Carbene, Alkylidene & Carbyne Ligands

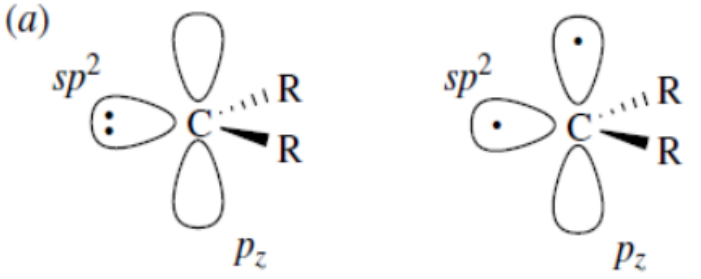
M. Sc. Chemistry – 4th Sem (Ia)
Ph. D. Course Work/NET/JRF CSIR

Prof. (Dr.) Naresh Kumar
University Dept. of Chemistry
B. N. Mandal University, Madhepura

Metal Carbene Complex

Organic species having only six electron on C-atom in its valance shell containing to non-bonding electron is called carbene ligand. It may be paired which spin multiplicity (Sm=2S+1=1) is singlet or unpaired electron is spin multiplicity is triplet. It is two electron donor. Complexes containing carbene ligands are called carbenoids. So there are two types of Carbene

(i) Fischer Type Carbene
(ii) Schrock Carbene

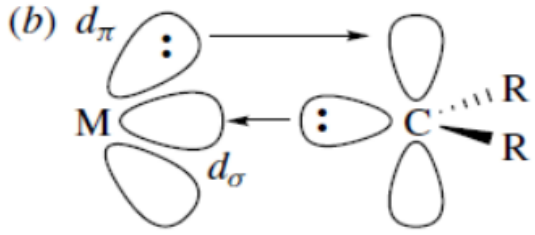


Singlet carbene

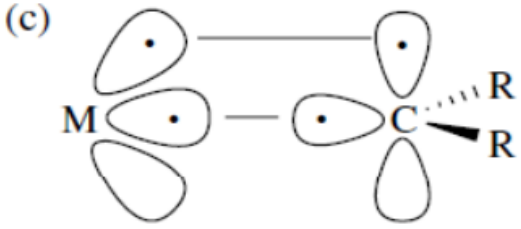
Non-bonding e- are paired
Sp2 hybrid
-Dimagnetic
-Sm=1
Less stable

Triplet carbene

NBE are unpaired
Sp2 Hybrd
Sm=3
Paramagnetic
More stable



Fischer carbene

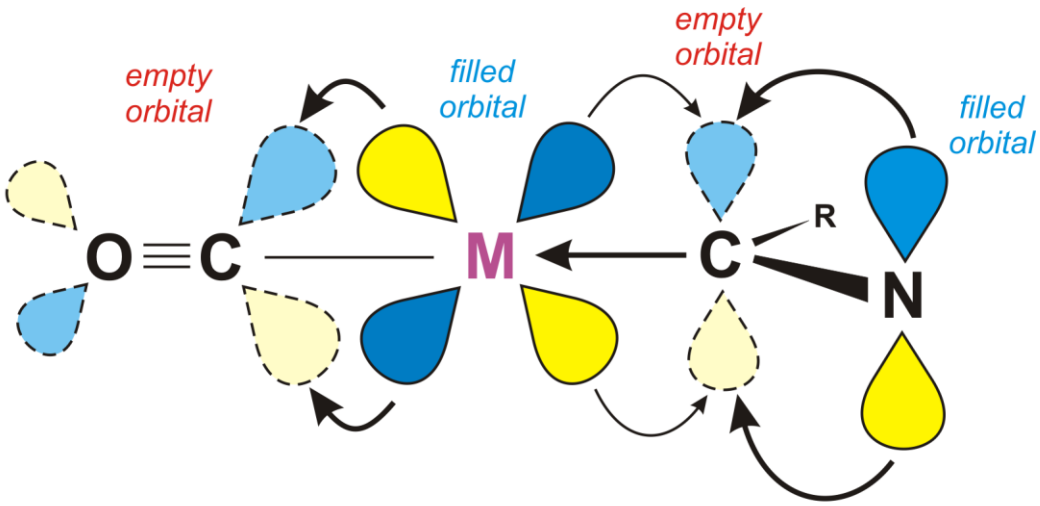


Schrock carbene

Stability of carbene depends upon nature of R attached with carbon. It may be similar or disimilar group. It may be electron with drawing group (F, Cl etc) or electron releasing group (OH, OR, NH_2 etc).

Fischer Carbenes

The bonding description commonly used to describe Fischer Carbenes is to treat the carbene as a neutral 2e- donor ligand that really only makes a single bond to the metal. In considering the carbene as a neutral ligand, it has one filled orbital (***sp*²** hybrid) that donates its lone pair to an empty orbital on the metal in a typical ligand fashion. But it also has one empty orbital (pure ***p*** character) that wants to interact with a lone pair of electrons in order to form a stabilizing bonding interaction. This is a singlet state carbene formalism and the possible orbital interactions are shown below:



competition for π-backbonding from the metal and the lone pair orbital(s) on the functional group(s) to the carbene empty orbital (N and S the best, then O, Ph, and other π-donating or lone pair containing groups)

If the metal is electron deficient (perhaps due to all the good π-acceptor CO ligands) then it **can't** π-donate very well to the carbene. Thus we end up with a M-C single bond (*even though we draw a double bond*!) and some multiple bond character between the carbene carbon and the π-donor groups attached to it (like a NR_2, OR, SR, Ph, etc).

