C-M(3) and M(1)-C antibonding interactions (in 6a' of Scheme 2) control the dihedral angle, θ.

Similar geometric preferences are expected in $HM_2M'Cp(CO)_7(\mu\text{-}CR)$ which is obtained by replacing $M(CO)_4$ unit of **2** by isolobal M'Cp(CO) unit. But experimental results do not support this. Complexes with the general formula $HM_2M'Cp(CO)_7(\mu\text{-}CR)$ prefer a μ_3 arrangement for the carbyne ligand. There are three of them known, all with methoxy carbyne (**XVII** to **XIX**, table 1).[15,16] Methoxy carbyne was found to give μ_2 bonding in the "all-carbonyl" complexes (**III**, **VII** and **X**,

Scheme 3

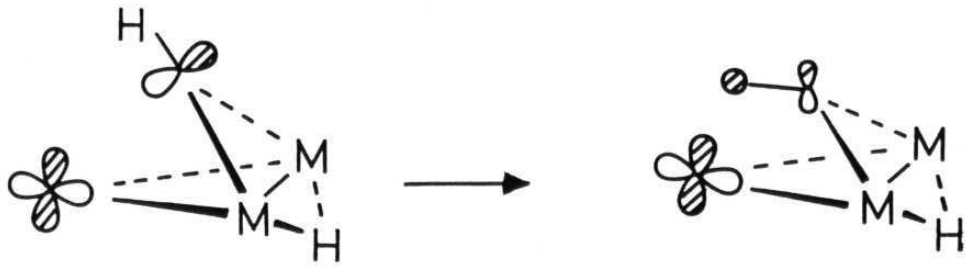
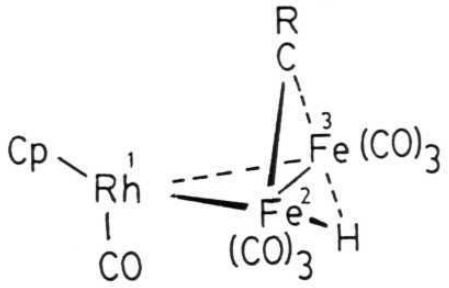


Table 1). The changes in the electronic structure that follow from a substitution of $M(CO)_4$ by MCp(CO) is analyzed below.

Electronic Structure of $HRhFe_2(CO)_7Cp(\mu\text{-}CH)$, 9.

There are several trinuclear structures where three carbonyls are replaced by a Cp group (**XVII -XIX, XXI**, Table 1).[15,16] All of these compounds have a short M(1)-CR distance even when the substituent R is an alkoxy group. A partial bridging nature is proposed between the unique carbonyl and two



9

metals to account for the 18 electron count in these complexes.[15,16] We have seen that Fe(3) and Os(3) complexes also show short M-C distances but there is no bonding interaction to assign μ_3 bonding mode to the CR group. Do these compounds with Cp ligands also fall in to this category? Electronic structure calculations on $HRhFe_2(CO)_7(\mu\text{-}COMe)$ reported earlier[15] have indicated the presence of a clear Rh-C σ bond and μ_3 arrangement for the bridging carbyne group. We have tried to the see the differences between $HFe_3(CO)_{10}(\mu\text{-}CH)$ and $HRhFe_2(CO)_7Cp(\mu\text{-}CH)$ in the following way. Fig. 2 (right) shows

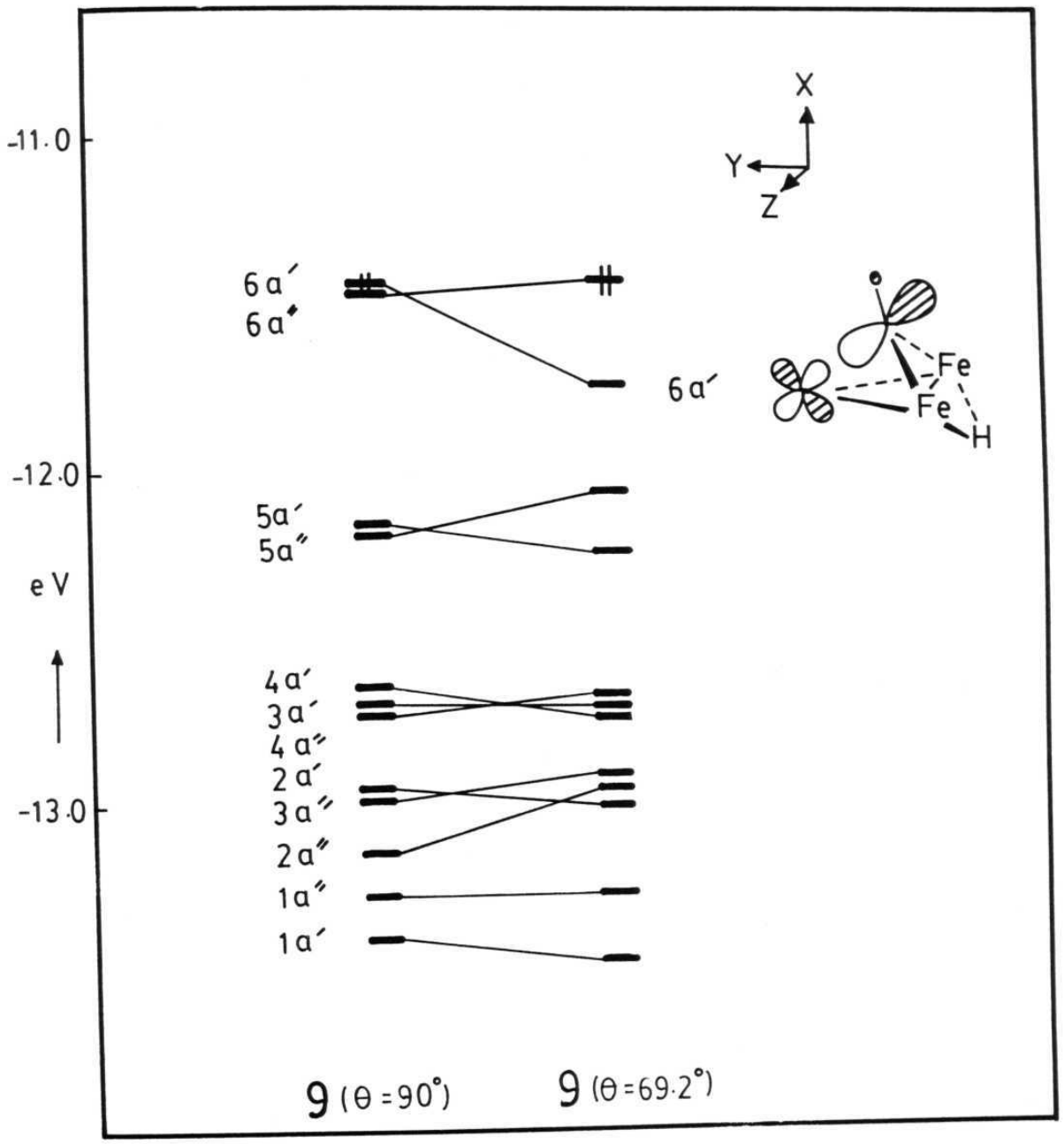


Fig. 4.7 Correlation diagram showing correlation of the MOs of $HRhFe_2(CO)_7Cp(\mu\text{-}CH)$ at $\theta = 90^{\circ}$ and at $\theta = 69.2^{\circ}$.

an interaction diagram for the construction of the MOs of **9** (90^{o}) from the fragments RhCp(CO) and $HFe_2(CO)_6$, **5**. The MOs of RhCp(CO) are very much similar to its isolobal fragment $Fe(CO)_4$, but higher in energy. In the low symmetry of Cp(CO)Rh t_{2g} is split into three well separated levels. HOMO of RhCp(CO), interacts with LUMO of **5** to give 7a'' of **9**. LUMO and HOMO-1 of RhCp(CO) (4a' and 3a') and the HOMO of **5** are involved in a three orbital stabilizing interaction. The resultant HOMO, 6a', of **9** is bonding between Rh and C. The corresponding orbital in **3a** (HOMO-1) is the result of a two orbital interaction that leads to Fe(1)-Fe(2) bonding and Fe(1)-C antibonding. Fig. 4.4b shows the contour plot for the MO 6a' of **9**. This particular bonding interaction is possible because of the directional properties and the higher energy of the MOs of Rh(CO)Cp in comparison to that of $Fe(CO)_4$.[27] Besides there is no antibonding MO in **9** corresponding to the 3a' MO of **3a** (Scheme 2). Calculations are repeated on **9** at $\theta = 69.2^{o}$. Fig. 4.7 shows the correlation between the MOs of **9** at $\theta = 90^{o}$ and $\theta = 69.2^{o}$. 6a' orbital comes down in energy with the decrease in θ. 6a' shows Rh-C σ bonding interaction at $\theta = 69.2^{o}$. The overlap population between Rh and C(H) in **9** increases largely with decreasing θ (0.175 at $\theta = 90^{o}$ and 0.354 at $\theta = 69.2^{o}$), indicating the developing Rh-C σ bond. Therefore the carbyne group should be treated as a μ_3 bridging group. Thus the directionality of RhCp(CO) orbitals pave the way for μ_3 arrangement for the carbyne bridge in **9**. In structures **XVII** to **XIX** (table 1), θ is less than 70^{o} and M(1)-C distance indicates μ_3 arrangement. Calculations made on **9** and $HRhFe_2Cp(CO)_7(\mu$-COMe), **XVII** as a function of variation in θ show energy minima at $\theta = 70^{o}$ which are very close to the experimental observation for **XVII** (69.2^{o}).

4.4 Conclusions

The electronic structure of $HFe_3(CO)_{10}(\mu\text{-}CH)$ shows that the $p_\perp$ orbital of carbynyl carbon finds antibonding interaction with all the three metals in HOMO-1. A delicate balance between this antibonding interactions control the observed changes in the angle θ between the M(1)-M(2)-M(3) and M(2)-C-M(3) planes. The coefficient size on carbon p orbital varies as a function of R group in the carbyne bridge, which is responsible for the decrease in θ with decreasing electron donating nature of R. No M(2)-C-M(3) π delocalization should be expected in $HM_3(CO)_{10}(\mu\text{-}CR)$ compounds. Electronic structure of $HM_3(CO)_{10}(\mu\text{-}CR)$ compounds suggest only μ_2 arrangement for the bridging carbyne despite short M(1)-C distance. The directionality of MOs of RhCp(CO) unit in $HRhCp(CO)Fe_2(CO)_6(\mu\text{-}CR)$ is different from that of $HFe_3(CO)_{10}(\mu\text{-}CR)$ and stabilizes a μ_3 carbyne bridge.

