CHAPTER 4

Electronic Origin for the Geometric Preferences of Carbyne Bridges in $\text{HM}_3(\text{CO})_{10}(\mu-\text{CR})$ Complexes
4.1 Abstract:

The electronic factors that control the variation of the bridging carbyne unit in $\text{HM}_3(\text{CO})_{10}(\mu-\text{CR})$ from $\mu_2^-$ to $\mu_3^-$ have been studied by Extended Huckel calculations on the model $\text{HFe}_3(\text{CO})_{10}(\mu-\text{CH})$, 3a. HOMO-1 of 3a has antibonding character between the $p_\perp$ orbital of carbyne and all the three metals. Substituents on the carbonyl carbon influence this metal-carbon antibonding interaction, but not equally with all metals. This leads to a variation in the dihedral angle $\theta$ between the M-M-M plane and M-C-M plane as a function of $R$. Molecular orbital patterns indicate only $\mu_2$ arrangement for carbyne in all $\text{HM}_3(\text{CO})_{10}(\mu-\text{CR})$ compounds. The $\mu_3$ arrangement of carbyne in $\text{HRhFe}_2(\text{CO})_7\text{Cp}(\mu-\text{COMe})$ 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, \( \mu_1-\mu_4 \).\(^1\) \( \mu_1, \mu_2 \) and \( \mu_3 \) bridging carbyne arrangements are in principle possible with a trinuclear carbyne complex. There has been no characterised example of a monohapto (\( \mu_1 \)) carbyne ligand attached to a trinuclear cluster. \( \mu_3 \) carbyne bridging mode is well known in the trinuclear complexes, \( 1\text{IC} \), isolobal to tetrahedrane. \( \mu_2 \)-CR on trimetallic templates presents a different story.\(^2\)-\(^{19}\) A perusal of available structures, (Table 1) indicates that the \( \mu_2\)-CR attachment is a very delicate one. With changes in the substituent R, the CR group could shift gradually from a \( \mu_2 \) to a \( \mu_3 \) position. The electronic factors that control such a gradation are discussed in this chapter.

\[
\begin{align*}
&\text{R} \\
&\text{C} \\
&\text{M} \\
&\text{L}_n \text{M} \\
&\text{M}_n \text{L}_n \\
&\text{1} \\
&\theta \\
&\text{R} \\
&\text{C} \\
&\text{M} \\
&\text{L}_n \text{M} \\
&\text{M}_n \text{L}_n \\
&\text{2a} \\
&\text{R} \\
&\text{C} \\
&\text{M} \\
&\text{L}_n \text{M} \\
&\text{M}_n \text{L}_n \\
&\text{2b}
\end{align*}
\]

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 \( \theta \) between the M(1)-M(2)-M(3) plane and the M(2)-C-M(3) plane is much larger than \( 90^\circ \), (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 $\theta$. Distances in angstrom units and angles in degrees.

