CHAPTER 3

Electronic Structure
and Reactivity of
Carbonyl Cation Bridged
Binuclear Transition Metal
Complexes
3.1 Abstract

Extended Huckel method is used to study the molecular orbital pattern of carbonyl 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 \((\text{CR})^+\) 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 carbonyl 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 \(\text{CR}^+\) bridge, as in 1 can contribute only two electrons to the complex formation. These two participate in regular M-C \(\sigma\) bonds. The unsaturation at the carbon centre remains in the form of the +ve charge.

\[
\begin{array}{ccc}
\text{R} & \text{C}^+ & \text{L}_n\text{M}-\text{ML}_m \\
\text{1} & \text{L}_n\text{M} \circ \text{ML}_n \circ \text{ML}_n \\
\text{2} & \\
\text{3} & \\
\end{array}
\]

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 \(\text{L}_n\text{M}=\text{CR}^+\) 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 \(\text{CR}^+\) 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.\textsuperscript{1a,1d,9} Hydrogen migration from the R group to bridging carbon gives alkenyl bridged complexes.\textsuperscript{10} Apart from these three, another interesting reaction is also observed. The reaction of \( \text{Cp(CO)Fe(\mu-CH)(\mu-CO)Fe(CO)Cp}^+ \), 4 with ethylene gives an adduct \( \text{Cp(CO)Fe(\mu-CC_2H_5)(\mu-CO)Fe(CO)Cp}^+ \), 5 (Scheme 1).\textsuperscript{3} When the hydrogen on the carbyne bridge in 4 is replaced by any R group, such an adduct is not formed.\textsuperscript{11,12} This reaction is very much similar to the well known hydroboration reaction\textsuperscript{14} where \( \text{R}_2\text{B-H} \) reacts with ethylene to give an adduct and hence the name hydrocarbation.\textsuperscript{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 delocalization in the M-C-M framework, 6, is indicated.\textsuperscript{1c,1d} In some other complexes, an
M-C double bond is suggested, 7. 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. 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. The electronic structure studies on the CH⁺ bridged piano-stool dimers is reported previously by Bursten et al. 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 \((\text{CO})_2\text{CpMn(μ-CH)}\text{MnCp(\text{CO})}_2\)^+, 9.

\((\text{CO})_2\text{CpMn(μ-CH)}\text{Mn(\text{CO})}_2\text{Cp}^+, 9\) 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

\[
\text{Cp(\text{CO})}_2\text{Mn} \quad \text{MnCp(\text{CO})}
\]

fragments CH⁺ and \([\text{Mn(\text{CO})}_2\text{Cp}]_2\), 10 (C₂ symmetry maintained). Details of the geometric and atomic parameters are given in
Fig. 3.1 Interaction diagram for the construction of molecular orbitals of $[\text{Mn(CO)}_2\text{Cp}]_2(\mu-\text{CO})(\mu-\text{CH})^+\ 9\ (C_2)$ from smaller fragments $(\text{CH})^+$ and $[\text{Mn(CO)}_2\text{Cp}]_2\ 10,\ (C_2)$. 
appendix. With a d⁶-d⁶ 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 analogy¹⁸ also supports this idea.

1b (π) orbital of 10 destabilizes the pₐ orbital of carbonyl 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 destabilizes 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 pₐ of carbon, leading to a proposal of cyclic π system in the molecule.¹³c,¹³d But 1b orbital of 9 is mostly based on the two metals. Interesting aspect of this interaction diagram is the presence of an almost pure carbon pₐ (5b) orbital as LUMO, 11 (Fig. 3.1). 9 is isolobal to cyclopropyl cation, C₃H₅⁺. 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 $\text{CH}^+$ have been reported previously.\textsuperscript{17} It was pointed out that the presence of carbon $p_\perp$ orbital as LUMO in $\text{Cp(CO)}\text{Fe(μ-CO)(μ-CH)Fe(CO)}\text{Cp}^+$, 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 $\text{CpFe(μ-NO)(μ-CH)FeCp}^+$ towards nucleophiles.\textsuperscript{17} In tune with this, $[\text{Mn(CO)}_2\text{Cp}]_2(\mu-\text{CH})^+$, 9 should also be highly reactive at the carbon centre towards nucleophiles. $[\text{Mn(CO)}_2\text{Cp}]_2(\mu-\text{CR})^+$ is found in solution as an intermediate in vinylidene interconversion on metallic template,\textsuperscript{1a} indicating the high reactivity at the carbon centre in these complexes.

