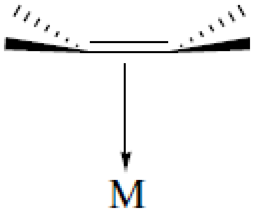
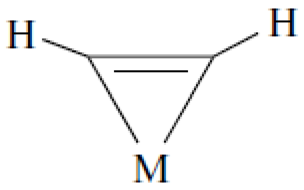
π bonded ligands

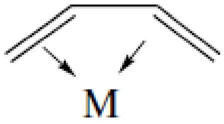


alkene complexes

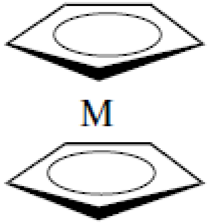


alkyne complexes

allyl complexes

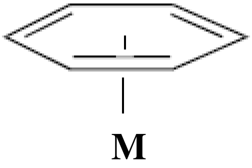


diene complexes

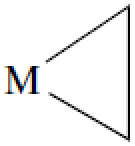


cyclopentadienyl complexes

arene complexes

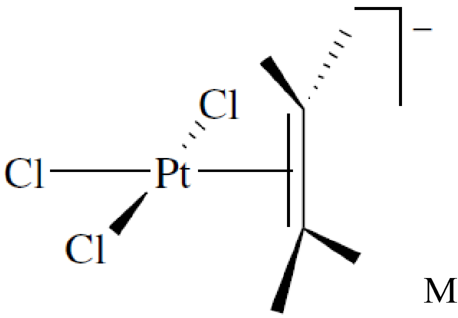


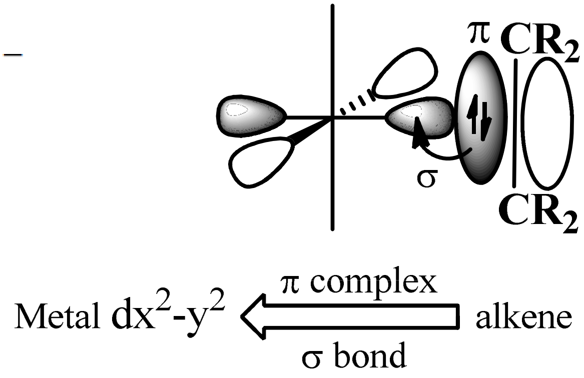
metallacycles

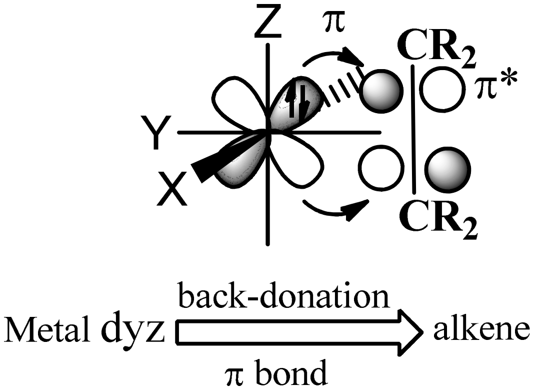


Transition metal alkene complexes

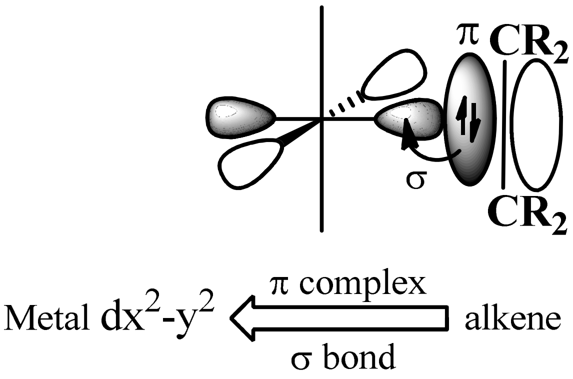
- The report in 1825 by William Zeise of crystals with composition, $KCl.PtCl_2.EtOH$, prepared from $KPtCl_4$ and EtOH was a topic of controversy for many years due to the nature of Zeise's structure - only possible by the dehydration of EtOH.

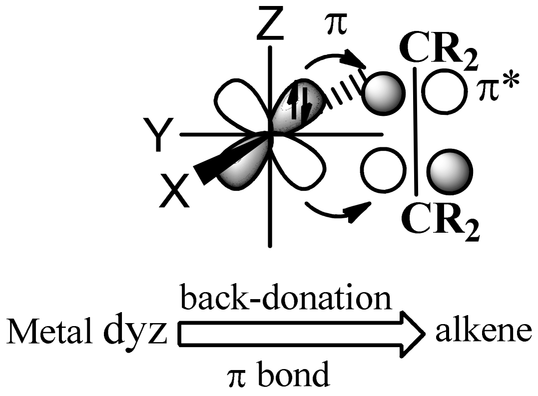






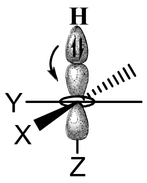
- Proof of Zeise's formulation came 13 years later when Birnbaum isolated the complex from a solution of platinic acid, $H_2PtCl_6.6H_20$, treated with ethylene.
- Zeise's salt was the first organometallic compound to be isolated in pure form.
- This discovery spawned a tremendous growth in organometallic chemistry and still serves as the simplest example of transition metal-olefin complexation.
- Zeise's salt has become one of the most cited examples of the Dewar-Chatt-Duncanson model for metal-olefin complexation.





- The ***Dewar-Chatt-Duncanson model*** explains the type of chemical bonding between an unsaturated ligand and a metal forming a **π complex**.
- The π-acid ligand donates electron density into a metal d-orbital **from a π-symmetry bonding orbital** between the carbon atoms.
- The metal donates electrons back from a filled t_{2g} *d*-orbital **into the empty π^* antibonding orbital** of the ligand (similar to dihydrogen σ-complexes)
- Both of these effects tend to **reduce the C-C bond order**, leading to an elongated C-C distance and a **lowering its vibrational frequency**.
- In the nickel compound $Ni(CH_2CH_2)(PPh_3)_2$ the C-C bond distance is 143 pm (vs. 134 pm for free ethylene).
- The interaction can cause carbon atoms to **"rehybridize“, for e.g in metal alkene complexes from sp^2 towards sp^3**, which is indicated by the bending of the hydrogen atoms on the ethylene back away from the metal.

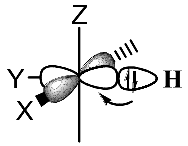
Metal Hydride



dz^2

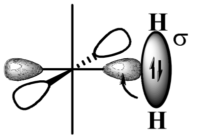
Hydride $\Downarrow \sigma$ Metal

or

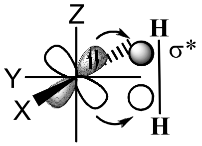


Metal dx^2-dy^2 $\xleftarrow{\sigma}$ Hydride

Metal Dihydrogen

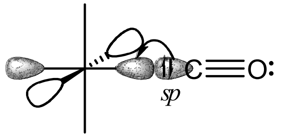


Metal dx^2-dy^2 $\xleftarrow{\sigma \text{ complex}}$ dihydrogen

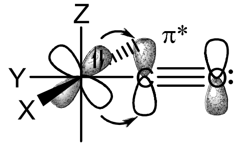


Metal dyz $\xrightarrow{\text{back-donation}}$ dihydrogen

Metal Carbonyl

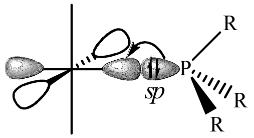


Metal dx^2-dy^2 $\xleftarrow{\sigma \text{ bond}}$ carbonyl

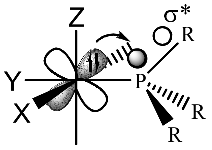


Metal dyz $\xrightarrow{\text{back-donation}}$ carbonyl

Metal Phosphine

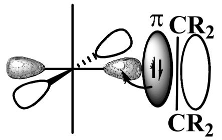


Metal dx^2-dy^2 $\xleftarrow{\sigma \text{ bond}}$ phosphine

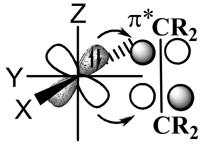


Metal dyz $\xrightarrow{\text{back-donation}}$ phosphine

Metal Alkene

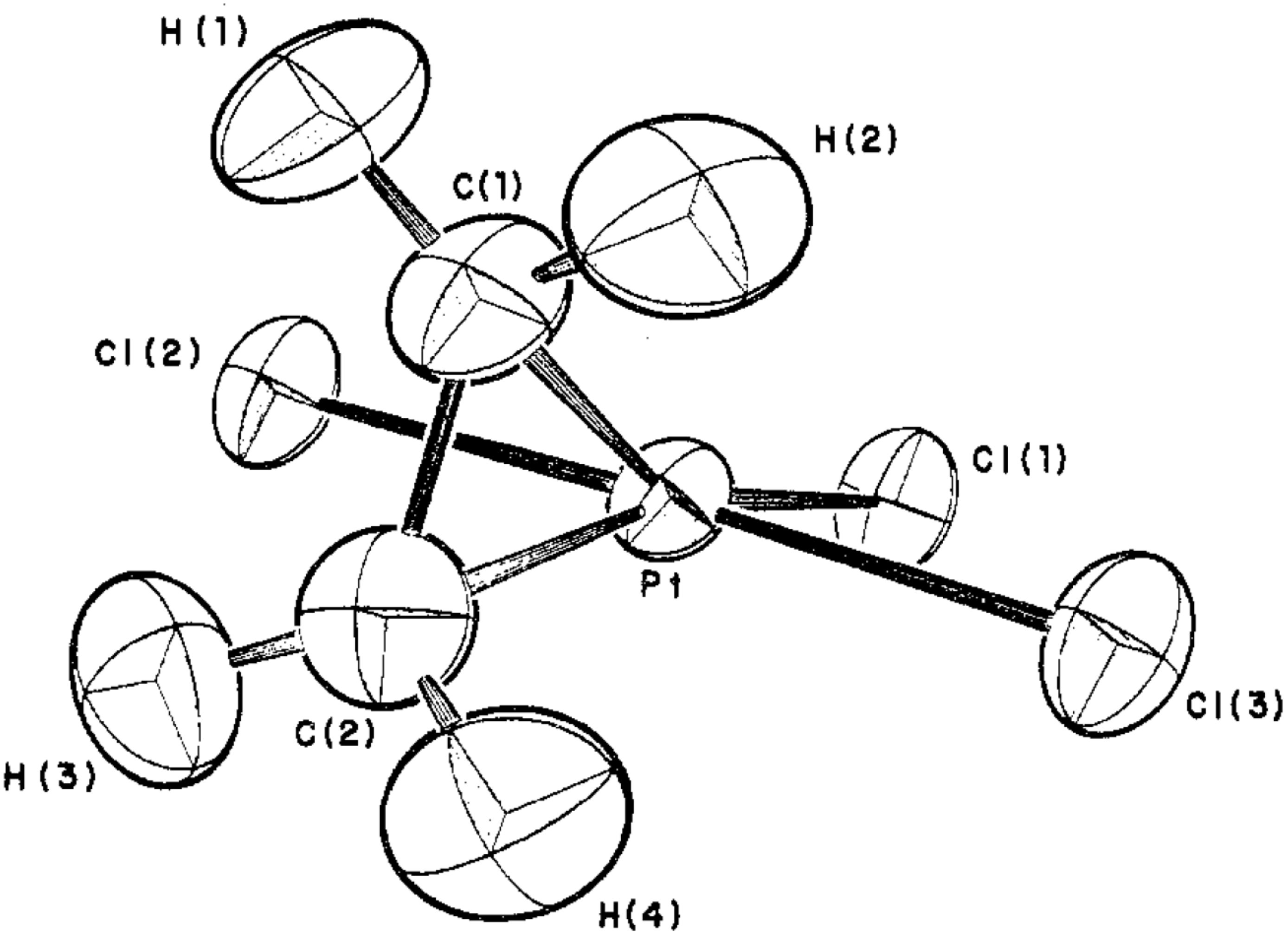


Metal dx^2-y^2 $\xleftarrow{\pi \text{ complex}}$ alkene

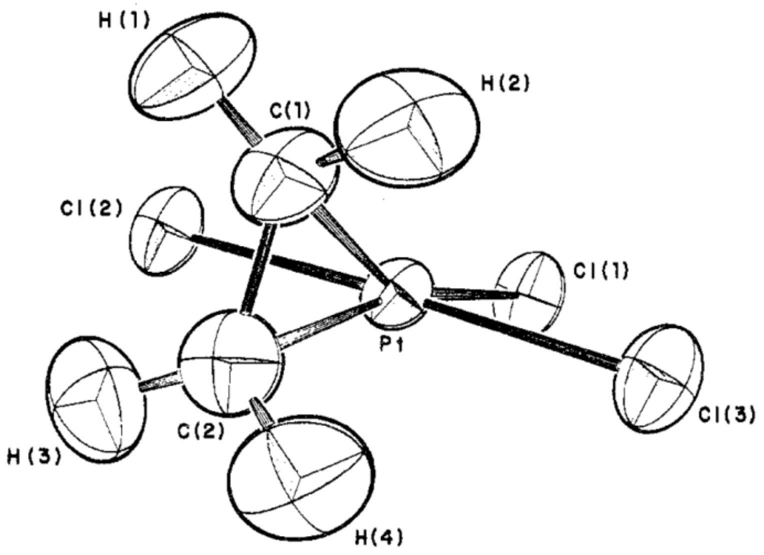


Metal dyz $\xrightarrow{\text{back-donation}}$ alkene

Molecular geometry of Zeise's salt (neutron diffraction)



Love et al. Inorg. Chem., 1975, 14, 2653-2657.



- The **$PtCl_3$ *moiety forms a nearly planar group*** with the Pt atom.
- The Pt-Cl bond trans to the ethylene group (2.340 Å) is significantly longer than the cis Pt-Cl bonds (2.302 and 2.303 Å) – ***trans effect !!***
- The C atoms are approximately equidistant from the Pt atom (2.128 and 2.135 Å).
- The distance from the ***midpoint of the C-C bond to the Pt atom is 2.022 Å.***
- The ***C-C distance, 1.375 Å, is slightly longer than the value found in free ethylene (1.337 Å)***, indicating some dπ-pπ* back-bonding from the platinum atom to C_2H_4.
- ***Back-bonding is also indicated by a bending of the four hydrogen atoms away from the Pt atom.***

- Both the ***magnitude of C-H bending*** and the ***C-C bond lengthening*** are considerably smaller in Zeise's salt than in metal complexes of C_2F_4 and $C_2(CN)_4$, suggesting that the amount of metal-ligand back-bonding may be greater in these complexes than in those involving ethylene.
- Indeed when the Pt(II)Cl_3 moiety is replaced by the much more π basic Pt(0)PPh_3 a greater back donation is observed with increased C-H bending and a longer C-C bond order.

