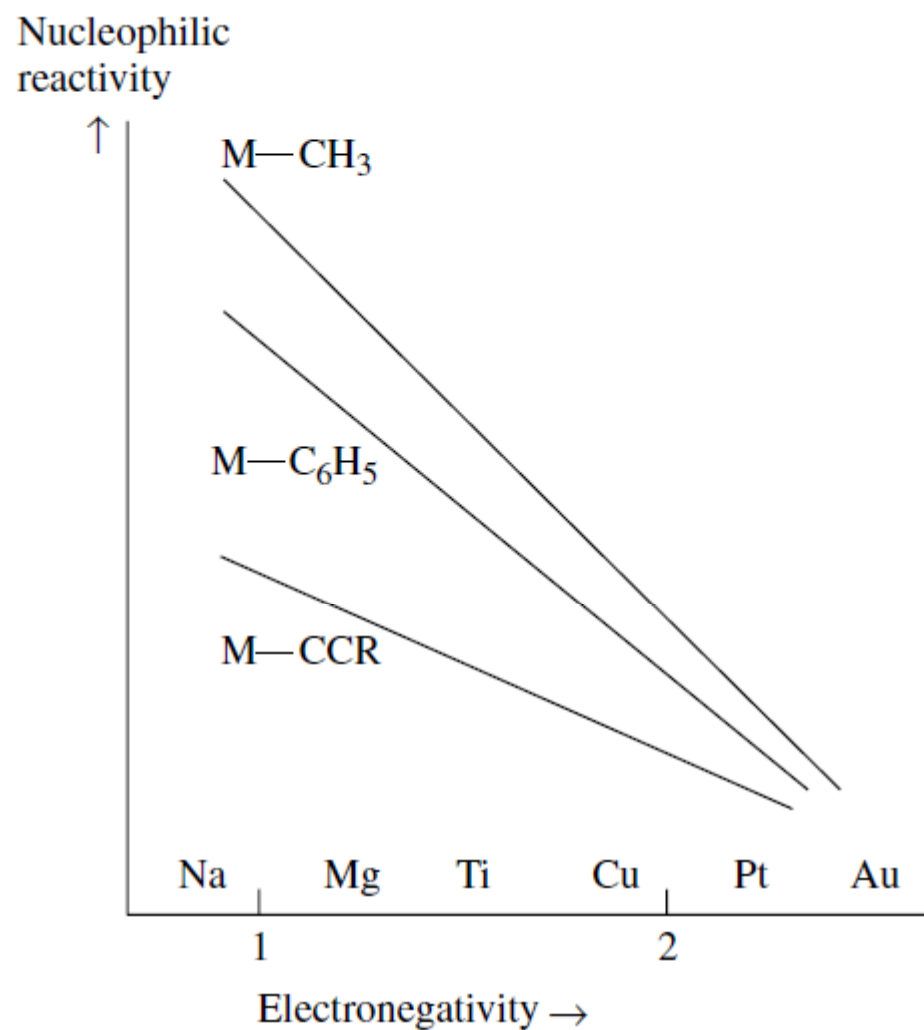


## $\sigma$ -Bonded ligands: Transition Metal Alkyls and Hydrides

- Simplest of organo-transitionmetal species
- Rare until and understanding of their stability in the 60's and 70's
- Metal alkyls can be considered as stabilized carbanions
- **R-Mg-X** provided the first general source of nucleophilic alkyl groups, complementing the alkyl halides ( $R^{\delta+}-X^{\delta-}$ ).
- Using the ionic model, metal alkyls result from combining an alkyl anion with a metal cation.



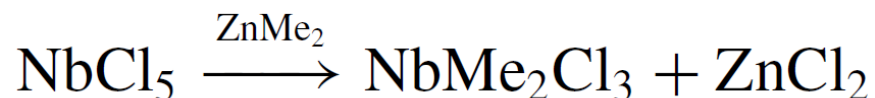
- The alkyl anion is stabilized to a different extent depending on the electronegativity of the metal involved and also the nature of the alkyl ligand itself, i.e. the hybridization of the C atom.



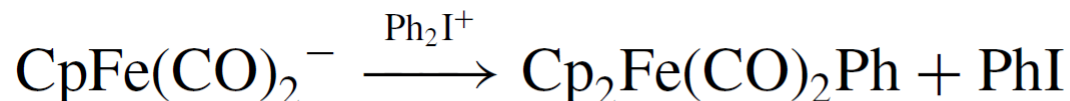
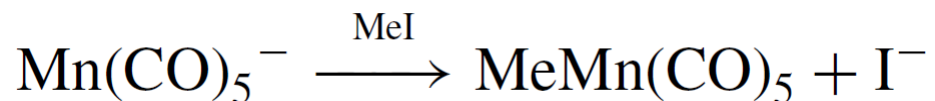
**FIGURE 3.1** Schematic diagram showing qualitatively how the nucleophilic reactivity of main-group and transition metal alkyls to protons or air oxidation depends on the alkyl itself and the electronegativity of the metal.

# Preparation of Metal Alkyls

## 1. Nucleophilic attack on the metal

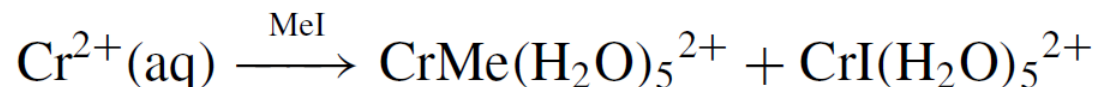
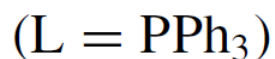
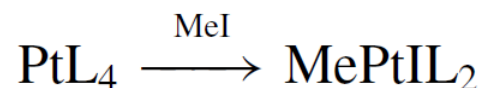
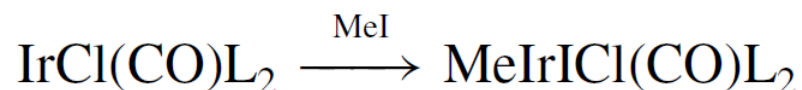


## 2. Electrophilic attack on the metal

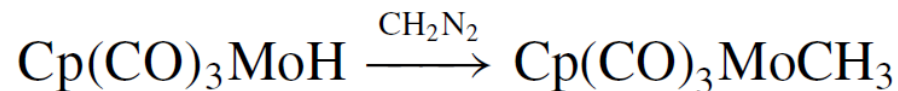
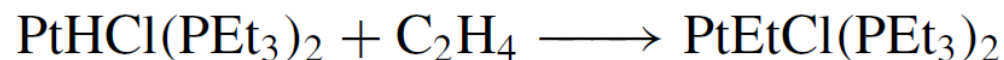