<table>
<thead>
<tr>
<th>Compound</th>
<th>M(1)-C</th>
<th>$\theta$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFe$<em>3$(CO)$</em>{10}$($\mu$-CO)$^{-}$</td>
<td>I</td>
<td>3.00</td>
<td>102.0</td>
</tr>
<tr>
<td>HFe$<em>3$(CO)$</em>{10}$($\mu$-CNMe$_2$)</td>
<td>II</td>
<td>2.89</td>
<td>96.8</td>
</tr>
<tr>
<td>HFe$<em>3$(CO)$</em>{10}$($\mu$-COMe)</td>
<td>III</td>
<td>2.70</td>
<td>91.0</td>
</tr>
<tr>
<td>HFe$<em>3$(CO)$</em>{10}$($\mu$-COH)</td>
<td>IV</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>HRu$<em>3$(CO)$</em>{10}$($\mu$-CO)$^{-}$</td>
<td>V</td>
<td>3.17</td>
<td>102.4</td>
</tr>
<tr>
<td>HRu$<em>3$(CO)$</em>{10}$($\mu$-CNMe$_2$)</td>
<td>VI</td>
<td>3.08</td>
<td>100.4</td>
</tr>
<tr>
<td>HRu$<em>3$(CO)$</em>{10}$($\mu$-COMe)</td>
<td>VII</td>
<td>2.90</td>
<td>94.4</td>
</tr>
<tr>
<td>HRu$<em>3$(CO)$</em>{g}$Py($\mu$-CNBz$_2$)</td>
<td>VIII</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>HRu$<em>3$(CO)$</em>{g}$PPh$_3$($\mu$-CNBz$_2$)</td>
<td>IX</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>HOs$<em>3$(CO)$</em>{10}$($\mu$-COMe)</td>
<td>X</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>HOs$<em>3$(CO)$</em>{10}$($\mu$-CNMe$_2$)</td>
<td>XI</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>HOs$<em>3$(CO)$</em>{10}$($\mu$-CPh)</td>
<td>XII</td>
<td>2.59</td>
<td>78.2</td>
</tr>
<tr>
<td>HOs$<em>3$(CO)$</em>{10}$($\mu$-CCH=CH$_2$)</td>
<td>XIII</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>HOs$<em>3$(CO)$</em>{10}$($\mu$-CCH$_3$)</td>
<td>XIV</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>HOs$<em>3$(CO)$</em>{10}$($\mu$-CC$_2$H$_5$)</td>
<td>XV</td>
<td>2.64</td>
<td>82.1</td>
</tr>
<tr>
<td>HOs$<em>3$(CO)$</em>{10}$($\mu$-CH)</td>
<td>XVI</td>
<td>2.35</td>
<td>69.7</td>
</tr>
<tr>
<td>HRhFe$_2$Cp(CO)$_7$($\mu$-COMe)</td>
<td>XVII</td>
<td>2.21</td>
<td>69.2</td>
</tr>
<tr>
<td>HCoFe$_2$Cp(CO)$_7$($\mu$-COMe)</td>
<td>XVIII</td>
<td>2.00</td>
<td>64.7</td>
</tr>
<tr>
<td>NiFe$_2$Cp(CO)$_7$($\mu$-COMe)</td>
<td>XIX</td>
<td>1.96</td>
<td></td>
</tr>
<tr>
<td>(AuPPh$_3$)$<em>3$(CO)$</em>{10}$($\mu$-COMe)$^a$</td>
<td>XX</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(AuPPh$_3$)Fe$_2$CoCp(CO)$_7$($\mu$-COMe)</td>
<td>XXI</td>
<td>1.93</td>
<td></td>
</tr>
<tr>
<td>HOs$_3$(M$\mu$-CPh)(CO)$_g$(=COMe)$_2$</td>
<td>XXII</td>
<td>2.29</td>
<td>66.6</td>
</tr>
<tr>
<td>HOs$<em>3$(CO)$</em>{10}$($\mu$-C(PhC=C(Ph)-Re(CO)$_4$PMe$_2$Ph)</td>
<td>XXIII</td>
<td>3.09</td>
<td>99.1</td>
</tr>
</tbody>
</table>

$^a$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 \( \theta \) is as small as 64.7° (2b). 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 \( \theta \) is large (as large as 102° when \( R=O^- \), V, table 1). As the electron donating capacity of the \( R \) group decreases, \( \theta \) 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), \( \theta \) is less than 70° and a semi-triply bridging nature of the CH group is suggested on the basis of distances. What is the electronic origin for this change of \( \theta \) 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 \( \theta \) (70°) can the CR group be described as \( \mu_3 \)? Is there any \( \pi \) 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, $\theta$. It has been suggested that the metal M(1) donates electrons to the $\pi^*$ orbital of C-OMe or C-NMe$_2$ bridging groups. 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 $\mu_3$ 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)$_{10}$($\mu$-CR) and in HM$_2$M'Cp(CO)$_7$($\mu$-CR) are different? There are several examples in literature where short interatomic distances do not 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 $\theta$ as a function of substituent (R) on the bridging carbyne (CR) in 2. The electronic structure of the model compound HFe$_3$(CO)$_{10}$($\mu$-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 $\theta$. Electronic structure of HOs$_3$(CO)$_{10}$($\mu$-CH), XVI is studied to explain its special properties. The MO pattern of HRhFe$_2$Cp(CO)$_7$($\mu$-CH) is also studied to explain the $\mu_3$ arrangement of CR bridge in XVII and XVIII. Fragment Molecular Orbital approach$^{22}$ within the Extended Hückel method$^{23}$ is used in these studies.
4.3 Results and Discussion