4.5 References

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CHAPTER 5

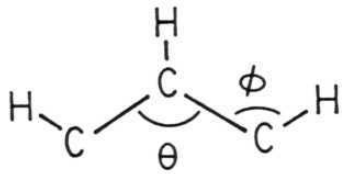
To Tilt or Not To Tilt? The Dilemma of C_3R_3 Bridged Binuclear Transition Metal Complexes

5.1 Abstract

The symmetrical or tilted positioning of μ-C_3R_3 groups that straddle an otherwise symmetrical metal-metal bond is dictated by the geometric flexibility available with the terminal ligands of the metal. The C_3Cl_3 in $[(OC)Ni(\mu\text{-}C_3Cl_3)Ni(CO)]_2Cl_2$ is symmetrical because the Ni(CO)Cl groups are free to pyramidalize around the metal so that simultaneous binding is possible for both metals with the bridging ligand. The additional bridging CR group in $L_2W(\mu\text{-}CR)(\mu\text{-}C_3R_3)WL_2$ prevents substantial pyramidalization at the WL_2 centre. In unsymmetrical metal environments, the middle carbon of the C_3R_3 group tilts toward the ML_n fragment that provides the more diffuse frontier orbitals. For example, $(\eta^5\text{-}C_5Ph_5)Ni(\mu\text{-}C_3Ph_3)Ni(\eta^4\text{-}C_4Ph_4)$ has the middle CR group tilted to $(\eta^4\text{-}C_4Ph_4)Ni$.

5.2 Introduction

Reaction of many carbyne bridged binuclear transition metal complexes with alkynes or carbenes result in compounds containing C_3R_3 bridging ligands (see chapters 1 and 2). In this chapter, we discuss the preferential bonding of C_3R_3 bridges on the bimetallic template. Though unstable as an isolated species, the C_3R_3 unit, **1**, has been stabilized as a ligand in transition metal complexes.[1-4] In binuclear complexes the C_3R_3 appears as a bridging ligand, that straddles the metal-metal bond, **2**.[2-4] The bridging C_3R_3 is symmetrical (**2a**) in some of the binuclear complexes,[3] while in others the C_3R_3 unit is tilted towards one of the metals (**2b**).[2,4] This tilting of the bridging ligand is anticipated when the two metals are not the same or when the metal environments are otherwise unsymmetrical.[2] The appearance of C_3R_3 group in an unsymmetrical bridging position in some complexes which are otherwise symmetrical is unexpected. We study this problem here. Our analysis is supported by Extended Huckel calculations.[5]



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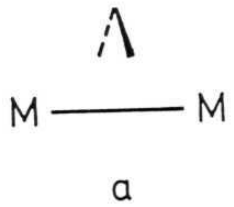

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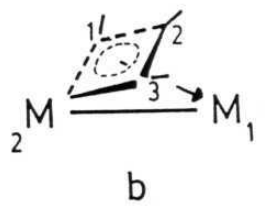

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2

A list of binuclear complexes with bridging C_3R_3 group that have been studied by X-ray crystallography is given in Table 1. The ratio M(1)C(2) / M(2)C(2) indicates the extent of tilting of the C_3R_3 group (**1,2**). Clearly there are complexes with varying

Table 1: Structural details of the binuclear complexes with bridging C_3R_3 ligands studied by diffraction methods.

Molecule	M_1C_2/M_2C_2[a]	θ[b]	Φ[b]	Terminal LML angle[b]	C_1-C_2[b]	References
$[(OC)_2Ni(\mu\text{-}C_3Cl_3)(\mu\text{-}Cl)]_2$	1.93/1.93	99.7	124.0	96.9	1.40	3a, 3b
$(CNBu^t)_2Pt[\mu\text{-}C(C_6H_5)COC(C_6H_5)]Pt(CNBu^t)$	2.48/2.50	99.0		95.6	1.43	3c, 3d
$(CO)_2(\eta^5\text{-}C_5H_5)W[\mu\text{-}C(C_6H_4Me\text{-}4)COC(C_6H_4Me\text{-}4)]W(CO)_2(\eta^5\text{-}C_5H_5)$	2.64/2.65	98.0			1.53	3e
$(Me_3SiCH_2)_2W[\mu\text{-}C(Ph)C(Ph)C(SiMe_3)][\mu\text{-}CSiMe_3]W(CH_2SiMe_3)_2$	2.45/2.68	106.0	129.5	101.7	1.41	4a, 4b
$(O\text{-}iPr)_2W[\mu\text{-}CHCHC(SiMe_3)][\mu\text{-}CSiMe_3]W(O\text{-}iPr)_2$	2.23/2.72	100.9	124.8	102.4	1.42	4b
$(CO)_2(\eta^5\text{-}C_5H_5)W[\mu\text{-}C(C_6H_4Me\text{-}4)C(Me)C(Me)]Fe(CO)_3$	2.10/	101.9	126.3		1.44	2a, 2b
$(CO)_2(\eta^5\text{-}C_5H_5)W[\mu\text{-}C(C_6H_4Me\text{-}4)C(Ph)C(Ph)]Rh(\eta^5\text{-}C_9H_5)$	2.14/	101.2	126.0		1.44	2c
$(CO)_2(\eta^5\text{-}C_5H_5)Mo[\mu\text{-}C(C_6H_4Me\text{-}4)C(OMe)CH]Fe(CO)_3$	2.17/	103.4			1.41	2j
$(CO)_2(\eta^5\text{-}C_5H_5)W[\mu\text{-}C(CO_2Me)C(CO_2Me)CO]W(\eta^5\text{-}C_5H_5)(CO)_2$	2.22/				1.45	2g
$(\eta^5\text{-}C_5H_5)Rh[\mu\text{-}C(CF_3)C(CF_3)CO]Rh(\eta^5\text{-}C_5H_5)$	2.17/				1.44	2h
$(CO)_2(\eta^5\text{-}C_5H_5)Mo[\mu\text{-}C(Me)C(Me)CO]Ni(\eta^5\text{-}C_5H_5)$	2.29/	99.9				2i
$(\eta^5\text{-}C_5(C_6H_5)_5)Ni[\mu\text{-}C_3(C_6H_5)_3]Ni(\eta^4\text{-}C_4(C_6H_5)_4)$	2.11/2.44				1.41	2k
$(O_2C_2H_7)Pd[\mu\text{-}C_3(C_6H_4OMe\text{-}4)_3]Pd[\mu\text{-}C_3(C_6H_4OMe\text{-}4)_3]Pd(O_2C_2H_7)$	2.32/2.58	97.5	133.1	89.1	1.41	2l, m

a The metal that is closer to C_2 is labelled as M_1(2b). M_2C_2 values are not reported in some unsymmetrical bridging structures.

b Average values. Distances are in Å. Angles are in degrees.

degree of C_3R_3 tilting. However the geometric parameters of the C_3R_3 unit (bond lengths and bond angles, table 1) remain more or less constant. Even the slightest deviation in the environment of the two metals, as in (η^4-C_4R_4)Ni(μ -C_3R_3)Ni(η^5-C_5R_5), (R=Ph) leads to the tilting of the C_3R_3 bridge.[2k] Are there any electronic reasons for the tilting of the central carbon of the C_3R_3 towards Ni(η^4-C_4R_4) rather than towards Ni(η^5-C_5R_5)? The simplest explanation that has been offered for tilting is as follows.[2k] When the C_3R_3 group straddling the M-M bond cannot have effective bonding with both the metals, tilting helps in increasing the binding to any one of the metals. If this is correct, we would like to know how the bonding increases with tilting and what controls the direction of the tilt.

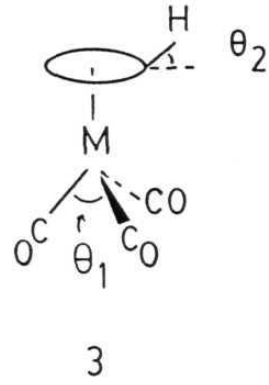
We provide an explanation for the observed geometries based on the diffuse nature and the directionality of the frontier molecular orbitals of the fragments involved. A discussion on the directionality and the extension in space of the frontier molecular orbitals of various fragments is given first. This is used to explain the structure of $(C_4R_4)Ni(\mu\text{-}C_3R_3)Ni(C_5R_5)$[2k] and other unsymmetrical bimetallic systems. A study of the symmetric M_2L_4 fragments, one with symmetrical and another with tilted μ-C_3R_3 ligands, follows next. A comparison of these provides useful insights.[5a]

5.3 Results and Discussion

The Directionality and the Extension in Space of ML_n and $M(C_nH_n)$ Frontier Molecular Orbitals

Considerable information is available about the nature of the frontier orbitals of ML_n fragments as a function of L. The

number, symmetry properties, energy and extent in space of frontier orbitals of ML_n fragments determine their interaction with other ligands completing the metal coordination sphere.[6] For example, the frontier MOs of $(\eta^n\text{-}C_nH_n)M$ become more diffuse as the value of n decreases.[6a] The origin of this effect has been manifested in the increasing (CO)M(CO) angle, θ_1, in $(\eta^n\text{-}C_nH_n)M(CO)_3$ complexes as a function of decreasing n, **3**. The

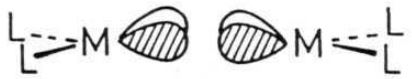


3

n	3	4	5	6
M	Co	Fe	Mn	Cr
θ_1	104.0°	97.0°	92.0°	88.0°
θ_2	25.0°	6.0°	0.0°	-3.0°

angles are 88°, [n=6, $C_6H_6Cr(CO)_3$][7a], 92°, [n=5, $C_5H_5Mn(CO)_3$],[7b] 97°, [n=4, $C_4Me_4Fe(CO)_3$],[7c] 104°, [n=3, $C_3Ph_3Co(CO)_3$][7d]. The attempts by smaller, rings to optimize their interactions with the metal results in the observed variation in θ_2 as a function of ring size.[6] It is as if the direction of three ligands in an octahedron controls the direction of the remaining three ligands. Thus $(\eta^4\text{-}C_4H_4)Ni$ has more diffuse orbitals than $(\eta^5\text{-}C_5H_5)Ni$.

A similar situation exists even in binuclear transition metal templates. The highest lying d orbitals of the $L_2M\text{-}ML_2$ fragments are the $d_{yz}\text{-}d_{yz}$ combination, **4**. The directionality of these orbitals can be changed by pyramidalization at the metal. The corresponding orbitals are directed better towards a bridging ligand, **5**. We shall see below how such pyramidalizations control metal bridging ligand interactions.



