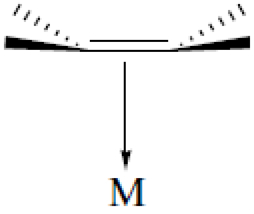
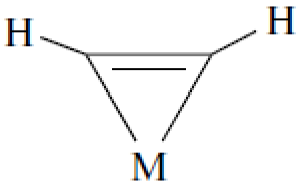
π bonded ligands

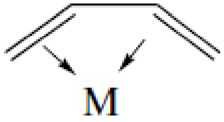
alkene complexes



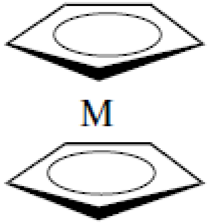


alkyne complexes

allyl complexes

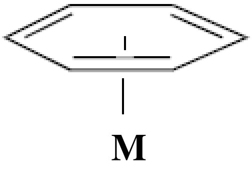


diene complexes

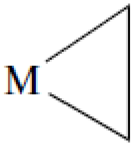


cyclopentadienyl complexes

arene complexes

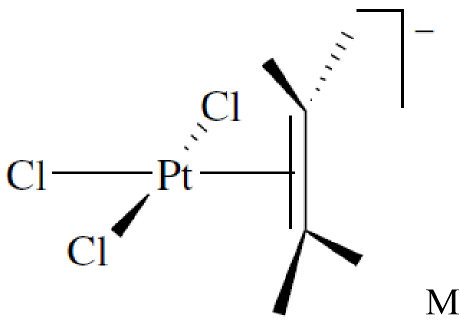


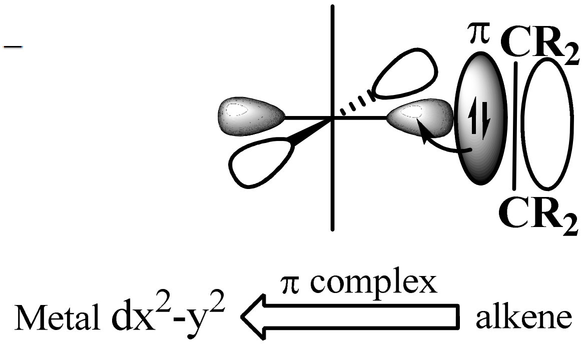
metallacycles

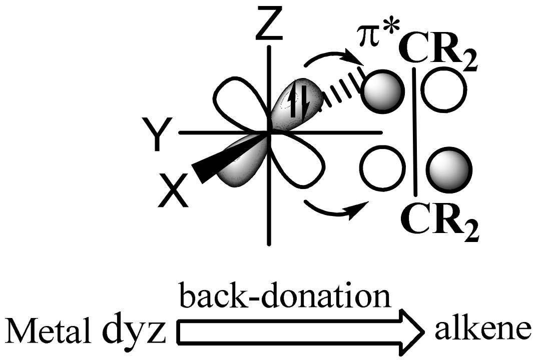


Transition metal alkene complexes

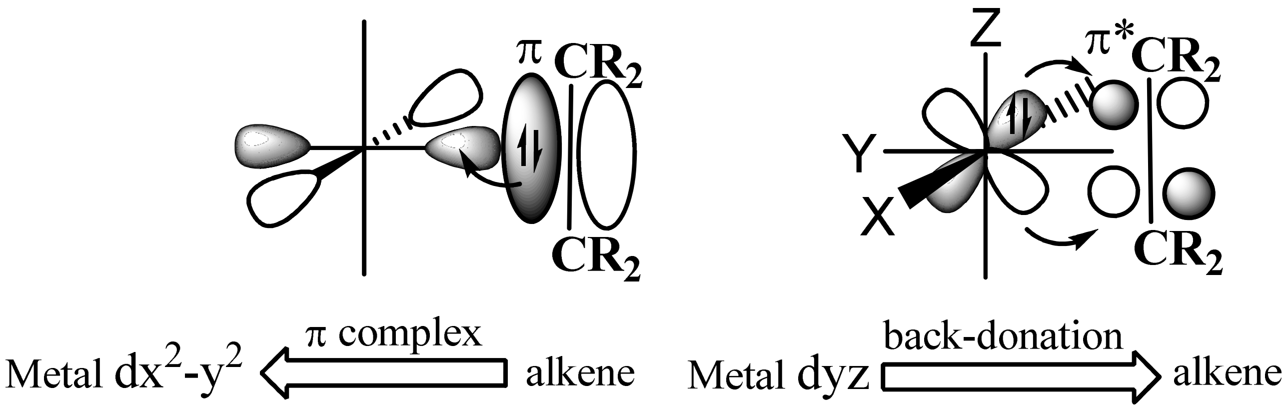
- The report in 1825 by William Zeise of crystals with composition, $KCl.PtCl_2.EtOH$, prepared from $KPtCl_4$ and EtOH was a topic of controversy for many years due to the nature of Zeise's structure - only possible by the dehydration of EtOH.





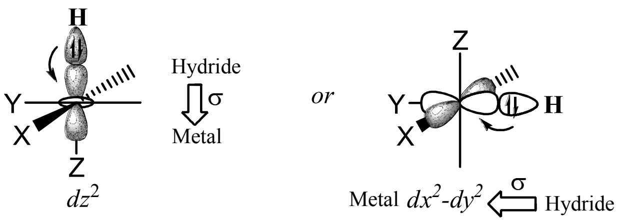


- Proof of Zeise's formulation came 13 years later when Birnbaum isolated the complex from a solution of platinic acid, $H_2PtCl_6.6H_20$, treated with ethylene.
- Zeise's salt was the first organometallic compound to be isolated in pure form.
- This discovery spawned a tremendous growth in organometallic 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.