## Preparation of Metal Alkyls contd.

### 3. Oxidative addition

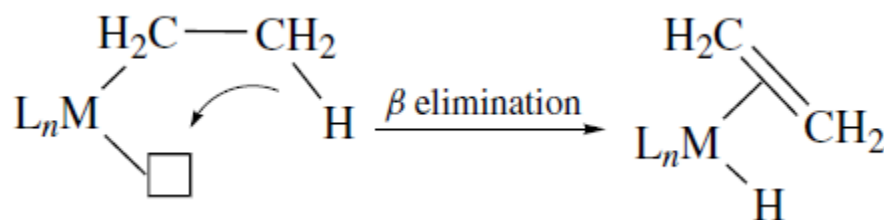


### 4. Insertion



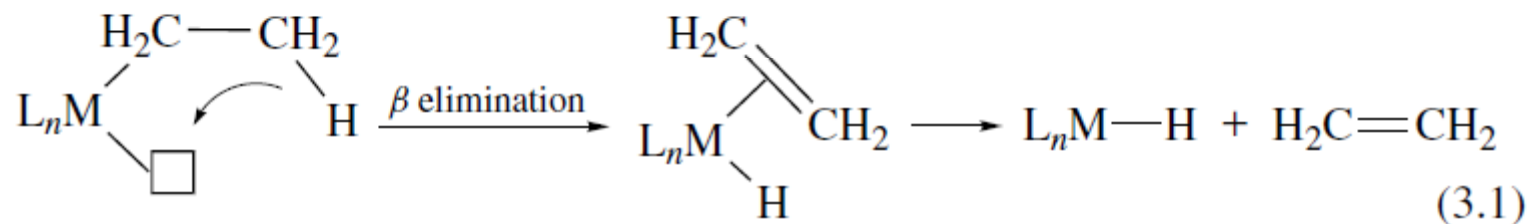
# $\beta$ Elimination

- The major decomposition pathway for metal-alkyls is  $\beta$  elimination which converts a metal alkyl into a **hydridometal alkene** complex.



- This is a very common reaction which can occur whenever
  1. The  $\beta$  carbon of the alkyl bears a hydrogen substituent.
  2. The  $M-C-C-H$  unit can take up a roughly coplanar conformation, which brings the  $\beta$  hydrogen close to the metal.
  3. There is a vacant site on the metal, symbolized here as  $\square$ , cis to the alkyl.
  4. The reaction is much more rapid for  $d^2$  and higher metals than for  $d^0$  and main-group alkyls (agostic interactions - later)

- The  $\beta$  carbon of the alkyl bears a hydrogen substituent.
  - The M–C–C–H unit can take up a roughly coplanar conformation, which brings the  $\beta$  hydrogen close to the metal.
- it is the  $\beta$  hydrogen of the alkyl that is transferred to the metal to give the product hydride.



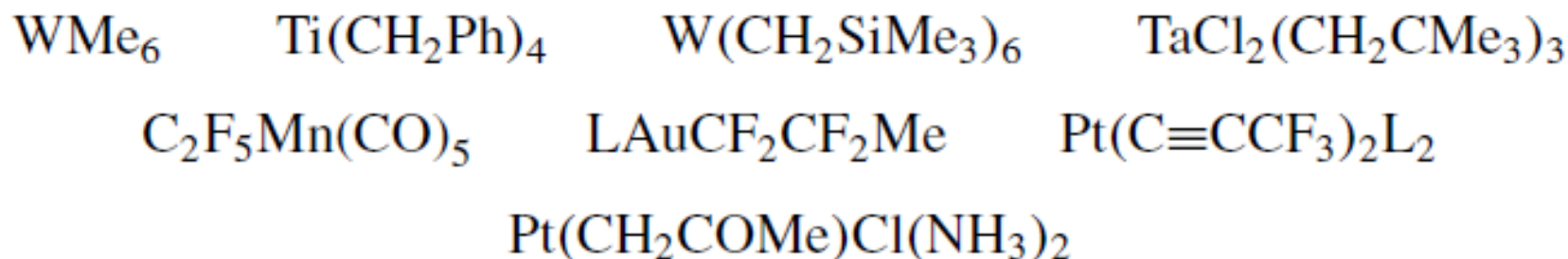
- There is a vacant site on the metal, symbolized here as  $\square$ , *cis* to the alkyl.
- The reaction is much more rapid for  $d^2$  and higher metals than for  $d^0$  and main-group alkyls.
- The elimination is believed to be concerted
- C–H bond breaking and M–C and M–H bond making happen at the same time.

- The term “vacant site” does not simply mean that there should be a gap in the coordination sphere large enough to accommodate the incoming ligand.
- There must also be an empty orbital ready to accept the  $\beta$ -H, or more exactly, the pair of electrons that constitutes the  $\beta$  C-H bond.
- The electron count of the product alkene hydride is  $2e^-$  more than that of the alkyl starting material.
- An  $18e^-$  alkyl is much more reluctant to  $\beta$ -eliminate via a  $20e^-$  intermediate than is a  $16e^-$  alkyl, which can go via an  $18e^-$  alkene hydride.
- Even if the alkene subsequently dissociates, which is often the case, we still have to stabilize the  $20e^-$  transition state leading to the alkene hydride intermediate if we want the reaction to be fast.
- An  $18e^-$  alkyl therefore is said to be coordinatively saturated. By this we mean that an empty orbital is not available.