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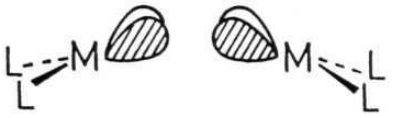

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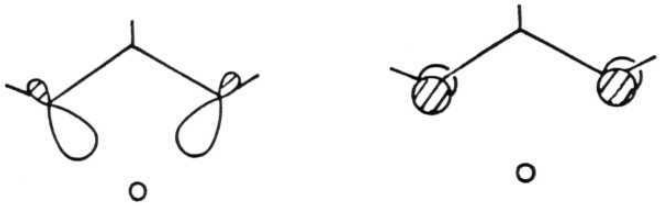
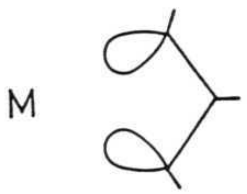
Frontier MOs of C_3R_3 Ligand and the Structure of μ-C_3R_3 Complexes with Unsymmetrical Metal Environments

The molecular orbitals of the C_3R_3 ligand have been studied in detail.[8] Here we point out the differences in the orientation and extension of the σ and π frontier orbitals. In the fragment C_3R_3 the geometry around carbons differ considerably from the standard sp^2 situation. The average internal CCC angle, θ, is decreased to around 100° while the RC(1)C(2) or RC(3)C(2) angle, ϕ, is increased to around 125° (**1**). The low value of θ is similar to that found in metallacyclobutadienes.[1a-i] The hybrid orbital lobes, which constitute the σ frontier orbitals, are directed towards the M-M bond, **6a**. The point at which the

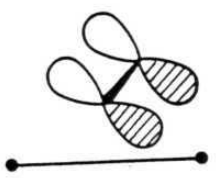


6a

6b

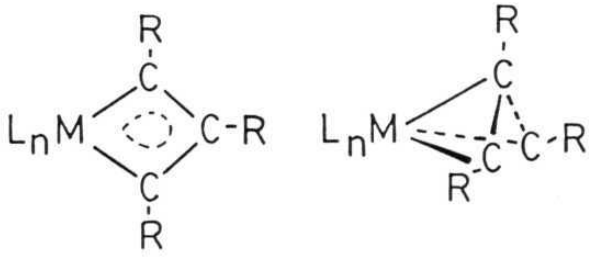


7a



7b

M-M bond passes through the C(1)C(2)C(3) plane is indicated by the small circle underneath the carbons. In contrast the p orbitals that constitute the π MOs of C_3R_3 are parallel to the M-M axis, **6b**. **7a** and **7b** respectively represent these orbital lobes in the M(2)C(1)C(2)C(3) plane and as a projection in a plane containing the two metals and the middle carbon of C_3R_3. The σ and π MOs that arise from these individual orbitals will retain these spatial directions. Formally, the C_3R_3 ligand may be treated as a -3 ligand in $L_2W(\mu\text{-}C_3R_3)(\mu\text{-}CR)WL_2$, so that W is d^1. This is appropriate for the W system which has relatively high AO energies in relation to the MOs of C_3H_3. C_3R_3 then corresponds to allyl anion in the π frame with two σ hybrid orbitals each with two electrons. Since the molecular orbitals in the σ plane of C_3R_3 will be less diffuse in comparison to the π MOs, the metal fragments with contracted frontier orbitals should prefer bonding in the σ-plane (metallacyclobutadiene), **8**. On the other hand metals with more diffuse frontier orbitals should prefer an allyl type of interaction, **9**.



8 9

It is only natural to expect the bridging group not to adopt a perpendicular orientation with respect to an M-M bond which does not provide a symmetrical environment. The direction of the tilting should depend on the details of metal-μ-C_3R_3 interactions. The orbitals of the tilted C_3R_3 are directed better for σ type interaction with one metal and π type interaction with

the other. The highly directional σ type MOs (**6a,7a**) overlap better with the metal orbitals that are less diffuse. Consequently the middle carbon of the C_3R_3 will be tilted to the other metal allowing favourable metal-polyene π interaction. The direction of the tilting then should depend on the terminal ligands on the metal that control the nature of its frontier orbitals.

As discussed above in (η^5-C_5Ph_5)Ni(μ -C_3Ph_3)Ni(η^4-C_4Ph_4), the (η^4-C_4Ph_4)Ni unit has more diffuse frontier orbitals than those of (η^5-C_5Ph_5)Ni. Therefore in the binuclear template (η^5-C_5Ph_5)Ni-Ni(η^4-C_4Ph_4), the (η^5-C_5Ph_5)Ni unit should prefer to interact with the σ orbitals of C_3R_3. This would bring the central CR group towards the Ni(η^4-C_4Ph_4) unit so that it can interact with the π-plane. The X-ray structure of ($C_5(C_6H_5)_5$)Ni(μ -$C_3(C_6H_5)_3$)Ni($C_4(C_6H_5)_4$) supports this idea.[2k]

The direction of tilting in the complexes where the two metals are different[2] also can be understood using similar arguments. In all such examples noted in table 1, $CpM(CO)_2$ fragment provides less diffuse metal orbitals and prefer a σ type of bonding with the C_3R_3 bridging ligand. The other metal, which in most cases is equivalent to ML_3, provides comparatively more diffuse orbitals for the complex formation and prefers the π type of bonding with the bridging ligand and so the central carbon of the C_3R_3 group is expected to bend away from the $CpM(CO)_2$ unit. X-ray structures clearly show the resulting near planar arrangement of $[(CO)_2Cp]MC(1)-C(2)-C(3)$. Crystal structure of $Cp(CO)_2Mo[\mu-C(Ph^t)C(OMe)CH]Fe(CO)_3$ clearly shows how pyramidalization at $Fe(CO)_3$ adjust itself to give more

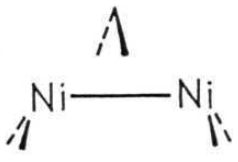
diffuse orbitals.[2j] For example the (CO)Fe(CO) angle is less than average and $Fe(CO)_3$ unit rotates itself to adopt a nonsawhorse geometry.[9]

Structure of the μ-C_3R_3 Complexes with Symmetrical Metal Fragments.

There are two types of complexes known with symmetrical binuclear metal fragments and μ-C_3R_3 ligands. The first type involves Ni_2 or Pt_2 metals with two terminal ligands each. The second type has a bridging carbyne ligand in addition to the μ-C_3R_3 in a W_2 system. In $[(CO)Ni(\mu\text{-}C_3Cl_3)Ni(CO)]_2Cl_2$ [3a,3b] and $(NCBu^t)_2Pt[\mu\text{-}C(Ph)COC(Ph)]Pt(NCBu^t)_2$ [3c,3d] the bridging C_3R_3 unit is perpendicular to the M-M axis. The LML angle in Ni_2 complex is 96.8° and in Pt_2 complex is 95.6°. The environment is pyramidal, the two ligands bent away from the bridging C_3R_3 group. Interaction diagrams have been constructed for the complex $(CO)_2Ni(\mu\text{-}C_3H_3)Ni(CO)_2^+$ from the smaller fragments $(CO)_2Ni\text{-}Ni(CO)_2$ and $C_3H_3^+$ at four different geometries **10-13**,

10

12



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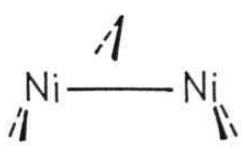

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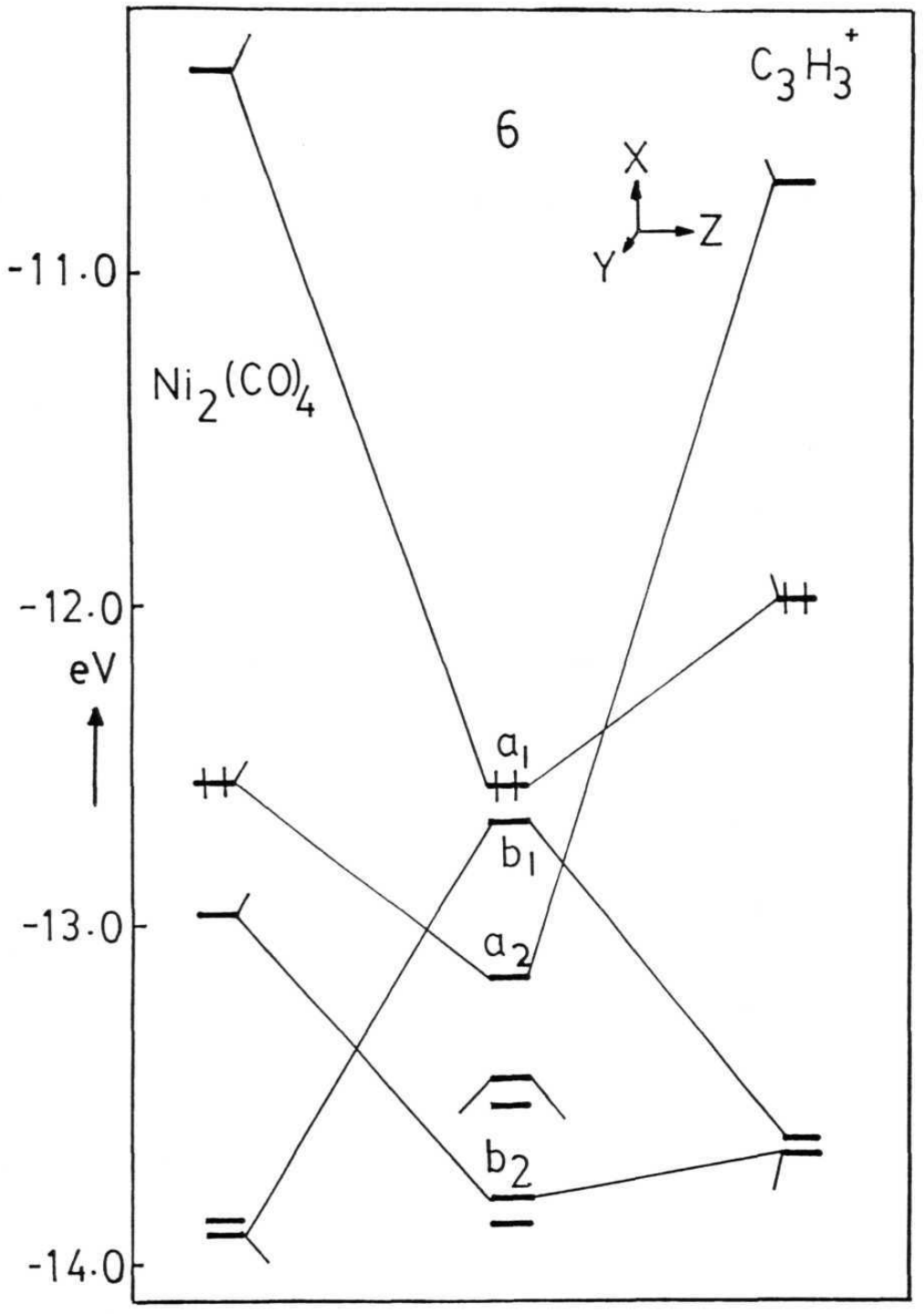


Fig. 5.1 : Interaction diagram for the construction of **10** (C_{2v}). Important orbitals are shown in figure 2.

using the fragment molecular orbital approach within the Extended Huckel method. Fig. 5.1 represents the interaction diagram for the construction of **10**. The bridging of C_3R_3 fragment to the metallic framework primarily stems from three MOs, a_1, a_2 and b_2. In addition to these MOs there are MOs resulting from several 4e-2 orbital interactions. One of these appear in the frontier range (b_2, HOMO-1). The interaction diagrams for **11-13** are similar. The orientation of the orbitals on the metal controls the extent of bonding between the bridging group and the metals. A decrease in LML angle and the pyramidalization at the metal

Table : Overlap between the fragment molecular orbitals (FMOs) of $(OC)_2NiNi(CO)_2$ and C_3R_3 in geometries 10 - 13.

