Chapter 4: Studies on Ti₈C₁₂ Cluster and Transition Metal-Containing Poly-yne.

[4.0] Abstract ... 137
[4.1] Electronic structure study of the reactivity centres in Ti₈C₁₂ clusters ... 138
[4.2] Electronic structure studies on Transition Metal-containing poly-yne ... 161
[4.3] conclusions ... 193
Abstract

The reactivity centres of $\text{TigC}_12$ (for the three structures suggested in conformity with experimental observations) have been studied by extended Huckel theory. The $\text{C}_2$ unit can complex with transition metal fragments such as $\text{Pt(PH}_3)_2$ with the unusual net result of transferring two electrons to $\text{TigC}_12$. The metal centre, Ti can accommodate extra two-electron donors like CO. Model systems are used to explain the carbon and metal environment in $\text{TigC}_12$.

Transition metal-containing poly-ynes are studied using the tight-binding extended Huckel method. The band gap between valence and conduction bands is found to be dependent both on metal and on the bridging ligand between the two metals. Not only the substitution on phenyl ring but its topology also affects the band gap of the polymer. The cyano substitution on phenyl ring is found to be more effective in reducing the band gaps of these polymers.
[4.1] Electronic Structure study of the reactivity centres in Ti$_8$C$_{12}$ clusters

The discovery of fullerenes has given a strong boost to cluster chemistry.$^1$ Another exciting development in cluster chemistry is the observation of metallocarbohedrenes.$^2$ During reactions of Ti atoms and hydrocarbons such as CH$_4$, C$_2$H$_2$, C$_3$H$_6$, C$_2$H$_4$ and C$_6$H$_6$ in a time of flight mass spectrometer coupled with a laser vaporisation source, a dominant peak at 528 atomic mass units was observed.$^2$ In order to characterise this "super magic" peak (so called because of its high intensity), a series of studies with varying isotopic labelling was undertaken by Castleman et al.$^2$ The results showed that the cluster contains 12 carbon atoms but no hydrogens. The remaining mass has been accounted as Ti and thus the super magic peak represents Ti$_8$C$_{12}$$^+$.$^2-4$ This was further supported by high resolution distribution pattern analysis. The high intensity of the peak suggested that the neutral Ti$_8$C$_{12}$ might be equally stable. The intense activity in icosahedral clusters of various kinds led to the first suggestion of a structure based on icosahedron 1 with T$_h$ symmetry (Fig.1) for Ti$_8$C$_{12}$.$^2,5$ The gas phase "titrations" of mass selected Ti$_8$C$_{12}$ cluster with ND$_3$ in thermal reaction cell revealed that eight equally coordinated Ti sites are present in the cluster. This finding supported the structure 1 with all Ti metals exposed at the cluster surface. This is related to the familiar organic dodecahedrane C$_{20}$H$_{20}$ provided the twenty hydrogen atoms are removed.$^6$ The C$_{20}$, dodecahedrane, is expected to be highly strained species.$^7$ The pyramidality required at each carbon is considerably larger than that for C$_{60}$.$^8$ Replacement of eight carbon atoms of C$_{20}$ by Ti gives Ti$_8$C$_{12}$. As a result, the symmetry reduces to T$_h$. These
Fig. 1: Ti₈C₁₂ in Tₘ (1), D₂h (2) and Tₐ (3) symmetries, (4) and the model system Ti(HC=CH₂)₃ (5).
clusters are named as **metallocarbohedrenes** (Met-Car). Many theoretical studies have been directed to establish the structure of the first Met-Car, a Ti₈C₁₂ cluster. Geometry optimization with T₄h symmetry (1) has shown Ti₈C₁₂ to have a triplet state. The Jahn-Teller distorted structure with D₂h symmetry, 2 (Fig. 1), is calculated to be a singlet and lies lower in energy by about 28.5 kcal/mol than 1. In another study, a Ti₈ skeleton based on a face-bridged tetrahedron, was considered. This structure, 3 (Fig. 1), was optimized to be a minimum in the quintet state, and was found to be lower in energy than 1 by about 300 kcal/mol. These three structures are consistent with the experimental observations. Titration with NH₃ and CH₃OH produces Ti₈C₁₂(NH₃)₈ and Ti₈C₁₂(CH₃OH)₈, detected in mass spectral analysis. Later, the synthesis of Met-Cars has been extended so as to obtain other early transition metals (viz. V₈C₁₂, Zr₈C₁₂ and Hf₈C₁₂). Duncan et al have reported the observation of chromium, iron and molybdenum Met-Cars. In addition to these, there are also reports on mixed-metal Met-Cars.

There are several interesting features in these structures. The C₂ units in 1 and 2 are similar to those in tetrametalated ethylene with pyramidalized carbon and is reminiscent of the structure of a metal-ethylene π-complex with all the substituents of the ethylene bent away from the metal (4). This suggests the possibility of bonding arrangement for an incoming metal fragment to interact with the C₂ in Mg₈C₁₂. While isomer 2 has three different sets of C₂ units (the C-C distances are 1.299, 1.392 and 1.478Å), the basic framework in 1 and 2 is the same. Structure 3, a tetracapped tetrahedron, also presents interesting analogies. The C₂ unit is
Table 1.

Extended Huckel Parameters.\textsuperscript{25, 30}

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<th>Atom</th>
<th>Orbital</th>
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Table 2.