Electronic Structure of $\text{HFe}_3(\text{CO})_{10}(\mu-\text{CH}), \text{3a}$. 

$\text{HFe}_3(\text{CO})_{10}(\mu-\text{CH}), \text{3a}$, in which the dihedral angle $\theta$ formed by the two planes, Fe(1)-Fe(2)-Fe(3) and Fe(2)-C-Fe(3) is kept at 90° 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 $\text{3a}$ are constructed from the MOs of smaller fragments $\text{Fe(CO)}_4$, 4, and $\text{HFe}_2(\text{CO})_6(\mu-\text{CH}), \text{5}$. The MOs of fragment 5, in turn are constructed from those of the carbyne group, 6, and of the remaining fragment $\text{HFe}_2(\text{CO})_6$, 7 (Fig. 4.1). The carbyne group has a $\sigma$ orbital and two unhybridized p orbitals one in the plane of the fragment ($p_\| \sigma$) 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 $\sigma$, $\pi$ and $\delta$, 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 $p_\| \pi$ of 6 to give 4a'' of 5, corresponding to an M-C $\sigma$ bond. 1a' of 5 is a $\pi$ 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_{⊥} of carbyne. In 4a' of 5, p_{⊥} 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

\[ \text{Scheme 1} \]

![Diagram of Scheme 1](image-url)
Fig. 4.1 Interaction diagram for the construction of the MOs of the fragment $\text{Fe}_2(\text{CO})_6(\mu-H)(\mu-\text{CH})$, 5 from smaller fragments CH, 6 and $\text{Fe}_2(\text{CO})_6(\mu-\text{H})$. 
us to consider the fragment 5 to be analogous to the cyclopropenyl anion. 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 HFe₂(CO)₆(M-CH), 5 with the familiar Fe(CO)₄ group 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) \( \pi \) delocalization. In addition
Fig. 4.2 Diagram showing the interaction of fragment $\text{HFe}_2(\text{CO})_6(\mu-\text{CH}),$ 5 (left) with $\text{Fe}(\text{CO})_4$ to give $\text{HFe}_3(\text{CO})_{10}(\mu-\text{CH}),$ 3 and (right) with $\text{Rh}(\text{CO})\text{Cp}$ to give $\text{HRhFe}_2(\text{CO})_7\text{Cp}(\mu-\text{CH}),$ 10 (at $\theta = 90^\circ$).
to this interaction, carbynol 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) $\delta$ orbital while the interaction with Fe(1) may be described as $\sigma^*$. In 3a' there is an antibonding interaction between one of the carbynyls 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 $\sigma$ 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. The Fe(2)-C and Fe(3)-C bonds are regular two centre two electron bonds which leaves 4 $\pi$ electrons (one each from CR, Fe(2) and Fe(3) 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' ($\pi$) and 6a' ($\pi^*$) 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 $d_{xy}$-$d_{xy}$ $\delta$ ($\delta_1$) and bonding interaction with $d_{x^2-y^2}$-$d_{x^2-y^2}$ $\delta$ ($\delta_2$) 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 \( \text{HFe}_3(\text{CO})_{10}(\mu-\text{CH}) \), 3a and (right) leading to \( \text{HOS}_3(\text{CO})_{10}(\mu-\text{CH}) \), 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°. 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⊥ 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 carbonyl 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° to 65° some bonding interactions (1a', 1a'') are developed between Fe(1) and carbonyl 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)$_{10}$($\mu$-CH), 3a and (b) in HRhFe$_2$Cp(CO)$_7$($\mu$-CH), 9, both at $\theta = 90^\circ$. 