**Electronic Structure of $(\text{C}_5\text{Me}_5)\text{Rh(μ-C(C}_6\text{H}_4\text{Me-4))}(\mu-\text{CO})\text{Rh(C}_5\text{Me}_5)^+$** 12.\textsuperscript{2i}

$\text{CpRh(μ-CH)(μ-CO)RhCp}^+$, 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, $\text{CH}^+$ and

![Diagram](image-url)

12 $L=\text{C}_5\text{Me}_5$ $R=\text{C}_6\text{H}_4\text{Me}$

13 $L=\text{C}_5\text{H}_5$ $R=\text{H}$
CpRh(μ-CO)RhCp, 14. In 14 apart from the ligand based orbitals (not labeled), the following metal based orbitals are occupied. 1b₁(δ), 1a₁(δ), 1b₂(δ*), 1a₂(δ*), 2a₁(σ), 2b₂(σ*), 2b₁(π), 3a₁(π). The HOMO is the 3a₁ (in-plane π orbital) between the two metals. LUMO is the 3b₂ (in-plane π* orbital). 2a₂ (out-of-plane π* orbital) is the LUMO+1. In 14, both 2a₁(σ) and 2b₂(σ*) are occupied indicating the absence of M-M σ interaction. Two M-M π* orbitals 2b₁ and 3a₁ are occupied.

Interaction of fragment 14 with CH⁺ leads to 13 (Fig. 3.2). The major interactions are between 3b₂ (π*) of 14 and b₂ orbital of CH⁺ leading to M-C bond formation. The resultant 3b₂ of 13 is slightly pushed up by the interaction with the 1b₂ and 2b₂ orbitals of 14. The a₁ orbital of CH⁺ pushes the a₁ orbitals of 14, 3a₁ orbital of 14 is pushed up into the unoccupied region of 13. Instead the 3b₂ of 13 is occupied. The a₂ orbitals do not find a match among the orbitals of CH⁺ and remain untouched. 2a₂ of 14 becomes LUMO 2a₂ of 13. The p┴ orbital of CH⁺ stabilizes the 2b₁ of 14. The corresponding antibonding combination 3b₁ is LUMO+1 in 13, mainly concentrated on the p┴ orbital of carbon. All the bonding and antibonding interactions of metal-metal axis are occupied. 1b₂(δ*), 1b₁(δ), 1a₁(δ), 2a₂(δ*), 2a₁(σ), 2b₂(σ*), 3b₁(π) and 3b₂(π*). 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.²¹ The 1b₁ orbital of 13 is the bonding combination of the π orbital of 14 and the p┴ orbital leading to a proposal of cyclic π delocalization. But 1b₁ 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. 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, \( C_3H_3^+ \).

Extended Huckel calculations are performed on various other carbonyl cation bridged bimetallic systems. They include 

\[
[\text{Fe(CO)Cp}]_2 (\mu-CO)(\mu-CH)^+ , \quad [\text{Fe(CO)Cp}]_2 (\mu-CO)(\mu-CCH_3)^+ , \\
[\text{Fe(CO)}_4]_2 (\mu-CCH_3)^+ , \quad [\text{RuCp(CO)}]_2 (\mu-CO)(\mu-CMe)^+ , \\
[\text{FeCp}]_2 (\mu-dmpm)(\mu-CO)(\mu-COME)^+ .
\]

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. The LUMO of these compounds is in favour of this observation.