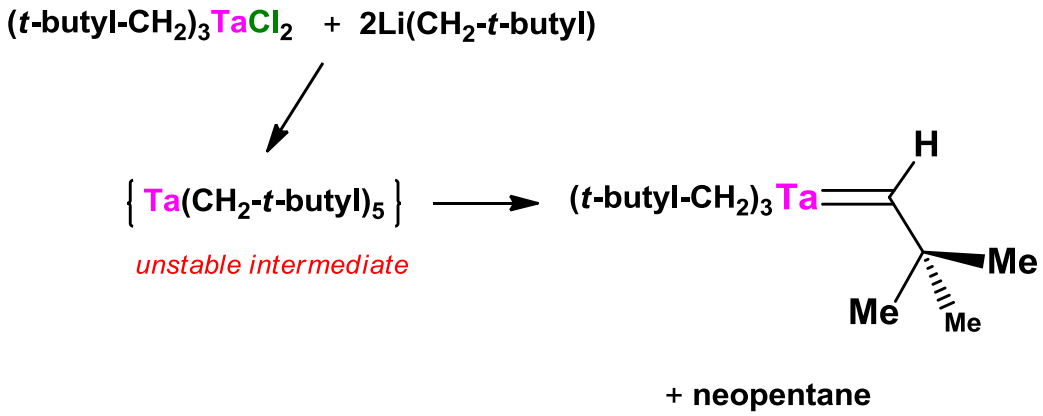
Most Fischer Carbenes have d^6 metal configurations (assuming that we electron count the carbene ligand as a neutral 2 e- donor), but d^4 and d^8 systems are known.

The bond strength in Fischer Carbenes depends on several factors:

	Weak M=C	**Strong M=C**
Metal	Electron-deficient (electron withdrawing ligands like CO, NO, 1st row metal, electronegative metal)	Electron-rich (electron donating ligands, 3rd row metal)
Carbene groups	Good donating groups that can π-bond to the carbene (like NR_2, SR, OR, Ph); *more than one donating group really weakens the M-C bond*!!	Simple sigma donors like H or CH_3 that can't π-donate to the Carbene carbon atom.

Schrock Alkylidenes

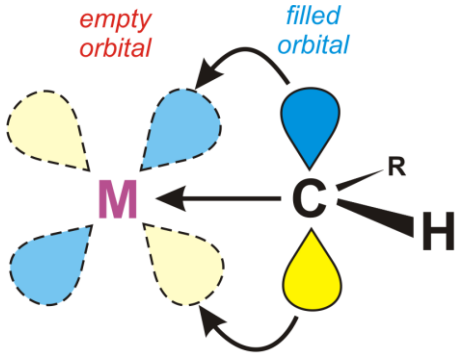
In 1973 Richard Schrock, prepared the first early transition metal complex with a metal=carbon double bond:



Fischer Carbenes	**Schrock Alkylidenes**
Nucleophillic attacks at carbon atom of carbene (carbon is electron deficient)	Electrophillic attacks at carbon atom of alkylidene (carbon is electron-rich)
Electrophillic attacks on metal center (metal is more electron-rich, often d^6 18 e- system)	Nucleophillic attacks on metal center (metal is electron-deficient, usually d^2 or d^0 16 or 14 e- count)
Carbene is *stabilized* by heteroatom groups that can π-bond to it. Likes NR_2, SR, OR, or Ph groups.	Alkylidene is *destabilized* by heteroatom groups that can π-bond to it. Strongly prefers H or simple alkyl groups.
Later transition metals favored, especially with d^6 counts (carbene as neutral 2e- donor ligand)	Early transition metals favored, especially with d^0 centers (alkylidene as dianionic 4e- donor)

The bonding description commonly used to describe Schrock Alkylidenes is to treat the alkylidene as a dianionic 4e- donor ligand, which is what the electron counting and valence rules from the first chapter would indicate.

The filled *p*-orbital on the alkylidene carbon nicely explains the tendency for electrophiles to attack at this site, while in a Fischer carbene this same orbital is formally empty and thus susceptible to a nucleophillic attack.

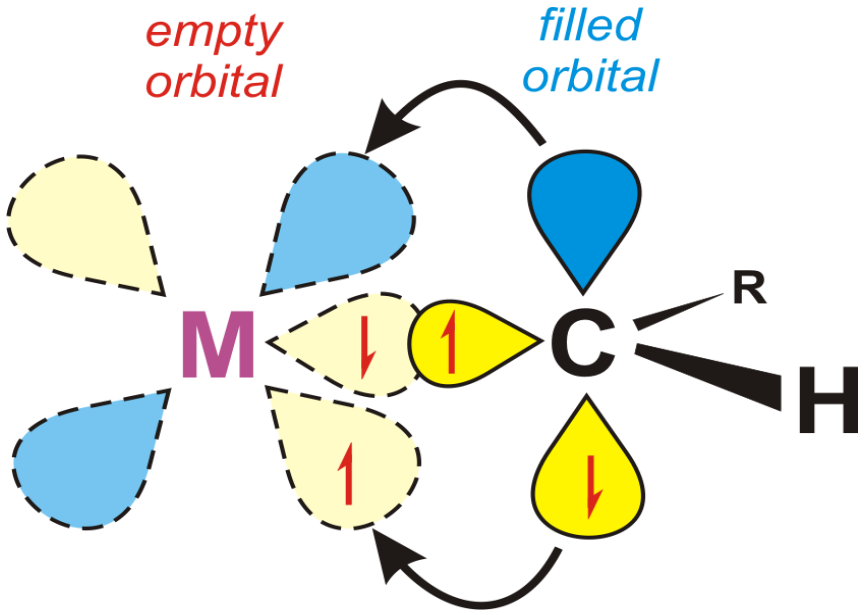


both the sp^2 and p orbitals on the alkylidene are filled (thus the -2 charge) and both can strongly donate to the empty orbitals on the early transition metal (only one empty d orbital is shown)