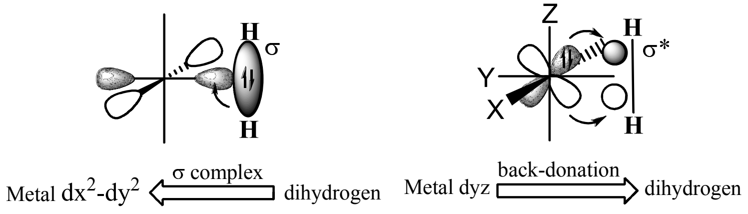


- The ***Dewar-Chatt-Duncanson model*** explains the type of chemical bonding between an unsaturated ligand and a metal forming a **π complex**.
- The π-acid ligand donates electron density into a metal d-orbital **from a π-symmetry bonding orbital** between the carbon atoms.
- The metal donates electrons 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.

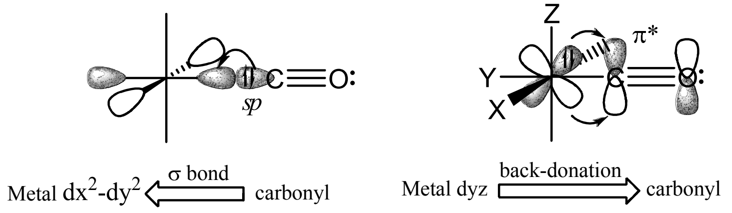
Metal Hydride



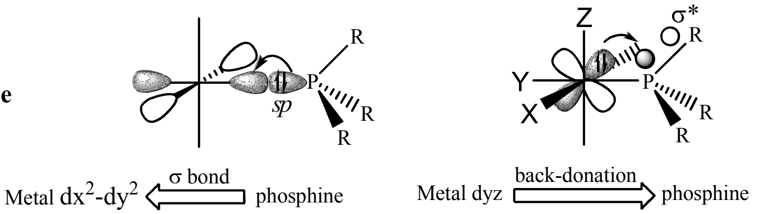
Metal Dihydrogen



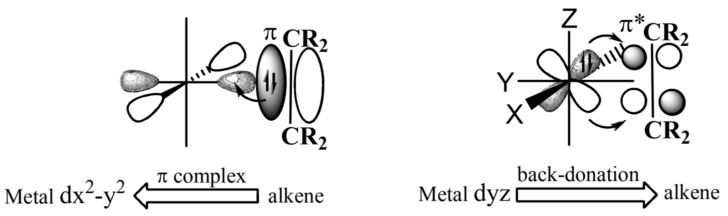
Metal Carbonyl



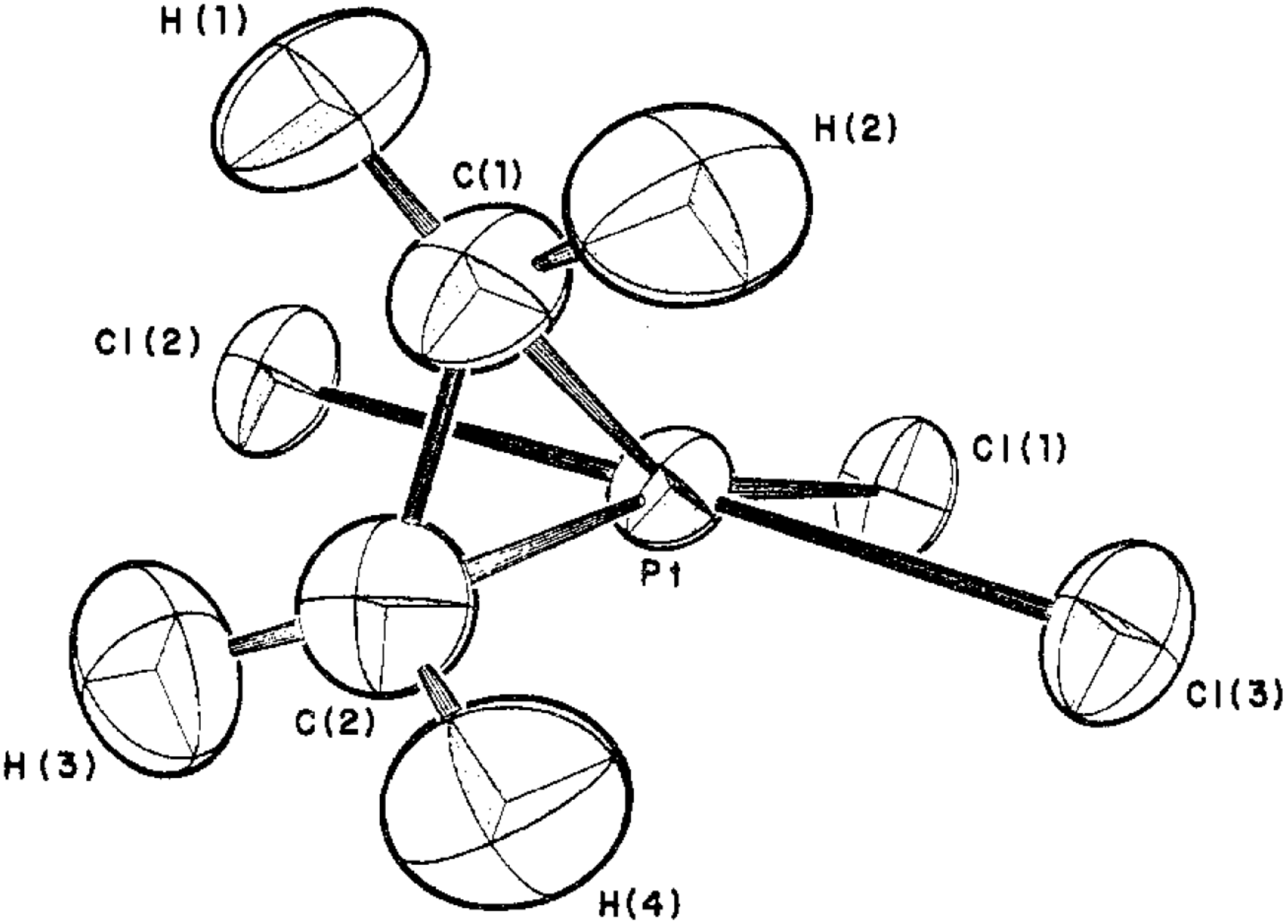
Metal Phosphine



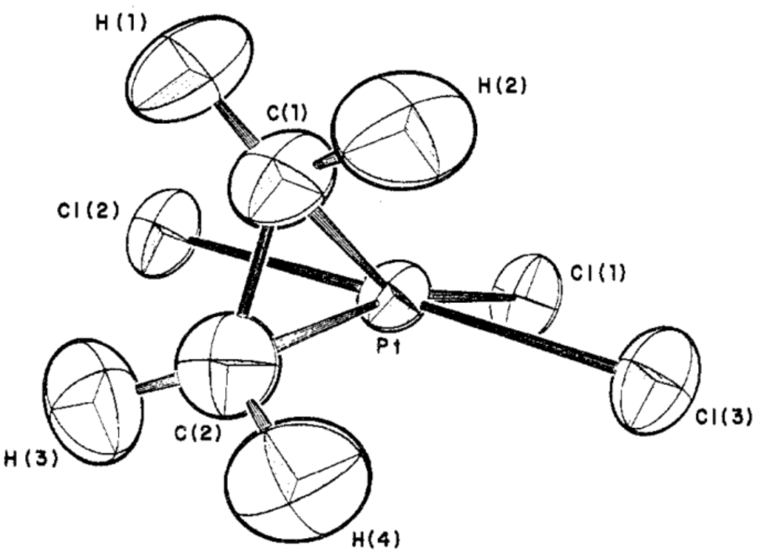
Metal Alkene