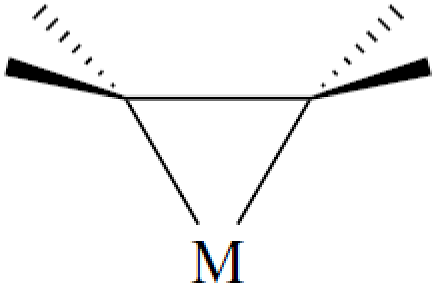
	C-C (Å)
$K[PtCl_3(C_2H_4)]$	**1.375**
$Pt(PPh_3)_3(C_2H_4)$	**1.430**

Table VI. Comparison between Ethylene and TCNE Complexes

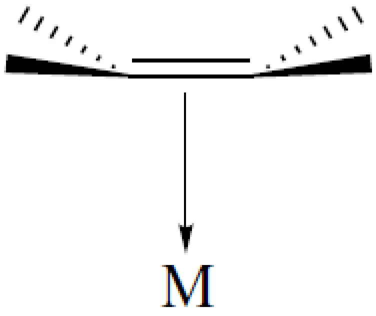
Compd	C–C, Å	Δ(C–C),[a] Å	α,[b] deg	Method	Ref
C_2H_4	1.337 (2)	0.0	0.0	*c*	22
$Rh(C_2H_4)(C_2F_4)(C_5H_5)$	1.358 (9)	0.021	42.4	*d*	34
$KPt(C_2H_4)Cl_3 \cdot H_2O$	1.375 (4)	0.038	32.5	*e*	This work
$Nb(C_2H_4)(C_2H_5)(C_5H_5)_2$	1.406 (13)	0.069	52.5	*d*	36
$C_2(CN)_4$	1.344 (3)	0.0	0.0	*d*	37
$Ni[C_2(CN)_4](t\text{-}C_4H_9NC)_2$	1.476 (5)	0.132	56.8	*d*	32
$Ir[C_2(CN)_4](CO)(Br)(PPh_3)_2$	1.506 (15)	0.162	70.4	*d*	38
$Ir[C_2(CN)_4](CO)(C_6N_4H)(PPh_3)_2$	1.526 (12)	0.182	67.4	*d*	33

[a] Δ(C–C) is the difference between the C–C distances of the complexed and uncomplexed forms of the ligand. [b] α is the angle between the normals to the two CH_2 or $C(CN)_2$ planes (see ref 32). [c] Electron diffraction. [d] X-Ray diffraction. [e] Neutron diffraction.

- In extreme cases of strong backbonding from a π basic metal to the alkene ligand a ***metallacyclopropane*** structure is a better description.
- The metal-alkene system can now be considered as an ***η^2 structure***
- In this η^2 structure
  - The C atoms of the alkene rehybridize close to sp^3
  - There are two σ bonds to the metal centre
  - the Dewar-Chatt-Duncanson model no longer applies
- These two extremes are often referred to as **X_2 type** and **L type** ligands

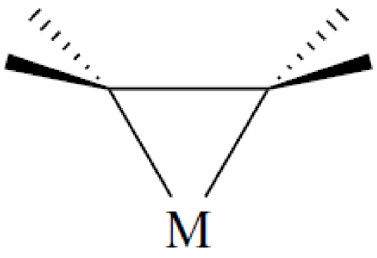


X_2



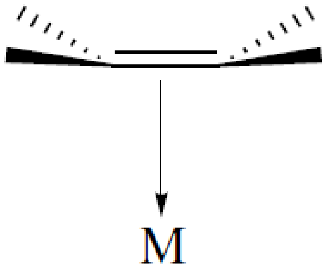
L

- In both cases the ligand is considered as a $2e^-$ donor in the covalent model.
- In the ionic model, the X_2 configuration has a 2- charge and is considered a $4e^-$ donor.
- In the ionic model, the L configuration does not change the oxidation state of the metal and is still considered a $2e^-$ donor.
- **One can consider L as an intermediate structure in the oxidative addition of the alkene ligand to form X_2**
- In the X_2 form the C atoms of the alkene rehybridize close to *sp*^{3}
- Apart from crystallographic studies ^{1}H and ^{13}C NMR spectroscopy are useful tools in determining the nature of a metal alkene bond.



X_2

Ionic model: 2- charge 4e donor
Covalent model: 0 charge 2e donor

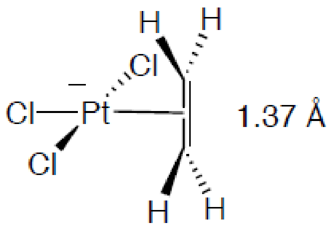


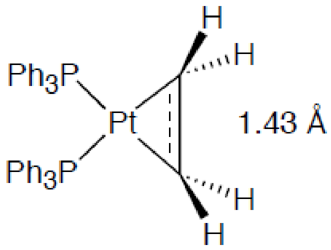
L

Ionic model: 0 charge 2e donor
Covalent model: 0 charge 2e donor

- The difference between the L and X_2 structural configurations are also borne out in their electronic and hence chemical properties.
- In the ***L configuration the C atoms tend to carry a*** δ^+ ***charge*** due to σ donation to the metal which is not reciprocated by back donation from the metal.
- Metal-alkene complexes having the L type configuration are therefore ***susceptible to nucleophilic attack at the alkene C atoms***.
- This is in contrast to electrophilic attack often observed for free alkenes. This change in reactivity upon complexation is also known as ***"umpolung"*** which can be translated as a ***reversal in polarity***.
- In the ***X_2 configuration the C atoms are negatively charged*** and are susceptible to electrophilic attack.

- Factors favoring X_2-type binding
  - strong donor ligands
  - a net negative charge on the complex
  - low-oxidation state metals



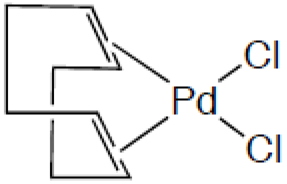


- Reactivity difference between the bonding types:
  - L-type: the alkene is electron deficient and prone to attack by nucleophiles
  - X_2-type: the carbons are carbanion-like and prone to attack by electrophiles

- Olefin binding strength is very sensitive to steric changes:

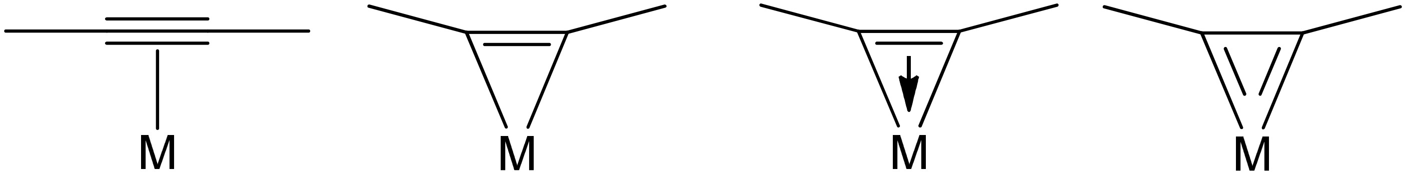
  ethylene > propylene > *cis-2-butene* > *trans-2-butene*

- Chelating dienes form more stable complexes than simple alkenes.



Transition metal alkyne complexes

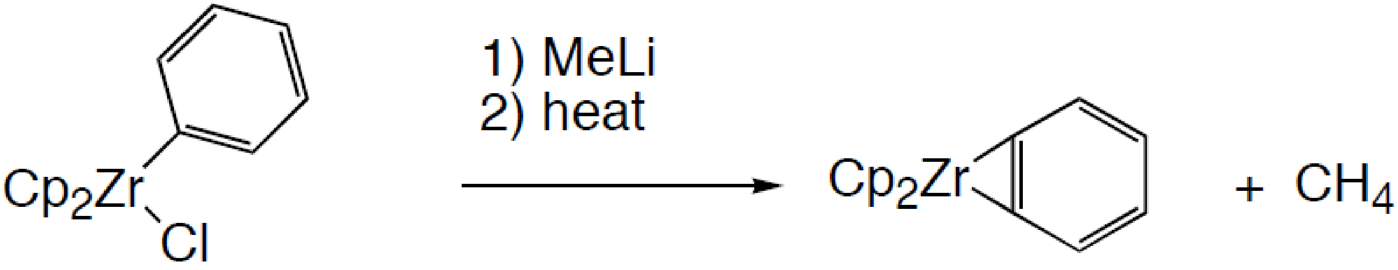
- Alkynes behave in ways broadly similar to alkenes, but being more electronegative, they tend to encourage back donation and bind more strongly.
- The substituents tend to fold back away from the metal by 30°–40° in the complex, and the M−C distances are slightly shorter than in the corresponding alkene complexes.



	η^2	η^2	η^2	η^2
Ionic model:	**2e (0)**	**4e (2-)**	**6e (2-)**	**8e (4-)**
Covalent model:	**2e (0)**	**2e (0)**	**4e (0)**	**4e (0)**

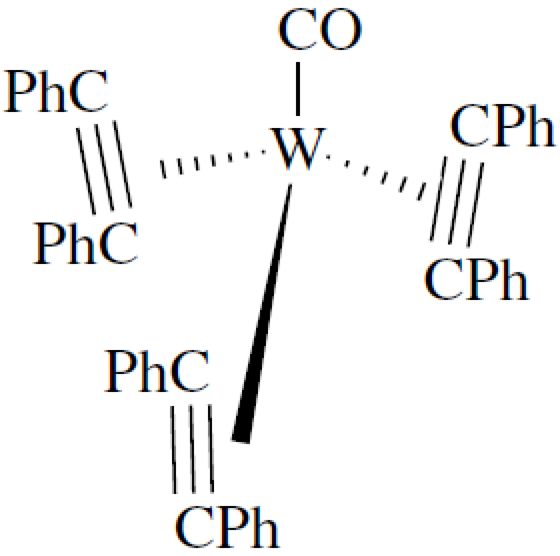
Why are alkynes more electronegative than alkenes?

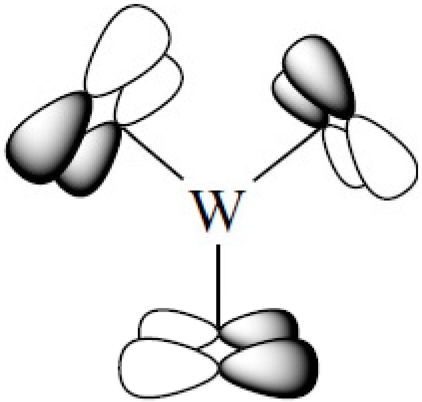
- Metals can stabilize alkynes that cannot be observed as free compounds



Chem. Rev., **1988**, *88*, 1047-1058

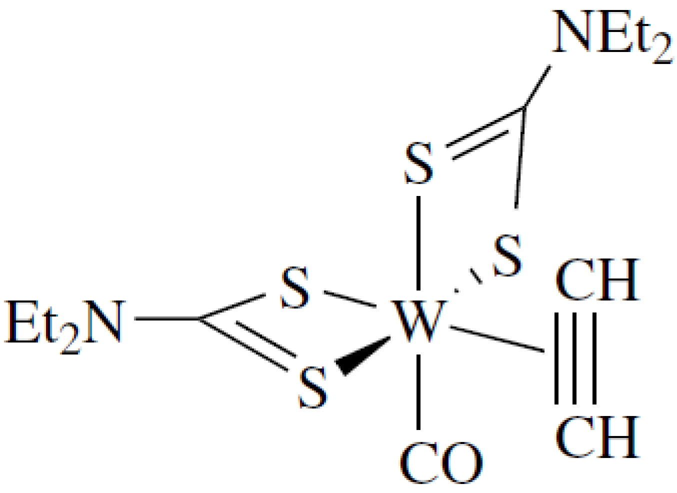
- Alkynes can also form complexes that appear to be coordinatively unsaturated.





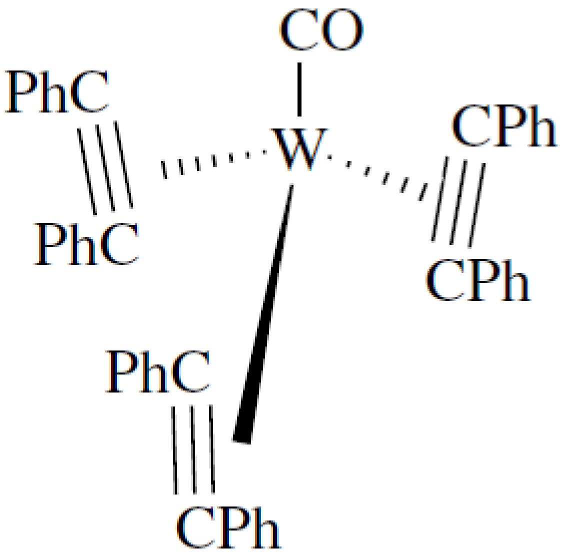
14e species?

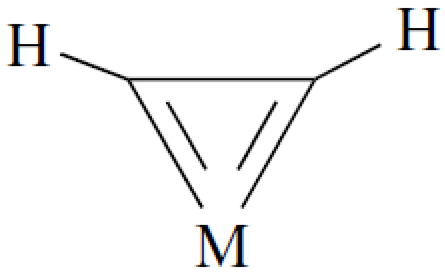
- Coordinatively unsaturated metal alkynes (contd.)

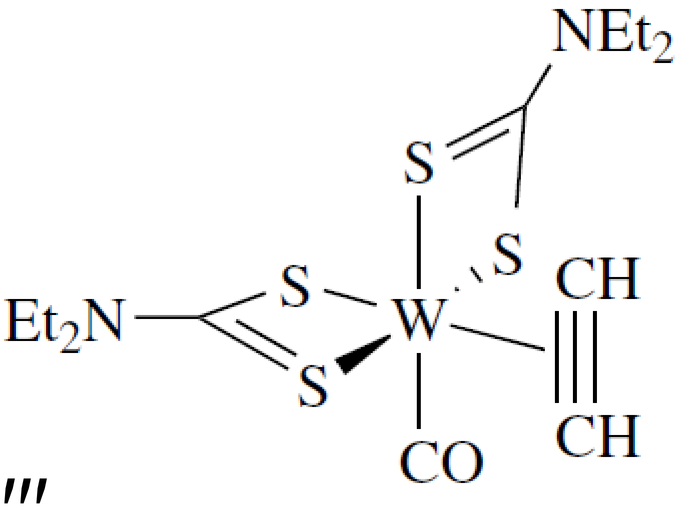


16e species?

- In such cases the alkyne also ***donates its second C=C π-bonding orbital***, which lies at right angles to the first.
- ***The alkyne is now a 4e donor.***





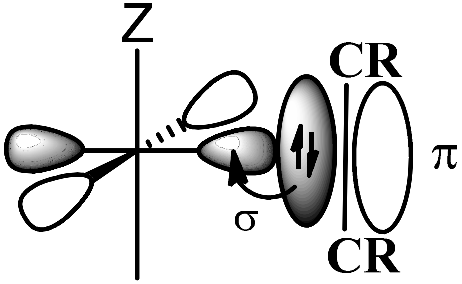


both 18e species !!!

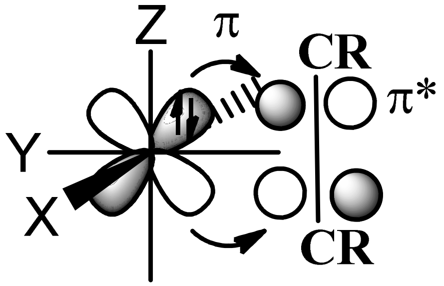
(2x 4e donor & 1 x 2e donor)

- Four electron alkyne complexes are rare for d^6 metals because of a 4e repulsion between the filled metal dπ and the second alkyne C=C π-bonding pair.