Important bond lengths of various isomers.\textsuperscript{9,11}

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<th>Structure</th>
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<tr>
<td>1</td>
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different from those in 1 and 2, but is similar to one of the minima calculated for tetrалithioethylene with two terminal lithiums and two bridging lithiums in the two \( \pi \)-planes.\(^{26}\)

The metal environment in 1 and 2 can be compared to that in trivinyl metal complex, with the three ligands arranged in a pyramidal fashion. This helps the metal in Met-Cars to accommodate extra ligands. There are two types of metal environments in 3. Four metal atoms form an inner tetrahedron and the other four cap the faces of this inner tetrahedron. Four Ti atoms around one \( C_2 \) unit form a butterfly arrangement with the two inner titanium atoms as the hinge. This leads to an outer metal a bonded to three \( C_2 \) units and an inner metal having \( \pi \)-interaction with three \( C_2 \) units. Keeping these structural possibilities in view, this chapter discusses the interaction of fragments such as \( \text{Pt(PH}_3)_2 \) and carbon monoxide at various sites in the Ti\(gC_12 \) skeleton. The electronic structure calculations were performed using the fragment molecular orbital approach\(^{27}\) within the extended Huckel theory\(^{28}\) with parameters given in Table 1 and 2.

The electronic structure of 1 and 2 was studied previously by \textit{ab initio} MO and density functional theory calculations.\(^9\) But the electronic structure of 3 is not known except the report of the optimized structure.\(^{11}\) This chapter deals with the electronic structure of 1, 2 and 3 with the main emphasis on assessing the reactivity centres in the cluster.
Fig. 2: Interaction diagram between Ti₈ and C₁₂ to give the energy levels of Ti₈C₁₂(1). Tₜ₈ symmetry labels are used.
Electronic structure of 1 and 2

The electronic structure of 1 is constructed by the interaction of Ti\(_g\) and C\(_{12}\) (Fig. 2). Only the important interactions are shown. The \(\sigma\) orbitals of C\(_{12}\) (2tg and 1ag) interact with Ti\(_g\) fragment leads to 2tg and 1ag, the \(\sigma\) bonding orbitals in Ti\(_g\)C\(_{12}\). The \(\pi\) bonding combinations between carbon \(n\) orbitals (1tg to 1eg) and Ti\(_g\) fragment, that is 1t\(_u\) and 1t\(_g\) in Ti\(_g\)C\(_{12}\) are lower in energy than the \(\sigma\) combination. The second set of \(\pi\)-bonding MOs (3tg, 4tg, 1e\(_u\) and 1a\(_u\)) resulting from carbon \(n^*\) orbitals (1a\(_u\) to 2t\(_u\)) lie above the \(\sigma\) levels in energy. This interaction diagram clearly shows that there is a greater contribution from carbon \(\pi^*\) levels at the frontier range. Below this, one finds the carbon \(\sigma\) contribution. The HOMO is a doubly degenerate 1e\(_u\) set with only two electrons and leads to a triplet ground state.

The electronic structure of 2 is not very different from 1. There are three groups of orbitals in 2. The group at HOMO is rich in metal d-orbitals with carbon \(n^*\) participation. The second group below this has predominantly carbon p-orbitals of the C-C bond direction along with some contribution from the metal d-orbitals. The third group which is below the second one is mainly contributed by the carbon s-orbitals. In general, these descriptions of the electronic structure of 1 and 2 agree well with the previous theoretical calculations.
Fig. 3(a): Interaction diagram between Ti$_4$ and C$_2$ to give the energy levels of Ti$_4$C$_2$ with C$_{2v}$ geometry.
Electronic structure of 3

The coordination around carbon in 3 is different from 1 and 2. To understand this new geometry at the C$_2$ unit, we have taken a smaller fragment Ti$_4$C$_2$ of Ti$_8$C$_{12}$ (3). The molecular orbitals of Ti$_4$C$_2$ are constructed from the fragments Ti$_4$ (in butterfly geometry) and C$_2$ (Fig. 3a). The symmetric combination of $a$ and the $\pi^*$ orbitals of C$_2$ are empty; whereas, the C-C $a$, the antisymmetric combination of lone pairs and $n$ orbitals are filled in C$_2$. The molecular orbitals of M4 are similar to those of the butterfly clusters. The long metal-metal distance restricts the energy spread to be small. The $\pi$ orbitals of C$_2$ ($b_1$) interact with $\varnothing$ and $4b_1$ of the Ti$_4$ unit leading to $1b_1$ and $2b_1$ of Ti$_4$C$_2$. The non-bonding $\sigma$-orbitals of C$_2$ ($a_1$) and $1a_1$ of Ti$_4$ leads to $1a_1$ of Ti$_4$C$_2$. These $1b_1$, $2b_1$ and $\varnothing$ MOs in Ti$_4$C$_2$ are responsible for $\sigma$-bonding between the outer Ti and C$_2$. these interactions mainly lead to $\pi$-bonding between the inner Ti atoms in the Ti$_4$ and the C$_2$ units. The HOMO of Ti$_4$C$_2$ is purely metal based arising from $1a_2$, which has $n$ anti-bonding interactions between the inner and outer Ti atoms. The interesting feature of this diagram is the HOMO-1 (4b$_2$) of Ti$_4$C$_2$, a bonding MO between % orbitals of C$_2$ and $z^2$ orbitals on outer Ti atoms.

With this understanding of Ti$_4$C$_2$, we proceed to form Ti$_{8}$C$_4$ by taking two Ti$_4$C$_2$ units (see Fig.3(b) for MO's of Ti$_{8}$C$_4$). The important developments during dimerization are formation of MOs viz. $1e$, $2a_2$2$a_1$, $1b_2$ and $3a_1$, corresponding to metal-metal bonds. The le and $2a_2$ MOs are responsible for bonding between inner Ti atoms. The MOs $1a_1$, $2a_1$ and $1b_2$ are mainly responsible for bonding between inner and outer Ti atoms.
Fig. 3(b): Construction of energy levels of Ti₈C₁₂ (3) from Ti₈C₄ and 4C₂ units. For Ti₈C₄ and 4C₂'s the D₂d symmetry labels are used and Tₐd symmetry labels are used for Ti₈C₁₂.
The MOs 3a\textsubscript{1} and 4a\textsubscript{1} are mainly outer Ti metal-based orbitals. In short, dimerization of Ti\textsubscript{4}C\textsubscript{2} brings in metal-metal interactions between inner-inner and inner-outer Ti metals.