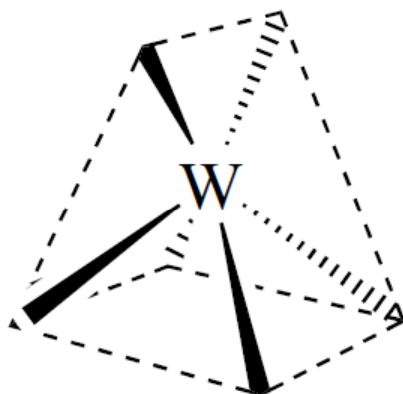
# Stable Transition Metal Alkyls

To have a kinetically stable alkyl, we must **block the  $\beta$ -elimination pathway** for Decomposition – 5 possibilities

## 1. Alkyls that have no $\beta$ hydrogen:

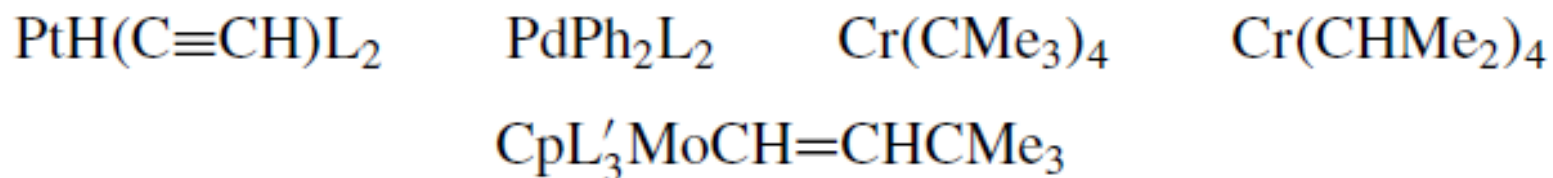


- Albright and Eisenstein predicted that  $d^0$   $MX_6$  species such as  $WMe_6$  would be **trigonal prismatic** where X is not a  $\pi$  donor, **not the octahedral structure usually found for  $ML_6$**



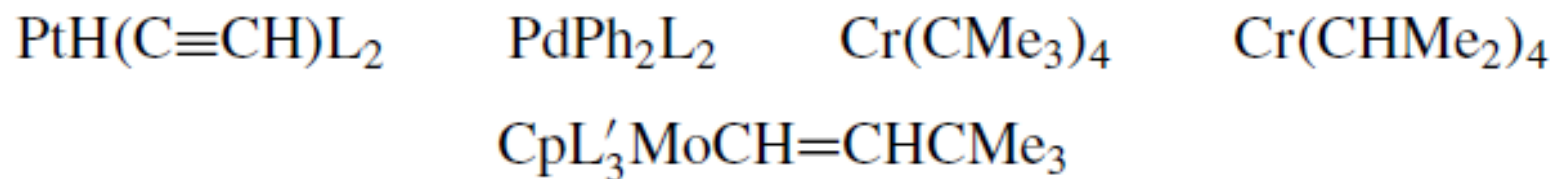
- Often, substitution with electron-withdrawing or bulky groups (e.g.  $-CH_2Ph$ ,  $-CH_2SiMe_3$ ) also gives stable alkyls.

**2. Alkyls for which the  $\beta$  hydrogen is unable to approach the metal as a result of the geometry or bulk of the ligand:**



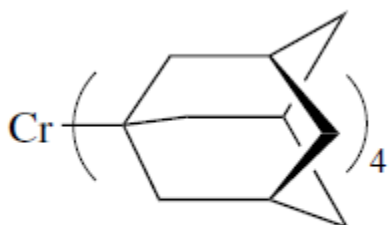
- The vinyl and phenyl groups both have  $\beta$  hydrogens, but they do not  $\beta$ -eliminate easily.
- One reason may be that the  $\beta$  hydrogens are further from the metal in these  $\text{sp}^2$ -hybridized systems with  $120^\circ$  angles at carbon, less favorable for delivery of the  $\beta$ -H than in the  $\text{sp}^3$  ethyl group ( $109^\circ$ ).
- In addition, as is the case for other electronegative alkyl groups, the phenyl and vinyl groups have stronger M–C bonds than does the ethyl group.

(2 contd.)

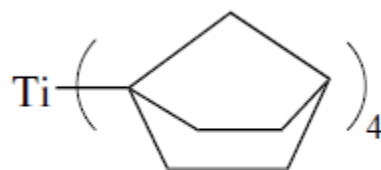


- The iso-propyl and tert-butyl chromium complexes are unusual as their steric bulk prevents the  $\beta$ -C-H bond from reaching the metal.
- These structures seem to be sterically saturated.

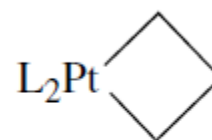
### 3. Alkyls in which the M–C–C–H unit cannot become *syn*-coplanar:



[Cr(1-adamantyl)<sub>4</sub>]



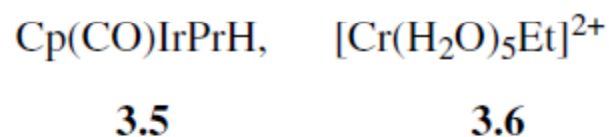
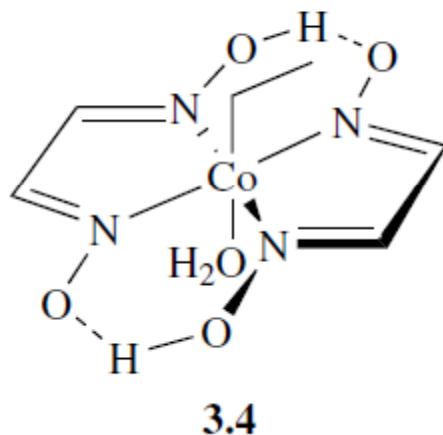
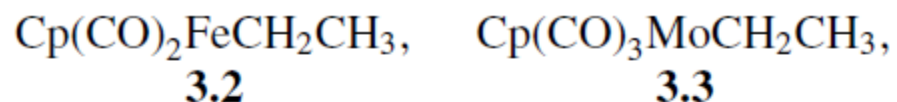
Ti(6-norbornyl)<sub>4</sub>



L<sub>2</sub>Pt(CH<sub>2</sub>)<sub>3</sub>

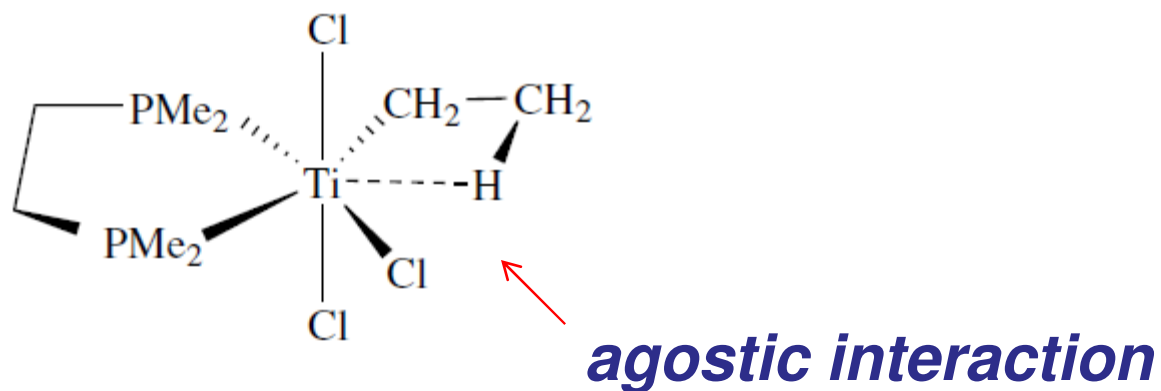
- The examples containing non-coplanar M–C–C–H groups mainly involve cyclic alkyls, in which the rigidity of the ring system holds the M–C–C–H dihedral angle near 60° and far away from the value of 0° required for β elimination – steric effects may also play a role.