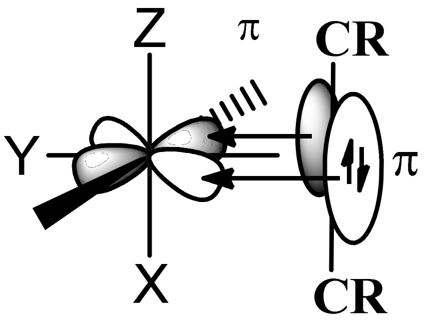
Metal Alkyne Bonding Scheme



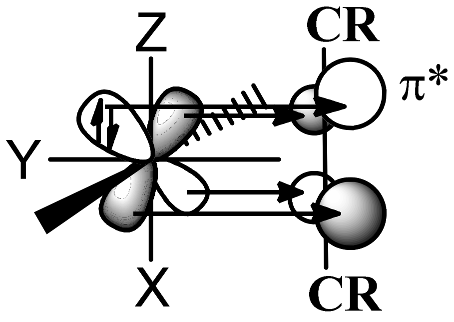
Metal dx^2-y^2 $\Longleftarrow$ alkyne
σ bond



back-donation
Metal dyz $\Longrightarrow$ alkyne
π bond

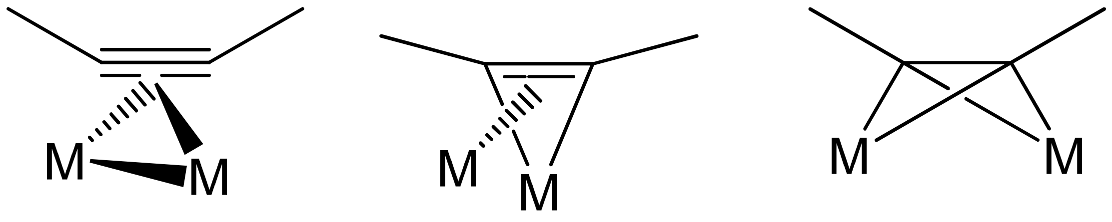


Metal dxy $\Longleftarrow$ alkyne
π bond

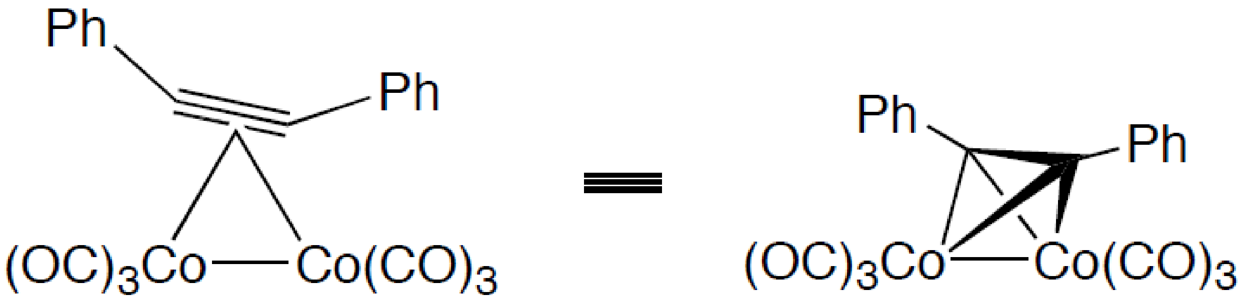


back-donation
Metal dyz $\Longrightarrow$ alkyne
δ bond

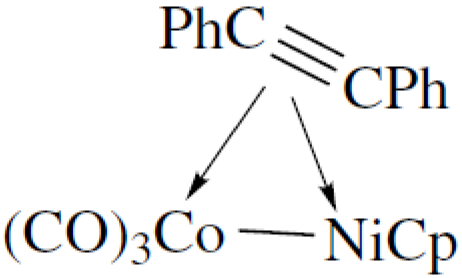
Bridging metal alkyne complexes



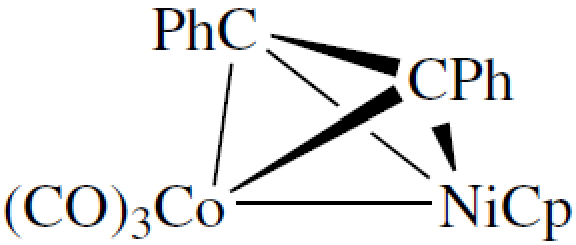
	η^2	η^2	η^2 *(wrt each metal)*
Ionic model:	**4e (0)**	**6e (2-)**	**8e (4-)**
Covalent model:	**4e (0)**	**4e (0)**	**4e (0)**



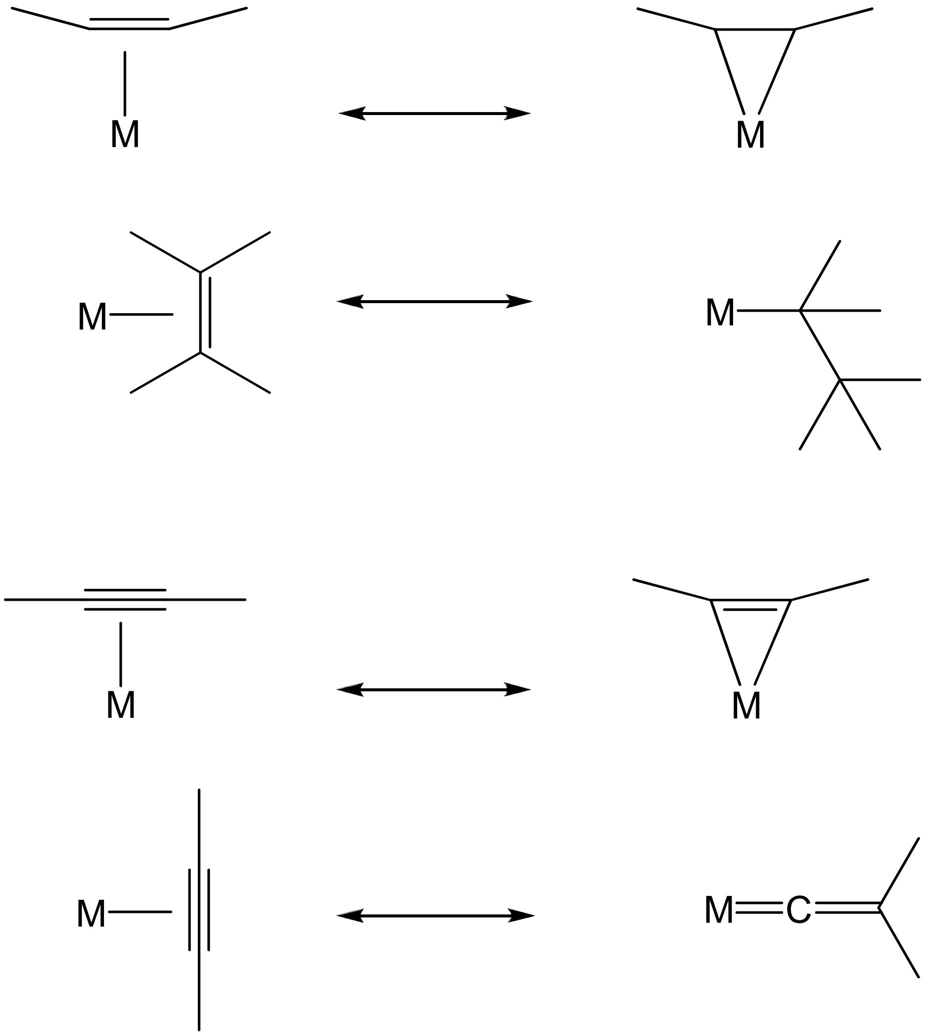
- Alkynes readily bridge an M−M bond, in which case they can act as conventional 2e donors to each metal.



- The alternative tetrahedrane form is the equivalent of the metalacyclopropane picture for such a system.

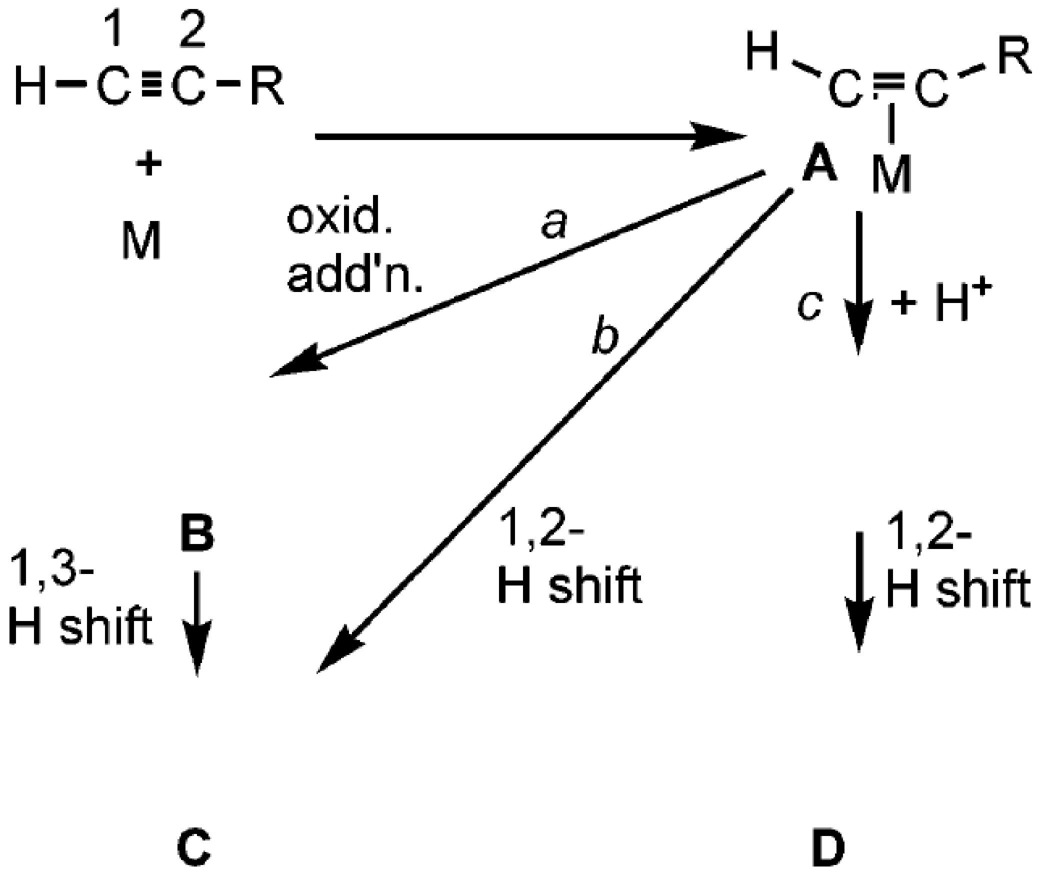


Isomers

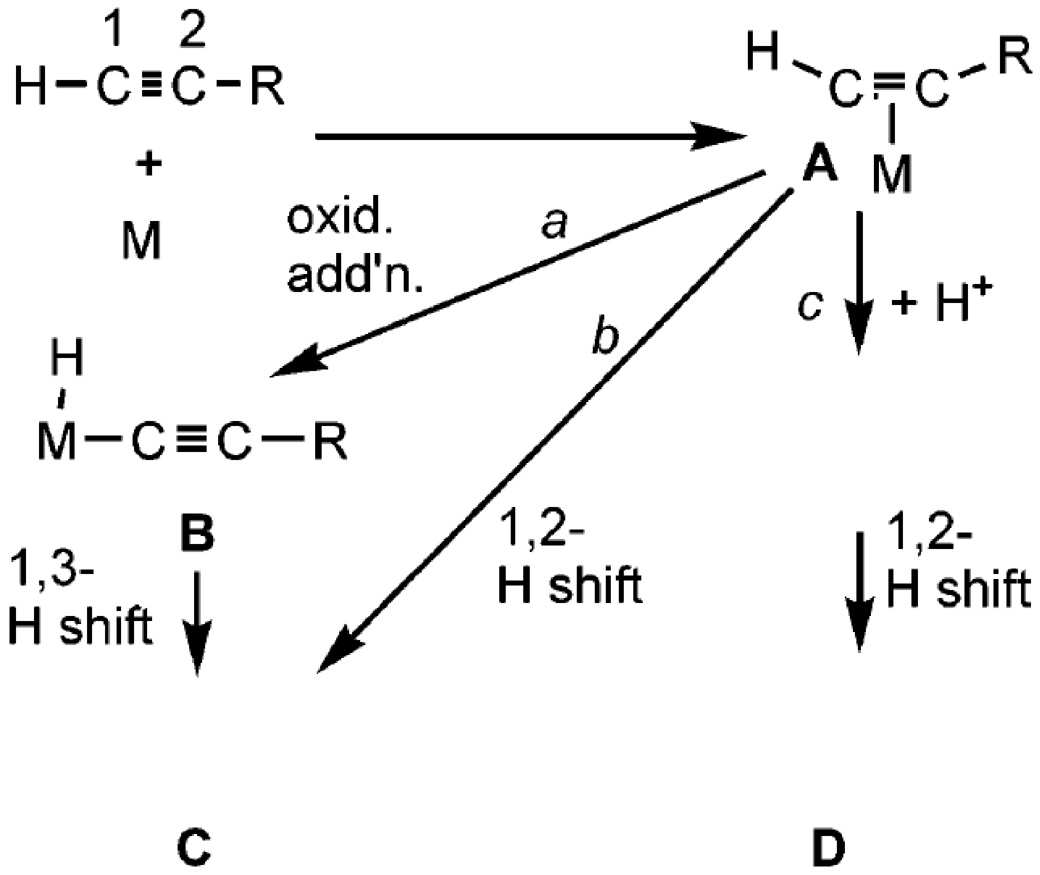


metal vinylidene

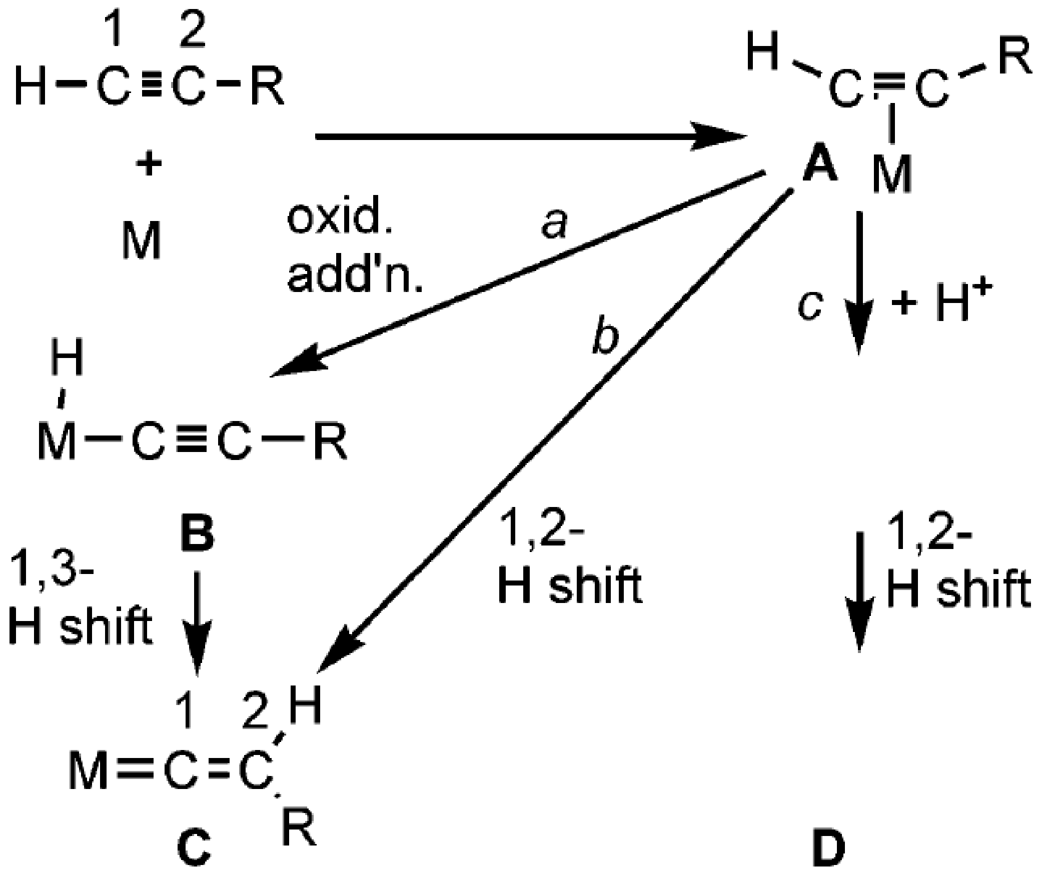
Proposed Alkyne-to-Vinylidene Mechanisms