\textbf{TigC\textsubscript{12}}, 3, can now be obtained by adding the remaining C\textsubscript{2} units to TigC\textsubscript{4}. Some of the important interactions in the formation of 3 are shown in Fig. 3b. The MOs of 4C\textsubscript{2} units are given on the right-hand side of the diagram. MOs 1a\textsubscript{1} and 2a\textsubscript{1} are symmetric combination of rc-orbitals of C\textsubscript{2} units. 4a\textsubscript{1} of TigC\textsubscript{4} interacts with 2a\textsubscript{1} leading to \textit{\sigma}-bonding between the outer Ti atoms and C\textsubscript{2}. 1e and 2e of the 4C\textsubscript{2} units are \textit{\pi} orbitals which interact with inner Ti atoms in a \textit{\sigma}-fashion and with outer metals in a \textit{n}-fashion. The non-bonded \textit{\sigma}-orbitals 4a\textsubscript{1}, 3e and 5a\textsubscript{1} of the C\textsubscript{2} units form mainly \textit{\sigma}-bonds with outer metals. The \textit{\pi} MOs 1b\textsubscript{1}, 4e and 5e of the C\textsubscript{2} units are mainly responsible for \textit{\sigma}-bonding with inner metals and anti-bonding \textit{\pi}-interactions with outer metals. The HOMO of 3 is triply degenerate with two electrons which makes the system susceptible to Jahn-Teller distortion. One way of stabilizing the system is by exciting one electron from 2a\textsubscript{u} to HOMO, which gives a spin multiplicity of 5,\textsuperscript{12}

\textit{Oxidation state of metal atoms in TigC\textsubscript{12}}

Each metal atom in 1 may be viewed as a trivinyl derivative. This leads to a +3 oxidation state at the metal with a d\textsuperscript{1} configuration. Similarly, each C\textsubscript{2} unit can be viewed as tetrametallated ethylene, that is C\textsubscript{2}\textsuperscript{4-}. The Mulliken charge on the metal atom is +0.41 and on C is -0.27. Isomer 2 can also be viewed in the same way as 1 since the structural features of them are similar. In 2 also, the Mulliken charge on the metal is
Fig. 4(a) and (b): Interaction diagram between (a) C₂H₄ and Pt(PH₃)₂, (b) Ti₈C₁₂ (1) and Pt(PH₃)₂.
approximately +0.41. But the C's have charges of magnitude -0.21, -0.26 and -0.34 for the three different carbons.

The oxidation states of the two types of metals in isomer 3 are different. Since each metal in the outer tetrahedron is bonded to three C₂ units, the outer metal may have a +3 oxidation state. There are four outer Ti atoms which leads to each C₂ having a -2 charge. This electron counting leaves the inner Ti atoms in a zero oxidation state as the interactions with C₂ units may be treated as π-type. But this is not in tune with the calculations which show that the inner Ti atoms have more charge than the outer ones (0.54 Vs 0.11).

Another way of counting electrons leads to the following. Each inner Ti interacts with 3C₂ units. The metal-carbon distance (2.2Å) is very close to that of a σ-bond between them (in Ti-vinyl systems the Ti-C single bond distance is 2.2Å²⁹). Thus, each inner metal is connected to six carbons; whereas, each outer one is connected to three carbons only. Formal oxidation state counting would have led to four outer metals with +3 and each inner metal with +6. But the latter is impossible in an early transition metal. This would also leave each C₂ formally as C₂⁻⁶ with a C-C single bond. The truth is somewhere in between these extremes. All that can be said safely is that the inner Ti metal is at a higher oxidation state than the outer one. The overlap population between inner Ti-C is 0.26. But between the outer Ti-C it is 0.76 due to the extra π-bonding. The C-C overlap population (1.23) shows C-C to be close to a double bond (the C-C bond distance is 1.34Å).
Fig. 4(c): Interaction diagram between Ti$_8$C$_{12}$ (3) and Pt(PH$_3$)$_2$. 

151
Carbon environment in Ti₈C₁₂. Interaction of C₂ with Pt(PH₃)₂

The carbons in a transition metal ethylene complex are pyramidalized towards the metal. The C₂ unit in 1 and 2 is pyramidalized in the same way. Even though the C₂ unit in 3 is of a different type, it is also pyramidalized. Thus, the C₂ units in Ti₈C₁₂ should act as ethylenes towards transition metal fragments. To study this type of bonding in detail, we have considered the interaction of Pt(PH₃)₂ with Ti₈C₁₂. Pt(PH₃)₂C₂H₄ is a well known π-complex where the Pt-C bond occurs mainly from the interaction of the π⁺ (b₂) MO of ethylene (Fig.4(a)) with the hybridized d-orbital (b₂) of Pt(PH₃)₂. Fig. 4 gives the interaction diagram between Pt(PH₃)₂ (with standard geometry) and isomers 1 and 3. Isomer 2 was left out due to its close resemblance to 1. The equivalent orbital of ethylenic b₂ in 1 is 3tg and 2t_u. Since 3tg is an occupied orbital unlike b₂ in C₂H₄, the interaction between 3tg and b₂ of Pt(PH₃)₂ should have caused destabilization. However, the two electrons fill the degenerate HOMO fully instead of going to an anti-bonding orbital. Thus, Pt(PH₃)₂ may be treated as a two-electron donor to Ti₈C₁₂ (1).