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(III)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**

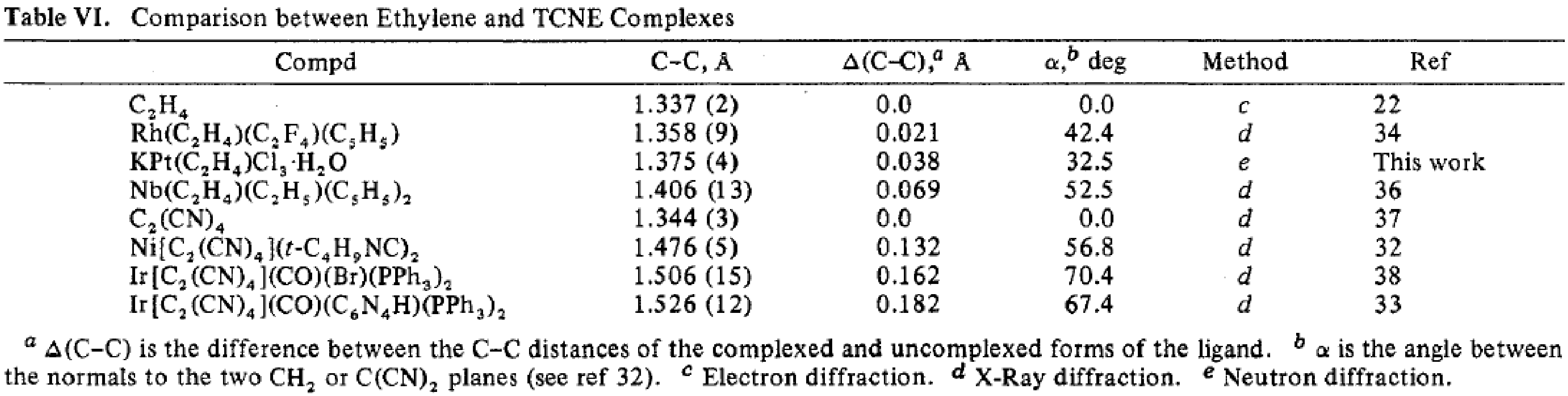
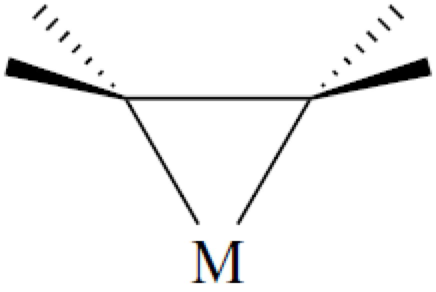


Table VI. Comparison between Ethylene and TCNE Complexes

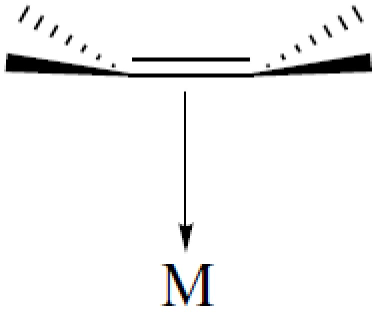
Compd	C–C, Å	Δ(C–C),[a] Å	α,[b] deg	Method	Ref
C_2H_4	1.337 (2)	0.0	0.0	*c*	22
$Rh(C_2H_4)(C_2F_4)(C_5H_5)$	1.358 (9)	0.021	42.4	*d*	34
$KPt(C_2H_4)Cl_3 \cdot H_2O$	1.375 (4)	0.038	32.5	*e*	This work
$Nb(C_2H_4)(C_2H_5)(C_5H_5)_2$	1.406 (13)	0.069	52.5	*d*	36
$C_2(CN)_4$	1.344 (3)	0.0	0.0	*d*	37
$Ni[C_2(CN)_4](t\text{-}C_4H_9NC)_2$	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 ***metalacyclopropane*** 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