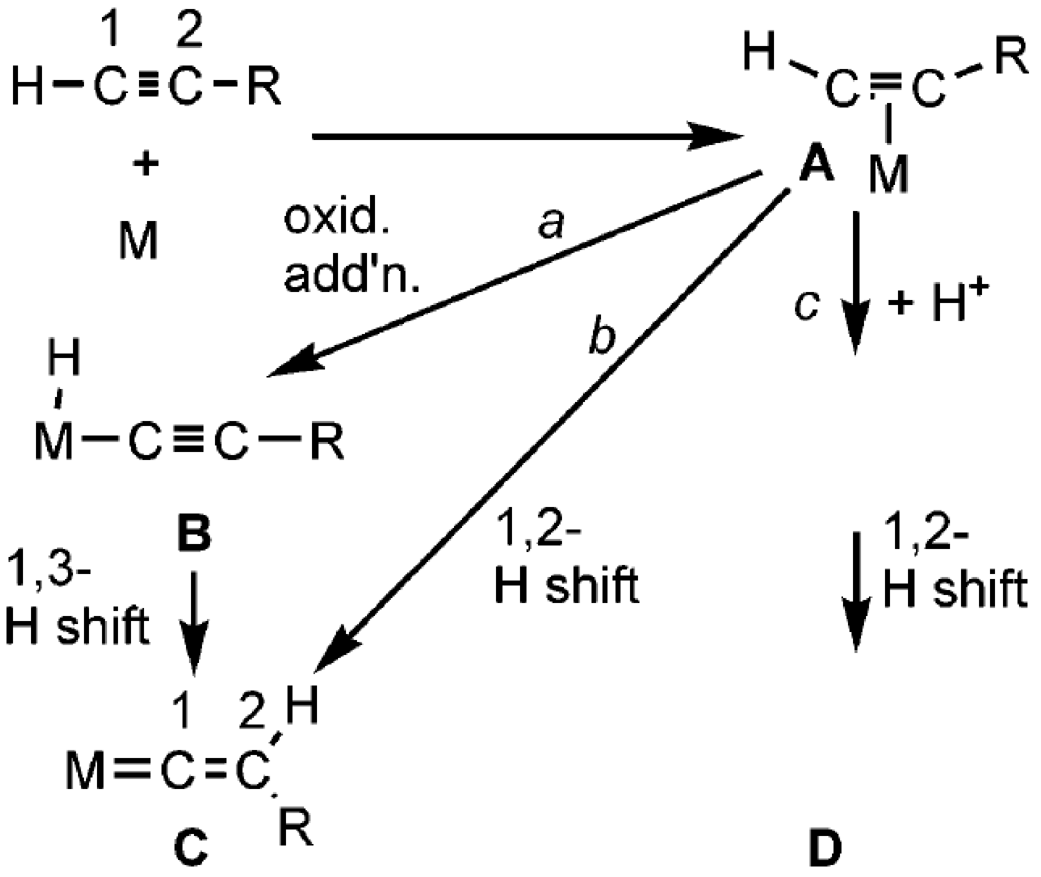
Proposed Alkyne-to-Vinylidene Mechanisms



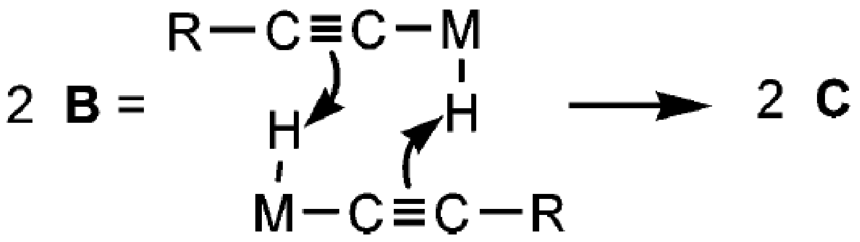
Proposed Alkyne-to-Vinylidene Mechanisms



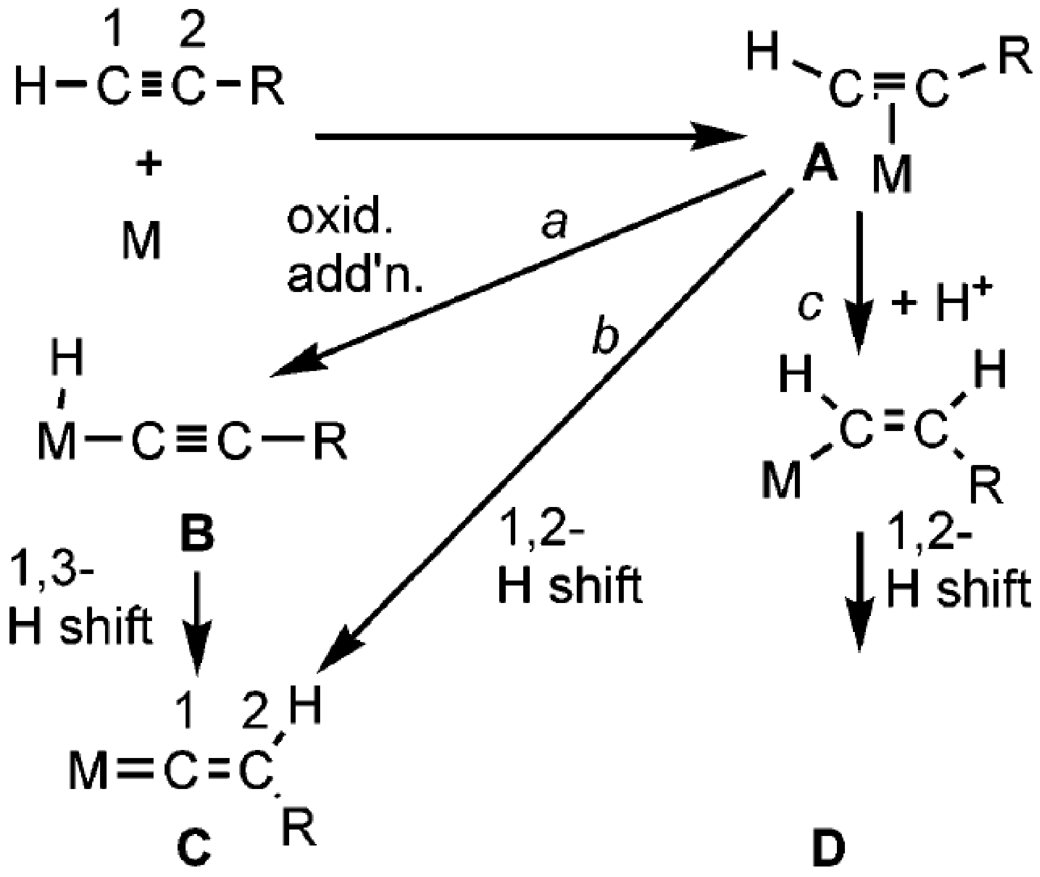
Proposed Alkyne-to-Vinylidene Mechanisms



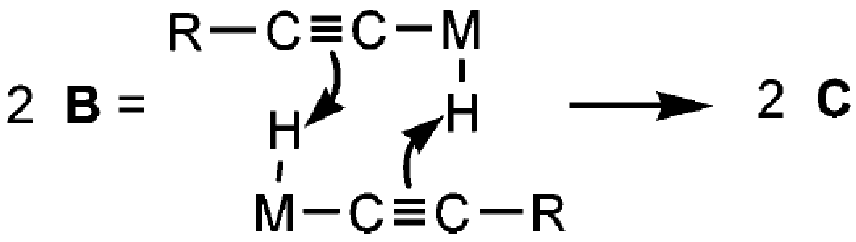
proposed bimolecular 1,3-H shift on **B**:



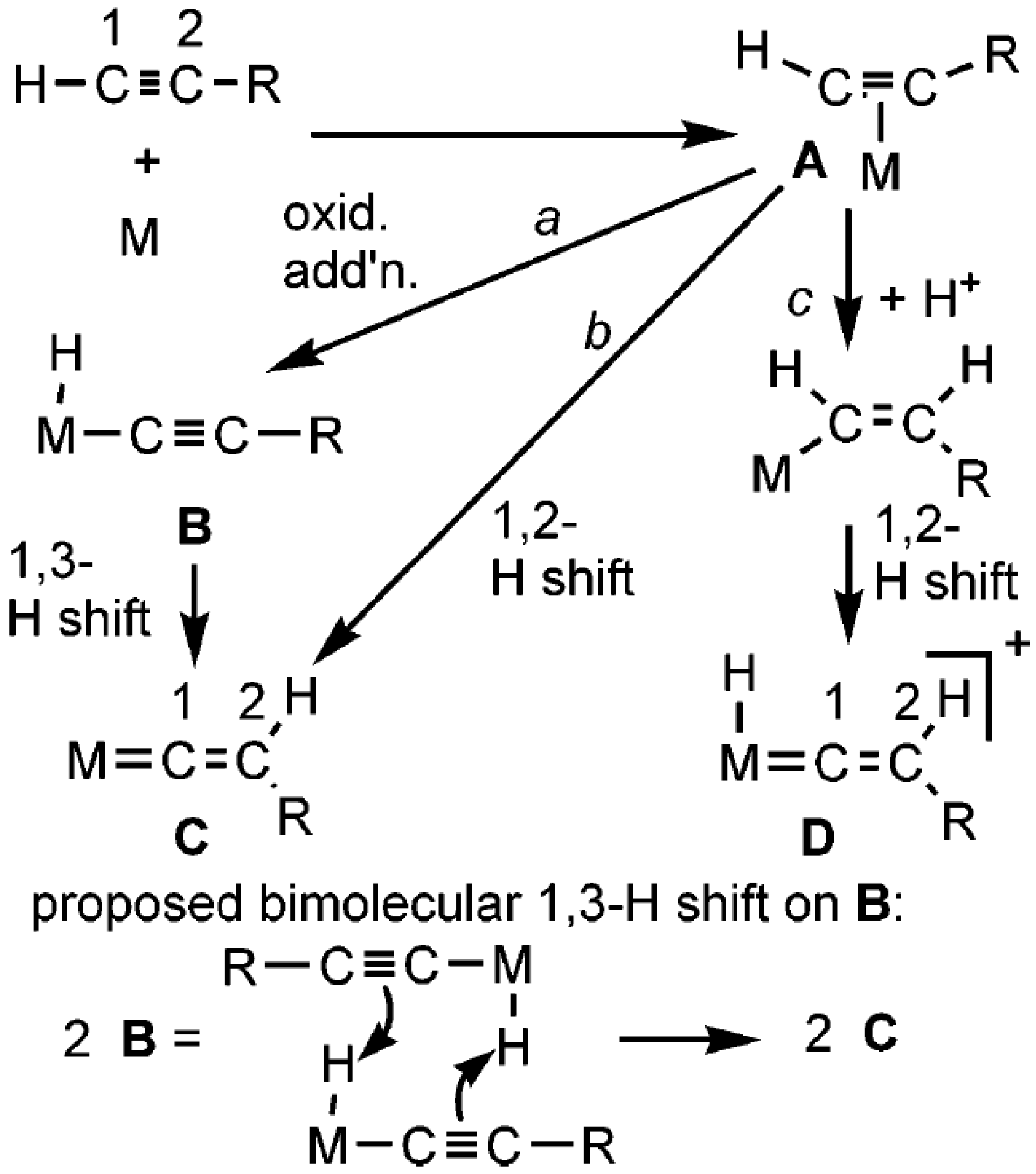
Proposed Alkyne-to-Vinylidene Mechanisms



proposed bimolecular 1,3-H shift on **B**:

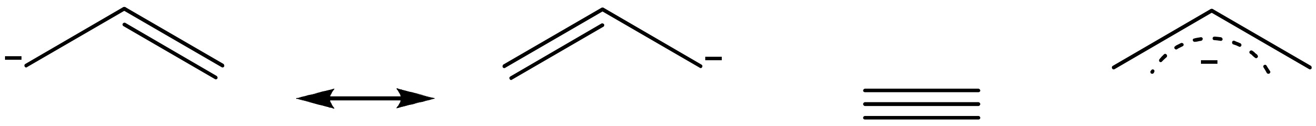


Proposed Alkyne-to-Vinylidene Mechanisms

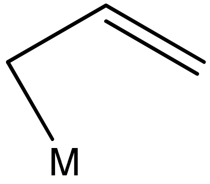


Transition metal allyl complexes

- The allyl group, commonly a spectator ligand, binds in one of two ways.
- In the η^1 **form it is a simple X-type ligand** like Me
- In the η^3 **form it acts as a LX enyl ligand**.
- It is often useful to think in terms of the resonance forms **(2e + 1e donor)**