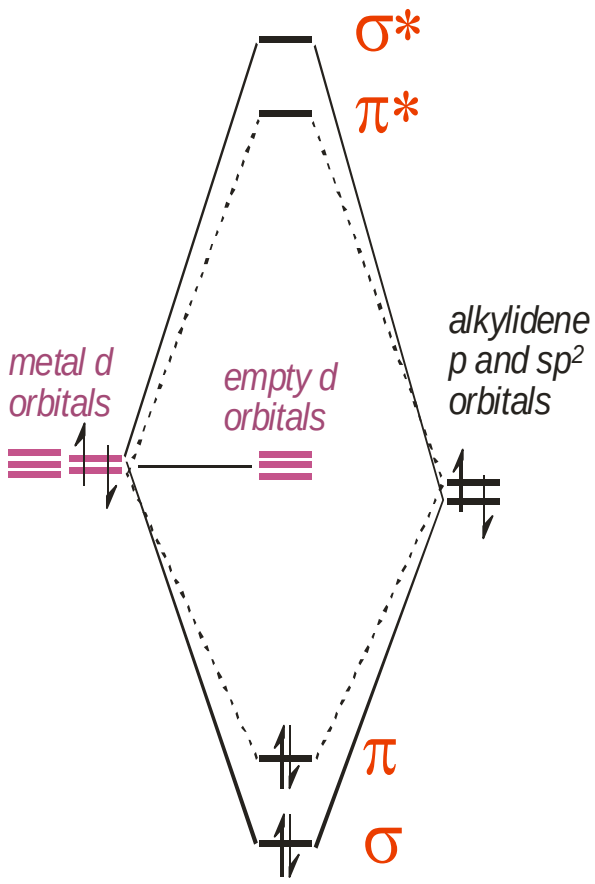
Similarly, the d^0 metal center in the typical Schrock alkylidene usually only has a 12 to 16 e- count (often 14 e-), this means that there are several empty low energy orbitals that are very attractive to any nucleophile that can sterically access the metal center. In Fischer carbenes, the metal is typically d^6 and 18e-, thus there are no empty orbitals on the metal for a nucleophile to attack.

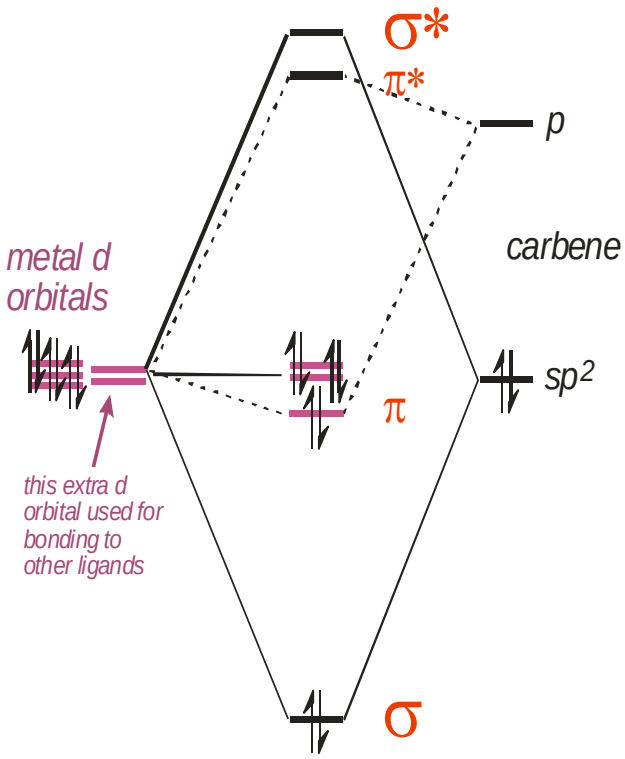
One other way to view a Schrock alkylidene is as a neutral ligand, just as with a Fischer carbene, but that it is in the triplet carbene state and interacting with a spin unpaired d^2 metal center:

The view of an alkylidene as a neutral triplet carbene forming a strong covalent double bond to a triplet metal center is very analogous to the covalent C=C double bond in organic chemistry.



Molecular orbital (MO) diagrams for generic Schrock alkylidene and Fischer carbene ligands are shown below starting with both carbon fragments as neutral triplet (alkylidene) and singlet (carbene) groups:





Schrock alkylidene
Metal = d^2
alkylidene triplet state
(Ta^{3+}, Nb^{3+}, etc)

Fischer carbene
Metal = d^6
carbene singlet state
(Cr^0, Mo^0, Re^{+1}, etc)

Note that the higher energy early transition metal orbitals match up much better with the higher energy triplet alkylidene orbitals – this leads to considerably stronger covalent bonding (both MO diagrams are on the same energy scale).

So How Should I Electron Count??

The various methods of electron-counting carbenes and alkylidenes are:

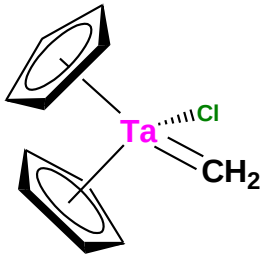
1) both as neutral 2 e- donor ligands (but still draw a M=C double bond)

2) both as dianionic 4 e- donor ligands

3) Fischer carbenes as neutral 2 e- donor ligands. Typically group 6 or higher metals with a d^6 or d^8 electron count (sometimes d^4).

4) Schrock alkylidenes as dianionic 4 e- donor ligands. Typically group 4 or 5 metals with d^0 electron counts. Also later transition metals in high oxidation states (d^0, d^2, or d^4).

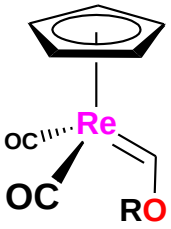
Example: Identify the following complexes as Fischer carbene or Schrock alkylidene.