4. An 18-electron species with firmly bound ligands, which will not dissociate to generate a vacant site:



- these systems have no vacant site **and others that have such a site**, but not cis to the alkyl
- $[\text{Cr(OH}_2)_5\text{Et}]^{2+}$  is not an  $18e^-$  species, but as a  $d^3$  Cr(III) complex it is **coordination inert**

## 5. Some $d^0$ alkyls:



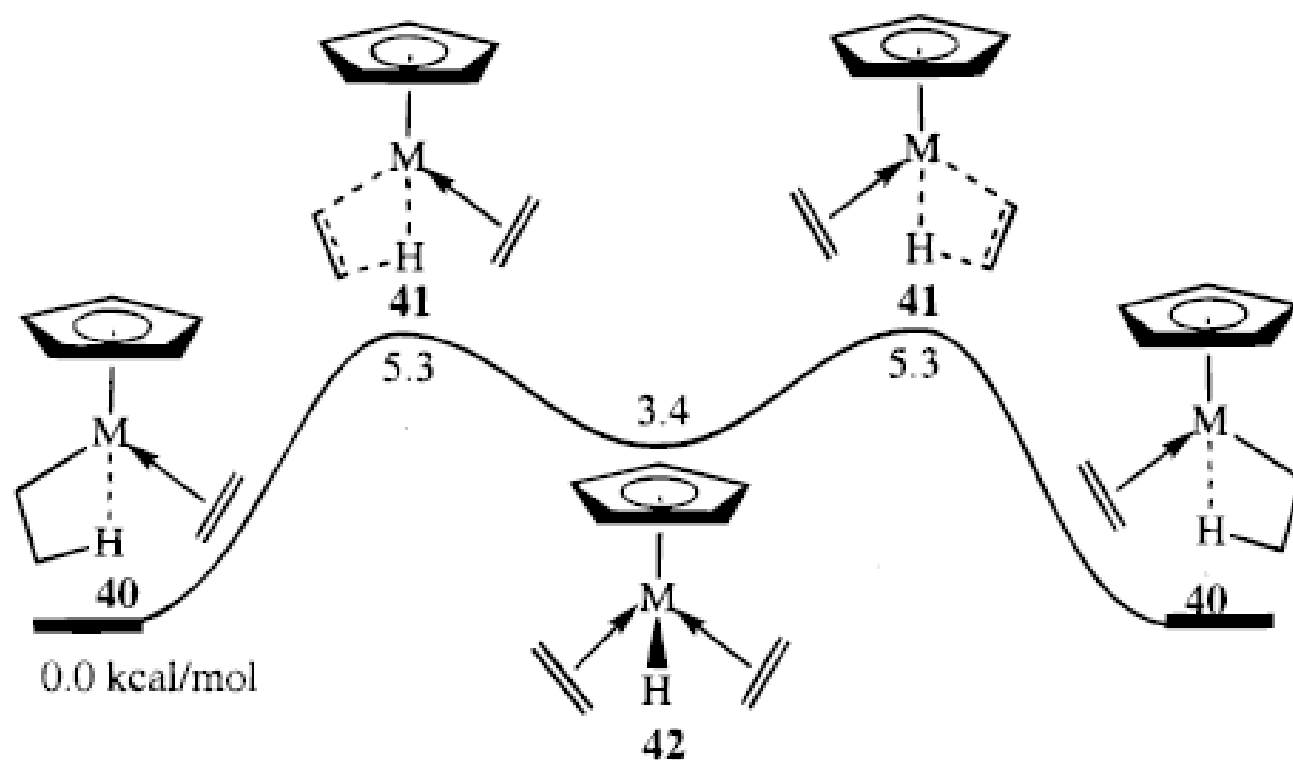
Rarer are those species in which all the criteria appear to be favorable but in which  $\beta$  elimination still does not occur.

- Requirements for  $\beta$  elimination include a  $2e^-$  vacant site (an empty d orbital) on the metal and an available electron pair (a filled d orbital) for breaking the C–H bond (back donation).
- There is a very close analogy between these requirements and those for binding a soft ligand such as CO ( $\sigma$ -donor,  $\pi$ -acceptor ligand).

**Both processes require a metal that is both  $\sigma$  acidic and  $\pi$  basic**

- In the case of CO, binding leads to a reduction in the CO bond order. In the case of the  $\beta$ -C–H bond of an alkyl group, this binding can reduce the C–H bond order to zero, by cleavage to give the alkene hydride complex.

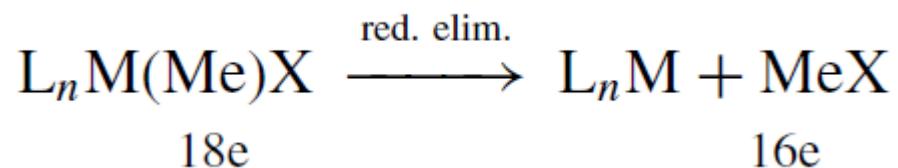
- Alternatively, if the metal is a good  $\sigma$  acid but a poor  $\pi$  base ( $Md^0$ ), an agostic system may be the result, and the C–H bond is only weakened, not completely broken.
- Many of the characteristic reactions of organometallic chemistry require both  $\sigma$ -acid and  $\pi$ -base bifunctional character. This is why transition metals, with their partly filled d orbitals, give these reactions so readily.



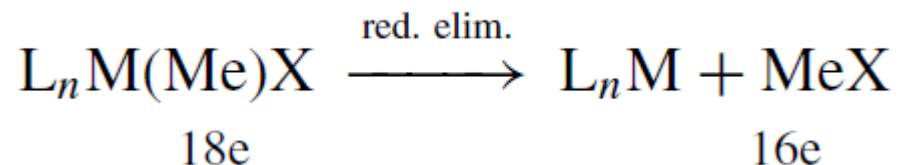
**Figure 20.** Hydrogen transfer along hydrogen-exchange mechanism involving a five-coordinated intermediate for  $\text{CpM}(\text{C}_2\text{H}_5)(\text{C}_2\text{H}_4)$ .