**Electronic structure of \( \text{Cp(CO)}_2\text{Mn(}\mu-\text{C(C}_6\text{H}_4\text{Me-4)})\text{Pt(PH}_3\text{)}_2^+ \),** 15

A few examples are known where the \( \text{CH}^+ \) bridges a heterobimetallic template. Two different electron distributions are proposed. One with metal carbon double bond, 7 where the charge is suggested to be localized on \( \text{ML}_n \) unit. The other is with a metal carbon triple bond where the charge is suggested to be localized on \( \text{M'L}_m \). 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 \( \text{M-C} \) 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 \( \text{Cp(CO)}_2\text{Mn(}\mu-\text{CH})\text{Pt(PH}_3\text{)}_2^+ \), 16, a representative of compounds of
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

\[
\begin{align*}
\text{Cp(CO)$_2$Mn} & \quad \leftrightarrow \quad d^6M L_5 \quad \leftrightarrow \quad \text{CH}_2 \\
(PR_3)_2Pt & \quad \leftrightarrow \quad d^6M L_2 \quad \leftrightarrow \quad \text{CH}_2 \\
\text{Cp(CO)Co} & \quad \leftrightarrow \quad d^8M L_4 \quad \leftrightarrow \quad \text{CH}_2 \\
(\text{PH}_3)\text{Au} & \quad \leftrightarrow \quad d^{10}s^1M L \quad \leftrightarrow \quad \text{H}
\end{align*}
\]

Extended Hückel 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 $\delta$ orbital of the M-M axis, 11. The interaction diagram between Cp(CO)$_2$Mn=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 $\pi$ 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 \((\text{CO})_5\text{W}(\mu-\text{CR})\text{Pt(PH}_3)_2\)^{+3a} also is similar to that of 15. In \(\text{Cp(CO)}_2\text{Mn(\mu-C(C}_6\text{H}_5\text{Me-4)})\text{Pt(PMe}_3)_2\)^{+3b}, a partial bridging interaction between one of the carboxyls 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 \(\text{Cp(CO)}_2\text{W(\mu-CH)Au(PH}_3)_2\), 17.**

\(\text{Cp(CO)}_2\text{W(\mu-C(C}_6\text{H}_4\text{Me-4)})\text{Au(PPh}_3)_2\)^{+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 suggested for 8.\(^{7b}\) The molecular orbitals of 17 are constructed from those of the fragments \((\text{CO})_2\text{CpW≡CH}\) and \(\text{Au(PH}_3)_2\) (Fig. 3.3). The energies of HOMO and LUMO of \(\text{Au(PH}_3)_2\) are not close to the energies of the frontier orbitals of \(\text{Cp(CO)}_2\text{W≡CH}\). The fragment \((\text{CO})_2\text{CpW≡CH}\) has a \(\sigma\) and two \(\pi\) occupied orbitals along the W-C axis (Chapter 2). LUMO is a W-C \(\pi^*\) orbital. The interaction diagram clearly shows that there is no significant interaction between the two fragments. The in plane \(\pi\) orbital of
3.3 Interaction diagram for the construction of molecular orbitals of $\text{Cp(CO)}_2\text{W(μ-CH)Au(PH}_3\text{)}$ 17 from smaller fragments $\text{Cp(CO)}_2\text{W}_\text{μCH}$ and $\text{Au(PH}_3\text{)}$. The occupied orbitals of $\text{Au(PH}_3\text{)}$ are very low in energy (HOMO is at $-14.28$ eV.)
Cp(CO)$_2$W≡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°) 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$_2$H$_3^+$, 20. The Au-C overlap population of 0.343 is arising mostly from the MO shown in 21. Cp(CO)$_2$W 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]$_2$(μ-CO)(μ-CH)$^+$, [Fe(CO)$_4$]$_2$(μ-CMe)$^+$, [Co(CO)Cp]$_2$(μ-CMe)$^+$, Cp(CO)$_2$Mn(μ-CR)PtL$_2^+$ etc. but not CpRh(μ-
\( \text{CR)}(\mu-\text{CO})\text{RhCp}^+, \text{Cp(CO)}_2\text{W}(\mu-\text{CR})\text{AuL}^+, \text{CpFe}(\mu-\text{CH})(\mu-\text{NO})_2\text{FeCp}^+ \text{ etc.}\) are expected to be electrophilic.