neutral carbene

Ta(+3)	d^2
2 Cp^-	12 e-
Cl^-	2 e-
CH_2	2 e-
	18 e-

d^2 early TM using neutral carbene indicates a Schrock alkylidene complex



neutral carbene

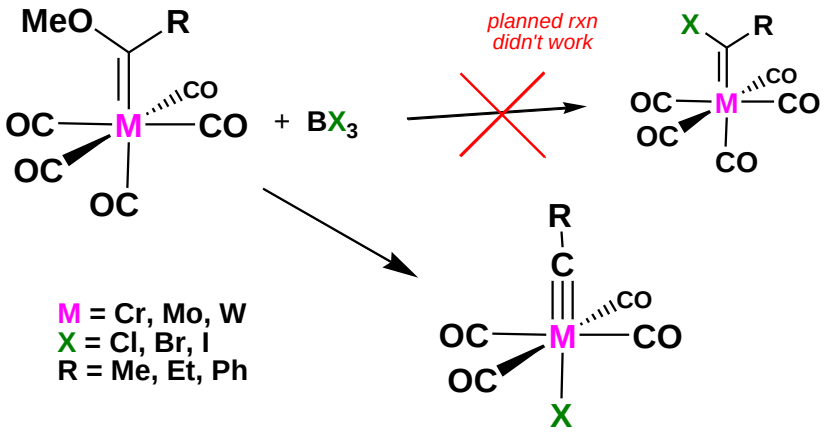
Re(+1)	d^6
Cp^-	6 e-
2CO	4 e-
C(OR)H	2 e-
	18 e-

d^6 mid-TM using neutral carbene indicates a Fisher carbene complex

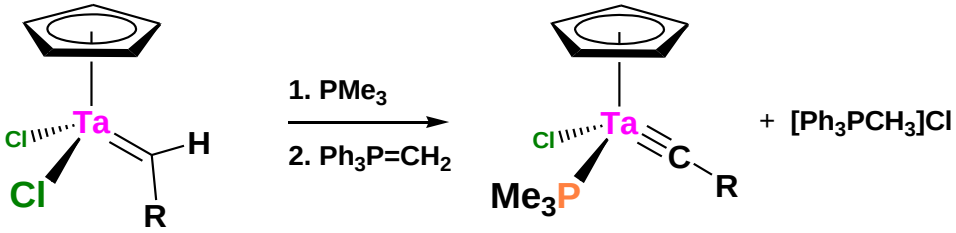
Carbynes/Alkylidynes

The two π-bonds available in alkynes, either only one or both may be donated to a metal to form carbine complex. Alkynes have two π bonding and two π* antibonding orbitals, which are quite capable of interacting metal orbitals. Out of these one or two electron pairs may be donated to metal atom. It is assumed that these are utilized in a mononuclear complex eg. in Mo (Meso. tetra-p-tollyl porphyrin) (HC≡CH). The two π-bonds in acctylenes are placed perpendicular to each other, hence these can not function as a bidentate ligand easily. Only in binuclear complexes these can be utilized for linking two metal atoms, e.g. dicobalt octa carbonyl when reacts with acetylene, it links as a bidentate ligand replacing two molecules: $Co_2(CO)_8 + HC{\equiv}CH \rightarrow Co_2(CO)_6(C_2H_2) + 2CO$ In this complex two π electron pairs are donated to cobalt atom and HC≡CH molecule forms a bridge between two cobalt atoms. Similar to carbonyl complexes, these complexes also follow EAN – rule.

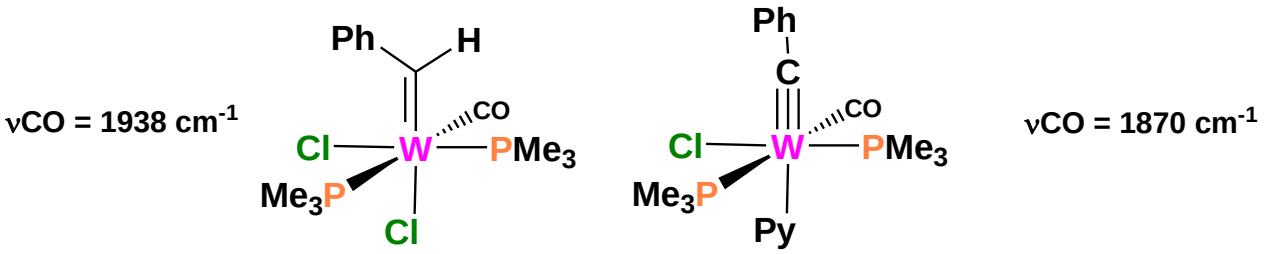
E. O. Fischer accidentally prepared the first M≡C-R triple bonded compound in 1973:



He called this a carbyne after alkyne, which refers to a C≡C triple bond. Early transition metal versions were prepared first by Schrock in 1978 via α-deprotonation of the alkylidene:



These were called alkylidynes by Schrock. Fortunately, while there are some differences between early and later transition metal carbon triple bonds, we can treat them as basically being the same. Thus, one can simply treat carbynes and alkylidynes as trianionic (-3) 6e- donating ligands. They are very strong donors as might be expected from the relatively low electronegativity of carbon and the -3 formal charge.



Methods of Preparation

Simple method of their preparation involve replacement of carbonyl etc. from metal complexes by alkyne:

(a) $M(CO)_6 + RC \equiv C\ R' \xrightarrow{UV} M(CO)_5\ (RC \equiv CR') + CO$
$(M = Mo, W)$

(b) $Mn(CO)_3\ (\eta^5 - C_5H_5) + RC \equiv CR \rightarrow Mo\ (RC \equiv CR)(\eta^5 - C_5H_5)_2 + CO$

(c) $MC(CO_3)(\eta^5 - C_5H_5)_2 + Ph\ C \equiv C\ Ph \xrightarrow{UV}$

$Mn(CO)_2(\eta^2 PhC \equiv CPh)(\eta^5 - C_5H_5) + CO$

(d) $Fe(CO)_5 + RC \equiv C\ R \rightarrow Fe(CO)_4(\eta^2 - RC \equiv CR) + CO$

(e) $MH_3(\eta^5 - C_5H_5)_2 + RC \equiv CR \rightarrow MH(\eta^5 - RC \equiv CR)(\eta^5 - C_5H_5) + H_2$

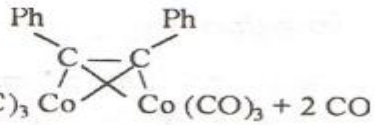
$(M = Nb, Ta)$

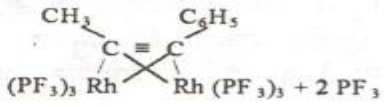
(f) $K_2\ Pt\ Cl_4 + Bu'\ C = C\ Bu' \rightarrow [Pt\ Cl\ (M - Cl)(\eta^2 - Bu^1C \equiv C\ Bu^1)_2] + 2KCl$