Structure 2 also has pyramidalized C₂ units. Out of three types of C₂ units, the C₂ unit which has a short C-C bond gives maximum stabilization with Pt(PH₃)₂. The interactions between Pt(PH₃)₂ and 2 are not very different from 1. The result is donation of electrons from the metal fragment to 2.
Fig. 5(a) and (b): Interaction diagram between (a) Ti(HOCH2)3 and (CO)3, (b) Ti8C12 (1) and (CO)3.
Though the geometry around $C_2$ unit in 3 is different from the other two, it is possible to trace pyramidalized $n^*$ orbitals. In 3, the MO 6tg is similar to $\pi^*$ of $C_2H_4$ which interacts with the $b_2$ orbital of Pt(PH$_3$)$_2$. HOMO-1 of 3 is also of appropriate energy to mix with $b_2$ of Pt(PH$_3$)$_2$. Another stabilization in this complex is from the 3eg orbitals of 3 mixing with $b\backslash$ of the metal fragment. Pt(PH$_3$)$_2$ donates two electrons on complexing with 1, 2 or 3. The two electrons from Pt(PH$_3$)$_2$ fill the LUMO of 2; whereas, they stabilize the half-filled HOMOs in 1 and 3. Therefore, the C-C overlap population values 1.10, 1.28 and 1.23 are changed to 0.94, 1.10 and 1.08 in 1, 2 and 3 respectively after complexing with Pt(PH$_4$)$_2$.

**Metal environment. Interaction with carbonyls**

Our calculations on model system Ti(CH=CH$_2$)$_3$ (5) has shown that the metal in the non-planar geometry of this complex represents the metal in Ti$_8$C$_{12}$. Since we are interested in extra ligand complexion on metal in Ti$_8$C$_{12}$, we have studied the complexation of CO on 5. Fig. 5a gives the interaction diagram between 5 and (CO)$_3$ fragments with standard titanium-carbonyl distances. The angle 80.0° was fixed between carbonyl-titanium-carbonyl. The staggered form which gives pseudo-octahedral geometry is found to be more stable. The hybridized metal orbitals in 5 are 4e, 3a and 5e. The major interactions are between 3e, 4e and 5e set of 5 and 1e and 2e set of (CO)$_3$. The $\sigma$ interactions occur between 1e and 2e of 5 and 1e of (CO)$_3$. The symmetric combination of the $7t^*$ orbitals of (CO)$_3$, (that is 3a and 3e) do not have orbitals of right symmetry to mix with 5. There is a stabilization of 10 eV in the formation of the carbon monoxide complex as judged by the change in the sum of one electron energies.
Fig. 5(c): Interaction diagram between $\text{Ti}_8\text{C}_{12}(3)$ and $(\text{CO})_3$. 
The metal contribution in 3tg and 2tg of 1 and 5tg and 2eg orbitals of 3 (which are based on the outer tetrahedron of titaniums) are similar to 5e, 4e and 3e orbitals of 5. Fig. 5 shows the interaction between Ti8C12 (in structures 1 and 3) and (CO)3, which is more or less similar to that between 5 and (CO)3. Isomer 2 also shows an interaction similar to 1. All the Ti metals in 1, 2 and outer Ti metals in 3 have shown enough capacity of complexing with carbonyls. There is an enormous stabilization of 10.20, 10.19 and 11.40 eV for 1, 2 and 3 respectively as calculated from change in the sum of one-electron energies in complexation with (CO)3.

The Mulliken charge on the metal changes drastically on complexation with carbon monoxide. The charges are from +0.41, +0.40 and +0.11 on 1, 2 and 3, to -0.08, -0.33 and -0.68 respectively after complexing with CO. These changes also indicate the electrophilic nature of the metal in the cluster. The outer Ti metal in 3 is most electrophilic, next is the metal in 2 followed by 1. There are changes in overlap population also. The M-M overlap populations of 0.10, 0.11 and 0.18 in 1, 2 and 3 decreases to 0.03, 0.05 and 0.09 respectively after complexing with CO. The M-C overlap population (0.66 and 0.75 in 1 and 3, and 0.53, 0.61 and 0.72 for, medium and long C2 units in 2) also decreases to 0.45 and 0.59 in 1 and 3, and 0.35, 0.41 and 0.48 for the three C2 units in 2. In general, this may be considered as a result of donation of electrons from carbonyl to the cluster where predominantly M-C and M-M anti-bonding MOs are at the receiving end.

We conclude that despite the structural differences, all the Ti metals in 1, 2 and outer Ti metals in 3 show the capability of complexing with
COs. It may be possible that by allowing three COs at each metal, the macro-complex Ti₈(CO)₂₄ may be obtained. Since we get a high stabilization for each (CO)₃ unit on one metal, Ti₈C₁₂ may be used as a CO absorber.

Thus, in conclusion, the Ti₈C₁₂ cluster is a highly electron-deficient species. The cluster is ready to accept electrons from traditional ligands such as CO and also from transition metal fragments. In soot obtained in the experiments of Castleman, Ti₈C₁₂ may exist as associated clusters with the interaction of Ti metal in one cluster with C₂ units in the other. Metallocarbohedrens should also be good ligands for forming large clusters.
References

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(e) Byun, Y.G.; Freiser, B.S. J. Am. Chem. Soc. 1996, 775, 3681.


The search for polymers for specific applications has been an active field of research for many years. Polymer chemistry has become an interdisciplinary field which includes purely organic polymers, inorganic complexes and also organic charge transfer salts. These polymers find many practical applications, e.g. photovoltaic devices based on poly-acetylene and (SN)x films, current and optical switching in thin films of Cu(tetracyanoquinodimethane), high density rechargeable batteries, molecular-based electronic devices, stabilization of n-type silicon photoelectrochemical cells in material science and switchable ion conducting membrane and controlled release of drugs from microelectrodes in biological science.

Recently, interest in the search for low-band-gap polymers has increased due to its conductivity and good non-linear optical properties. Among the conjugated polymers, poly(isothionaphthene) was known to have one of the smallest energy gap (E=1.0 eV) found experimentally. Theoretical calculations based on the model of Longuet-Higgins and Salem (LHS) have shown the band gaps to be of about 0.7 eV and 0.5 eV for poly (bis-isothionaphthene-methine) and poly (isonaphthothiophene-thiophene) respectively.