## Reductive Elimination

- A second very common decomposition pathway for metal alkyls is *reductive elimination*



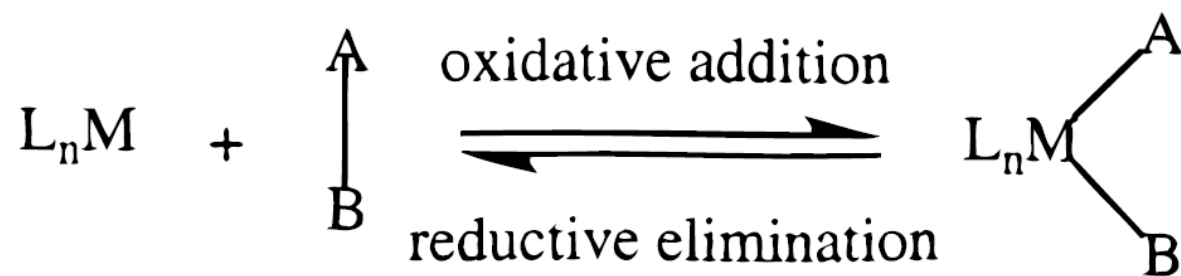
- This leads to a decrease by two units in both the electron count and the formal oxidation state.*
- In principle, it is available to all complexes, even if they are  $d^0$  or  $18e^-$ , *provided a stable oxidation state exists two units more reduced than the oxidation state in the starting alkyl.*
- In many instances reductive elimination is not observed, for example, if X is a halogen.
- The position of equilibrium for alkyl halides usually lies to the left; in other words,  $18e$  species is usually more stable thermodynamically.



- On the other hand, when X = H, the reaction is usually both kinetically facile and thermodynamically favorable, so isolable alkyl hydrides are rare.
- Where X = CH<sub>3</sub>, the thermodynamics still favor elimination, but the reaction is generally much slower kinetically.

*It is often the case that reactions involving a hydrogen atom are much faster than those involving any other element; this is because H carries no electrons other than bonding electrons, and these are in a 1s orbital, which is capable of making and breaking bonds in any direction in the transition state.*

- The sp<sup>3</sup> orbital of the CH<sub>3</sub> fragment is directed in space, and so there can often be poorer orbital overlap in the transition state.



OS = 0

16e

CN =  $n$

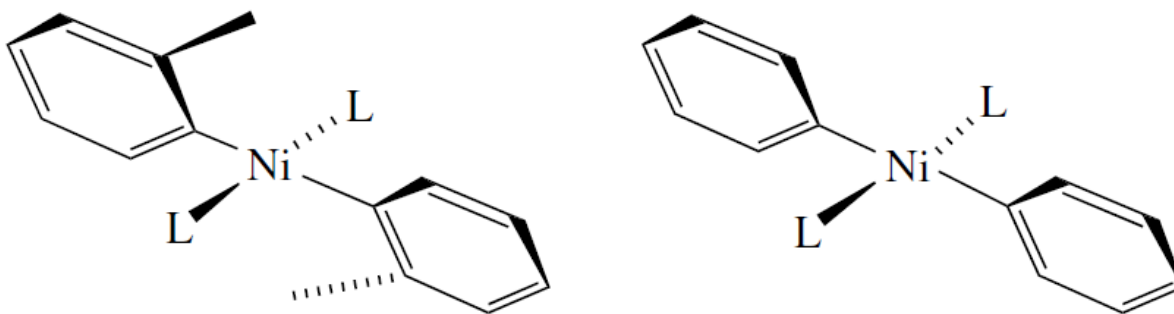
OS = 2

18e

CN =  $n + 2$

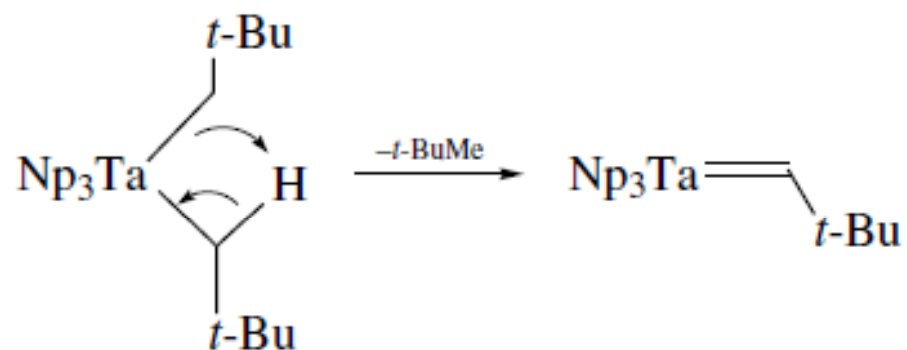
## Stability from Bulky Substituents

- Bulky ligands provide a general strategy for stabilizing many different classes of organometallic complex.
- Associative decomposition pathways for alkyls, such as by reaction with the solvent or with another molecule of the complex, can also be important, especially for 16e metals. These can often be suppressed with bulky coligands.
- For example, square planar Ni(II) alkyls are vulnerable to attack along the z *direction perpendicular to the plane*. The *o*-tolyl complex (below), in which this approach is blocked, is more stable than the analogous diphenyl.