Molecular Orbital	FMO Overlaps			
	10	11	12	13
a_1	0.2809	0.2833	0.2261	0.2358
a_2	0.2305	0.2495	0.1479	0.1621

center (**11,13**) helps in directing the metal orbitals toward the orbitals of C_3R_3 group. This increases the bonding of the C_3R_3 ligand to both the metals. Table 2 shows the fragment molecular orbital overlap values, corresponding to a_1 and a_2, between fragments $C_3H_3^+$ and $(CO)_2Ni\text{-}Ni(CO)_2$, for the complexes **10-13**. These values clearly indicate that the larger overlaps are obtained when the allyl group is symmetrical (**10** and **11** > **12** and **13**). Thus symmetrical structures **10** or **11** are more

favourable. Further, maximum overlap occurs in **11** when the C_3R_3 is symmetrical and the CO ligands are bent away from the bridging ligand. Finally overlap values between fragment molecular orbitals of $(CO)_2Ni\text{-}Ni(CO)_2$ and $C_3H_3^+$ in geometries **10-13** indicate that structure **11** is most favourable for $(CO)_2Ni(\mu\text{-}C_3H_3)Ni(CO)_2^+$. A Walsh diagram (Fig. 5.2) for the process **11 ---> 13** indicates that only three orbitals a_1, a_2, b_1 show major change in energy. Bonding combinations a_1 and a_2 rise in energy due to decrease in the bonding nature. Antibonding orbital b_1 falls in energy, but cannot compensate for the destabilization caused by a_1 and a_2. As a result, destabilizing interactions predominate the process and **11** is more stable than **13**. In the process **10** ---> **12**, the a_1 orbital do not show any change and the changes in the other orbitals, are as usual. This indicates that process **10** ---> **12** is less unfavourable. The symmetrical structure is more stable here also. The crystal structure of the two Ni complexes have symmetrical C_3R_3 groups. The freedom available at the terminal ML_2 group for pyramidalization adds to the stabilization of symmetrical structures. If C_3R_3 is taken as a -3 ligand, the Ni atoms will be d^8 with two vacant d orbitals. The C_3R_3 can also be regarded C_3R_3 as a +1 ligand in which case Ni will be d^{10}. Charge analysis indicate that actual description should lie somewhere in between. It is difficult therefore to conclude that the $M\text{-}C_3R_3$ antibonding MO decreased in energy on tilting by mixing with vacant metal d orbitals.

$L_2W(\mu\text{-}CR)(\mu\text{-}C_3R_3)WL_2$ (d^1-d^1) complexes are examples of the second kind.[4a,b] The MOs mainly responsible for the $M\text{-}C_3R_3$ bonding remain more or less similar to those in Ni_2 or Pt_2

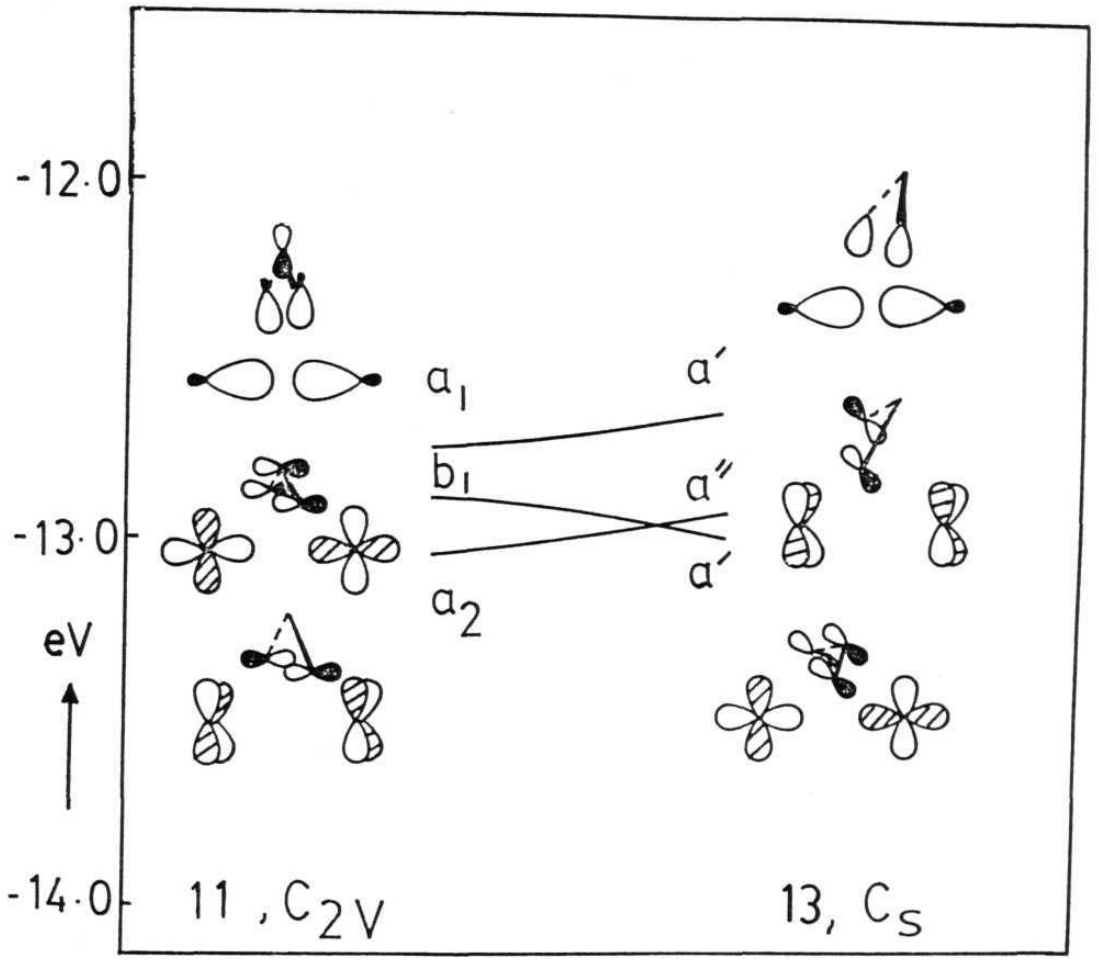


Fig. 5.2 : Walsh diagram for the process **11** (C_{2v})----> **13** (C_s).

complexes.[10a] It is the restriction of the terminal ligands that are very different here. The tungsten complexes have two bridging groups (CR and C_3R_3) with opposing requirements on the directionality of the frontier orbitals of the metal. Pyramidalization at the metal in any one direction will have opposite effects on the bridging ligands. The only alternative is to tilt the C_3R_3 group, which allows different terminal LML angles at the metal centres without pyramidalization of L_2MM unit. This does not increase the stability of the tilted structure dramatically. EH calculations for the process **2a** ---> **2b** on the model $Me_2W(\mu$-CH)(μ-C_3H_3)WMe_2 indicate that **2b** structure is marginally more favourable than **2a**. The HOMO (a_1) is the antibonding combination of a filled-filled interaction and HOMO-1 (a_1) is a bonding combination. On tilting the C_3R_3 group towards one metal, a_1 decreased in energy (Fig. 5.3). The a_2 orbital increase in energy due to increase in bonding interaction and results in a''. In this case a_1 ---> a' decrement in energy is more predominant. On the whole only a slight stabilization arises in the process **2a** ---> **2b**. In solution a dynamic equilibrium exists between the two possible tilted geometries even though in the solid state, the C_3R_3 is tilted towards a metal.[4b] Pyramidalization at the metal centres to increase metal C_3R_3 bonding in the symmetrical structure is not possible because of the second bridging group, μ-CR.

It should be possible to constrain the terminal ligands in Pt_2 and Ni_2 complexes to force the μ-C_3R_3 group to be unsymmetrical. If the terminal ligands have large bite size and a geometry that cannot support pyramidalization at the metal, it should lead to unsymmetrical bridging. Similarly restricting the

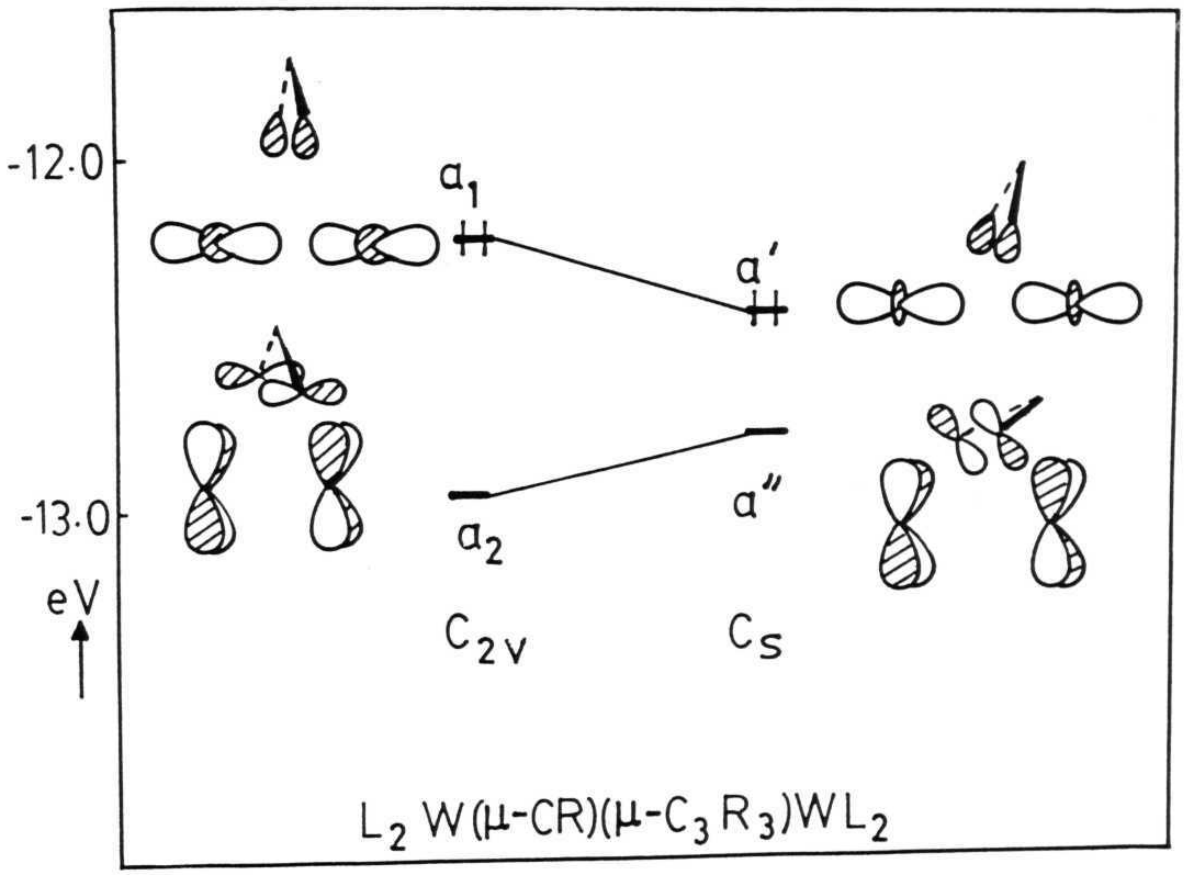


Fig. 5.3 : Walsh diagram for the tilting of μ C_3R_3 in $L_2W(\mu - C_3R_3)$ $(\mu - CR)WL_2$.

terminal ligand bite size to small values and forcing pyramidalization at the metal centre as in $[(CO)Ni(\mu\text{-}C_3Cl_3)Ni(CO)]_2Cl_2$ and $(NCBu^t)_2Pt[\mu\text{-}C(Ph)COC(Ph)]Pt(NCBu^t)_2$ will increase the stability of the complexes with symmetrically bridging C_3R_3 group.