Conjugated polymers incorporating transition metal atoms in the main skeleton has attracted much attention in recent years. In expectation of the interesting physical properties associated with a long conjugated
Scheme 1

\[ \text{[} \text{Pt(PH}_3\text{)}_2 \text{Y-C≡C-}]_n \]

\[ \text{[} \text{Pd(PH}_3\text{)}_2 \text{Y-C≡C-}]_n \]

\[ \text{[} \text{Ni(PH}_3\text{)}_2 \text{Y-C≡C-}]_n \]

\[ \text{[} \text{Fe(PH}_3\text{)}_4 \text{Y-C≡C-}]_n \]

a) Y: none  
b) Y: C≡C  
c) Y: C≡C--C≡C

d) Y: C≡C

e) Y: C≡C

f) Y: C≡C

\[ \text{[} \text{CN-CN-}] \]

g) Y: C≡C

\[ \text{[} \text{CN-CN-}] \]

h) Y: C≡C

\[ \text{[} \text{CN-CN-}] \]

i) Y: C≡C

\[ \text{[} \text{NH}_2 \text{-}] \]
structure due to $d\pi$(metal)-$p\pi$(acetylenic carbon) interaction, novel straight-link oligomers composed of metal atoms of the platinum group and conjugated poly-yne systems have been synthesized.\textsuperscript{14}

Hagihara et al have prepared the polymers mainly of the type $[\text{M(PBu}_3\text{)}_2\text{(-C≡C-(R)-C≡C-)}]_n$ where $n>200$, $\text{M} = \text{Ni, Pd, Pt}$; $\text{R} = \text{none, p-C}_6\text{H}_4$ etc.\textsuperscript{14} They analyzed the electronic spectra of the three polymers $[\text{trans-M(PBu}_3\text{)}_2\text{-C≡C-}]_n$ ($\text{M} = \text{Ni, Pd and Pt}$) and assigned the lowest energy bands to metal to ligand charge transfer transitions which have $\lambda_{\text{max}}$ values of 342, 382 and 414 nm (that is 3.6, 3.2 and 3.0 eV) respectively.\textsuperscript{15} Later, the preparation of these metal poly-yne polymers have been extended from group 10 to group 8 and 9.\textsuperscript{16,17}

To explain the conductivity and other physical properties of these polymers, one has to know the electronic structure of these materials. To the best of our knowledge, there is only one electronic structure discussion of these polymers so far.\textsuperscript{18} In the present study, we have tried to decrease the band gap by changing the metal-metal distance (by changing the various connecting ligands in the polymer back bone), and examined some substituents on the bridging ligands.

We have taken polymers $[-\text{C≡C-Y-M(PH}_3\text{)}_m]_n$ where $\text{Y} = \text{none, C}, \text{p-C}_6\text{H}_4\text{-C≡C}; \text{M} = \text{Pt, Pd, Ni and } m = 2$ for Pt, Pd, Ni and 4 for Fe to study the electronic structure (Scheme 1). The band structures, density of states (DOS) and crystal orbital overlap populations (COOP) have been calculated using the tight-binding extended Hückel method\textsuperscript{19} (parameters are listed in Table 1 and 2).
Table 1

Extended Huckel parameters that are used in the present study\textsuperscript{20}.

<table>
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<tr>
<th>Atom</th>
<th>Orbital</th>
<th>$H_{ii}$ (eV)</th>
<th>$\zeta_1$</th>
<th>$c_1$</th>
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Table 2

Important bond lengths used in the present study.\textsuperscript{21}

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<td>C≡C</td>
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<td>C-C ((in\ phenyl\ ring)) ((sp))</td>
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<tr>
<td>NC─(\textcircled{\circ})</td>
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<td>N-H</td>
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Fig. 1(a): Energy bands of the model polymer $[\text{Pt(PH}_3)_2-\text{C}≡\text{C}]-_n$. 
\textit{Band structure of Pt polymers}

The development of bands from the molecular energy levels for the Pt polymers in our study agrees well with the previous calculations.\textsuperscript{18} Hence only the electronic structure of these polymers are discussed in this chapter. The band structure, density of states and the crystal orbital overlap populations for the polymer \textit{la} are given in \textbf{Fig.1a-e}. The projected DOS has shown that the valence bands and conduction bands are rich in contribution from metal (Fig.1b). There is a predominant participation of ligand in both the bands (Fig.1c). Scheme-2 gives the crystal orbitals corresponding to unoccupied and occupied bands of the model polymer \textit{la} at \(k = 0\) (zone center) and \(k = \pi c/a\) (zone edge).

The lowest unoccupied band, \(3b_2\), is ligand \(n\) mixed with the metal \(z\) at the zone center (\(k=0\)) in anti-bonding fashion and \(n\) of ligand mixed with metal \(z\) at zone edge (\(k=\pi a\)) in a bonding fashion (Fig. 1, Scheme 2). The anti-bonding interactions decrease and development of bonding interactions increase between the metal and the ligand as \(k\) changes from 0 to \(\pi /a\). The Pt-C crystal orbital overlap population (Fig.1d) shows that the bonding interactions are much stronger than the anti-bonding interactions. The crystal orbital overlap population between the two carbons of acetylene shows that it is of anti-bonding type (Fig.1e). In summary, the unoccupied band, \(3b_2\), is a ligand \(n\), in bonding fashion with the metal \(z\) orbital.

At the Fermi level, the valence bands \(2b_1\) and \(2b_2\) are metal \(xy\) and \(yz\) anti-bonding bands with very little energy difference between them.
Scheme 2

K=0
Unoccupied bands:

3b₂

occupied bands:

1a₁

K=π/a

occupied bands:

2b₁

K=0

occupied bands:

K=π/a

H₃P–Pt–PH₃
Ligand $\pi_1$ and $\pi_2$ orbitals mix with the metal xy and yz (Scheme 2). These interactions are very weak bonding type at zone center ($k=0$), and ligand is in $\pi^*$ character (Scheme 2). While at zone edge the ligand $\pi$ orbitals interact with metal orbitals in an anti-bonding fashion. The crystal orbital overlap population shows strong anti-bonding between platinum and carbon and bonding between the two carbons of the acetylene (Fig.1d,e). This indicates that the nature of the polymer at the Fermi level is $\pi$ anti-bonding between ligand and the metal with a bonding interaction within the ligand (acetylene).