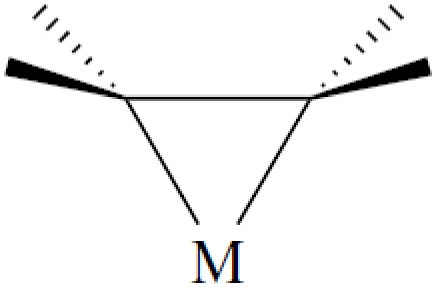


X_2

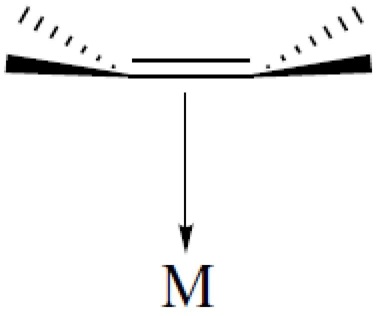


L

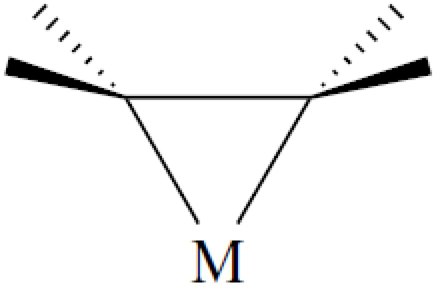
- In both cases the ligand is considered as a 2e donor in the covalent model.
- In the ionic model, the X_2 configuration has a 2- charge and is considered a 4e donor.
- In the ionic model, the L configuration does not change the oxidation state of the metal and is still considered a 2e donor.
- **One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



X_2

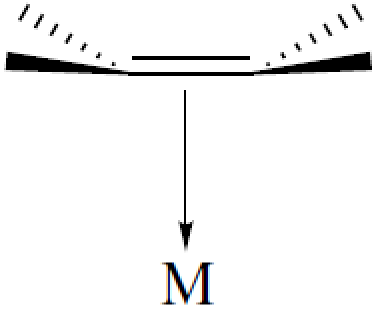


L



X_2

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

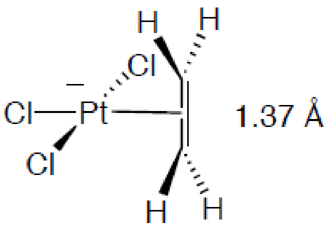


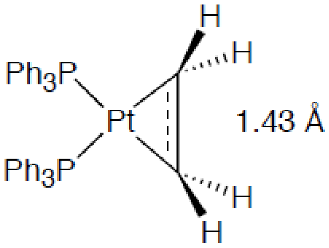
L

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



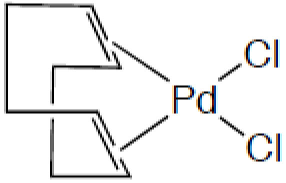


- Reactivity difference between the bonding types:
  - L-type: the alkene is electron deficient and prone to attack by nucleophiles
  - X_2-type: the carbons are carbanion-like and prone to attack by electrophiles

- 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.



Synthesis of Metal Alkenes

1. Substitution in a low-valent metal:

$$AgOSO_2CF_3 + C_2H_4 \longrightarrow (C_2H_4)AgOSO_2CF_3$$

- Reversible binding of alkenes to Ag^+ is used to separate different alkenes chromatographically on silver-doped gas chromatography columns.

$$Cp(CO)_2Fe(Me_2C{=}CH_2)^+ \xrightarrow{\text{1-hexene}} Cp(CO)_2Fe(\text{1-hexene})^+$$

- Less hindered alkenes usually bind more strongly

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

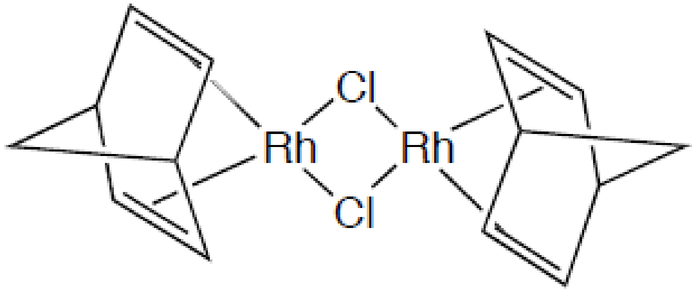
2. Reduction of a higher valent metal in the presence of an alkene:

$$\mathrm{(cod)PtCl_2 + C_8H_8{}^{2-} + cod \longrightarrow Pt(cod)_2}$$

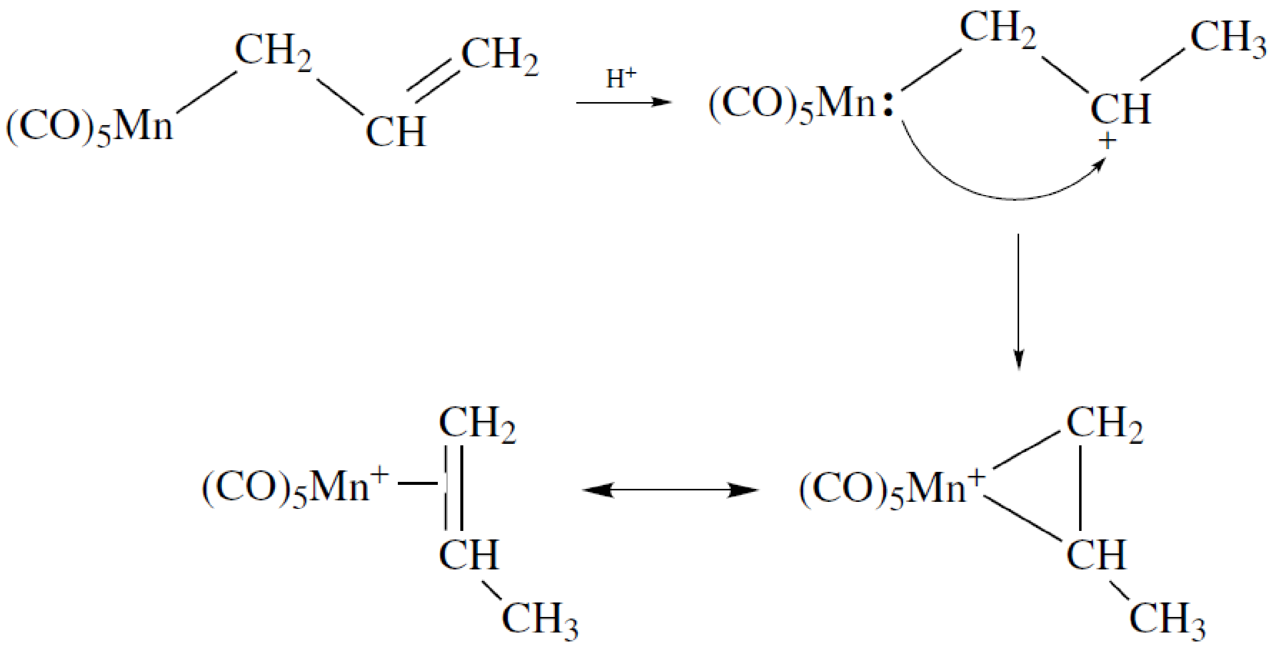
- Here the ligand acts as the reducing agent also (cod = cyclooctadiene)

$$\mathrm{RhCl_3 + nbd + CH_3CH_2OH \longrightarrow [(nbd)Rh(\mu\text{-}Cl)]_2 + CH_3CHO + HCl}$$

- Here the solvent ethanol acts as the reducing agent (a common occurrence in inorganic synthesis)



3. From alkyls and related species:



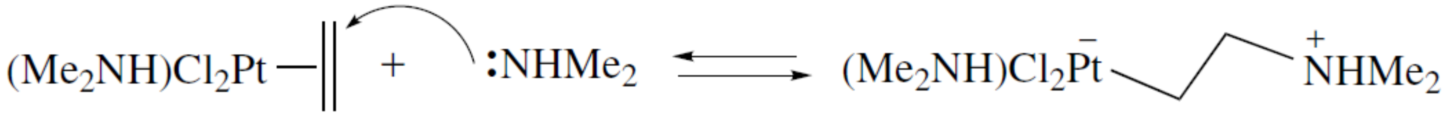
- Protonation at the terminal methylene in the η^1-allyl Mn complex creates a carbonium ion having a metal at the β position. Since the carbonium ion is a zero-electron ligand like a proton, it can coordinate to the 18e metal to give the alkene complex.

Reactions of metal alkenes

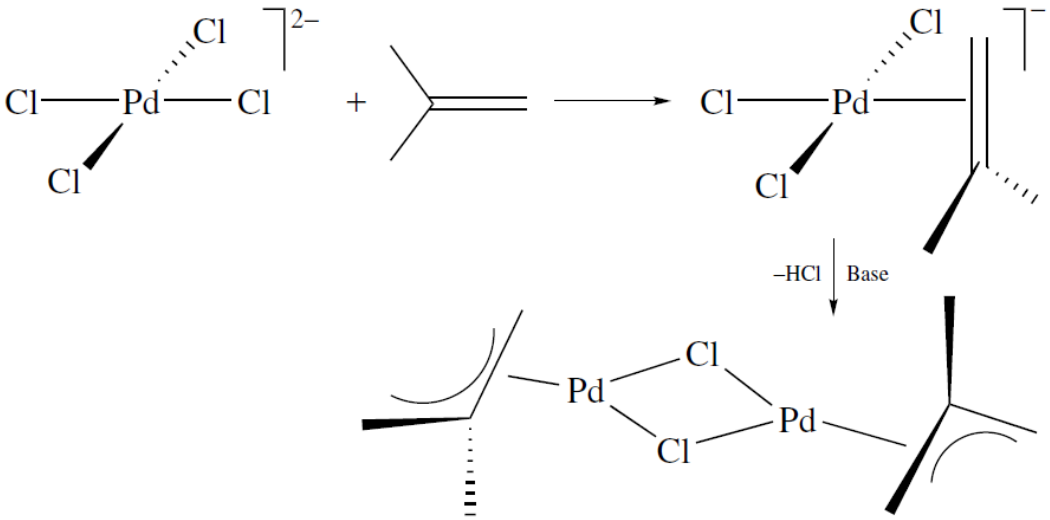
1. Insertion into M-L σ bonds to form higher alkanes

$$AuMe(PPh_3) + CF_2{=}CF_2 \longrightarrow \{(CF_2{=}CF_2)AuMe(PPh_3)\} \longrightarrow Au(CF_2{-}CF_2Me)(PPh_3)$$