**Hydrocarbation Reaction**

Reaction of \( \text{Cp(CO)}\text{Fe}(\mu-\text{CH})(\mu-\text{CO})\text{Fe(CO)}\text{Cp}^+, 4 \) with ethylene gives \( \text{Cp(CO)}_2\text{Fe}(\mu-\text{CCH}_2\text{CH}_3)(\mu-\text{CO})\text{Fe(CO)}\text{Cp}^+, 5 \) (Scheme 1).\(^{11}\) This reaction is found to be very general and found to take place with every possible alkene. \( \text{Cp(CO)}\text{Fe}(\mu-\text{CO})(\mu-\text{CEt})\text{Fe(CO)}\text{Cp}^+, 5 \) 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 \( \sigma^* \) orbital of the methyldiylnyl 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 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 \((CO)CpFe(\mu-CO)(\mu-CH)Fe(CO)Cp^+\) 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 C1-C2, and C3-H bonds and C1-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 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-CCH3)Fe(CO)Cp+, 22 is also carbon based p orbital. But it has a π* interaction with a psuedo p orbital of the CH3 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

Scheme 4

H
Fe

Fe
C
Fe

H
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(μ-CH)PtL₂⁺, (CO)₅W(μ-CH)PtL₂⁺, [Ru(CO)Cp]₂(μ-CO)(μ-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.¹¹,²¹,²² The well characterized examples are [Cp(CO)Fe]₂(μ-CO)(μ-CSMe)⁺, 2₃,²¹ and [Cp(CO)Co]₂(μ-CMe)⁺, 2₄.²²,²² 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
goes into the LUMO of 4 i.e. 11. Since 11 is antibonding between $p_\perp$ orbital of carbon and $\delta$ 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.\textsuperscript{21} This supports the idea that the odd electron in 23 is localized on carbon only. Co(CO)Cp is isolobal to CH\textsubscript{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°.

**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 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)\textsubscript{4}Re(\textit{u}-Br)(\textit{u}-C(C\textsubscript{6}H\textsubscript{5}))Re(CO)\textsubscript{4}, 26,\textsuperscript{23} the fragment Re(CO)\textsubscript{4} is a $d^7$-ML\textsubscript{4} unit and is isolobal to CH\textsubscript{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\textsuperscript{-} and CR\textsuperscript{+}
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)$_4$]$_2$(μ-Br)(μ-CH), 33 shows that $\sigma$, $\sigma^*$, $\pi$, $\pi^*$ and $\delta$, $\delta^*$ orbitals of M...M axis are occupied. The $\pi$ and $\delta$ combinations of M...M are stabilized by the participation of the $\pi$ and $\pi^*$ combinations of HC...Br unit respectively, but the MOs are mostly on metal and Br. The carbon based $p^\parallel$ orbital is destabilized to become the LUMO. It is antibonding with the M-M $\delta$ 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]$_2$(μ-Cl)(μ-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]$_2$(μ-Cl)(μ-CH), 34 shows that the $\sigma$ and $p^\parallel$ orbitals of carbyne are involved in M-C bond formation. The $p^\parallel$ orbital of carbyne is stabilized by the $\delta$ orbital of the metallic template, leading to the Re-C-Re $\pi$ delocalization. In a $d^3$-$d^3$ metal electron count, three of
the metal based orbitals are occupied. They are $\delta^*$, $\sigma^*$ and $\pi^*$. LUMO is an M-M $\pi$ orbital. This indicates that only an M-M single bond is present in 27, along with Re-C-Re $\pi$ delocalization. The charge matrix shows a large concentration of charge in the carbynyl carbon.