$2a_1$ and $1a_2$ bands are flat without any change in the slope of the bands, as $k$ changes from 0 to $\pi/a$ (Fig.1a). These two bands are purely metal based $xz$ and $z^2$ whose symmetry does not allow any interaction with the bridging ligand for polymer propagation. This makes these bands to be unaffected throughout the Brillouin zone.

$1b_1$ and $1b_2$ are the pure ligand $\pi$ bands at the zone center. There is development of bonding interaction between these ligand $n$ and metal $xy$ and $yz$ as $k$ changes from 0 to $\pi/a$. This makes these bands to get stabilized at the zone edge. The band $1a_1$ is a bonding interaction between metal $x^2-y^2$ and ligand $a$ orbital at zone center; while, at zone edge it is bonding with metal $y$. As the metal $p$ orbitals are relatively high in energy than the metal $d$-orbitals, this band goes up in energy at zone edge. Pt-C and C-C (acetylene) crystal orbital overlap populations show the bonding nature within the energy range of these three bands (Fig.1d,e).
Fig. 1(b): Projected DOS of Pt (shaded part) in \([\text{Pt(PH}_3\text{)}_2\text{-C}\equiv\text{C-}]_n\) polymer.
Fig. 1(c): Projected DOS of acetylenic carbon (shaded part) in [Pt(PH$_3$)$_2$-C≡C-]$_n$ polymer.
Fig. 1(d): The crystal orbital overlap population between Pt and acetylenic carbon in $[\text{Pt(PH}_3)_2-\text{C=C-}]_n\text{polymer}$. $\varepsilon_f$ denotes Fermi energy level.
Fig. 1(e): The crystal orbital overlap population of C=C in $[\text{Pt(PH}_3)_2\text{-C=C-}]_n$ polymer. sf denotes Fermi energy level.
So far, we have discussed the band structures of model platinum mono acetylenic polymer \([Pt(PH_3)_{2-C≡C-}]_n\) la. Now, let us increase the unit cell size and the distance between the metals in the polymer by increasing the length of the bridging ligand. For this purpose, the polymers that have been taken are 1b and 1c (Scheme 1). 1b is a model for experimentally prepared polymer \([Pt(PBu_3)_{2-C≡C≡C-}]_n\) known as diacetylenic polymer. Similarly, 1c is also a model for experimentally known triacetylenic polymer \([Pt(PBu_3)_{2-C≡C≡C≡C-}]_n\).

The projected DOS of platinum is more at the Fermi level in 1b similar to that of polymer la. The Pt-C and C-C crystal orbital overlap populations are also similar to that of la. The band structures of this polymer may be described as if the second half of the band structure of Fig.1 were folded onto its first half. Since the unit cell for 1b is not exactly double of that of la, there are large adjustments in folding back. This folding back appears only for the bands in which the acetylenic participation is large. As the unit cell of 1b does not contain another platinum, the bands which are mainly metal based were not affected. The lowest unoccupied band is ligand \(n^*\) and the valence bands are metal xy and yz anti-bonding degenerate bands at the Fermi level. The crystal orbital overlap population of acetylenic \(\pi\)-orbitals has shown its participation at conduction band as well as at valence band. The crystal orbitals are same as in Scheme 2 except by increased number of carbons. These results are in tune with the experimental findings for \([-Pt(PBu_3)_{2-C≡C≡C-}]_n\), the lowest energy band in the electronic spectra is the metal to ligand charge transfer.
Polymer 1c also shows the similar trend, the unoccupied band is based on ligand $\pi^*$ and the valence bands are predominantly from the metal xy and yz antibonding combinations. The crystal orbital overlap population of acetylenic $\pi$-orbitals has also shown similar results like polymer 1b. Crystal orbitals for this polymer are similar to that of Scheme 2, except for increased number of carbons.

In the process of changing the bridging ligand, we have done the calculations for the polymers 1d, 1e, 1f, 1g, 1h and 1i (Scheme 1). All these polymers have shown results similar to that of 1a. The results of 1d agree well with the previous calculations. The conduction band is ligand $\pi$ mixed with the metal $z$ in bonding fashion. Valence band is not degenerate in these cases as the $C_2$ symmetry is missing in these polymers. In all these polymers, metal based $yz$ interacting with ligand $n$ is the valence band at the Fermi level. All cyano substituted polymers have lost their anti-bonding interactions between metal $yz$ and ligand $n$ and have become non-bonding as the valence band runs from $k = 0$ to $k = n/a$. In the case of amino substituted polymer, the metal participation was lost in valence band and it became pure ligand $n$ band as $k$ changes from 0 to $n/a$. These are the important changes of these polymers when compared to the polymer 1a.

*Band structures of Pd and Ni polymers*

To examine the effect of metal on the electronic structure of these polymers, we have done some calculations with Ni and Pd in group 10. The polymers that have been taken are 2a, 2b, 2d and 3a, 3b, 3d in the nickle group (Scheme 1).
The lowest unoccupied bands of palladium polymer, 2a, are ligand $n^*$ in bonding interactions with the metal $z$ and ligand $\sigma_u$ in anti-bonding interactions with metal $x^2-y^2$ (3a). Similarly, in the case of Ni (3a), the lowest unoccupied band is ligand $\pi^*$ in bonding interaction with metal $z$ which is similar to 1a. The 3a band is stabilized from $k = 0$ to $k = \pi/a$ in all the polymers 1a, 2a and 3a. It is ligand $\sigma_u$ mixing with metal at the zone center; while, ligand $\sigma_u$ is mixing with metal $x^2-y^2$ at zone edge. In the case of palladium (2a), 3a is stabilized more as $k$ changes from 0 to $n/a$ and mixes with 3b at zone edge. The valence bands are degenerate xy, yz for 2a and 3a at Fermi level as in the case of 1a. In both the cases, the 1a band rose in energy from $k = 0$ to $k = \pi/a$ similar to that of 1a. For 2a the increase in energy of 1a is to such an extent that it reaches between 2a (z$^2$) and 1a (xz) at zone edge. While, in the case of 3a, 1a further rises and is above the 2a and 1a and below 2b and 2b. This shows that the change in energy of 1a from zone center to zone edge increases from platinum to nickel (1.3, 1.6 and 1.7 eV for platinum, palladium and nickel respectively). This is may be due to the following: the band 1a is ligand $\sigma_p$ in bonding interaction with metal $x^2-y^2$ at zone center. At zone edge, it is $\sigma_g$ in bonding interaction with metal $y$. The sp hybridization also increases in acetylene as we go from 1a to 3a.