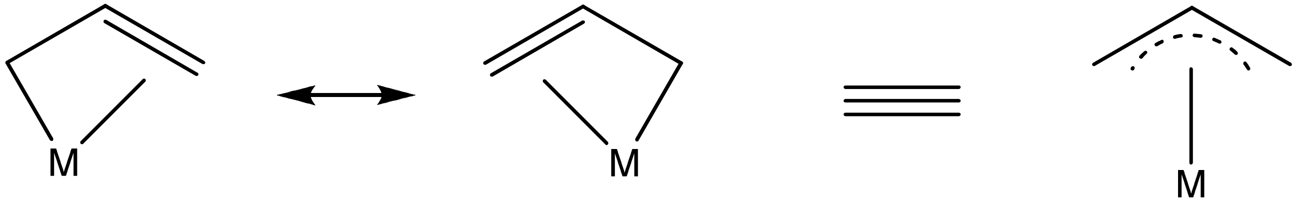


η^1

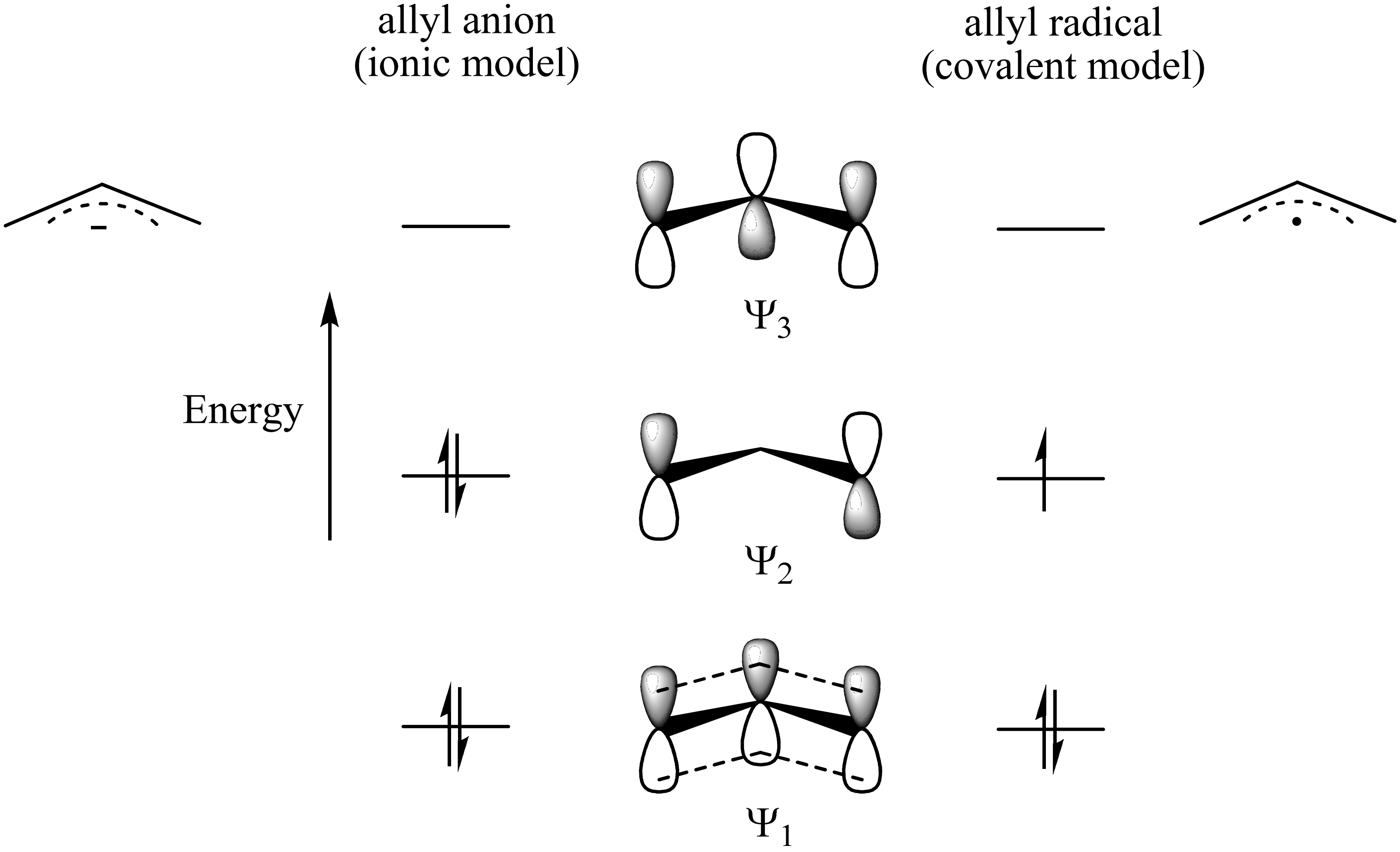


covalent model: 1e donor (0 charge)
ionic model: 2e donor (1- charge)

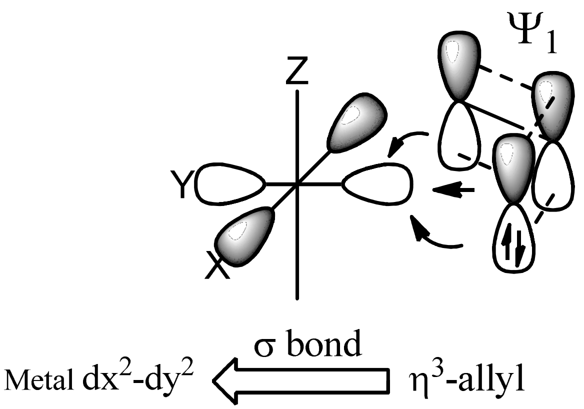
η^3

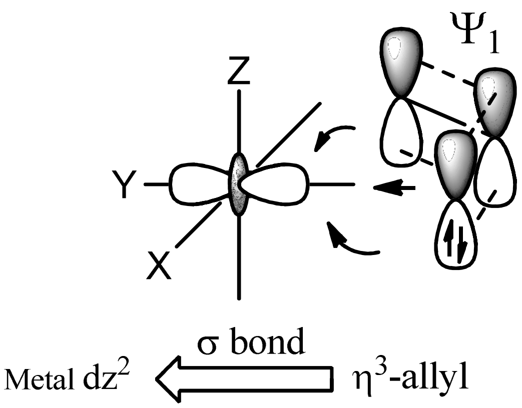


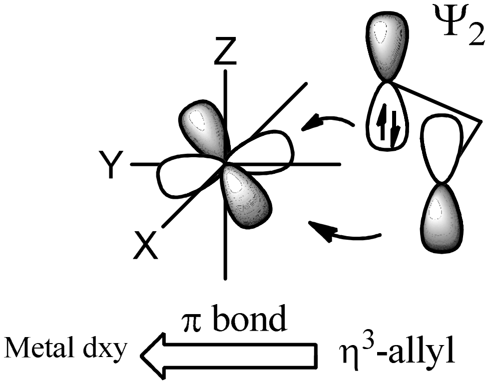
covalent model: 3e donor (0 charge)
ionic model: 4e donor (-1 charge)

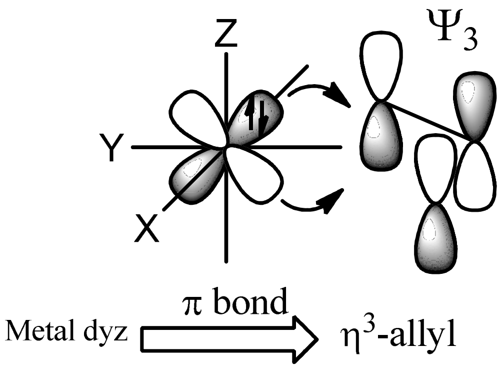


- As the number of nodes on the allyl ligand increase the MOs of the free ligand increase in energy, i.e. become less stable.

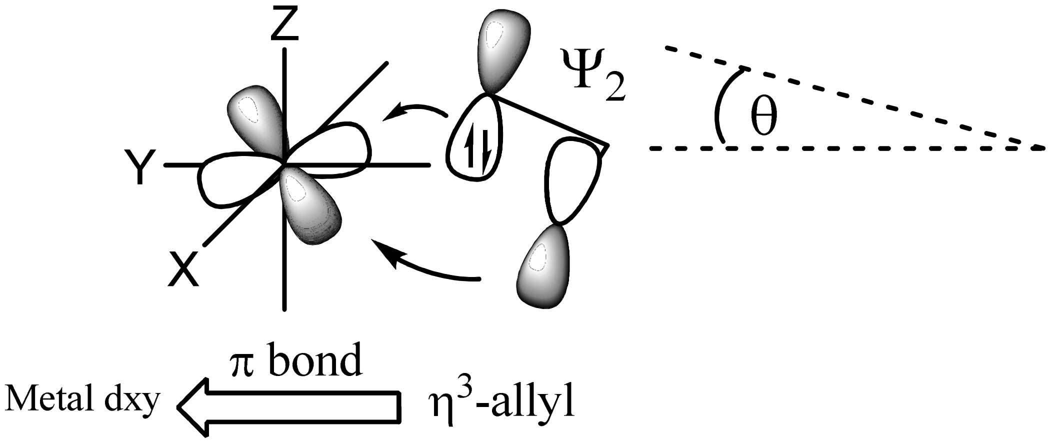


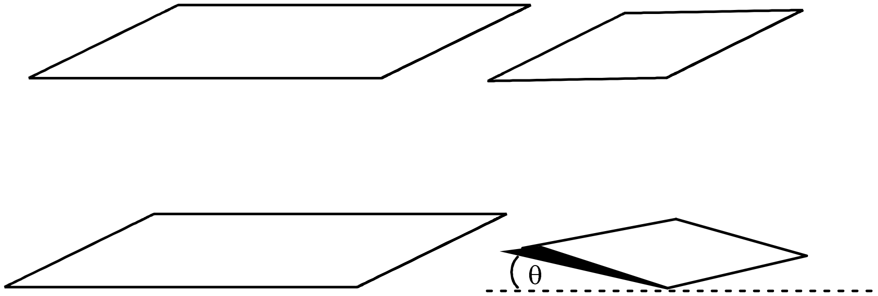




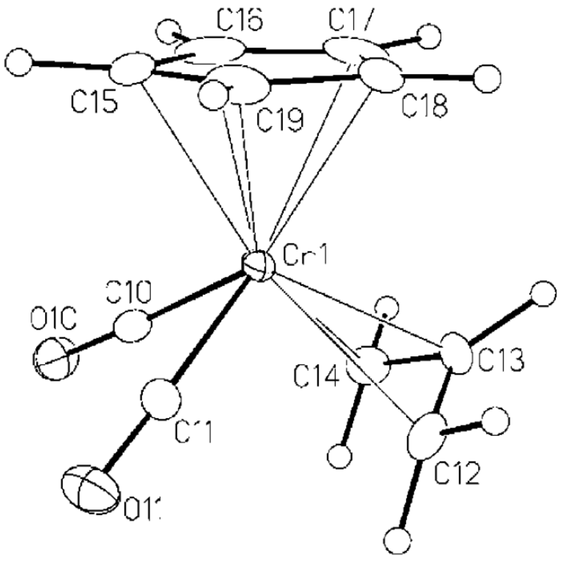


- **Frontier molecular orbitals of the metal allyl fragment:**
  - Ψ_1 is occupied by 2 electrons and has appropriate symmetry, energy and orientation to overlap with a suitable metal dσ orbital.
  - Ψ_2 is also occupied by 2 electrons (ionic model) and has appropriate symmetry, energy and orientation to overlap with a suitable metal dπ orbital.
  - Ψ_3 is unoccupied and has appropriate symmetry, energy and orientation to overlap with a suitable metal dπ orbital for back donation.

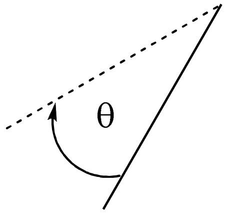


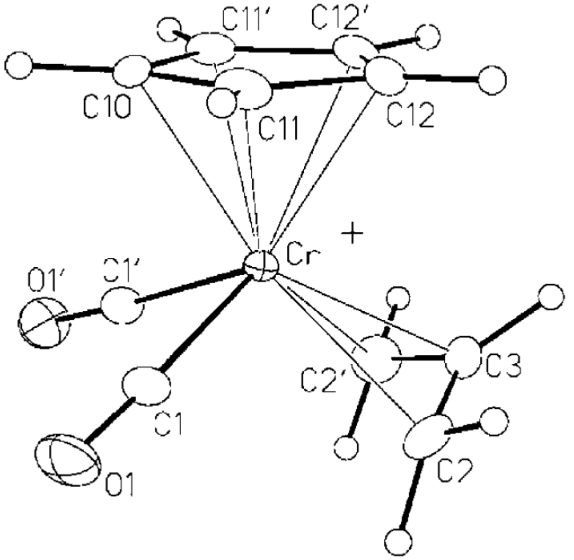


- The plane of the allyl is canted at an angle θ with respect to the coordination polyhedron around the metal (θ is usually 5°–10°).
- The extent of orbital overlap between Ψ_2 and the d_{xy} orbital on the metal is improved if the allyl group moves in this way.



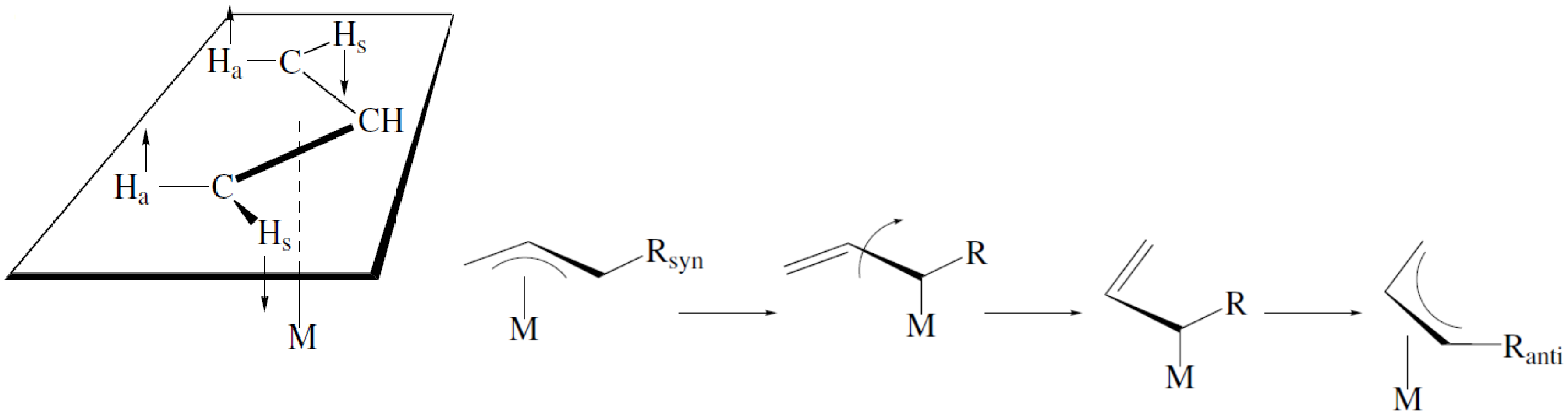
Neutral Cr(II) η^3-allyl complex





Cationic Cr(III) η^3-allyl complex

- In the cationic complex the $Cr(CO)_2$ plane is tilted fully 10° closer to the plane of the ring than it is in neutral complex.
- This substantial relaxation of the roughly square pyramidal coordination sphere may be attributed to the reduction in dπ back-donation from the oxidized metal center to the ancillary carbonyl and allyl ligand.