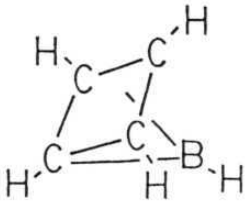
Isolobal Analogs of $\mu\text{-}C_3R_3$ Complexes

The concept of isolobal analogy has increased our understanding of the relations between organic and inorganic chemistry.[11] Here we shall see the main group equivalents of the binuclear transition metal complexes. This exercise provides another explanation for the tilting of C_3R_3 structures. We shall start with $(\eta^5\text{-}C_5Ph_5)Ni(\mu\text{-}C_3Ph_3)Ni(\eta^4\text{-}C_4Ph_4)$. The $(C_5Ph_5)Ni$ group is equivalent to $d^8\text{-}ML_3$ (treating C_4Ph_4 as a six electron dianionic ligand) and isolobal to BH (Scheme 1); thus, the

Scheme 1

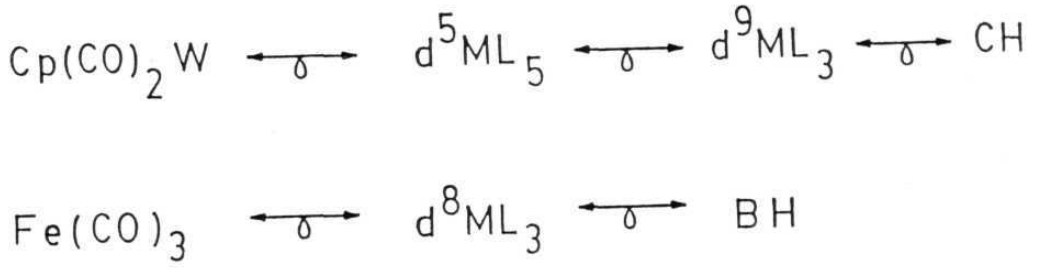
$$C_5Ph_5Ni \longleftrightarrow d^9ML_3 \longleftrightarrow CH$$

$$C_4Ph_4Ni \longleftrightarrow d^8ML_3 \longleftrightarrow BH$$



complex is equivalent to C_4H_4BH, **14**. The electron counting rules in polyhedral molecules indicates that this has to be square pyramidal,[12] while the compatibility of orbitals demands that the BH group to be at the apex.[13] Thus the distinction between the frontier orbitals of CpNi and $(C_4H_4)Ni$ is translated as similar to that between CH and BH.

Scheme 2



A similar treatment is available for $Cp(CO)_2W(\mu\text{-}C_3R_3)$-$Fe(CO)_3$ and related molecules.[2b] The following isolobal changes (Scheme 2) make this compound equivalent to the same C_4H_4BH, **14**, discussed above. This also leads to the expected direction of tilting as BH has more diffuse orbitals.

5.4 Conclusions

A bridging C_3R_3 group in a binuclear transition metal complex will tilt towards one of the metals under two conditions. First of these is the obvious situation where the two metals are not identical or the metal environments are otherwise dissimilar. Here the C_3R_3 will tilt towards the metal that provides more diffuse frontier orbitals. This enables the directed σ-type C_3R_3 orbitals to interact with the less diffuse orbitals provided by the other metal. The tilting of the middle carbon of the C_3Ph_3 group towards the $(\eta^4\text{-}C_4Ph_4)Ni$ in $(\eta^5\text{-}C_5Ph_5)Ni(\mu\text{-}C_3Ph_3)Ni(\eta^4\text{-}C_4Ph_4)$ is an example. However tilted geometries of C_3R_3 bridged complexes are observed even when the environments are symmetrical. If the directionality of the frontier orbitals of the metal fragments can be increased by pyramidalization at the metal centres metal-C_3R_3 binding can be maintained by both metals equally. Thus $(CO)_2Ni(\mu\text{-}C_3R_3)Ni(CO)_2^+$ has symmetrically bridging C_3R_3. However, if such pyramidalizations are not possible due to any reason, the bridging group would optimize bonding by tilting. This would lead to specific π interactions with one metal and σ interactions to the other. Thus bending of the terminal ligands is impractical in $L_2W(\mu\text{-}C_3R_3)(\mu\text{-}CR)WL_2$ because the increase in the binding gained to one bridging group will be canceled by the loss of binding to the other. This leads to the observed structure where the C_3R_3 is tilted towards one metal. Isolobal analogies also lead to similar results.

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CHAPTER 6

Analogy Between Trivalent Boron and Divalent Silicon

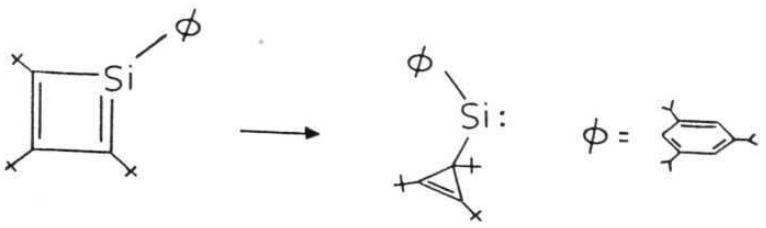
6.1 Abstract

The electronic configuration of divalent Si compounds with a sigma lone pair and an empty p orbital is similar to that of trivalent borane if a B-H bond is equated to the lone pair on Si. Following this analogy two novel compounds, :Si(μ-CH)(μ-H)Si:, **24** and :Si(μ-CH)$_2$Si:, **26**, are proposed. The energetics and geometries of the two compounds and their isomers (**24**, **26-39** and **41-65**) are studied using the MNDO and 3-21G* methods.

6.2 Introduction

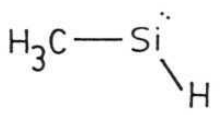
In chapters 1-4 we have discussed the theoretical studies on carbyne bridged binuclear transition metal complexes. The interesting chemistry of these compounds was controlled by the bridging carbyne group. It may be possible to find equally interesting chemistry of the bridging carbyne group when it is bridging two main group elements. An attempt in these lines lead us to propose some interesting analogies. The results are discussed.[1]

Group IV elements of the periodic table generally form tetravalent compounds. Lower valency arises in the heavier members of the group beginning with Ge because of the inert pair effect.[1,2] In carbon chemistry, low valent species such as carbenes, carbanions and carbo cations are known but they are highly reactive intermediates. Divalent silicon presents a different story. Even though silylenes such as $SiCl_2$ and SiF_2[3,4] are highly reactive, many silylenes especially with organic substituents are very stable in their singlet ground states.[5,6] The stability of silylenes in organosilicon compounds is unusual especially when we compare these with their carbon analogs. The divalent structures are preferred even when the alternative tetracoordinated Si structures are possible.[5,6] There are several examples that illustrate the preference of silicon to be divalent. Thermal isomerization of photogenerated 1-(2,4,6-triisopropylphenyl)2,3,4- tri-tert-butyl-1-silacyclobutadiene, **A** to (2,4,6-triisopropylphenyl)-(1,2,3-tri-tert-butylcyclopropenyl) silylene, **B** gives clear evidence of the stability of divalent silicon compounds.[7]



A B

Thermochemical evidence shows that the heats of formation of methylsilylene **1** and silaethylene **2** are comparable (difference is only 10 kcal/mol).[8] Various theoretical studies also support this observation and point out that **1** and **2** are very close in energy [9d] (the calculated energy differences between **1** and **2** vary from -0.4 to 4 kcal/mol). **3** is calculated to be more stable than silaacetylene **4**.[10] Hydroxysilylene (trans) **5** is lower in energy in comparison to silaketone, **6**, by 4.9 kcal/mol at 6-31G* level.[11] Aminosilylene **7** is found to be the global minimum on the potential energy surface of $NSiH_3$.[12] Corresponding silaimine isomer **8** is at least 18 kcal/mol high in energy. Similarly **9** is more stable than **10**.[13] Apart from these, isomers with one or more silylene units are found either as the global minimum or close to that for many organosilicon compounds. For example, 2-methylcycloprop-2-ene-1-silylene is shown to be the global minimum on the potential energy surface of C_3SiH_4.[14] These are all surprising results because the carbon analogs of each of these show a strong preference for the tetravalent arrangement. Here we present an analogy between compounds of divalent silicon and trivalent boron which help in arriving at unusual silicon compounds based on the structures of boron compounds.



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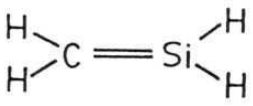

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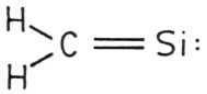

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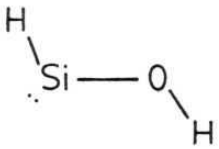

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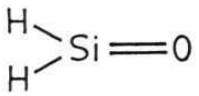

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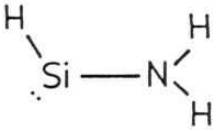

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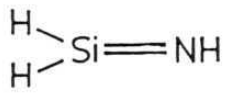

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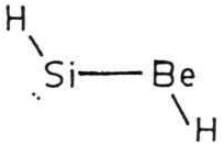

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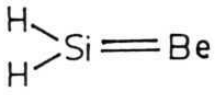

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6.3 Results and discussion

Isolobal Analogy Between BH and :Si

Simplest electronic structure description of divalent singlet silylene **12** involves two orbitals on silicon in addition to the two covalent bonds. One of them (a_1) is occupied with two electrons and the other (b_2) is empty (labels are according to C_{2v} point group). We propose an analogy between $H\text{-}BH_2$, **11** and $:SiH_2$, **12**. If the a_1 lone pair on **12** is taken as equivalent to the B-H bond in **11**, **11** and **12** may be treated as isolobal. Similarly divalent Si and the B-H group may be considered isolobal.[15] The diagonal relationship in the periodic table also suggests that there will be similarities between boron and silicon, e.g., they have comparable electronegativity and related characteristics[1,16].