The lowest unoccupied bands and valence bands of 2b and 3b are similar to those of 1b. 2a (z$^2$) and 1a (xz) are not degenerate in nickel (3b) and palladium (2b) polymers; while it is degenerate in platinum polymer (1b). The conduction and valence bands of polymers 2d and 3d
are also similar to those of 1d. The polymers 1d, 2d and 3d have narrow energy bands when compared to 1a, 2a, 3a and 1b, 2b and 3b.

**Band structures of Fe polymers**

In the process of studying the acetylenic polymers with different metals we have taken some acetylenic polymers of iron to analyze their band structures. Since iron is much cheaper than the platinum group metals, the polymers of iron will be much more attractive commercially.

Band structures, density of states and crystal orbital overlap populations of polymer 4a are given in Fig.2a-e. Scheme 3 gives the crystal orbitals corresponding to unoccupied and valence band of the polymer 4a at k = 0 (zone center) and k = 7t/a (zone edge). Projected DOS of iron is rich in valence bands; whereas, the projected DOS of ligand n is rich in conduction band (Fig.2b,c).

The lowest unoccupied band, 3e, is doubly degenerate ligand n* at Fermi level. Crystal orbital overlap population of acetylene shows that it is strongly anti-bonding at conduction band (Fig.2e). Similarly, the Fe-C crystal orbital overlap population is also strongly anti-bonding (Fig.2d). The \( \pi^* \) orbitals of ligand mix with metal xz and yz in an anti-bonding fashion at zone center (k=0). Metal participation decreases as k changes from 0 to \( \pi/a \); and finally, at zone edge, it disappears leaving 3e as the pure ligand n* (scheme 3).
Fig. 2(a): The energy bands of the Polymer [Fe(PH$_3$)$_4$-C≡C-]$_n$. 
Scheme 3

Unoccupied bands:

\[ K=0 \quad K=\pi/a \]

1e

2e

Occupied bands:

\[ K=0 \quad K=\pi/a \]

C

H₃P

Fe

H₃P

PH₃

PH₃

H₃P

Z

Y
Fig. 2(b): The projected DOS of Fe (shaded part) in $[\text{Fe(PH}_3)_4\text{-C=C-}]_n$ polymer.
Fig. 2(c): The projected DOS of acetylenic carbon (shaded part) in $[\text{Fe}(\text{PH}_3)_4-\text{C}=\text{C}-]_n$ polymer.
Fig. 2(d): The crystal orbital overlap population between Fe and acetylenic carbon in [Fe(PH₃)₄-C≡C-]ₙ polymer. Ef denotes the Fermi energy level.
Fig. 2(e): The crystal orbital overlap population of $\text{C}≡\text{C}$ in $[\text{Fe(PH}_3)_4\text{-C}≡\text{C-}]_n\text{polymer}$. $\epsilon_f$ denotes the Fermi energy level.
At Fermi level, the valence band 2e is doubly degenerate with metal xz, yz anti-bonding combinations. Ligand $\pi_1^*$ and $\pi_2^*$ mix with metal xz, yz in bonding fashion at zone center (k=0). On the other hand, ligand n\ and $\pi_2$ mix with metal xz, yz in anti-bonding fashion at the zone edge (k=n/a) (scheme 3). The Fe-C crystal orbital overlap population has shown that it is strong anti-bonding between iron and carbon (Fig.2d). The crystal orbital overlap population between the two carbons in acetylene is bonding type (Fig.2e); that is, the n bonding between metal, and ligand and the n anti-bonding within the acetylene which is shown at the zone center is very transient. The anti-bonding interactions between the metal and the ligand and the bonding interactions within the acetylene will be dominant as k changes from 0 to $\pi/a$. In summary, the valence band is rich in metal participation and is anti-bonding with ligand n orbitals.

Pure metal (xy) band 1b₂ is not effected as k changes from 0 to n/a. The doubly degenerate ligand $\pi$ band (1e) runs down in energy from zone center to zone edge. It is pure ligand $\pi$ at k = 0; at k = n/a, ligand n mixes with metal xz and yz in bonding fashion (scheme 3). Projected DOS of iron shows that the participation is less in this band (Fig.2b). Fe-C and C-C crystal orbital overlap populations support bonding interactions within acetylene and between metal and ligand (Fig.2d,e). The 1a₁ band is pushed up in energy when k changes from 0 to n/a. At the zone center, metal z² interacts with ligand $\sigma_{py}$, while at the zone edge metal $p_y$ mixes with ligand $\sigma_{py}$ (Scheme 3).

As in the case of platinum, we have increased the unit cell size by increasing the number of acetylene groups in the polymer for bridging
ligands. The polymers that have been taken in this process are di and tri-acetylenic polymers 4b and 4c (Scheme 1). Similar to that of polymer 4a, the metal participation is rich in valence band and ligand $\pi$ participation is rich in conduction band. Lowest unoccupied bands are doubly degenerate ligand $\pi^*$ and valence bands are doubly degenerate metal $xz$ and $yz$ antibonding bands at Fermi level. This is similar to those found for mono acetylenic polymer, 4a.