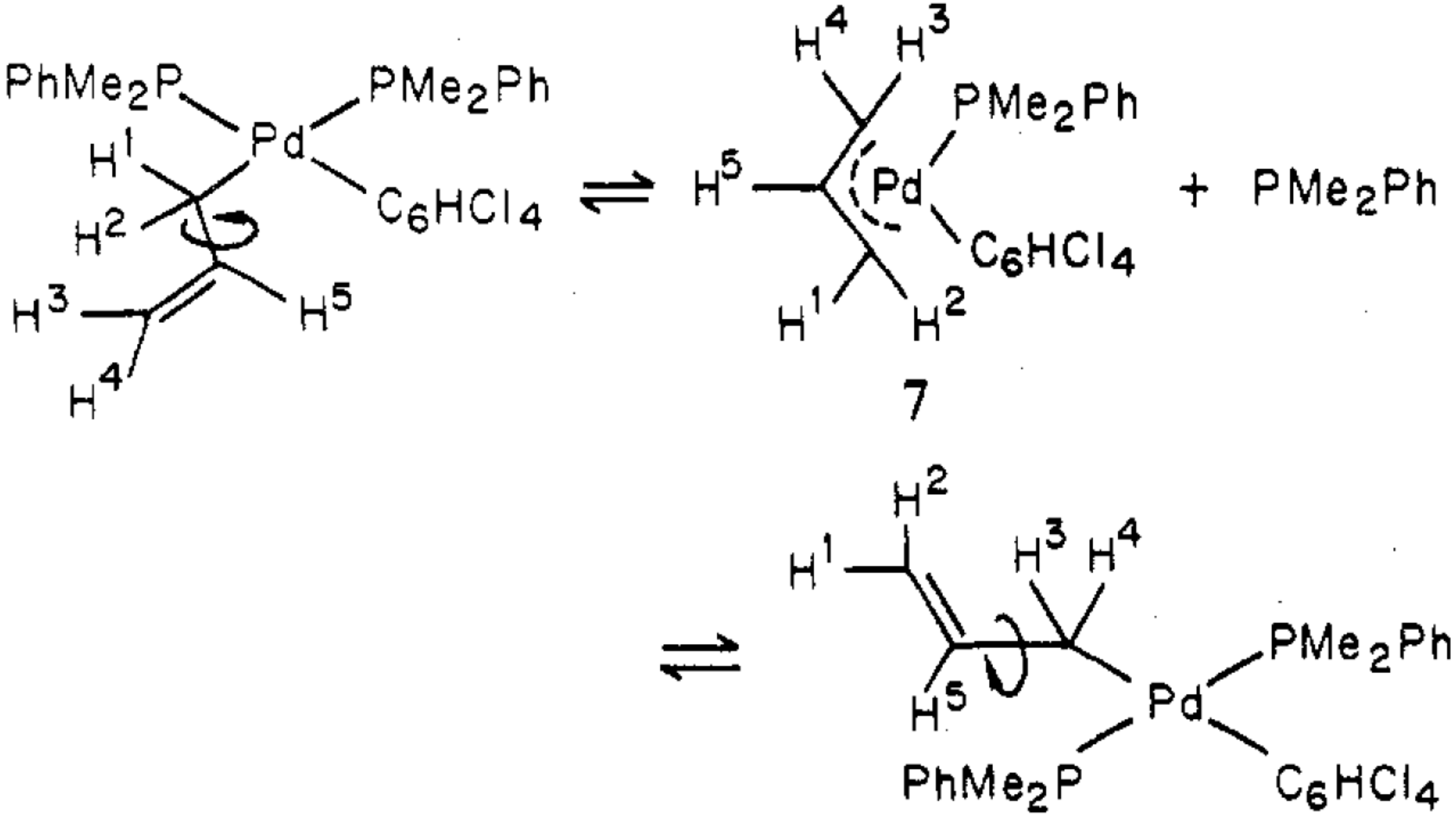


- The terminal CH_2 groups of the allyl are twisted about the C−C vector so as to rotate the ***anti hydrogens*** **(H_a)** away from the metal, and the ***syn hydrogens*** **(H_s)** toward the metal.

- This allows the bonding *p* orbital on these carbons to point more directly toward the metal, thus further improving the M-L overlap.

- The η^3-allyl group often shows ***exchange of the syn and anti substituents***. One mechanism goes through an η^1-allyl intermediate.

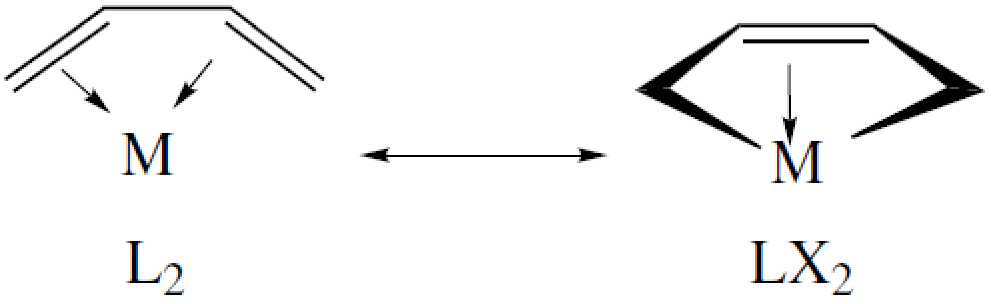
- This kind of exchange can affect the appearance of the ^{1}H NMR spectrum and also means that an allyl complex of a given stereochemistry may rearrange with time.



Numata et al. Inorg. Chem., 1977, 16, 1737.

Transition metal diene complexes

- The diene ligand usually acts as a 4e donor in its *cisoid* conformation.
- This L_2 f*orm is analogous to the Dewar-Chatt-Duncanson extreme for alkenes.*
- Analogous to metal alkene systems the LX_2 (enediyl or *$\sigma_2\pi$) form* ***to the metalacyclopropane*** extreme.

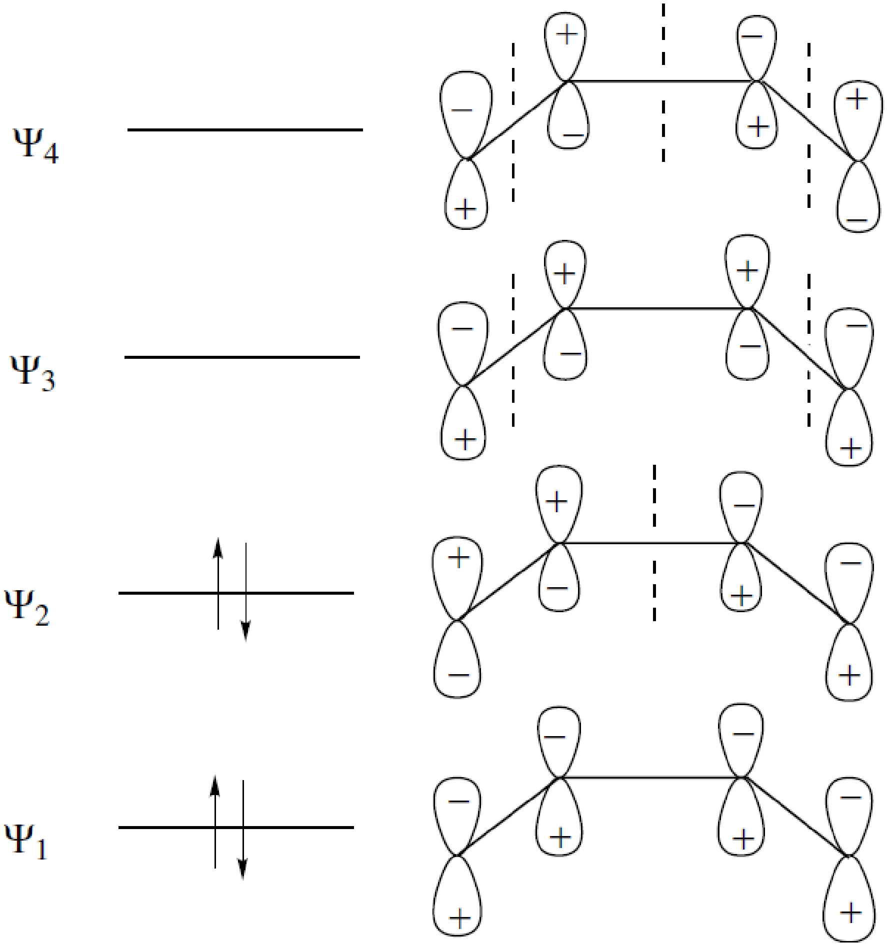


- The L_2 form is rarely seen with the LX_2 form becoming more important as the back donation increases.

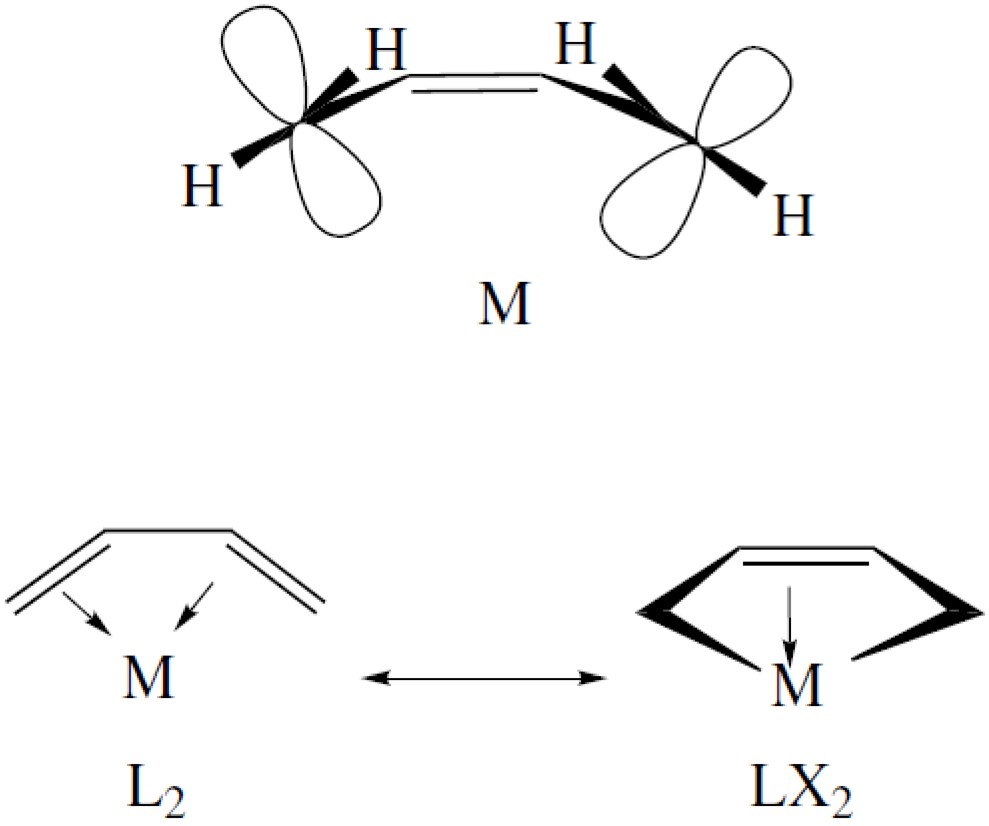
- The frontier orbitals of the butadiene, **ψ_2 (HOMO) and ψ_3 (LUMO)**, are the most important in bonding to the metal.
- Depletion of electron density in ψ_2 by σ donation to the metal and population of ψ_3 by back donation from the metal lengthens the C1-C2 bond and shortens the C2-C3 bond because ψ_2 is C1-C2 antibonding and ψ_3 is C2-C3 bonding.

Binding to a metal usually depletes the ligand HOMO and fills the ligand LUMO. This is the main reason why binding has such a profound effect on the chemical character of a ligand.

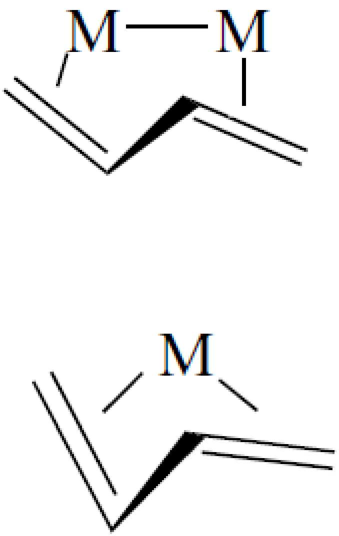
The structure of the bound form of a ligand is often similar to that of the first excited state of the free ligand because to reach this state we promote an electron from the HOMO to the LUMO.