2. Nucleophilic attack

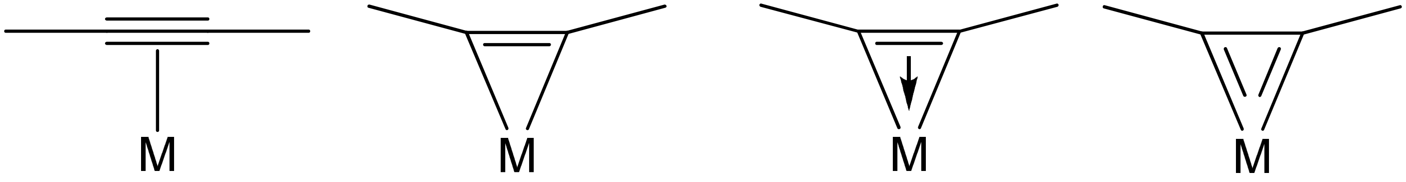


3. Oxidative addition



Transition metal alkyne complexes

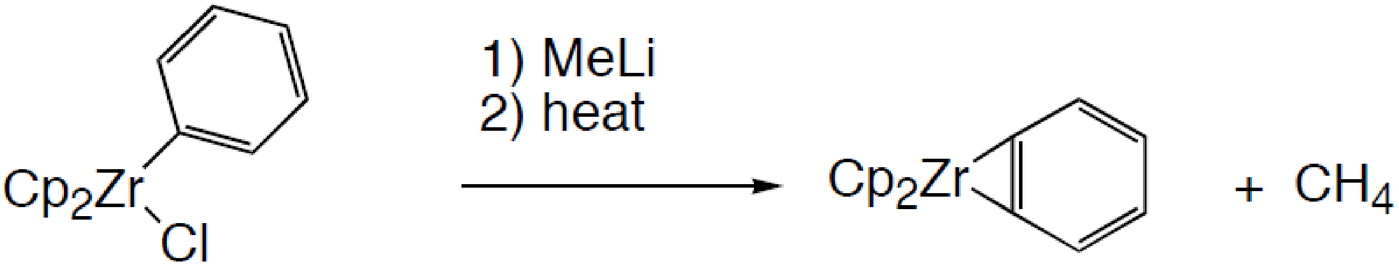
- Alkynes behave in ways broadly similar to alkenes, but being more electronegative, they tend to encourage back donation and bind more strongly.
- The substituents tend to fold back away from the metal by 30°–40° in the complex, and the M−C distances are slightly shorter than in the corresponding alkene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



	η^1	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)**

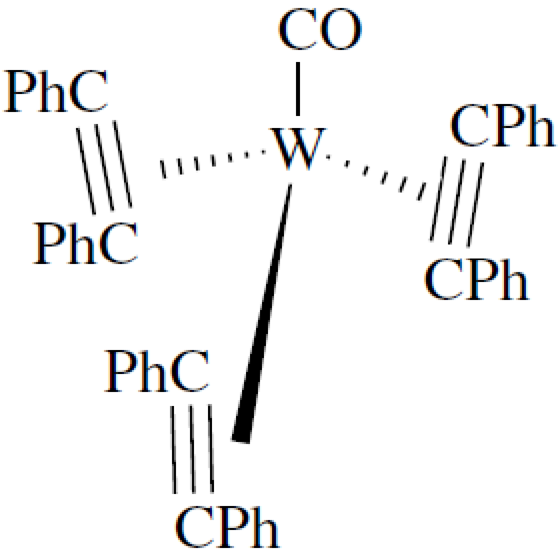
Why are alkynes more electronegative than alkenes?

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

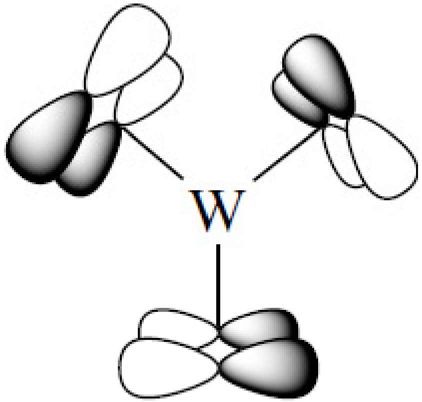


Chem. Rev., **1988**, *88*, 1047-1058

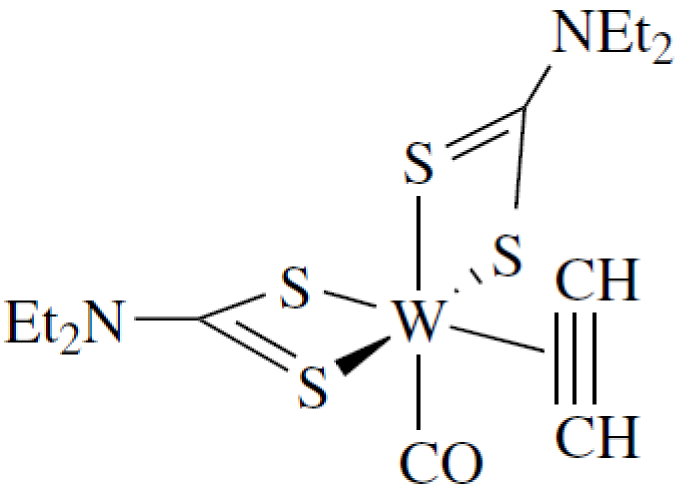
- Alkynes can also form complexes that appear to be coordinatively unsaturated.



14e species?