(ii) Reactions in which ethyne molecule replaces two monodeutate ligands:

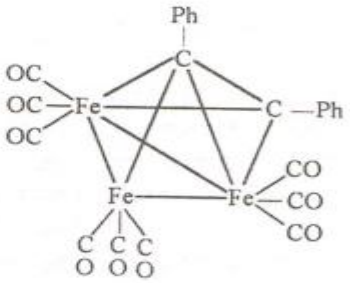
$V\ (CO)_4\ (\eta^5 - C_5H_5)_2 + RC \equiv CR \rightarrow V(CO)_2(\eta^2 - RC \equiv CR)(\eta^5 - C_5H_5)_2 + 2CO$

(iii) The two pairs of π-Electrons Donated in two Metal Atoms with the Alkyne Functioning as a Bridging Ligand:

(i) $Co_2(CO)_8 + Ph\ C \equiv C\ Ph \longrightarrow$  $+ 2\ CO$

(ii) $Rh_2(Ph_3)_8 + CH_3\ C \equiv C\ C_6H_5 \longrightarrow$ 

In these reactions generally polynuclear complexes are formed:

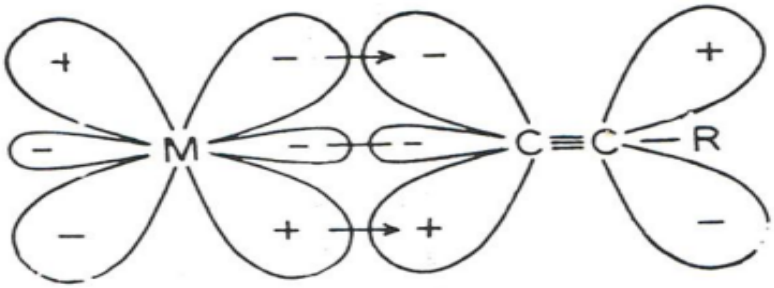
$Fe_3(CO)_{12} + Ph\ C \equiv CPh \longrightarrow$ 

The reaction of iron carbonyl with acetylene, RC≡CR often give special

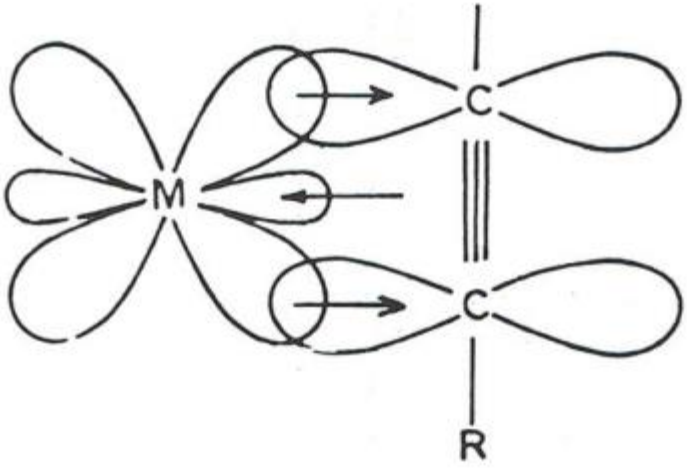
Bonding and structure

Alkynes with two π-bonds may bind metals utilizing one or both sets of π-electron pairs, thus providing greater possibilities for bonding by alkynes.

Algthough the boding in alkyne complexes could be easily interpreted in terms of Dewar – Chatt – Duncanson model, there is structural evidence that rehybridization occurs to form relatively strong σ-bonds. As the alkynylide $RC{\equiv}C^-$ is isoelectronic with NC and CO ligands, η' – alkynyl transition metal complexes containing M-C≡CR groups, may also be expected to have both σ-donor and α-acceptor character.



Bonding in transition metal-alkynyl complexes



The Dewar-Chatt Duncanson model of transition metal-alkyne bonding

In the formation of a σ-bond of the above type, the C≡C bond should be expected to become weaker; this is reflected in the lowering of the vC≡C absorption by about 150 Cm^{-1} in the metal acetylide compared to that in the free acetylenes.

X-ray structures (as the one above) usually show equal M-(μ-carbyne) bond distances completely supporting the idea that the bonding is delocalized. When there isn't M-M bonding present, most authors will draw a circle in the dimetallocyclobutane ring to indicate delocalized bonding (that doesn't necessarily mean it is aromatic, but it may be depending on the π- and *d*-electron count).

Reactions As expected, the reactivity of coordinated alkynes would be to some extent influenced by the nature of the metal involved. Thus alkyne complexes of transition metals in low oxidation states generally undergo reactions with electrophiles, while complexes of transition metals in higher oxidation states as well as cationic complexes are usually reactive towards nucleophilic moieties. A few examples of these types of behaviour are illustrated below:

(a) Displacement reactions

The displacement of one alkyne by another has been exploited for the preparation of new alkyne complexes:

$$Pt(PR_3)_2(HC\equiv CH)+RC\equiv CH \rightarrow Pt(PR_3)_2(RC\equiv CH)+HC\equiv CH$$

In these reactions the case of alkynes displacement can be represented as:
acetylene < alkylacetylenes < arylacetylenes < nitroacetylenes

The following two reactions represent two types of displacements from alkyne complexes with reagents other than alkynes:

$$Pt(PPh_3)_2(CH\equiv CH)+\underset{(excess)}{2PPh_3} \rightarrow Pt(PPh_3)_4 + HC\equiv CH$$

$$PtCl_3(HC\equiv CH)+en \xrightarrow{THF} [PtCl(en)(HC\equiv CH)]^+ Cl^-$$

Reaction on double bond of coordinated alkene:

(ii) Alkyne complexes also undergo a number of other interesting reactions, involving, for example, oligomerization and hydrometallation, e.g.:

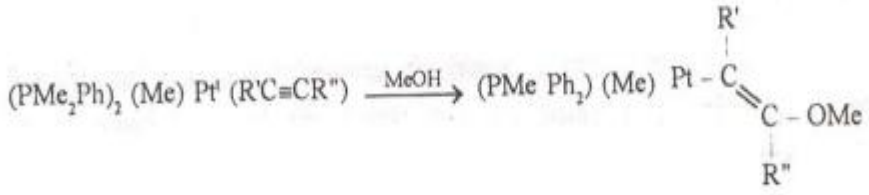
$$RC \equiv CH \xrightarrow{Pd(II)} [RC \equiv C - Pd^{II}] \xrightarrow[R'OH]{CO} RC \equiv CCO_2R'$$

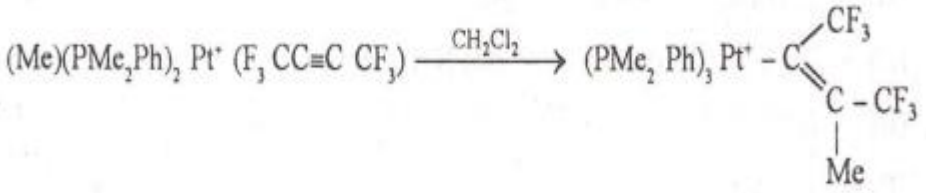
$$HC \equiv CH + H_2O \xrightarrow[150^0\,C,\,130\,atm]{Ni(CO)_4} H_2C = CHCO_2H$$

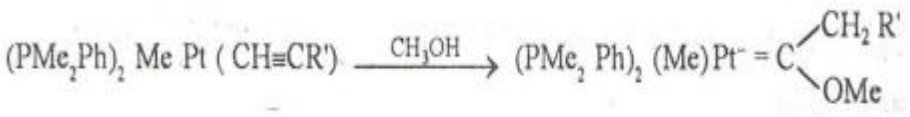
$$HC \equiv CH + CO + MeOH \xrightarrow[O_2]{PdCl_2\ /\ thiourea} MeO_2CCH = CHCO_2Me$$

(b) Reactions with Nucleophiles:

In these reactions the nucleophilic reagent reacts with metal in Cis-form or with proton of alkyne in trans form:

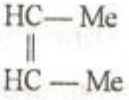


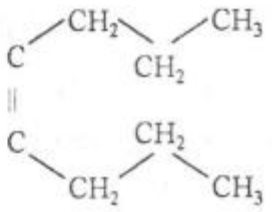




(c) Reaction with Electrophilies:

(i) $Pt(PPh_3)_2(\eta^2\ Ph\ C \equiv C\ Ph) \xrightarrow{HCl} Pt(PPh_3)\ Cl_2 + Ph'\ CH = CH\ Ph$

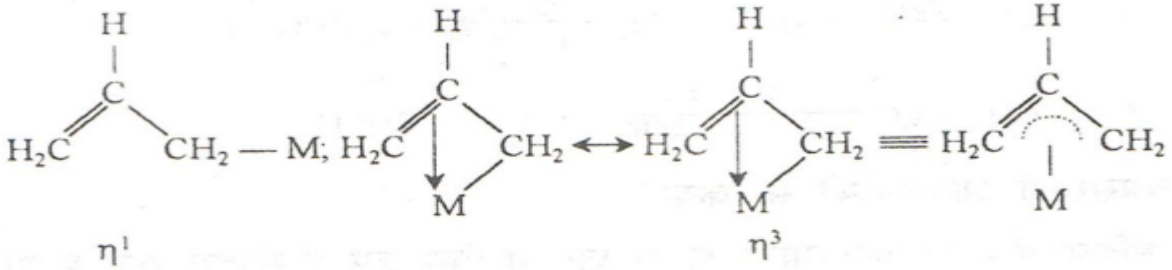
(ii) $Mo(\eta^2\text{-}MeC \equiv CMe)(\eta^5\text{-}C_5H_5) \xrightarrow[H_2O]{HCl}$  $+ Mo(Cl_2), (\eta^5\text{-}C_5H_5)_2$

(iii) $Ta\ H(\eta^2\text{-}C_3H_4\ C \equiv C\ C_3H_4)(\eta^5\text{-}C_5H_5)_2 + HBF_4 \rightarrow$ 

$Ta(\eta^5\text{-}C_5H_5)_2(BF_4)_2$

η^3- ALLYL COMPLEXES

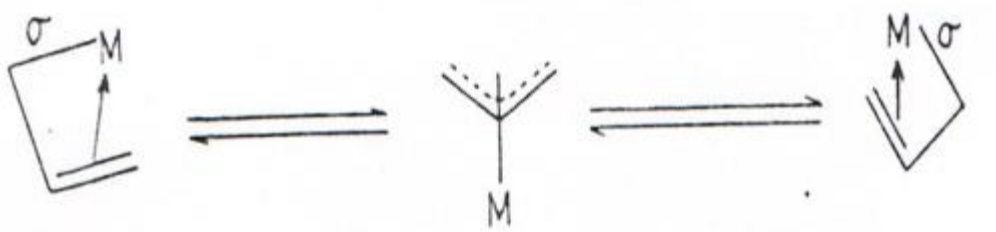
The preparation of η^3 allylic complexes has been one of the exciting developments in coordination chemistry. The significant feature of the allyl group, $H_2C{=}CH\text{-}CH_2$-, is its dual (mono – as well as tri - hapto) character of ligaqtion.



A large number of η^3–allyl complexes of almost all d' – d^x metals in the three (3d like Ti, Zr, V, Nb, Ta, Cr, Mo, W, Re, Fe, Co, Re, Fe, Co, Rh, Ir, Ni, Pd and Pt. It is further interesting to note that allylic groups can also act as bridging ligands.)

Further even when π - allyl group is a part of a larger ligand, it is known to form η^3 – complexes with transition metals. In addition to the η^3 bonding type allylic group can also function as a σ-ligand or as a σ, η^2 ligand.