The structural preferences shown by compounds containing trivalent boron and divalent silicon also support the proposed isolobal analogy. For example, among the isomers Si_2H_2, **13** is found to be more stable than **14**[13] and among the isomers of B_2H_4, **15** is more stable than **16**[17]. Similarly both **17**[18] and **18**[19] are shown to be local minima. In fact **17** is the global minimum on the PE surface of Si_2H_2. Both **19**[19] and **20**[20] are calculated to be stable structures. **21**[19] and **22**[21] are shown to have strong 2π electron delocalization and are global minima on their respective energy surfaces. The proposed analogy is further supported by the fact that $(CH)_5Si^+$ [22] and $(CH)_5BH^+$ [23] are proposed to have similar structural preferences. While these provide striking similarities between structures involving Si and BH

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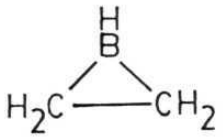
13 14

15 16

17 18



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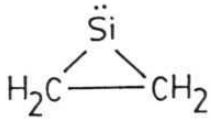

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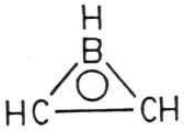

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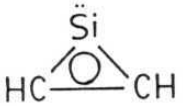

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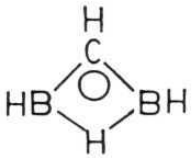

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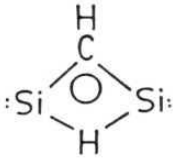

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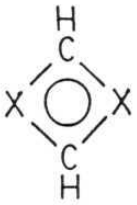
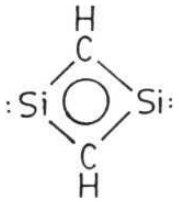


25 a b c

X = BH CH^+ Be



26

group, to our knowledge, such an analogy between trivalent boron and divalent silicon has never been pointed out.[24] Each of the experimental and theoretical observations have been rationalized in boron or silicon compounds individually. In this paper we introduce the isolobal analogy that exists between the divalent silicon and trivalent boron species and use this analogy to arrive at unusual compounds of silicon. Some of the unconventional structures that we arrive at replacing B-H units by silicon turn out to be the most stable isomers of a given molecular formula. The analogy may indeed be reversed to study compounds of boron based on those of silicon. It also lend itself to other obvious extensions.

Structures represented by two molecular formulae, CSi_2H_2 and $C_2Si_2H_2$ are dealt in detail in this chapter. The molecular formula CSi_2H_2 was selected from the stable structure **23** calculated for CB_2H_4.[25] Replacement of two BH groups by Si leads to **24**. Even though various alternatives are studied for **24**, this is found to be the global minimum in our study. Similarly $C_2Si_2H_2$ was selected from a series of isoelectronic structures for **25**. **25a** and **25b** have been studied experimentally and theoretically[26] **25c** is calculated to be a true minimum on the potential energy surface of $C_2Be_2H_2$.[26] The new analogy between BH and Si enables us to suggest **26** as a stable arrangement for $C_2Si_2H_2$. This as well as other isomers that do not involve divalent carbon have also been studied here.

The semi-empirical MNDO method is used initially to obtain relative energies. The geometries of the compounds are optimized using both old[28] and new[29] parameters of silicon

because it appeared that the new set of parameters were optimized for structures involving tetra and penta coordinate Si. This was necessary because it was not clear which set of parameters are best for divalent silicon. Table 1 gives an indication of the performances of the two sets in studying divalent silicon. Comparison to the best available ab initio calculation showed that MNDO1 (MNDO method using the old set of parameters for silicon) is closer to it than the MNDO2 (MNDO method using the new set of parameters for silicon). The AM1 method is not used because table 1 did not show any improvement for AM1 over MNDO. Ab initio calculations at the 3-21G* [30a] level on all the isomers of CSi_2H_2 and some important isomers of $C_2Si_2H_2$ are carried out. Vibrational frequencies of all the structures are carried out at 3-21G* level to note the nature of the stationary points observed on the potential energy surfaces of the two molecular formulae. To obtain more reliable total energy values, we have also performed single point calculations on **24**, **26-39** and **41-54** at ab initio HF/6-31G* [30b] and MP2/6-31G* [30c] level of theory using the geometry obtained at 3-21G* level.

The molecular orbital patterns and the relative stabilities of **24** and **26** should give further understanding of the proposed analogy. Silylenes are normally more stable in their singlet state[31] and hence the triplet structures are not studied. During the optimization no symmetry restrictions are imposed, but the electronic structures of the isomers of **24** and **26** are analyzed according to the closest possible symmetry.

Table 1

ΔH_f values for the two reactions at various levels (energy in kcal/mol).

Reaction	ΔH_f values			
	MNDO1[a]	MNDO2[b]	AM1[c]	ab initio
$H_2C{=}SiH$ ----> $H_2C{-}SiH$	-44.3	9.2	23.5	-0.4[d]
$HC{=}SiH$ ----> $H_2C{=}Si$:	-71.8	-20.2	11.1	-49.1[e]

[a] MNDO using old parameters for silicon: Ref. 28.

[b] MNDO using new parameters for silicon: Ref. 29.

[c] Ref. 26.

[c] DZ + d with CI ref. 7d. A discussion on the variation in this value is given in ref. 7a.

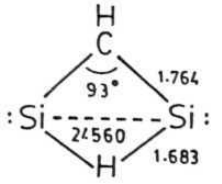
[d] DZ + d with CI ref. 7d.

[e] DZ + d with CI and Davidson correction. Ref.8b.

Structure and Stabilities of the isomers of CSi_2H_2.

Figure 6.1 gives several possible structural isomers of CSi_2H_2, (**24, 27-39**). The relative energies calculated at MNDO1 and MNDO2 are given in Table 2. Structures involving divalent carbene carbon atoms are not considered in the study because these are known to be very high energy species. MNDO1 and MNDO2 give contrasting results. According to MNDO1 calculations **24** is the global minimum. But calculations using MNDO2 suggest **35** as the global minimum. **24** is not a local minimum at the MNDO2 level. Ab initio calculations at 3-21G* level also suggest a global minimum for **24** and the relative energy ordering almost follows the MNDO1 results except in the case of structure **27** and **35**. Single point HF/6-31G* and MP2/6-31G* calculations does not change the energy ordering obtained at HF/3-21G* level. Unless otherwise mentioned, the discussion will be based on HF/3-21G* results.

Distinct groups of isomers emerge from these relative energies. Structures with both Si occupying divalent positions are in general the most stable ones. Next comes the structures with one divalent Si. We shall consider the structures with two divalent Si first (**24, 27-34**). All the structures with two divalent silicons and without a three membered ring **24, 27, 29-31** have π electron delocalization. All of them are local minima. **23**, C_{2v}, $^1A_1$ is the most stable isomer. The Si-C bond length in **24** is 1.764 Å. This is shorter than the standard 3-21G* Si-C single (1.925 Å) and only slightly longer than the Si=C (1.719 Å), indicating substantial double bond character. The electronic structure of **24** clearly shows that the hydrogen is bridging the two Si atoms in a closed 3c-



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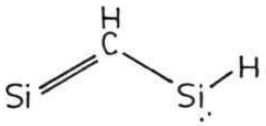

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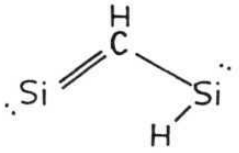

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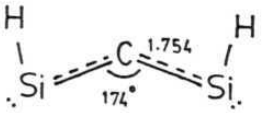

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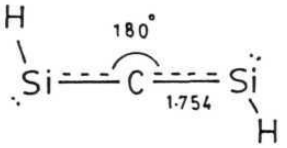

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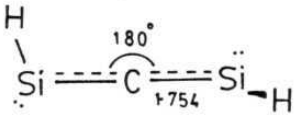

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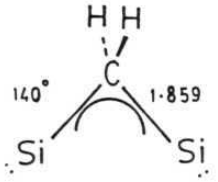

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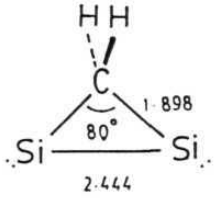

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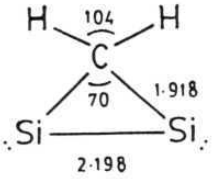

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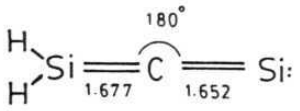

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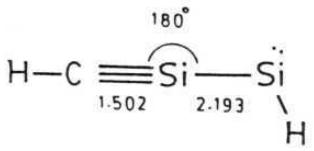

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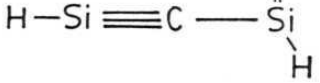

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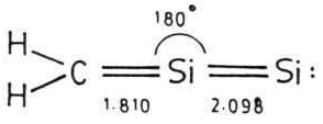

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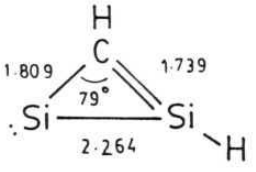

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Fig. 6.1 Observed geometric parameters of the isomers of CSi_2H_2 using 3-21G* method. Distances are in Angstroms and angles are in degrees.

Table 2

Relative energies (R.E.) of the isomers of CSi_2H_2 (energy in kcal/mol

Structure and symmetry	Relative Energies				
	MNDO1	MNDO2	HF/3-21G*	HF/6-31G*// HF/3-21G*	MP2/6-31G*// HF/3-21G*
24 $^1A_1$	0.00	39.93$_{C2v}$	0.00	0.00	0.00
27 $^1A'$	16.52	18.35	--a	--	--
28 $^1A'$	--a	20.24	--a	--a	--a
29 $^1A_1$	52.31	49.52	45.69	48.36	65.13
30 ^1A_G	54.12	47.47	45.77	48.48	64.43
31	--a	--a	--a	--a	--a
32 $^1A_1$	112.61	--a	92.45	88.91	72.94
33 $^1A_1$	50.83	57.05	69.78	66.75	63.38
34 $^1A_1$	58.61	96.96	34.89	31.89	26.79
35 $^1A_1$	60.74	0.00	16.85	21.13	24.92
36 $^1A'$	84.33	50.84	149.11	149.50	164.52
37	--a	--a	--	--	--
38 $^1A_1$	77.62	47.04	188.40	187.68	178.16
39 $^1A'$	--a	--a	12.25	12.44	13.22

-- not studied

--a does not correspond to a stationary point

2e interaction, Si-H distance being 1.683 Å. With a distance of 2.583 Å the Si-Si sigma bond is only slightly weakened by the bridging hydrogen. The three σ bonds around carbon (C-H, 2 Si-C) leaves one electron in the p orbital. The bridging hydrogen provides the second electron in the 2 electron delocalization of the π framework ($2b_1$). This is similar to other 2 π aromatic systems such as cyclopropenyl cation.