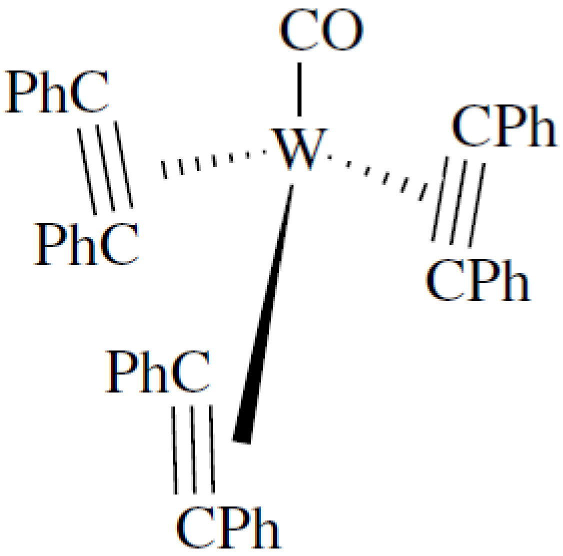


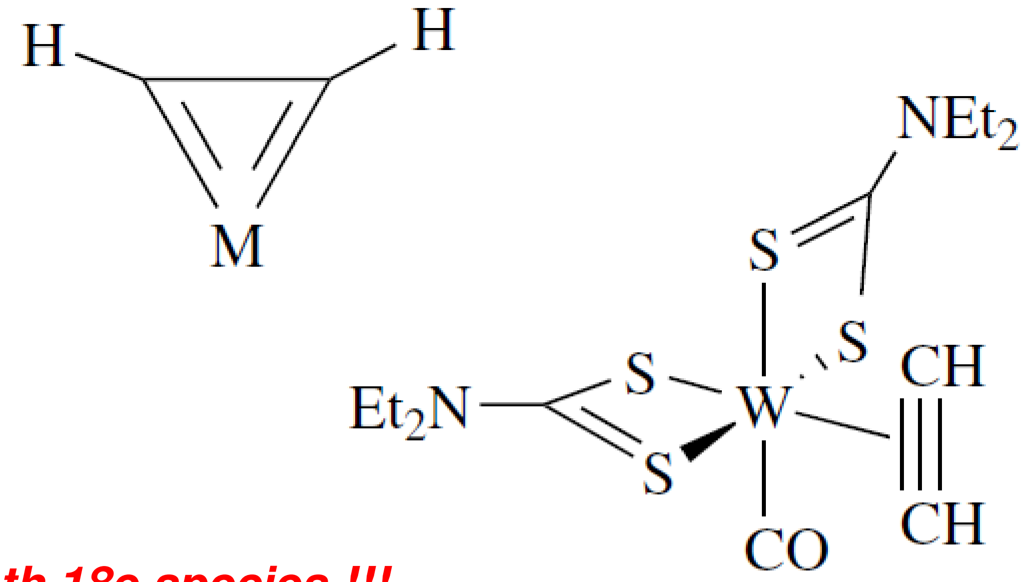
- Coordinatively unsaturated metal alkynes (contd.)



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.***



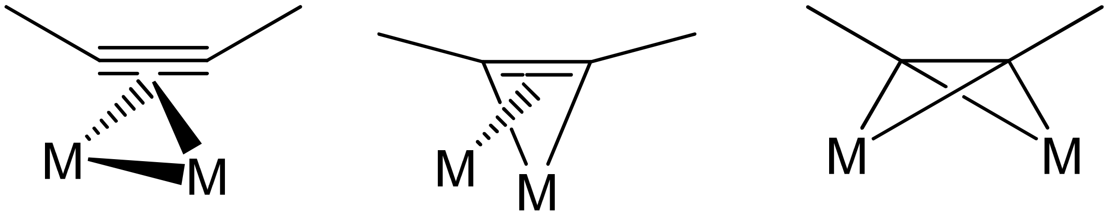


both 18e species !!!

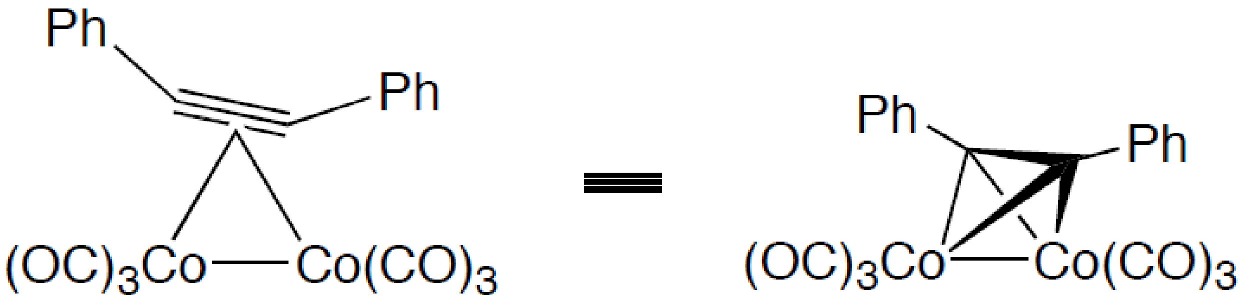
(2x 4e donor & 1 x 2e donor)

- 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.

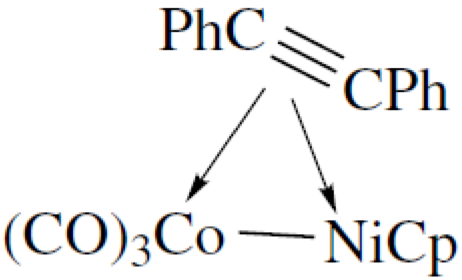
Bridging metal alkyne complexes



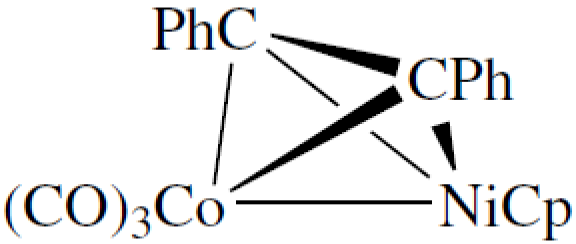
	η^2	η^3	η^4
Ionic model:	**4e (0)**	**6e (2-)**	**8e (4-)**
Covalent model:	**4e (0)**	**4e (0)**	**4e (0)**