In view of the above, one has to be very careful while suggesting the structures for allylic derivatives. The 18–electron rule is useful in distinguishing between η^3 – and η^1-allyl types, but the third type can be identified only by X-ray structure determination. The σ, η^2 – allyl derivatives are fluxional (cf. unit 8) with the metal changing positions from one side to another of the plane comprising the three allylic carbon atoms:



Just as alkene complexes show similarity to carbonyls, the delocalized allylic system CH_2-CH-CH_2 acting as a formal three – electron donor can be linked to NO ligands in metal nitrosyl derivatives. These allylic derivatives have also been visualized as a sort of halfsandwich, i.e., intermediate between alkene and the sandwich compounds.

Methods of Preparation

Several types of allylic η^3 – complexes have been prepared. Some of them are monoleptic, M(allyl)n, and some are heteroleptic, $M(allyl)_{n-a}\ X_a$:

1. Reaction of carbonyl complex with allylhalide:

(a) $$Na[Mn\ (CO)_5] + CH_2=CH - CH_2-Br \rightarrow (CO)_5\ Mn(\eta'-C_3H_5) + Na\ Br$$

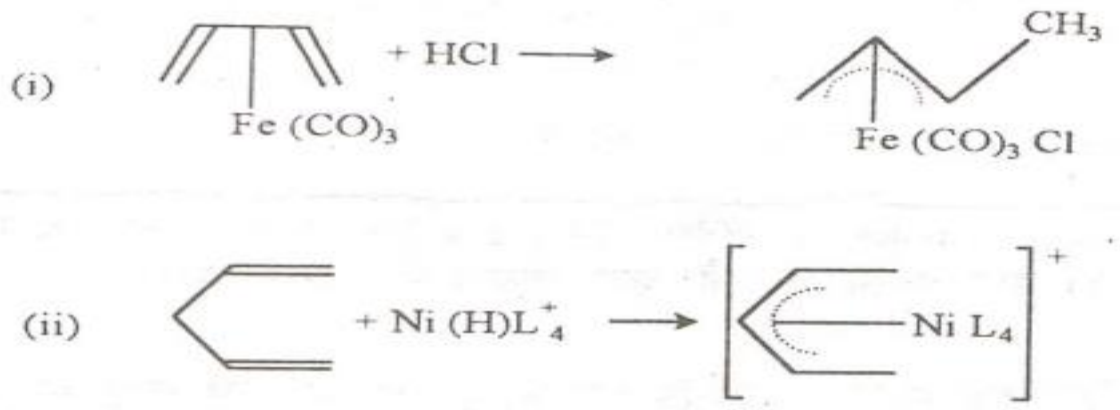
(b) $$(OC)_3\ Mn\ (n'-CH_2-CH=CH_2) \rightarrow (OC)_4\ Mn(\eta^3-C_3H_5)+CO$$

2. From Grignard's reagent.

$$NiCl_2 + 2CH_2=CHCH_2\ MgCl \rightarrow Ni(n^3-C_3H_5)_2 + 2Mg\ Cl_2$$

Other transition metals like Ti, Zr, Hf, Th, V, Nb, Ta, Cr, Mo, W, Fe, Co and Pt also follow this reaction. In some cases (e.g. Ni(II) and Pd (II)) this reaction takes place in equimolar ratio and the product is M(η^3-allyl)x.

Protonation of complexes (e.g. tetrahapto 1-3 Butadiene):

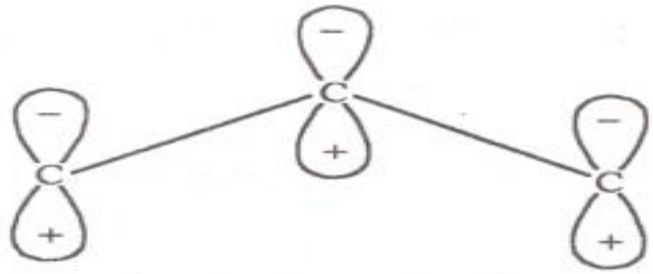


Bonding and structure

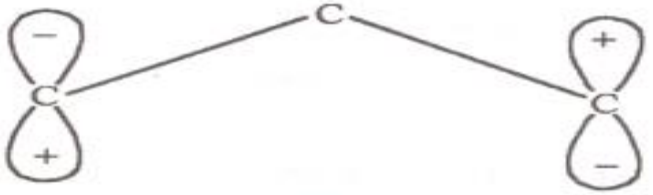
The bonding of the allylic group to the metal is believed to be similar to that of metal-alkene as explained on Dewar-Chatt-Duncanson model. For example, the allylic group donates its π electrons to metal atom forming aσ-type bond and accepts electrons into its antibonding π*-molecular orbitals in a π-type bond. These allylic complexes, therefore, involve a three electron delocalized allylic system. $H_2C = CH - CH_2$, as illustrated in Figure 3.9. Then η^3- allyl group is in general symmetrically displaced around the transition metal.

The η^3-allyl group forms two metal donor bonds (one σ and the other π) and one metal to ligand dπ-pπ bond. These three ligand molecular orbitals are obtained by linear combination of p-orbitals on three allylic carbon atoms.

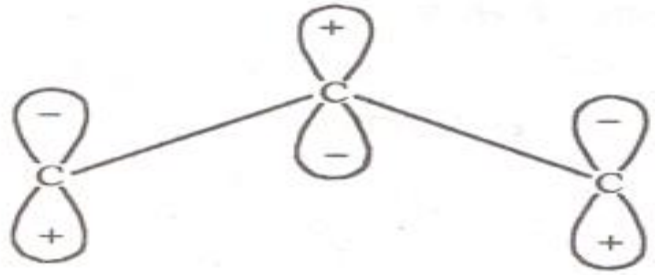
L-M electron donor bonds are formed by overlapping of metal s, d z^2 and pz orbitals with ψ_2. After this M–L back bodning takes place, when metal dxz orbital overlaps with ψ_3. The degree of participation of these orbitals in bonding depends upon their relative energies, radial diffuseness and orbital overlapping magnitudes.