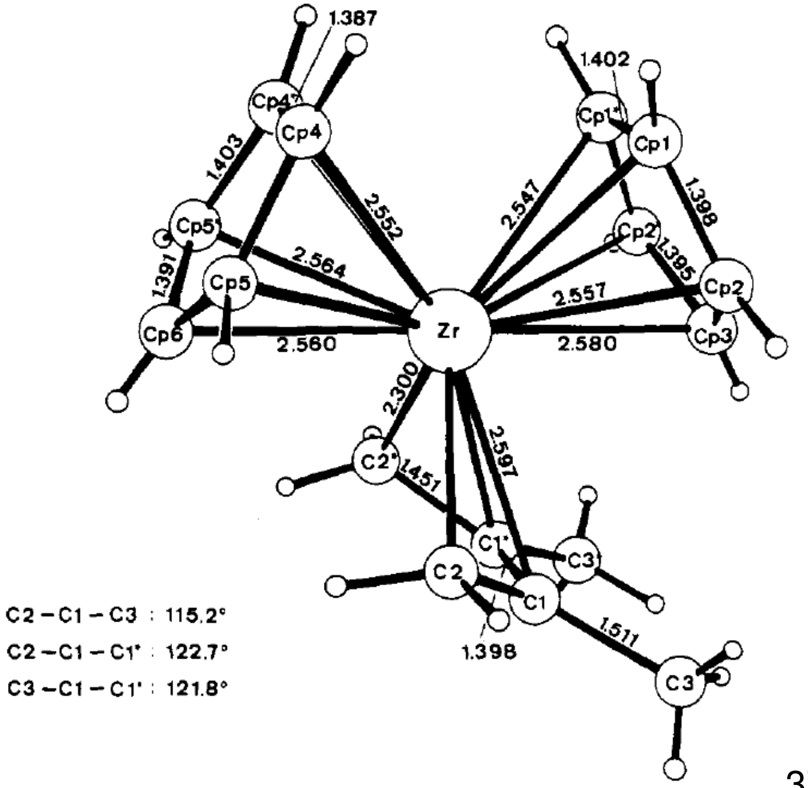


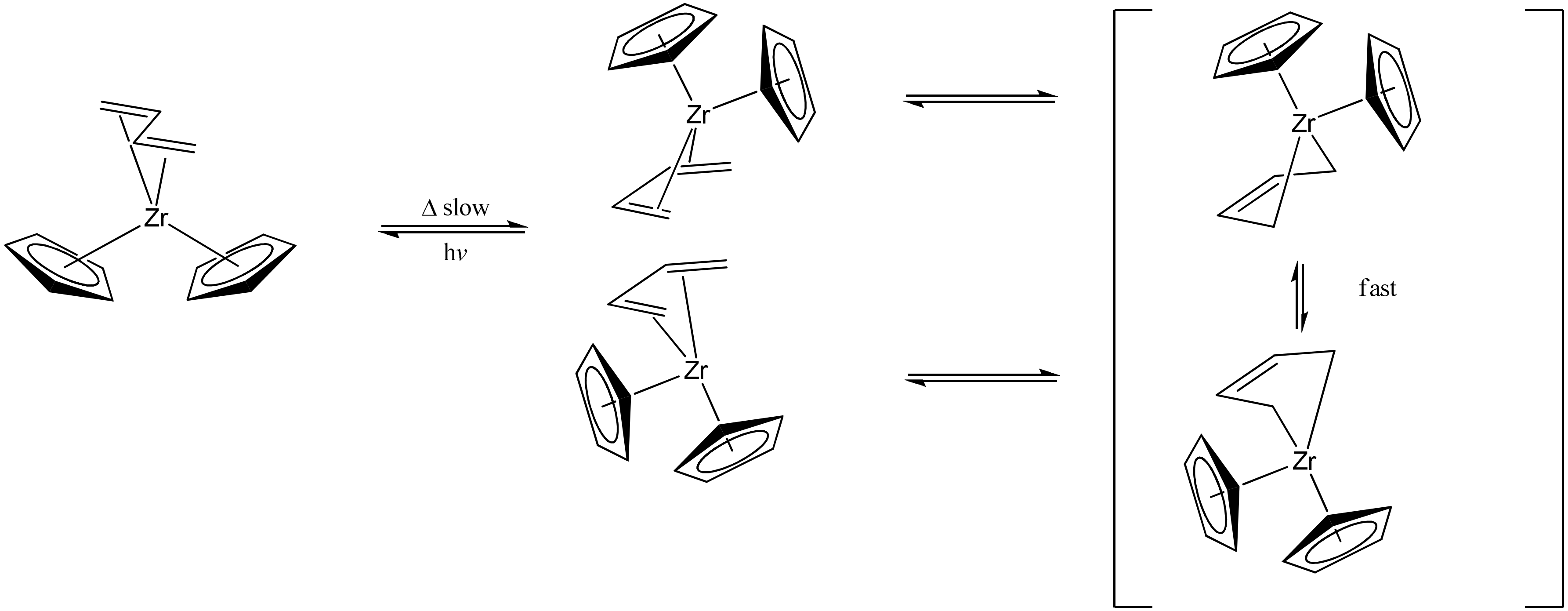
- **Depletion of electron density in ψ_2 by σ donation to the metal and population of ψ_3 by back donation from the metal lengthens the C1-C2 bond and shortens the C2-C3 bond because ψ_2 is C1-C2 antibonding and ψ_3 is C2-C3 bonding.**



- The binding of butadiene in the *transoid* form is much rarer.
- It is found in the osmium cluster $Os_3(CO)_{10}(C_4H_6)$ in which the diene is η^2 bound to two different Os centers.
- In $Cp_2Zr(C_4H_6)$ and $Cp^*(CO)Cr(C_4H_6)$ the diene is bound to a single metal centre as the transoid form. The cisoid isomer also exists here but it rearranges to give a 1 : 1 thermodynamic mixture of the two forms on standing - photolysis leads to the trans form.



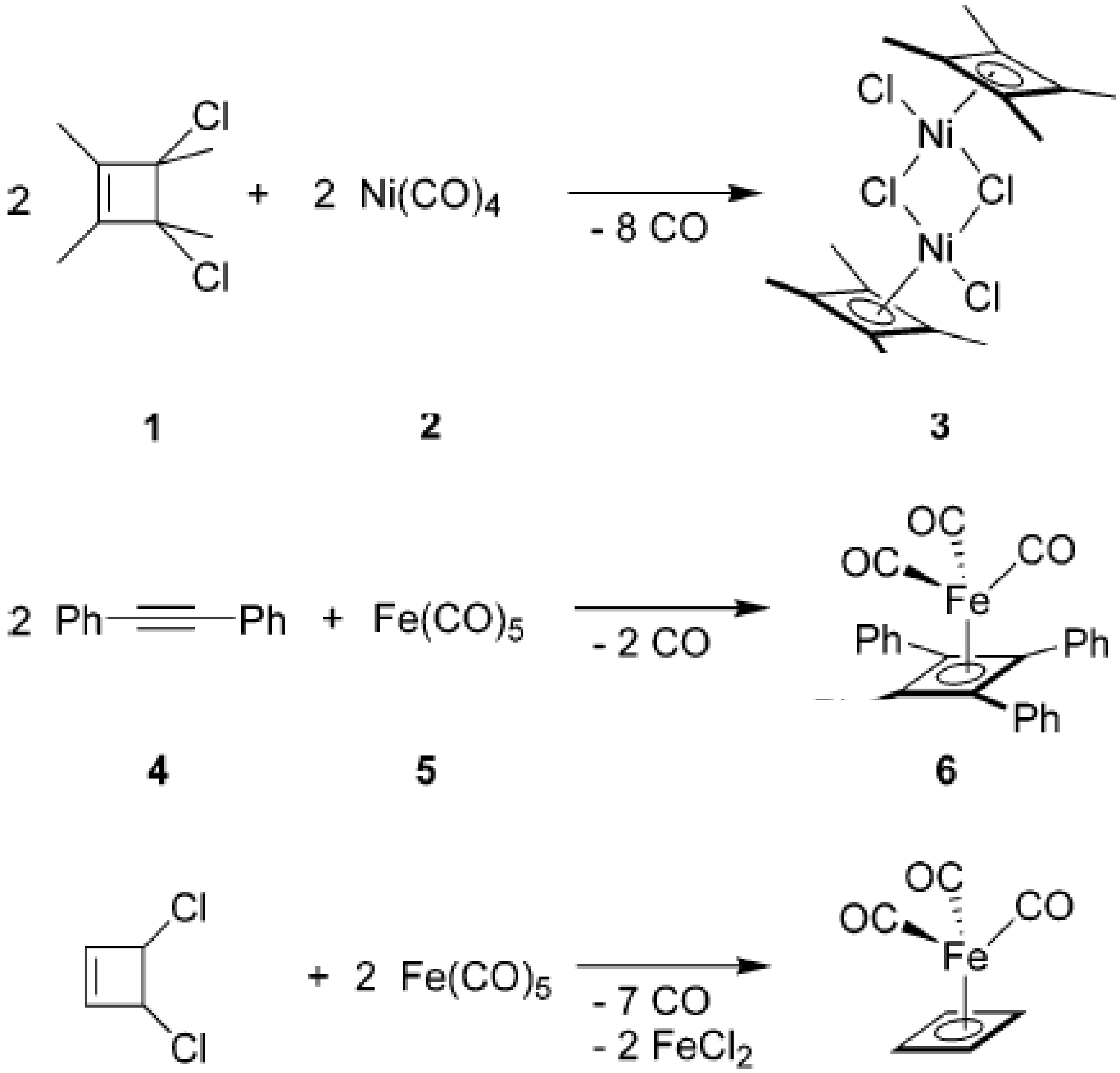



Zr
Δ slow
hν
Zr
Zr
Zr
fast
Zr

Transition metal cyclobutadiene complexes

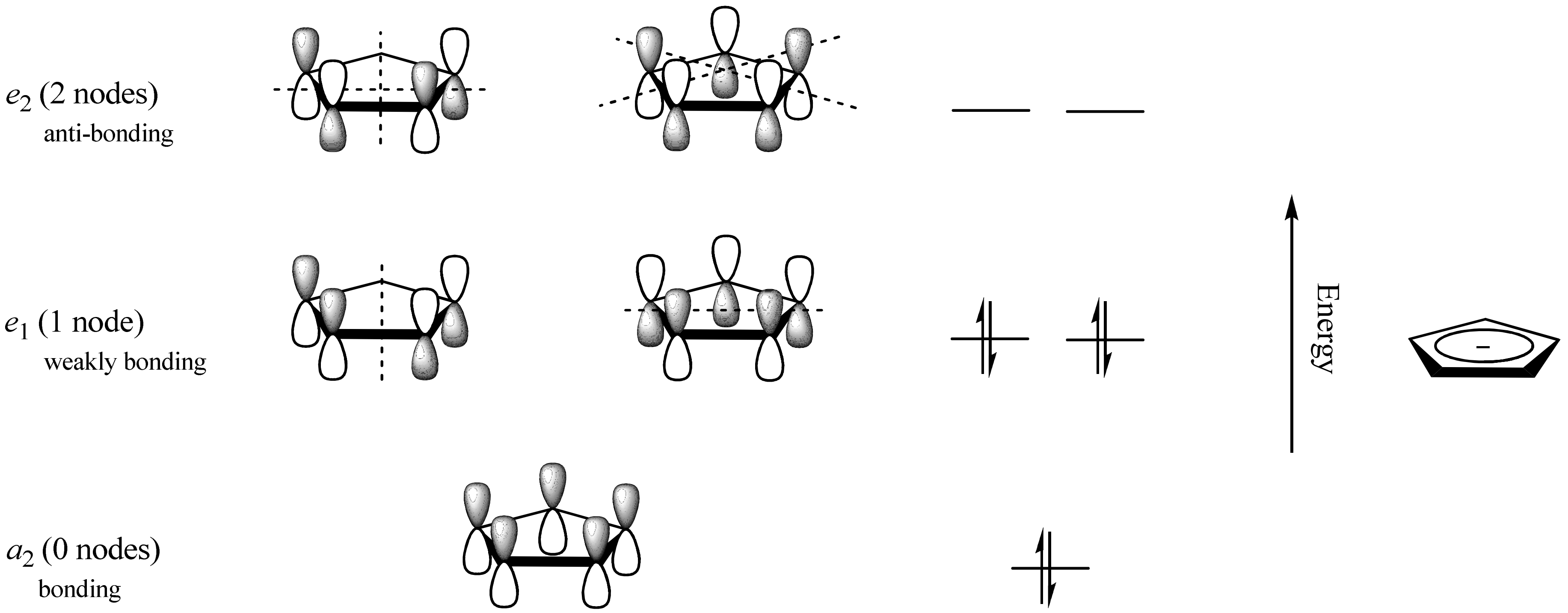
- Most of the neutral ligands we have studied (apart from carbenes) have been stable in the free state.
- Cyclobutadienes on the other hand are highyl reactive when not complexed to a late transition metal.
- The free molecule, with four π *electrons, is* antiaromatic and rectangular, but the ligand is square and appears to be aromatic.
- By populating the LUMO of the free diene the ligand is stabilized by metal back donation.
- Thus by gaining partial control of two more π *electrons* the diene attains an electronic structure resembling that of the aromatic six π*-electron dianion.*
- Ligand-to-metal σ *donation prevents the ligand from* accumulating excessive negative charge.
- This again is a clear example of the free and bound forms of the ligand being substantially different from one another.

Preparation



The Electronic Structure of Ferrocene

- The two cyclopentadienyl (Cp) rings of ferrocene may be orientated in the two extremes of either an eclipsed (D_{5h}) or staggered (D_{5d}) conformation.
- The energy of rotation about the Fe-Cp axis is very small (~ 4 $kJmol^{-1}$) and ground state structures of ferrocene may show either of these conformations.
- There is also very little difference in electronic states between the D_{5h} and D_{5d} symmetries however the D_{5d} point group irreducible representations are used here in the description of the electronic structure of ferrocene as they simplify the symmetry matching of ligand molecular orbitals and metal atomic orbitals.
- The primary orbital interactions that form the metal-ligand bonds in ferrocene occur between the Fe orbitals and the π-orbitals of the Cp ligand.
- If D_{5d} symmetry is assumed, so that there is a centre of symmetry in the ferrocene molecule through the Fe atom there will be centro-symmetric (*g*) and anti-symmetric (*u*) combinations.
- The five p-orbitals on the planar Cp ring (D_{5h} symmetry) can be combined to produce five molecular orbitals.



e_2 (2 nodes)
anti-bonding

e_1 (1 node)
weakly bonding

a_2 (0 nodes)
bonding

The π-molecular orbitals of the cyclopentadienyl ring (D_{5h})

- One combination has the full symmetry of the ring (a_2)
- There are two doubly degenerate combinations (e_1 and e_2) having one and two planar nodes at right angles to the plane of the ring.
- The relative energies of these orbitals increase as the number of nodes increases.
- The a_2 and e_1 orbitals are both fully occupied in the electronic configuration of the Cp^- anion whereas the e_2 orbitals are net anti-bonding and are unfilled.

- For a bis-cyclopentadienyl metal complex (η^5-Cp)$_2$M , such as ferrocene, the π-orbitals of the two Cp ligands are combined pairwise to form the symmetry-adapted linear combination of molecular orbitals (SALC's).

- To do this, the sum and difference of corresponding molecular orbitals on the Cp ligand must be taken, e.g. (ψ_1+ψ_1), (ψ_1-ψ_1); (ψ_2+ψ_2), (ψ_2-ψ_2) etc.

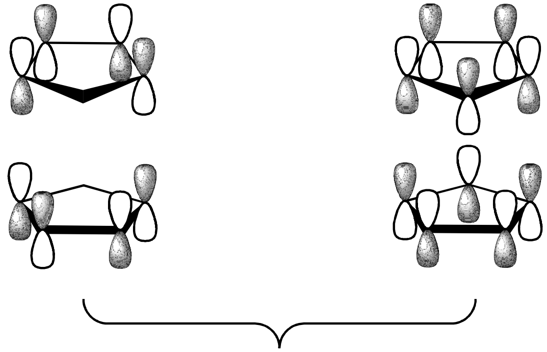
- For example, 'ψ_1+ψ_1' gives rise to a molecular orbital of a_{1g} symmetry.

- This gives rise to three sets of ligand molecular orbitals of gerade (*g*) and ungerade (*u*) symmetry ***with respect to the centre of inversion***;

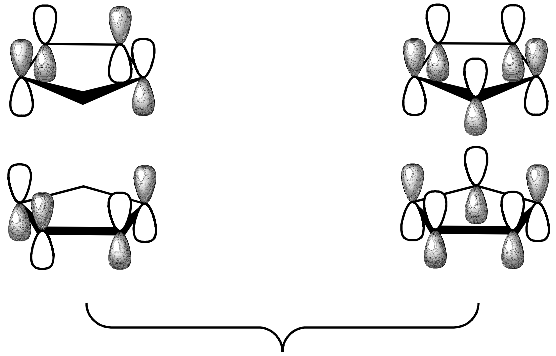
  - a low lying filled bonding pair of a_{1g} and a_{2u} symmetry
  - a filled weakly bonding pair of e_{1g} and e_{1u} symmetry
  - an unfilled anti-bonding pair of e_{2g} and e_{2u} symmetry.

- As the two Cp rings are *ca.* 4Å apart, the in-phase and out-of-phase combinations are expected to be close in energy.