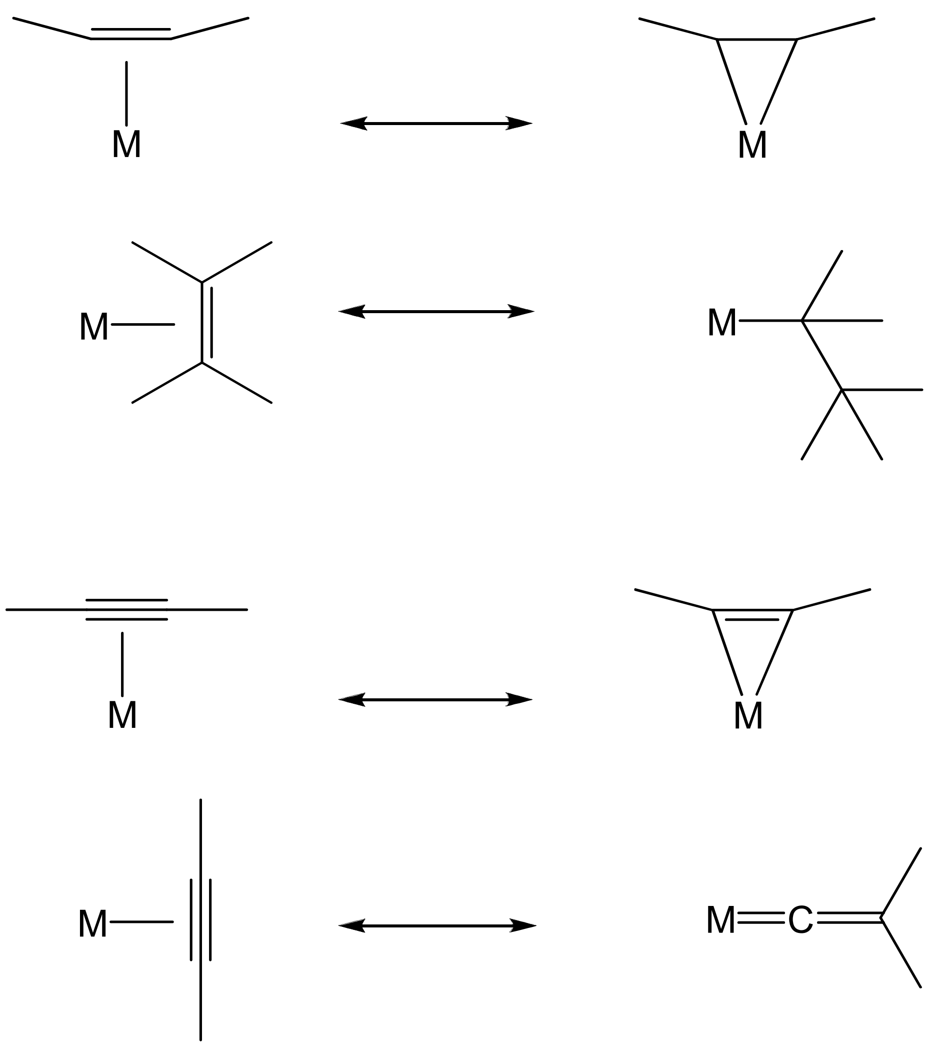
- Alkynes readily bridge an M−M bond, in which case they can act as conventional 2e donors to each metal.



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

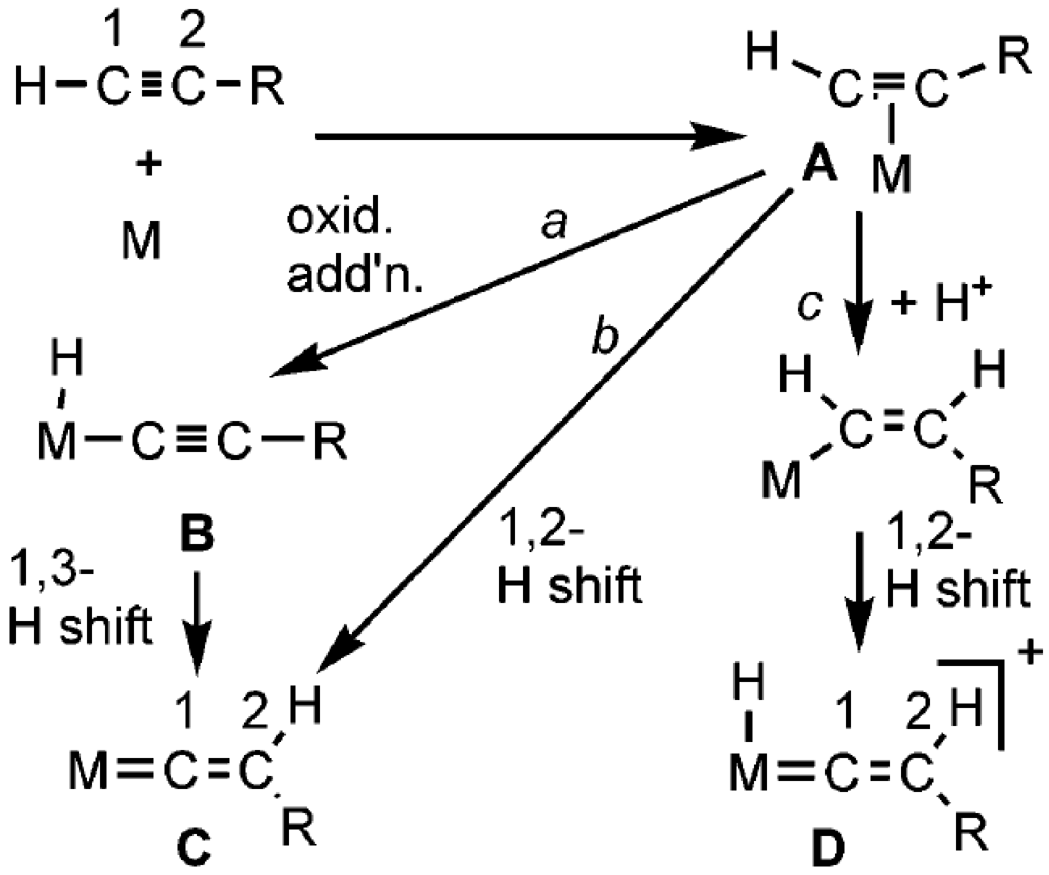


Tautomerization



metal vinylidene

Proposed Alkyne-to-Vinylidene Mechanisms



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