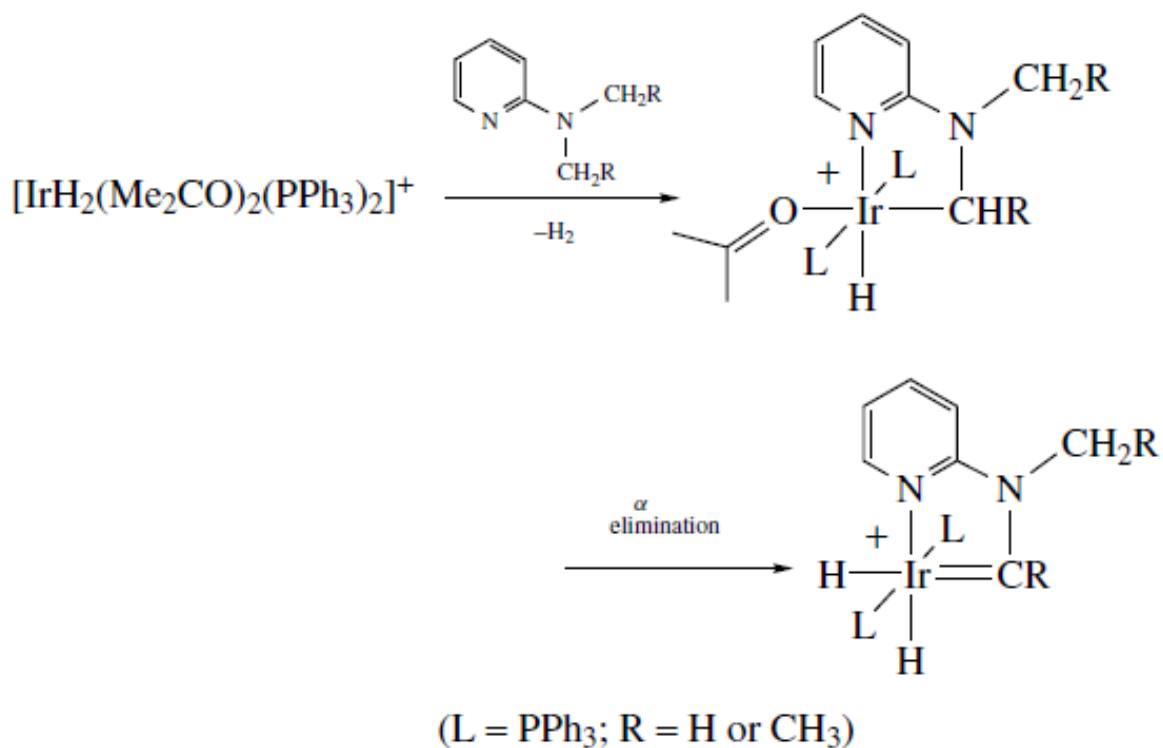


- **This steric factor has made the use of bulky alkyl groups**, such as neopentyl or trimethylsilylmethyl common in organometallic chemistry.

- Where  $\beta$  elimination cannot occur for the reasons discussed above,  $\alpha$  elimination sometimes takes over.
- This leads to the formation of species called carbenes, which have  $M=C$  double bonds.



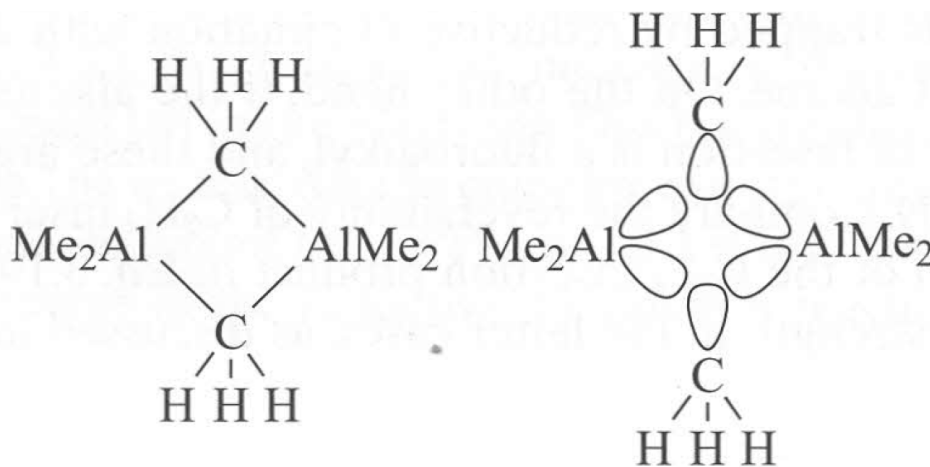
- Where a heteroatom such as N or O is present to activate the adjacent C–H bonds for reaction, double C–H bond cleavage can occur at the same carbon.



- The first cleavage, an oxidative addition, and the second, an  $\alpha$  elimination, can be observed stepwise for R = H.
- Even for the  $\text{ArNEt}$  analog (R =  $\text{CH}_3$ ), where there is a choice between  $\alpha$  elimination and  $\beta$  elimination in the second step, the product still comes exclusively from  $\alpha$  elimination.

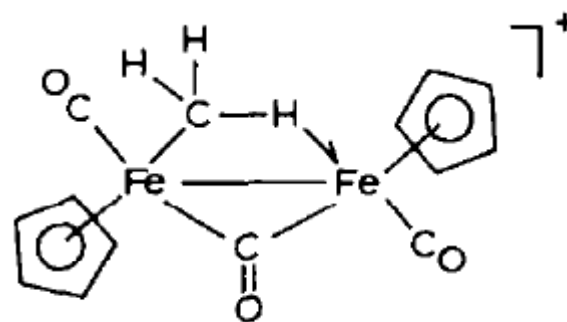
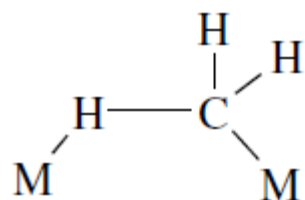
## Bridging Alkyls

- The methyl ligand which is normally a terminal ligand also has the capability of bridging two metal centers
- There are 3 ways in which a Me ligand can bridge two metal centres

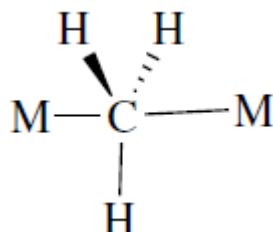


- In the case of main-group elements, such as Al, one Csp<sup>3</sup> orbital is shared between the two metals in a 2e<sup>-</sup> three-center bond involving only the metals and carbon.