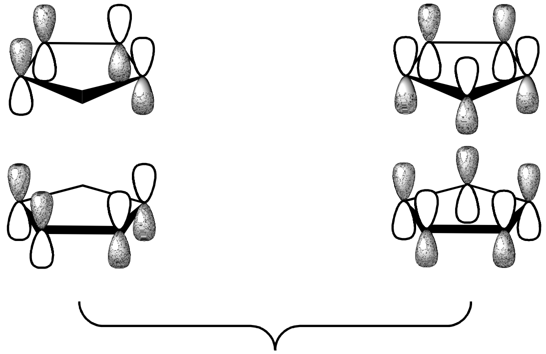
SALC's for a (η^5-Cp)$_2$M complex; $\Gamma_\pi = A_{1g} + A_{2u} + E_{1g} + E_{1u} + E_{2g} + E_{2u}$



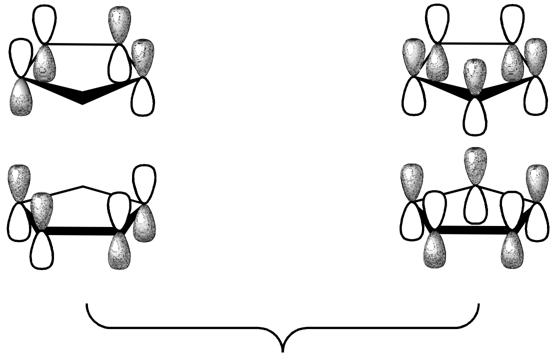
e_{2g}



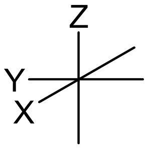
e_{2u}

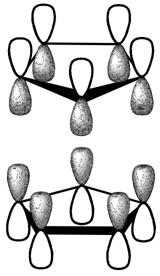


e_{1g}

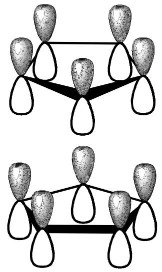


e_{1u}





a_{1g}



a_{2u}

- The metal orbitals transform as

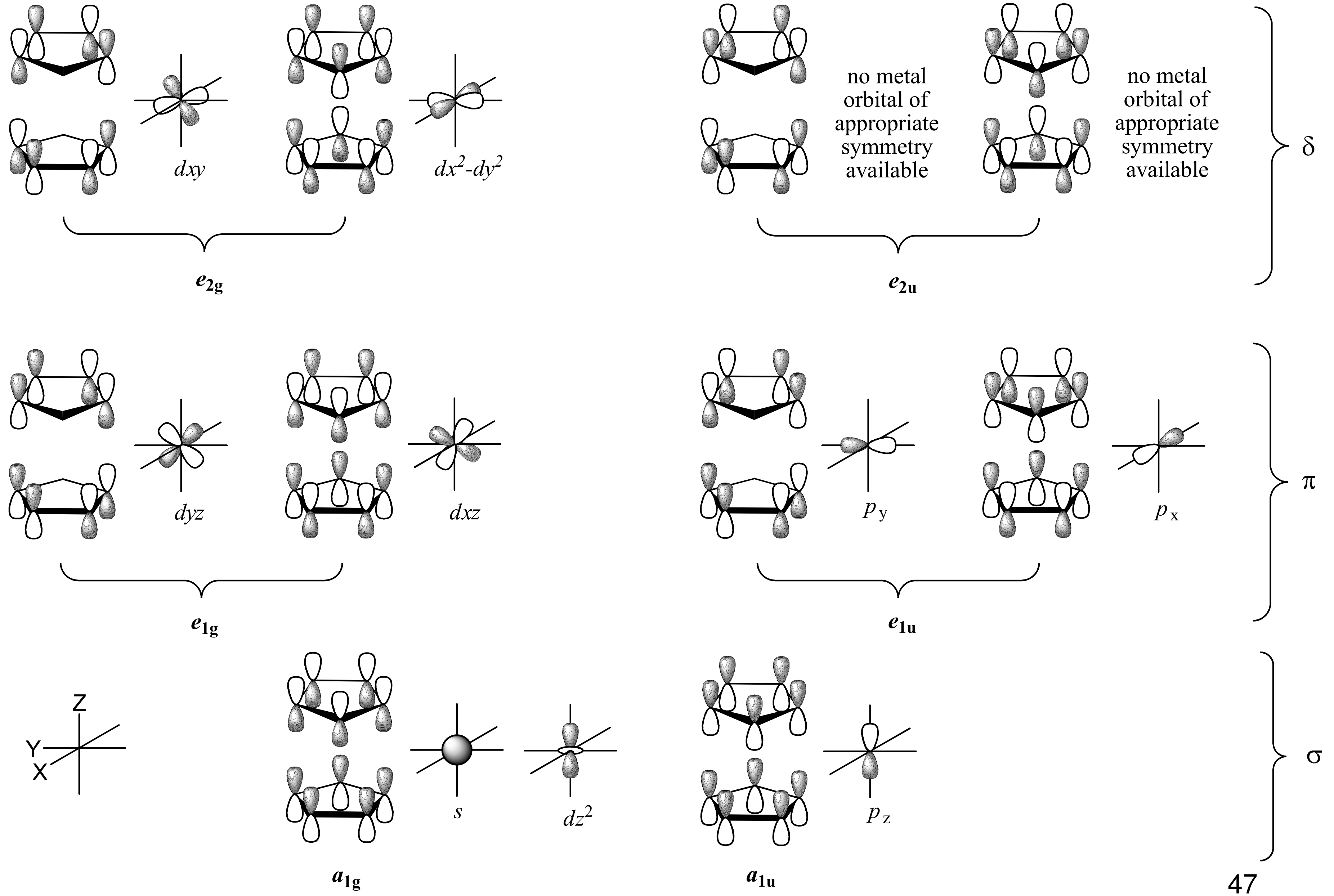
$$A_{1g}\,(d_{z^2}, s) + A_{2u}\,(p_z) + E_{1u}\,(p_x, p_y) + E_{1g}\,(d_{yz}, d_{xz}) + E_{2g}\,(d_{x^2} - d_{y^2}, d_{xy})$$

- Irreducible representation of SALC's :

$$\Gamma_\pi = A_{1g} + A_{2u} + E_{1g} + E_{1u} + E_{2g} + E_{2u}$$

- By considering these ligand molecular orbitals and how overlap with metal atomic orbitals can be affected the molecular orbital bonding picture of ferrocene can be constructed.
- For example, the a_{1g} SALC orbital can in theory overlap with the Fe 4s and 3dz^2 orbitals as they are also of a_{1g} symmetry. This interaction gives rise to the bonding and anti-bonding molecular orbitals of the complex a_{1g} and a_{1g}^* respectively.
- Each combination of ligand molecular orbitals and metal molecular orbitals leads to a bonding molecular orbital $[(\psi_{\text{ligand molecular orbital}})+(\psi_{\text{metal atomic orbital}})]$ and a corresponding anti-bonding molecular orbital $[(\psi_{\text{ligand molecular orbital}})-(\psi_{\text{metal atomic orbital}})]$ providing that the energies of the two component sets are sufficiently close for overlap.

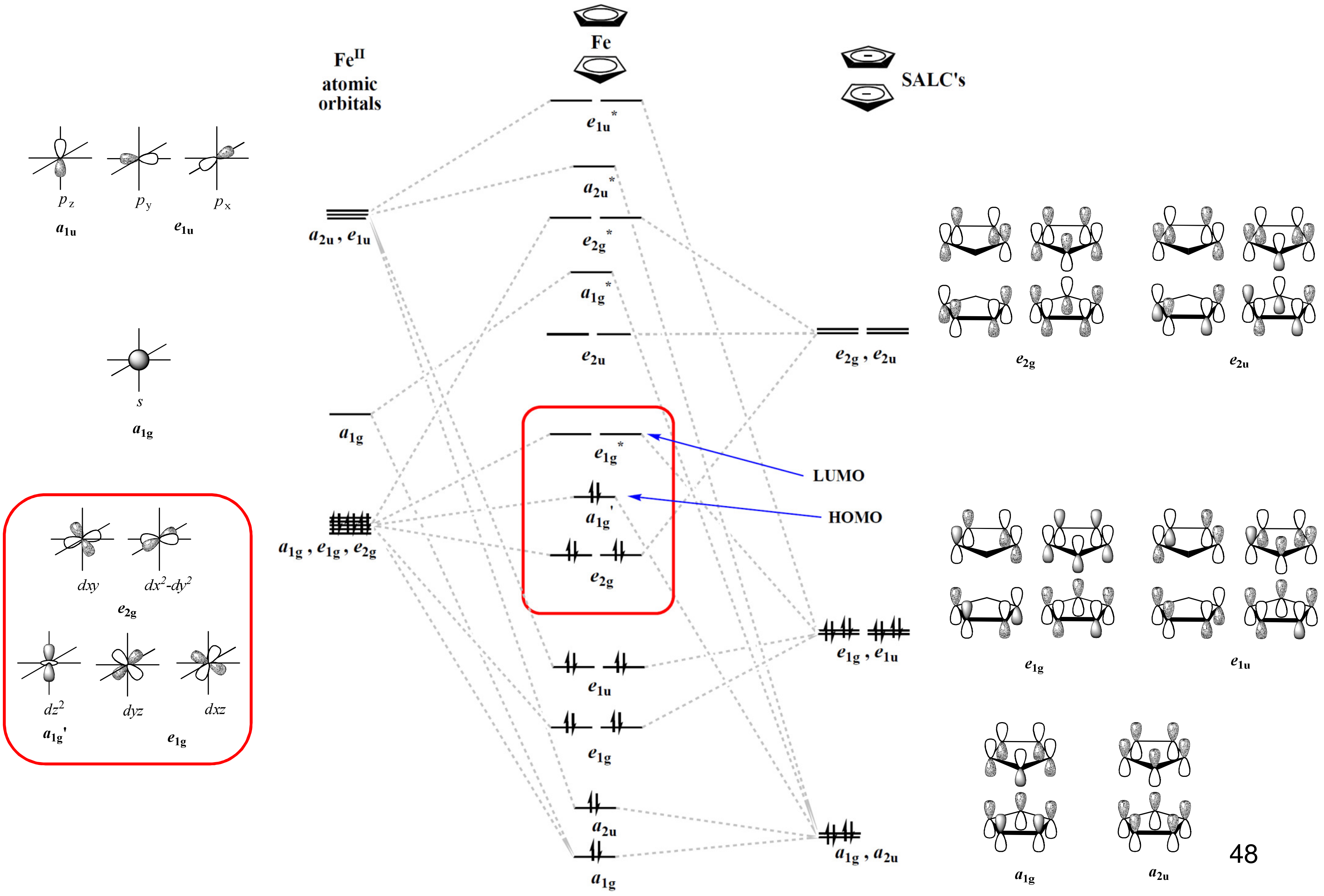
Symmetry matching of the SALC’s with the metal atomic orbitals



no metal orbital of appropriate symmetry available

no metal orbital of appropriate symmetry available

A qualitative molecular orbital diagram for ferrocene (D_{5d})



- Due to a difference in energies the a_{1g} molecular orbital is mainly ligand based with a slight admixture of the Fe 4s and 3dz^2 orbitals.
- Similarly the a_{2u} level has little if any metal character due to higher lying Fe 4p_z orbital with which it is formally able to combine.
- The e_{1g-} molecular orbital arises from the bonding combination of the ligand e_1 orbitals with the Fe 3d*xz* and 3d*yz* orbitals. This is the only symmetry combination of orbitals in the two Cp rings that has appreciable overlap with the metal 3d orbitals to act as an efficient donor and it is thus this interaction which is mainly responsible for the stability of the complex.
- The corresponding anti-bonding orbitals, $e_{1g}*$, are unfilled in the ground state of ferrocene but they are involved in excited state transitions.
- The e_{1u} bonding molecular orbitals are again mainly ligand based but with a small contribution from the higher energy Fe 3 p_x , p_y orbitals.
- The a_{1g}' molecular orbital mostly consists of the Fe 3dz^2 orbital as the ligand a_{1g} molecular orbital points between the nodes of the metal dz^2 orbital resulting in little or no overlap.
- The e_{2g} (dx^2-y^2, d*xy*) metal orbitals are considered non-bonding due to poor overlap with the ligand e_{2g} orbitals.

- Since the occupied orbitals are of either a, e_1 or e_2 type symmetry no intrinsic barrier to internal rotation is predicted as each of these molecular orbitals are symmetric about the axis of rotation.
- The very low values observed for this rotation (~ 4 kJmol^{-1}) may be attributed to van der Waals forces between the two Cp rings.
- The attachment of additional groups or ligands destroys the D_{5d}/D_{5h} symmetry of ferrocene thus altering the molecular orbital diagram.

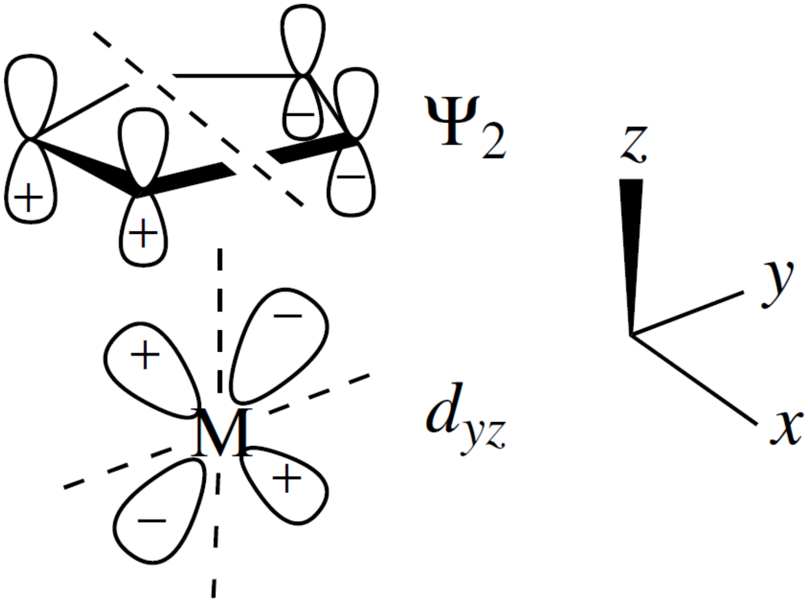
1. S. Barlow, H. E. Bunting, C. Ringham, J. C. Green, G. U. Bublitz, S. G. Boxer, J. W. Perry, S. R. Marder, *J. Amer. Chem. Soc.* 1999, 121, 3715-3723.

2. J. C. Calabrese, L. T. Cheng, J. C. Green, S. R. Marder, W. Tam, *J. Amer. Chem. Soc*. 1991, 113, 7227-7232.

3. D. R. Kanis, M. A. Ratner, T. J. Marks, *Chem. Rev.* 1994, 94, 195-242.

Half-Metallocene MO's

- The most important overlaps are ***ψ_1 with the metal dz^2***, ***and ψ_2 and ψ_3 with the d_{xz} and d_{yz} orbitals***



- ψ_4 and ψ_5 do not interact very strongly with metal orbitals, and ***the Cp group is therefore not a particularly good π acceptor.***
- This and the anionic charge means that ***Cp complexes are generally basic***, and that the presence of the Cp encourages back donation from the metal to the other ligands present.