In the process of changing the bridging ligands in the polymers, we have taken 4d, 4g and 4i (Scheme 1) for calculations to see the effect of the substituents in the 8th group. The results in 4d are similar to the previously known calculations. In these polymers, the valence and conduction bands are not degenerate as in 4a, due to the loss of $C_{4v}$ symmetry. At the Fermi level, the characteristics of the conduction and valence bands are similar to those of 4a. The conduction band is ligand $n^*$ and the valence band is having an antibonding interaction between the ligand $\pi$ and the metal $xz$. The valence band has lost its metal participation as $k$ changes from 0 to $n/a$ in the case of 4i; while, in the case of 4d and 4g, the antibonding interactions between metal and ligand have changed to nonbonding interactions. These results are very much similar to that of the platinum analogues.

Band gap as a function of bridging ligand and metal

The band gaps for various polymers are given in Table 3. Experimental results (wherever available) have been given in parentheses for substituted systems. The band gap decreases as we go from mono
Table 3: Calculated Band gaps for various polymers in the present study.

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<th>Band gap (eV)</th>
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*The values in parentheses are experimental results (ref. 15)*
acetylene (1a) to diacetylene (1b) and then to triacetylenic (1c) polymers. That is, by increasing the distance between the metals in the polymer the band gap is getting decreased. The lowest charge transfer electronic spectra of polymer [Pt(PBu3)2-C4-]n has been found at 414 nm (3.0 eV).15 For triacetylenic polymer, the minimum excitation energy is 2.7 eV.15 Our calculations have shown that the band gap for diacetylenic and triacetylenic model polymers is 2.4 eV and 2.2 eV respectively, indicating general agreement with the experimental results. Among the conjugated polymers, band gaps have been decreased by C=C back bone alteration and substituents.12 We have seen the same effect in the polymers 1d, 1e, 1f, 1g, 1h and 1i. When one acetylenic group in substituted by benzene in triacetylenic polymer, the band gap decreases from 2.2 eV to 2.1 eV. However, it is not a large decrease. Substitution of one cyano group on benzene ring in 1e decreases the energy gap to 2.0eV. If two cyano groups are at meta position (1f), the band gap is 1.9eV. When the two cyano groups are para to each other (1g), the decrease in band gap is large (the gap is 1.7eV). This shows that not only the substituents but also the topology of the substituents effect the band gaps. The band gap for ttracyano substituted phenyl polymer, 1h, is not up to the expectation. Amino substituents (1i) also have caused small band gaps; but, the changes are not as dramatic as for cyano substituents. Ni and Pd also have shown the same trend as Pt.

The band gap for 1f is 1.9eV; while, for 1g it is 1.7eV. The only difference between the two polymers is the topology of cyano groups. In 1f, the cyano groups are in meta position to each other; whereas, in 1g, cyano groups are in para position to each other. The change in the band structure
for these polymers is stabilization of conduction band. The conduction band of lg is lower in energy compared to the conduction band of 1f at Fermi level. The decrease in energy of conduction band from 1f to lg is 0.2eV. This is the difference that has been projected in the band gaps. The main change that has effected the conduction band of these two polymers is overlap between the phenyl and cyano groups. The overlap is more in lg compared to that of 1f. The crystal orbital overlap population for lg is 1.0; whereas, for 1fit is 0.5. This supports the decrease in energy of conduction band at Fermi level in lg compared to that of 1f.

In the case of Fe polymers, the decrease of band gap is sharp as we change the bridging ligands. From mono acetylenic polymer to diacetylenic polymer, the decrease in band gap is 1.6 eV. From diacetylenic to triacetylenic, the change is 0.6 eV. But, from 4c to 4d, the change is only 0.2eV. In the Fe polymers also, the substituents on phenyl groups have effected the band gaps. Two cyano groups in para to each other on phenyl, lg, has the band gap of 1.3 eV; whereas, for amino groups, 4i, the band gap is 2.0 eV.

Thus, present studies show that in the [Pt(PH3)2-C=C-]n polymer the valence band is mainly metal based and the conduction band mostly ligand based. Other polymers of the Pt with increased number of C2 units have also shown similar results. Therefore, the lowest energy band in the electronic spectra is the metal to ligand charge transfer, which is in tune with the experimental finding. Ni and Pd also have shown similar results. In the case of Fe polymer (4a) the conduction band is purely ligand based π* and the valence band is rich in metal participation showing the
similarities with the polymer 1a. When the bridging ligands are changed from one $C_2$ unit to two and three $C_2$ units, there is a general decrease in the band-gap. Not only the substitution on phenyl ring but also the topology of the substitution on phenyl ring also effects the band gap of the polymer. The cyano substitution is found to be more effective in reducing the band gaps of the polymer.
References


    (d) Akita, M.; Terada, M.; Oyama, S.; Moro-oka, Y. Organometallics 1990, 9, 816.
Theoretical calculations using extended Huckel method on $\text{Ti}_8\text{C}_{12}$ has shown the following results.

i) $\text{Ti}_8\text{C}_{12}$ cluster is found to be highly electron deficient species.

ii) The $\text{C}_2$ units in structures 1, 2 and 3 interacts with the transition metal fragment $\text{Pt}(...)$, with a net effect of electron transfer from $\text{Pt}(...)$ to $\text{Ti}_8\text{C}_{12}$.

iii) Despite the structural differences all the Ti metals in 1, 2 and outer Ti metals in 3 showed the capability of complexing with CO's.

iv) Due to the high electron deficient nature, $\text{Ti}_8\text{C}_{12}$ may exist as associated clusters in soot.

The band structure calculations on metal-containing poly-yne polymers have shown the following results.

i) The valence band is found to be metal based and the conduction band is found to be mainly ligand based, hence the lowest energy band in the electronic spectra is the metal to ligand charge transfer which is in accordance with the experimental findings.

ii) The band gap between valence and conduction bands depends on both the metal and the ligand.

iii) The calculated band gaps in model polymers $1b, 1c, 2b$ and $3b$ have reproduced the general trends found in experiments.

iv) The dicyano substitution on phenyl ring is found to be more effective in decreasing the band gap of these polymers.