Br(CO)W(μ-PF$_2$NMePF$_2$)$_2$(μ-Br)(μ-C(C$_6$H$_4$-Me))W(CO)Br, 28

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$_2$NRPF$_2$). Formally the (PF$_2$NRPF$_2$) fragment may be replaced by two PH$_3$ groups one each on the two metals. The metallic fragment becomes d$^5$-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$_3$)$_2$](μ-Br)(μ-CH), 35, shows only two of the metal
based orbitals $\sigma$ and $\pi^*$ are to be occupied ($d^2-d^2$). The $p_\perp$ orbital of carbon is stabilized because of its interaction with the $\pi$ orbital of metallic template. This orbital account for the 2 $\pi$ 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.

\[(\text{CH}_2\text{SiMe}_3)(\text{OC}_6\text{H}_3\text{Me}_2)(\text{Py})\text{Mo}_2(\mu-\text{H})(\mu-\text{CSiMe}_3), 29\]

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 $[\text{Mo(CH}_3)(\text{OCH}_3)(\text{NH}_3)]_2(\mu-\text{H})(\mu-\text{CH}), 36$

\[
\begin{array}{c}
\text{Py}(\text{OR}')\text{R'Mo} \\
\text{C} \\
\text{R} \\
\text{H}
\end{array}
\begin{array}{c}
\text{MoR'}(\text{OR}')\text{Py}
\end{array}
\]

29 $R=\text{SiMe}_3$ $R'=\text{CH}_2\text{SiMe}_3$ $R''=\text{C}_6\text{H}_3\text{Me}_2$

36 $R=R'=R''=\text{H}$

show that the M-M $\sigma$ and $\pi^*$ orbitals are occupied. The M-M $\pi$ orbital stabilizes the carbyne $p_\perp$ orbital to give $\pi$ delocalization to this compound. The corresponding antibonding combination is LUMO+3 and is mostly metal based. LUMO is a Mo-Mo $\pi^*$ 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 $\pi$ electron delocalization.

Another interesting compound is $\text{Cp}($CO$)\text{Re(\mu-NO)(\mu-C}(\text{C}_6\text{H}_4\text{Me-4}))\text{Fe(CO)}_3, 30.$\(^{3d}\) Both the bridging groups CR and NO are three electron donors as neutral ligands, but in general NO is treated
as NO⁺. The Extended Huckel calculations on the model
Cp(CO)Re(μ-NO)(μ-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(μ-COMe)(μ-
SCMe₃)Fe(CO)₃, 31²⁸ in addition to a carbyne bridge. The four
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(μ-CH)(μ-
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($\mu$-CR)($\mu$-Cl)Ru(PR$_3$)$_2$(CO), 32$^{29}$ is isolobal and isostructural to 31. EH calculations show that in 32 also the 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)$_4$]$_2$($\mu$-Br)($\mu$-CH), (CO)$_3$Fe($\mu$-CH)($\mu$-SR)Fe(CO)$_3$, Cp(CO)ClW($\mu$-CH)($\mu$-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 \((\text{CO})\text{CpFe}(\mu-\text{CO})(\mu-\text{CH})\text{Fe(CO)}\text{Cp}^+\) with ethylene occur in a least motion path which allows the donation of electron to the \(\pi^*\) orbital. 17 should not be considered as a carbynyl cation bridged complex. 26, 31 and 32 have electronic structures similar to that of \(\text{CR}^+\) 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.
3.5 References


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(b) While counting the electrons around the metals in finding the isolobal analogs, the bridging carbonyl, bridging Cl⁻ is considered as donating one electron to each metal. SR⁻ in 31 is considered to be donating two electrons each to the two metals.

(19) M-M bonding distance observed in several compounds but MO pattern precludes the possibility of M-M bonding interaction.


(b) Jemmis, E.D.; Sarma, K.S.; Pavan Kumar, P.N.V. J. Mol. Struc. (THEOCHEM) 1985, 121, 305.


(27) Many examples in which an additional MLₙ also bridging two metals are known. Detailed MO analysis of these compounds is given in chapter 4.

(b) Seyferth, D.; Archer, C.M. *Organometalics* 1985, 4, 2572.