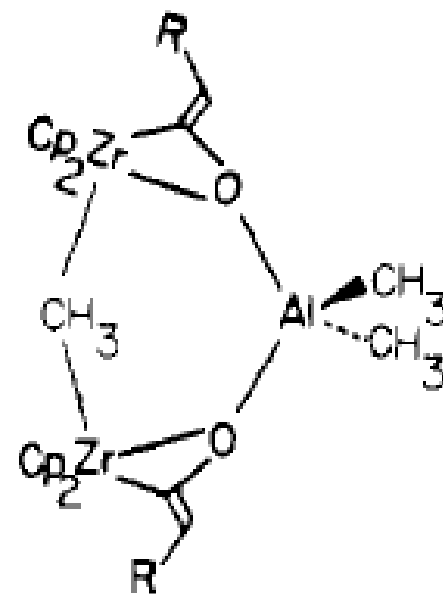
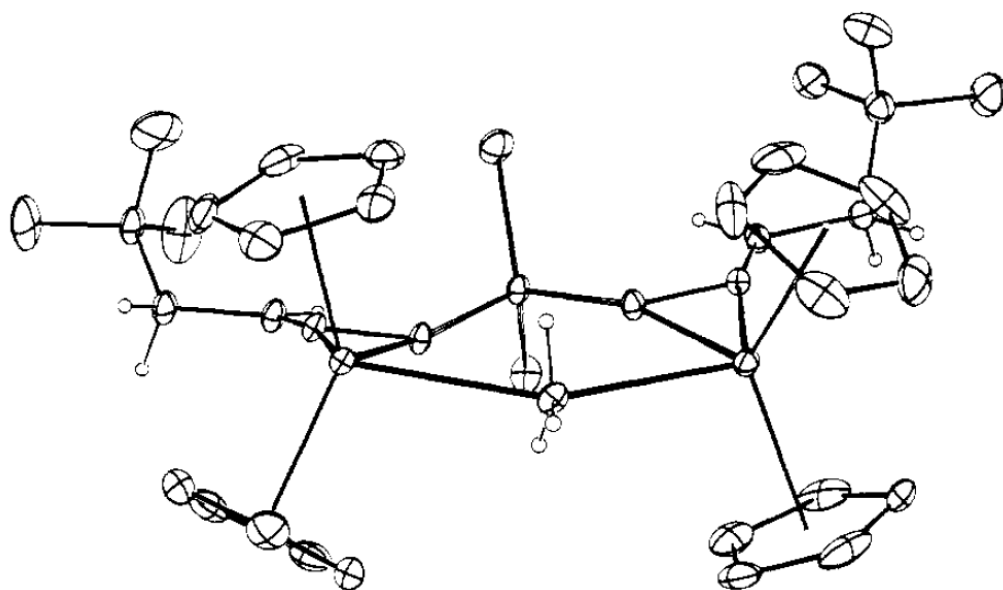
- the transition metals tend to prefer to bridge by an agostic C–H bond
- In  $d^2$ - $d^{10}$  transition metals capable of backbonding the Me group is usually terminal with the C–H bond acting as a  $\sigma$ -donor to the second metal.



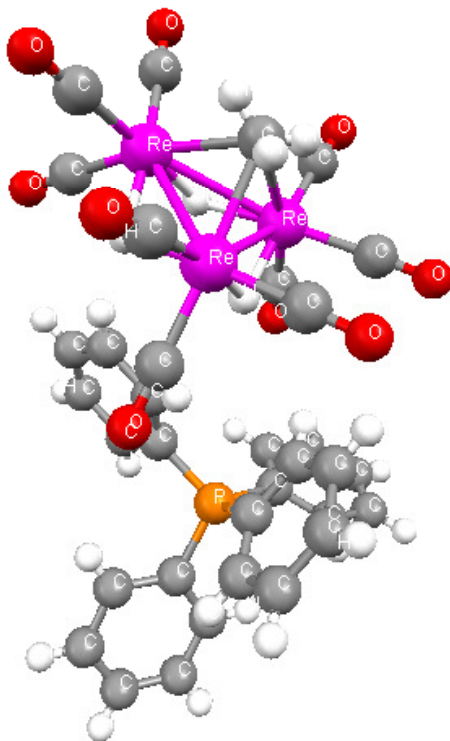
- Cases exist which involve an essentially planar methyl with the two  $d^0$  metals coordinated each side of the plane.



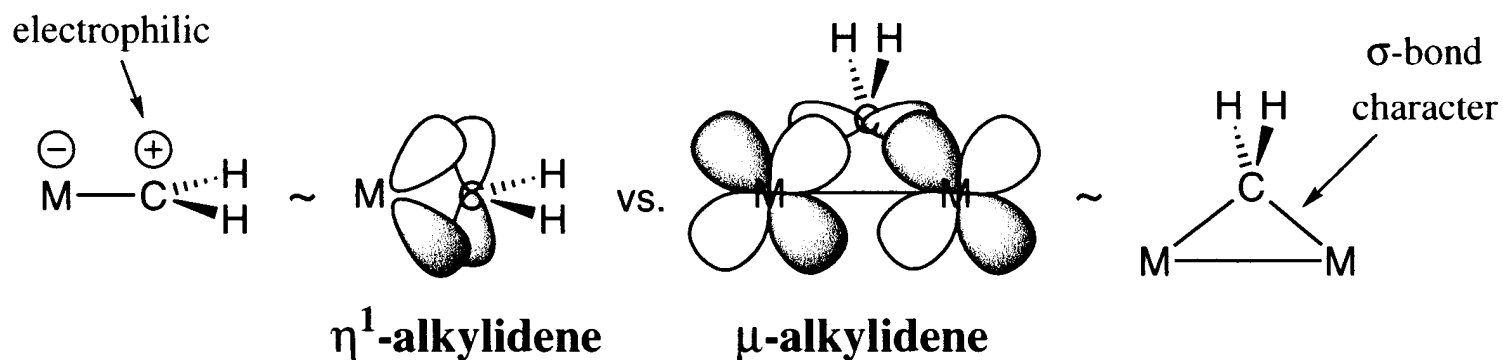
- **Trigonal-Bipyramidal Methyl Group Bridging Two Zirconocene-Ketene Centers**



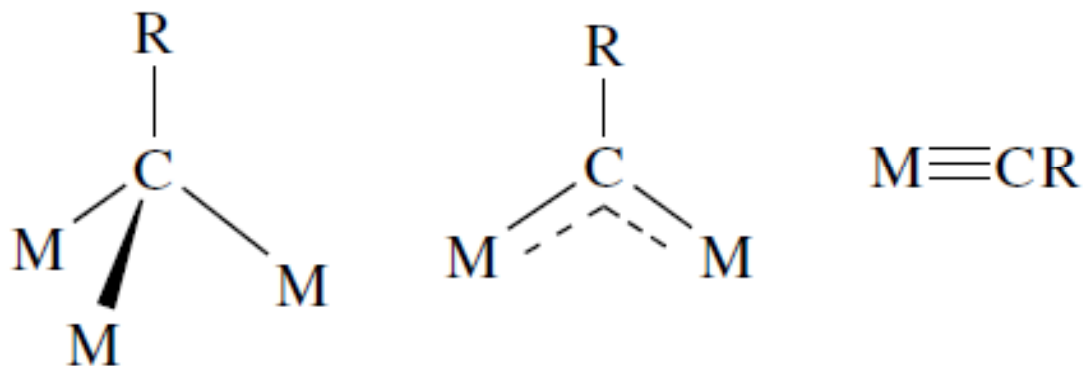
- There are some examples of even one  $\text{Csp}^3$  orbital shared between the three metals in a  $2e^-$  four-center bond involving only the metals and carbon.
- **A methyl group bridging on three metal atoms**  
the  $[\text{Re}_3(\mu\text{-H})_3(\mu_3\text{-CH}_3)(\text{CO})_9]^-$  Anion



- The divalent methylene moiety ( $\text{CH}_2$ ) can either form normal M-C bonds to two metals or act as a doubly bonded terminal carbene ligand to one metal.
- Terminal carbenes have a very extensive chemistry (later).