Fig. 4.5 Walsh diagrams showing the variation in the MO pattern of (a) HFe$_3$(CO)$_{10}$ (μ-CH) (b) HFe$_3$(CO)$_{10}$ (μ-CN) (c) HOs$_3$(CO)$_{10}$ (μ-CH) and (d) HOs$_3$(CO)$_{10}$ (μ-CN) 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 $\theta = 90^\circ$ and 0.061 at $\theta = 77^\circ$) and this cannot be taken as an evidence for increased Fe(1)-CR bonding interaction. The $\sigma^*$ interaction between Fe(1) and C(H) in 6a' increases with decreasing $\theta$. Therefore Fe(1)-C bond should not be expected at small $\theta$. Even though the Fe(1)-C distance 2.42 Å indicates a $\mu_3$ bridge (at $\theta = 77^\circ$), on the basis of MO pattern and overlap population analysis we should consider the carbyne as only a $\mu_2$ rather than a $\mu_3$ bridge in 3a. From the Walsh diagram Fig. 4.5a it is clear that the antibonding interaction between carbon $p_{\perp}$ orbital and the $\delta$ 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 $\theta$ 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 $p_{1}$ orbital as a function of $R$ in $H_2C\text{-}R$. 
electron energies. The decrease in $\theta$ decreases the $M(2)$-$C$-$M(3)$ $\pi^*$ 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 $\theta$. 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 $\theta = 93^\circ$. This is very close to the experimentally observed $\theta = 96.8^\circ$ for HFe$_3$(CO)$_{10}(\mu$-$\text{CNMe}_2)$.$^{3e}$ The Walsh diagram for a change in $\theta$ 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 $93^\circ$ in comparison to the $\theta = 77^\circ$ 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 $\theta = 90^\circ$ is shown in Fig.

\[
\begin{align*}
8a & \quad R = H \\
8b & \quad R = \text{NH}_2
\end{align*}
\]
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 $\delta$ orbital of M(2)-M(3) are more strong in 8a than in 3a (Fig. 4.3). This should lead to smaller $\theta$ in 8a than in 3a. The Walsh diagram Fig. 4.5c for HOs$_3$(CO)$_{10}$(μ-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 $\theta$ in 8a shows a minimum at 70°. This is very close to the experimentally observed $\theta = 69.7^\circ$ for HOs$_3$(CO)$_{10}$(μ-CH), XVI. Fig. 4.5c shows that in 8a also the variation in the $\theta$ is largely controlled by 6a' orbital only. In 8a at $\theta = 70^\circ$ also both MOs corresponding to $\sigma$ (1a') and $\sigma^*$ (6a') interactions between Os(1) and C are occupied. This suggests that in XVI the bridging carbyne should be treated as a $\mu_2$ 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.

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 $\theta$ in HOs$_3$(CO)$_{10}$(μ-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 carbonyl carbon and the $\delta$ orbital of M(2) and M(3) as a function of R.

In the case of regular $\mu_3$ 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).\textsuperscript{14} This originates from the antibonding Os(1)-C interaction in HOMO-1 (6$a'$). 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. 3$a$ is also expected to have an M-H interaction.

The above discussion on 3$a$ and 8$a$ suggests that the dihedral angle $\theta$ is dictated by the extent of antibonding interaction observed between M(2)-M(3) $\theta$ orbitals and the carbonyl carbon. Stronger antibonding interactions in 6$a'$ 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 6$a'$ of Scheme 2) control the dihedral angle, $\theta$.