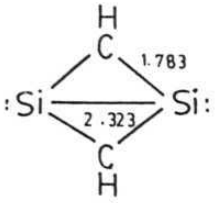
Open chain **27** is converted to the cyclic **39** on complete optimization at 3-21G* level. But MNDO1 shows a local minimum with an Si-C-Si angle of 118°. Various attempts to locate a stationary point close to structure **27** using 3-21G* failed. **27** has allyl 2 π electron delocalization at MNDO1 level. **28** is not a local minimum. Complete optimization leads to **24**. Among the geometrical isomers **29-31**, **31** does not correspond to a stationary point. **29**, $^1A_1$ and **30**, ^1A_G are planar with 2 π electron delocalization in the perpendicular plane. Both correspond to local minima. The central carbon in **29** and **30** have empty p orbitals which are stabilized by the lone pair participation. **29** with cis-hydrogen arrangement has an Si-C-Si angle of 173.83°. This is due to the lone pair--lone pair repulsion. The behaviour of the rotational isomers **29**, **30**, and **31** correspond to that of allenylic dication. Both **32**($^1A_1$), without Si-Si bond and **33**($^1A_1$) with Si-Si bond are found to have one negative eigenvalue each in the frequency analysis, they are transition states. The energy gap between the two at 3-21G* is 22.7 kcal/mol but decreases at 6-31G* and with the inclusion of electron correlations. **34**, $^1A_1$ with a planar tetravalent carbon is only 26.88 kcal/mol higher in energy than the global minimum, but it is also a transition

state point. It is 36.6 kcal/mol (at MP2/6-31G*//HF/3-21G*) lower in energy than **33** which has tetrahedral carbon. Similar energy order is found in the case of CB_2H_2 isomers (**33a** and **34a**).[24]

Among the isomers of CSi_2H_2 with one divalent and one tetravalent silicons (**35-39**), **37** does not correspond to a stationary point. **37** becomes **29** on complete optimization. **39** gets converted to either **24** or **28** depending on the C-Si-H angle used. **35** corresponds to local minimum, with its total energy only 16.85 kcal/mol higher than that of global minimum **24** at HF/3-21G* level. But this relative energy increases as electron correlation is added. This indicates that the ab initio result do not support the MNDO2 result which shows **35** to be the global minimum. **39** correspond to a local minimum with its energy only 12.25 kcal/mol higher to that of global minimum. However, MNDO does not show any local minimum for **39**. Complete optimization at MNDO1 and MNDO2 gives **27**. **39** has got $2\pi e$ cyclic delocalization as evident from MOs and bond lengths.

Structure and stabilities of the isomers of $C_2Si_2H_2$.

Fig. 6.2 gives some of the isomers (**41-64**) of **26** and their observed geometries at 3-21G* level. Here also isomers with divalent carbon are omitted. Table 3 gives the relative energies of various isomers of $C_2Si_2H_2$. In general, structures with two divalent silicon (**26**, **41-57**) are at lower energy than the structures with one divalent silicon (**58-64**) at MNDO1 level. This again indicates the preference of Si to be divalent. 3-21G* calculations are performed only on isomers with two divalent



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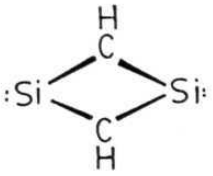

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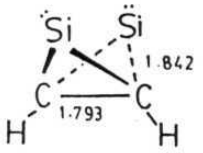

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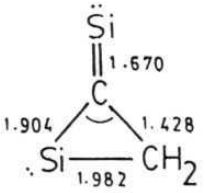

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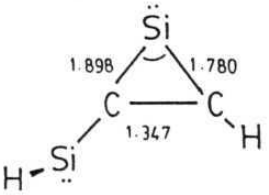

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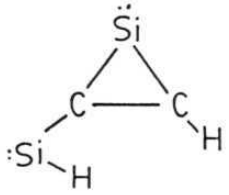

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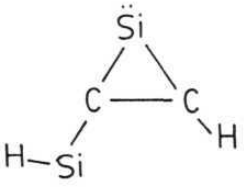

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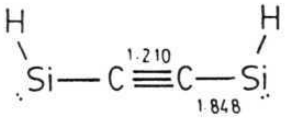

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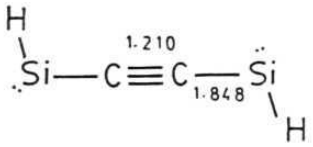

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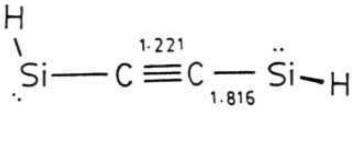

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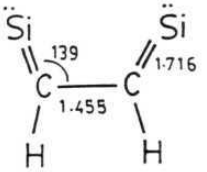

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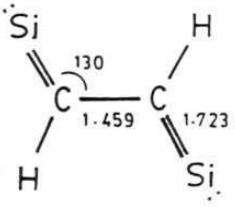

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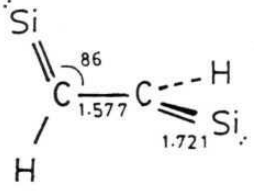

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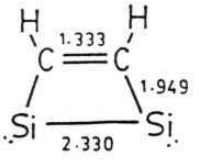

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Fig. 6.2 Observed geometric parameters of the isomers **26**, **41-54**) of $C_2Si_2H_2$ at 3-21G* level. Distances are in Angstroms and angles are in degrees.

Table 3

Relative energies (R.E.) of the isomers of $C_2Si_2H_2$ (energy in kcal/mol)

Structure and	symmetry	Relative Energies				
		MNDO1	MNDO2	HF/3-21G*	HF/6-31G*// HF/3-21G*	MP2/6-31G HF/3-21G*
26	$^1A_1$	34.52	--a	32.55	45.05	33.37
41		--a	--a	--a	--a	--a
42	$^1A_1$	0.00	9.56	0.21	9.62	18.53
43		--a	--a	--a	--a	--a
44	$^1A'$	11.34	0.00	0.00	0.00	0.00
45		12.21	12.60	7.15	10.13	28.94
46		--a	--a	--	--	--
47		--a	--a	--	--	--
48	$^1A_1$	20.06	6.24	22.46	31.82	59.99
49	$^1A'$	21.78	6.32	22.65	32.11	60.35
50		22.16	5.28	15.62	25.65	54.39
51	$^1A_1$	--a	27.97	34.07	38.95	53.77
52	^1A_G	--a	24.67	30.94	35.84	51.59
53	^1A	--a	--a	21.74	26.74	27.37
54	$^1A_1$	47.46	40.22	91.86	94.06	91.34

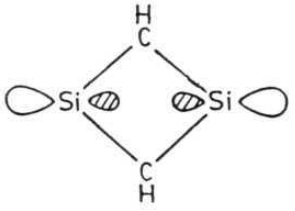
55	$^1A_1$	54.02	45.41
56	$^1A_1$	54.41	46.28
57	$^1A'$	56.32	--a
58	$^1A_1$	51.80	5.10
59	$^1A_1$	85.72	14.16
60	^1A_G	87.52	49.38
61		--a	--a
62	^1A_G	--a	39.41
63	$^1A_1$	106.92	47.30
64	$^1A_1$	110.60	32.95
65	^1A_G	--a	28.58

--a does not correspond to a stationary point

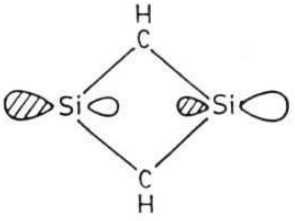
-- not studied

silicon atoms. Butterfly arrangement **42** is the global minimum at MNDO1 level. Puckered structure **41** becomes **26** after complete optimization at 3-21G* level. The tetrahedrane **43** leads to **42** on complete optimization.

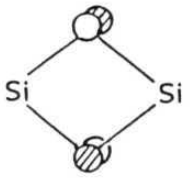
Calculations at MNDO1 and 3-21G* shows a local minimum for **26**. MNDO2 does not show a local minimum for **26**. Frequency calculations at 3-21G* indicates **26** to be a local minimum. The Si-C distance 1.783 Å is shorter than standard single bond distance and longer than standard double bond. Unlike $C_2B_2H_2$, (**25a**), **26** is completely planar. The Si-Si distance 2.323 Å indicates a single bond. The MO pattern indicates that only the bonding combination of lone pairs, **66**, is occupied. The corresponding antibonding combination **67** is unoccupied. Instead



66



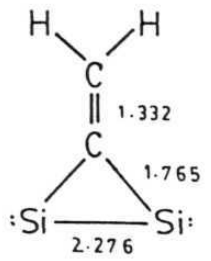
67



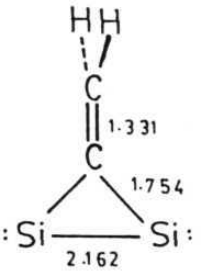
68

the HOMO is, **68**, which has 1,3-π^* interaction between the carbon atoms. The diagonal C-C distance is 2.707 Å. Thus **66** as well as **68** is responsible for the shorter Si-Si distance. In **42**, the Si-C distances 1.841 Å is slightly shorter than the standard single bond distance. The C-C distance of 1.793 Å indicates σ delocalization. MO pattern shows that both bonding and antibonding combinations of Si lone pairs are occupied.

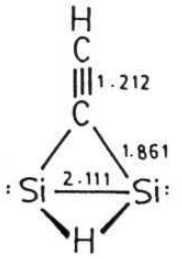
In **45** the out-of-plane arrangement of Si-H bond is preferred. **46** and **47** are not local minima but lead to **45** on optimization at MNDO1 and MNDO2. This is probably because of the



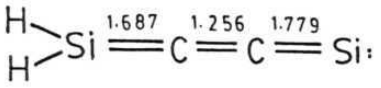
55



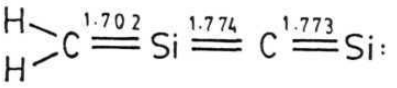
56



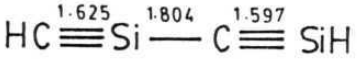
57



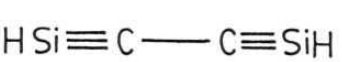
58



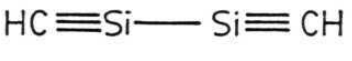
59



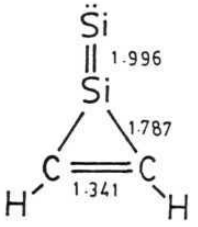
60



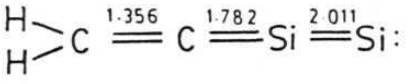
61



62



63



64

65

Fig. 6.3 Observed geometric parameters of the isomers (**55-65**) of $C_2Si_2H_2$ at MNDO1 level. Distances are in Angstroms and angles are in degrees.

stabilization of the p framework in **45** by the participation of the lone pair on the exo-silicon atom. The structures **42**, **44** and **45** are local minima. Only **50** correspond to a local minimum among the rotational isomers **48-50**. **48** and **49** are stationary points corresponding to transition states. **50** has two allyl π type Si-C-C orbitals in orthogonal planes whereas **48** and **49** have a C-C double bond and one butadiene type Si-C-C-Si π orbital with two electrons. The structures **51-53** are not stationary points at MNDO1 level. However, HF/3-21G* and MNDO2 calculations suggest that **52** corresponds to local minimum and **52** and **53** correspond to transition states. **54** is a high energy structure with two 7p electron distributed in the Si-C-C-Si framework and correspond to a transition state. Even though **54** and **55** are expected to have 2 electron delocalization in the π framework, the contribution from the p orbitals of Si is minimum in both the cases. The Si-Si distance in **54** is very close to single bond distance (2.343 Å) at MNDO1 level. The Si-C distances are considerably smaller than single bond distance.