Ψ_1 σ - donor (filled)

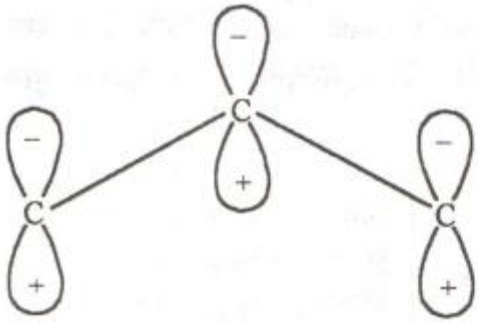


Ψ_2 σ - donor (filled)

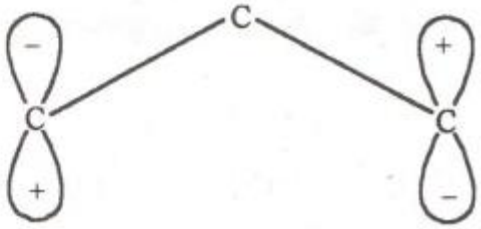


Ψ_3 σ - acceptor (empty)

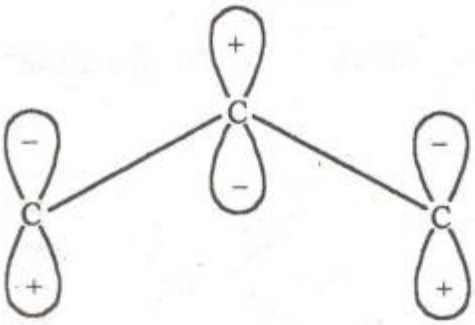
(a) π-allyl anion - orbital



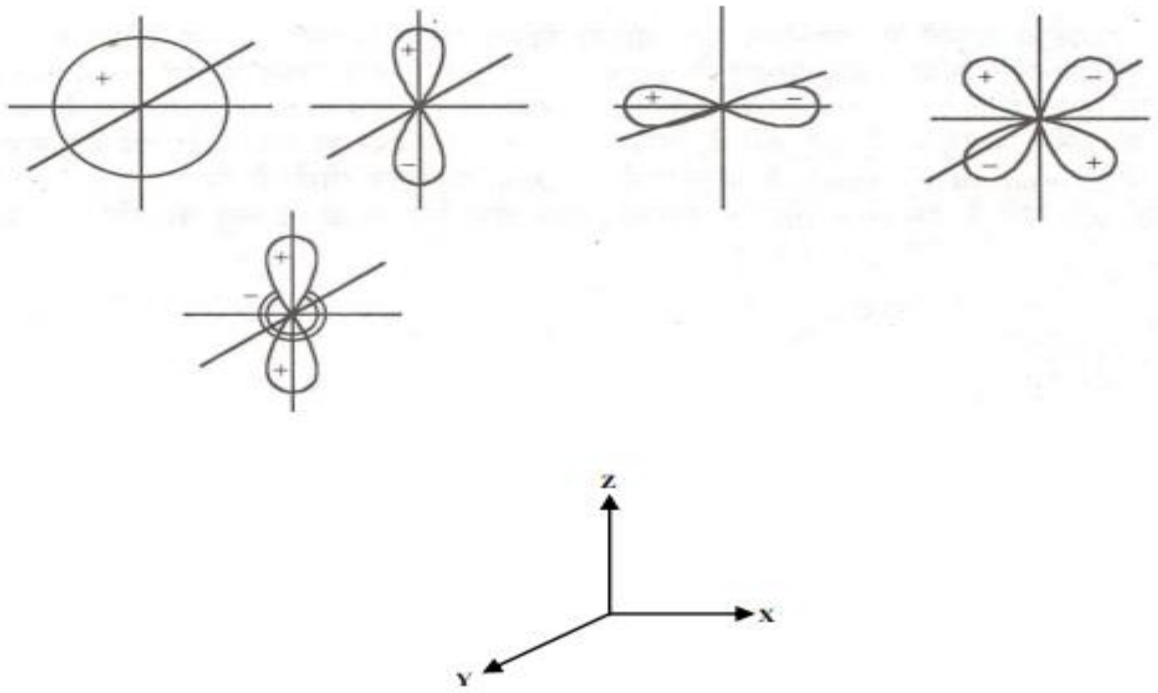
Ψ_1 σ - donor (filled)



Ψ_2 σ - donor (filled)



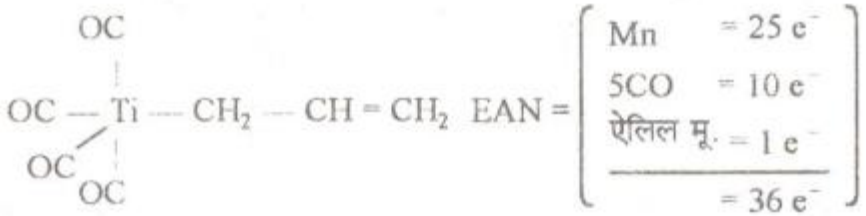
Ψ_3 σ - acceptor (empty)



(b) π-allyl M.O. and metal orbitals of corresponding symmetry

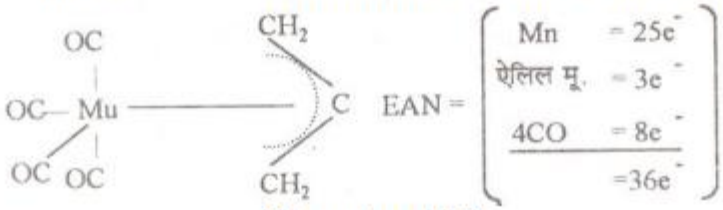
The structures of allyl-complexes have been established using x-ray and n-diffraction methods and follow EA N-rule :

In structure (I) allyl radical is monohapto ligand :



Structure (I)

In $Mn(CO)_4 CH_2 CH = CH_2$ (Structure II) it is trihapto ligand :



Structure (II)