Similar geometric preferences are expected in $\text{HM}_2\text{M'}\text{Cp(CO)}_7(\mu-\text{CR})$ 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 $\text{HM}_2\text{M'}\text{Cp(CO)}_7(\mu-\text{CR})$ prefer a $\mu_3$ arrangement for the carbyne ligand. There are three of them known, all with methoxy carbyne (XVII to XIX, table 1).\textsuperscript{15,16} Methoxy carbyne was found to give $\mu_2$ bonding in the "all-carbonyl" complexes (III, VII and X,
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)$_7$Cp(μ-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 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)$_7$(μ-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 see the differences between HFe$_3$(CO)$_{10}$(μ-CH) and HRhFe$_2$(CO)$_7$Cp(μ-CH) in the following way. Fig. 2 (right) shows
Fig. 4.7 Correlation diagram showing correlation of the MOs of HRhFe$_2$(CO)$_7$Cp(μ-CH) at $\theta = 90^\circ$ and at $\theta = 69.2^\circ$. 

9 ($\theta = 90^\circ$) 9 ($\theta = 69.2^\circ$)
an interaction diagram for the construction of the MOs of 9 (90°) from the fragments RhCp(CO) and HFe₂(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 t₂g 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 θ = 69.2°. Fig. 4.7 shows the correlation between the MOs of 9 at θ = 90° and θ = 69.2°. 6a' orbital comes down in energy with the decrease in θ. 6a' shows Rh-C σ bonding interaction at θ = 69.2°. The overlap population between Rh and C(H) in 9 increases largely with decreasing θ (0.175 at θ = 90° and 0.354 at θ = 69.2°), indicating the developing Rh-C σ bond. Therefore the carbyne group should be treated as a μ₃ bridging group. Thus the directionality of RhCp(CO) orbitals pave the way for μ₃ arrangement for the carbyne bridge in 9. In structures XVII to XIX (table 1), θ is less than 70° and M(1)-C distance indicates μ₃ arrangement. Calculations made on 9 and HRhFe₂Cp(CO)₇(μ-COCH₃), XVII as a function of variation in θ show energy minima at θ = 70° which are very close to the experimental observation for XVII (69.2°).
4.4 Conclusions

The electronic structure of $\text{HFe}_3(\text{CO})_{10}(\mu-\text{CH})$ 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 $\theta$ 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 $\theta$ with decreasing electron donating nature of $R$. No $M(2)$-$C$-$M(3)$ $\pi$ delocalization should be expected in $\text{HM}_3(\text{CO})_{10}(\mu-$CR$)$ compounds. Electronic structure of $\text{HM}_3(\text{CO})_{10}(\mu-$CR$)$ compounds suggest only $\mu_2$ arrangement for the bridging carbyne despite short $M(1)$-$C$ distance. The directionality of MOs of $\text{RhCp(CO)}$ unit in $\text{HRhCp(CO)Fe}_2(\text{CO})_6(\mu-$CR$)$ is different from that of $\text{HFe}_3(\text{CO})_{10}(\mu-$CR$)$ and stabilizes a $\mu_3$ carbyne bridge.
4.5 References

(1) Here, Alkylidynes are referred as $\mu_1$-CR complexes. For references corresponding to the $\mu_1-\mu_4$ CR bridging compounds, see Objective and Background.


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(21) The fact that the novel $M_3(CO)_{10}$ compounds are the original precursors for this series of compounds enhances the interest in these compounds.


(24) The possibility of considering the M-C(R)-M ring as an anion was suggested previously by Howell and Mathur in ref. 3d.


(26) Fe(CO)$_3$ group is considered to be donating one electron to the $\pi$ frame of the Fe(2)-C-Fe(3) in the following way. Fe(CO)$_3$ is a 14 electron unit. The 3c-2e bond with H has one electron. It shares an electron in the bond with Fe(CO)$_4$ and another with the bridging carbon in a $\sigma$ bond. This makes the Fe(CO)$_3$ group as a 17 electron unit. The 18th electron is placed in the Fe(2)-C-Fe(3) $\pi$ frame.