Structures **56** to **65** are studied only by the MNDO methods (Fig. 6.3). **56** may be considered as a combination of CH_2^+ and CSi_2^- ring but there is not much of a charge separation. The empty p orbital on the CH_2 group is stabilized by hyperconjugative donation from the two C-Si bonds of the CSi_2 ring. **57** is a non-classical structural isomer. Its structure is similar to **24** but it is nowhere close to the global minimum (56.3 kcal/mol above) at MNDO1 level. It has an acetylide group bridging the two Si atoms, but C-C distance of 1.212 Å indicates a strong triple bond. The Si-C distances (1.862 Å) are slightly longer than standard Si-C single bond distance (1.800 Å). The

bridging hydrogen represents a closed 3c-2e bond (Si-H: 1.662 Å) similar to the one in **24**. One more interesting observation is that the bridging hydrogen is not in the plane of the remaining atoms, but puckered by about **26**. This may not be the artifact of the method used because **17** and **18** are also calculated at various levels of theory to be puckered.

The structures with one divalent silicon are more classical. **61** is not a local minimum, but leads to **48**. Even though the remaining structures possess some π delocalization, all of them are higher in energy. Structures with non-vicinal Si atoms are more stable than the structures with 1,2 disilyl arrangements. **62** is also not a local minimum.

6.4 Conclusions

There is a clear isolobal analogy between H-B and :Si when they participate in covalent bonding in organometallic compounds. MNDO and 3-21G* calculations show that **24** is indeed a global minimum amongst $C_2Si_2H_2$. The 2 π electron delocalization in **24** causes extra stabilization. **26** is a local minimum with Si-Si bond shorter than single bond. **44**, with two silylene units and allylic delocalization is most stable among the isomers of $C_2Si_2H_2$. The analogy developed here along with higher level calculations should be useful in locating and predicting unusual structures for silicon compounds based on the known structures of boranes.

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APPENDIX

A.0

The parameters for all the atoms used in the Extended Huckel calculations are taken from previous studies: C[1], H[1], N[1], O[1], P[2], S[2], Cl[2], Au[2], Co[2], Fe[2], Mo[2], Pt[2], Rh[2], W[2], Ni[2], Re[3], Mn[4], Ti[4], V[4], Br[5]and Os[6].

A.1

The important geometric parameters (internal coordinates) for structure are given in Table 1. Weighted H_{ij} formula is used. Bond lengths in (Å) and angles in degrees.

Table 1

Parameter	Structure		
	19, D_{2h}	20, C_s	21, C_{2v}
W(1)-W(2)	2.550	2.915	2.550
W-C(Me)	2.100	2.100	2.100
W(1)-C(1)	1.910	2.158	1.910
W(2)-C(1)	1.910	1.730	1.910
C(1)-C(2)		3.900	1.410
C(2)-C(3)		1.300	1.410
C(2)-C(3)-H		150.0	127.0
W(1)-W(2)-C(Me)	125.0	125.0	125.0
W(2)-W(1)-C(Me)	125.0	115.0	125.0
C(Me)-W-C(Me)	110.0	103.0	110.0
W(1)-W(2)-C(2)	48.1	47.3	48.1

A.2

The important geometric parameters used in the calculations are given in Table 2. For **2**, the data is obtained from the $Cp(CO)_2Mo[\mu\text{-}C(C_6H_4Me\text{-}4)]Fe(CO)_2$[10] which is electronically equivalent and the atomic radii of Mo and W are very close to each other. The geometric parameters for 3 are adopted from the crystal structure of $HB(pz)_3(CO)_2W[\mu\text{-}C(C_6H_4Me\text{-}4)]Fe(CO)_3$ which is electronically equivalent. In **26** Fe-Mn : 2.56 Å in **27** Fe-Fe : 2.60 Å; in **28** Os-Ag : 2.74 Å are used. Weighted H_{ij} formula is used.

Table 2

Parameter	in **2**	in **3**	in **26**	in **21**	
Distances (in Angstroms)					
Fe-W	2.823	2.612	2.850	2.834	
Fe-C	2.008	1.826	2.050	1.950	Fe-C(O)
W-C	1.921	2.025	2.000	2.025	
C-C	---	---	1.300 (alkyne)	1.557	C-C(O)
Angles (in degrees)					
Fe-W-C	45.30	44.20	46.00	65.20	
W-Fe-C	42.80	50.60	44.56	77.30	
W-C-Fe	91.90	85.30	89.44	---	
W-C-C(O)	---	---	---	117.40	

The geometries for the model calculations are based upon the known complexes wherever possible. Mn-Mn: 2.76 Å; Mn-C: 2.01 Å; C-H: 1.08 Å; Fe-Fe: 2.50 Å; Fe-C: 1.86 Å; Ru-Ru: 2.62 Å; Ru-C: 1.91 Å; Rh-Rh: 2.51 Å; Rh-C: 1.92 Å; Rh-C(O):1.96 A^{o}. The Walsh diagram for the hydrocarbation reaction in Fig. 3.4 is described by a least motion between bridging CH of **4** and ethylene. The molecular planes of **4** and ethylene are kept parallel to each other initially. The initial distance between C(H) of **4** and the carbon of ethylene closest to it is 3.00 Å. The reaction path is defined as the decrement in this distance. Other necessary changes are made to get the final compound **5**. C_s symmetry is maintained. In **16** Pt-Mn: 2.63 Å; Pt-C: 1.97 Å; Mn-C: 1.83 Å. In **17** W-Au: 2.72 Å; W-C: 1.81 Å; Au-C: 2.21 Å. In **31** the Re-Re: 2.96 Å; Re-C: 2.14 Å; Re-Br: 2.56 Å. In **32** Re-Re: 2.60 Å; Re-C: 2.14 Å; Re-Cl (bridging): 2.42 Å; Re-Cl (terminal): 2.45 Å. In **33** W-W: 2.62 Å; W-C: 1.87 Å; W-Br: 2.56 Å. Octahedral arrangement around metal is maintained in both **31** and **33**. In **34** Mo-Mo: 2.38 Å; Mo-C: 1.96 Å; Mo-H: 1.75 Å. In **35**, Fe-Re: 1.91 Å; Fe-C: 1.91 Å; Re-C: 1.97 Å; Fe-N: 1.87 Å; Re-N: 1.80 Å; N=O: 1.20 Å. In **38** Fe-Fe: 2.5 Å ; Fe-C: 1.93 Å ; Fe-S: 2.30 Å. In **30** W-Ru: 2.77 Å; W-C : 1.94 Å ; Ru-C: 2.02 Å. Planar arrangement is adopted for the four membered rings of **32-36**.

A.4

The important geometric parameters used for the compounds **3, 3a, 8, 8a, 10, 12** and **XVI** are given in Table 3. The Walsh diagrams (Fig. 4.5) are constructed by varying θ from 105 to 65º. Weighted H_{ij} formula used. Distances are in angstrom units and angles are in degrees.

Table 3

Parameter	**3**	**3a**	**8**	**8a**	**10**	**12**	**XVI**
M(1)-M(2) =M(1)-M(3)	2.62	2.62	2.86	2.86	2.64	2.64	2.86
M(2)-M(3)	2.61	2.61	2.84	2.84	2.61	2.61	2.84
M(1)-C[a]	2.64	2.64	2.81	2.81	2.66	2.66	2.35
M(2)-C = M(3)-C	1.86	1.86	2.04	2.04	1.86	1.86	2.04
M(2)-H = M(3)-H	1.62	1.62	1.62	1.62	1.62	1.62	1.62
a	90.0	90.0	90.0	90.0	90.0	69.2	69.7

[a] Varies with the dihedral angle in the Walsh diagram.

A.5

The geometrical parameters used in the calculations are as follows. Bond lengths: Ni-Ni = 2.52 Å, Ni-CO = 1.8 Å, C-O = 1.14 Å, W-W = 2.56 Å, W-CH_3 = 2.1 Å, C-H = 1.08 Å, C(1)-C(2) = C(2)-C(3) = 1.41 Å. Bond angles: C(1)-C(2)-C(3) = 100°, C(1)-C(2)-H = 124°, OC-Ni-CO = 110°, Me-W-Me = 110°. Pyramidalization at Ni in **11** and **13** is achieved by bending the carbonyls down and decreasing the OC-Ni-CO angle from 110° to 98°. The OC-Ni-Ni angle is kept constant in the process. Tilting of the C_3H_3 group is performed so as to get the near planar arrangement of M(2)-C(1)-C(2)-C(3) without altering the geometry of C_3H_3 unit. M_2-C_2 distance is increased from 2.52 Å to 2.70 Å in this process.

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V I T A E

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List of Publications

1) "Theoretical Study of the Electronic Structure and Reactions of $R_2W(\mu\text{-}CR)_2WR_2$" Proc. Ind. Natl. Sci. Acad. **1986**, 52A, 764-775 B.V. Prasad, A.D. Prasad and E.D. Jemmis.

2) "Reaction of $L_2W(\mu\text{-}CR)_2WL_2$ with C_2R_2. A Theoretical Study." J. Am. Chem. Soc. **1987**, 109, 2560-2563 E.D. Jemmis and B.V. Prasad.

3) "The Fragment Molecular Orbital Approach in Organometallic Reactivity. Reactions on Binuclear Complexes." Proc. Ind. Acad. Sci. (Chem. Sci.) **1987**, 99, 156-111 E.D. Jemmis and B.V. Prasad.

4) "To Tilt or Not To Tilt. The Dilemma of the $\mu\text{-}C_3R_3$ ligands in Binuclear Complexes." J. Organomet. Chem. **1988**, 347, 401 E.D. Jemmis and B.V. Prasad.

5) "Theoretical Studies of (μ-CR) Bridging Ligands." Polyhedron, Symposium-in-Print **1988**, 7, 871 E.D. Jemmis and B.V. Prasad.

6) "Theoretical Studies on the ($\mu\text{-}S_2CR$) Ligands in Cyclopentadienyl Molybdenum Dimers" Inorg. Chem. Acta. **1989**, 162, 281-285 B.V. Prasad, C.S. Reddy and E.D. Jemmis.

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Submitted for publication

9) "Electronic Origin for the Geometric Preferences of carbyne Bridges in $HM_3(CO)_{10}(\mu\text{-}CR)$ Compounds" (Submitted to Inorg. Chem.) E.D. Jemmis and B.V. Prasad.

To be submitted for publication

10) "Carbynyl Cation Bridged Binuclear Transition Metal Complexes" (to be submitted) E.D. Jemmis and B.V. Prasad.

11) "Electronic Structure and Reactivity of Bimetallacyclopropene Complexes" (to be submitted) E.D. Jemmis and B.V. Prasad.