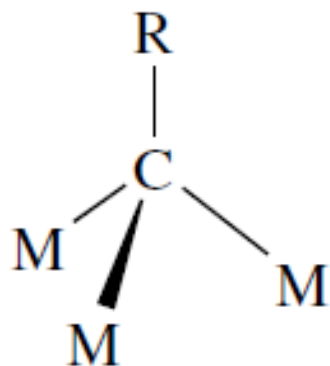


- Trivalent CH can bridge to two or three metals or act as a terminal carbyne ligand.

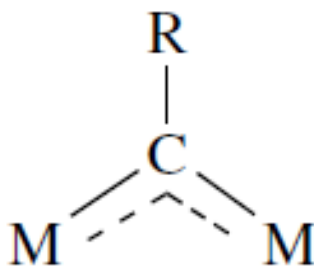


Hybridization of carbon ?

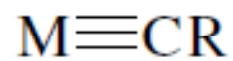
- Trivalent CH can bridge to two or three metals or act as a terminal carbyne ligand.



$sp^3$

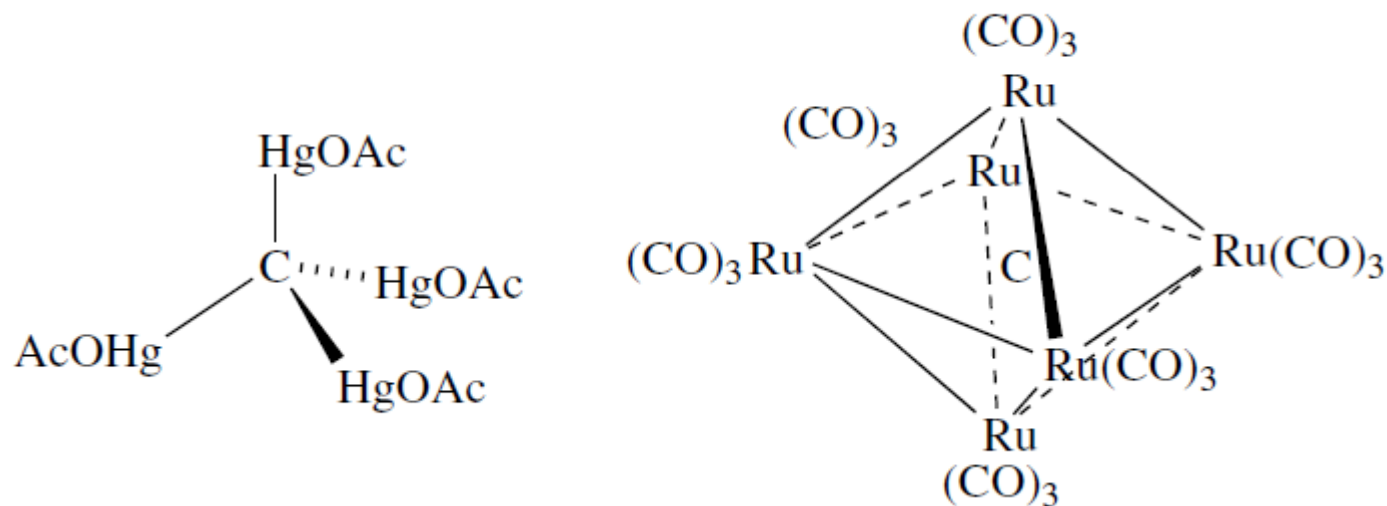


$sp^2$



$sp$

- Carbon itself being tetravalent, can bridge four independent metals or more commonly be found as an interstitial atom in a metal cluster binding up to 6 metals at one time!

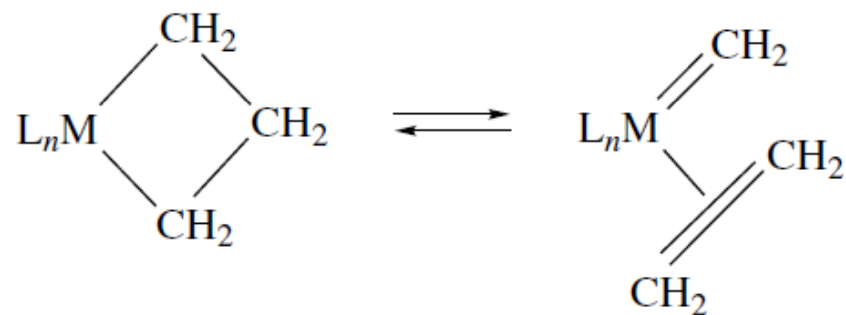


Hybridization of carbon ?

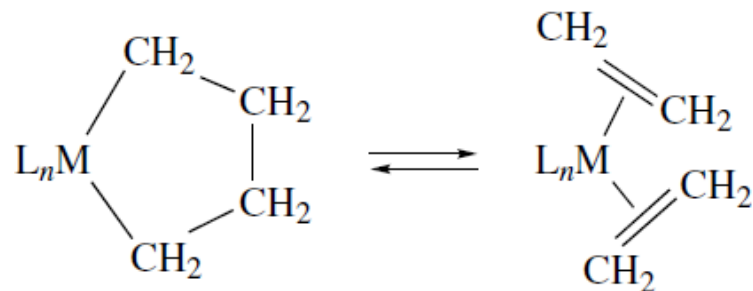
# Metalacycles

- Cyclic dialkyls  $M(CH_2)_n$  are **metalacycles**.
- *Metalacyclopropanes* ( $n = 2$ ) are more usefully thought of as metal–alkene complexes, but the higher homologs do indeed behave like dialkyls and have certain characteristic properties.
- *Metalacycles* are associated with two important reversible reactions.

- The  $n = 3$  metalcycle known as metalacyclobutane, rearranges to give an alkene and a carbene.



- The  $n = 4$  carbon known as a metallacyclopentane rearranges to give two alkenes



- In each rearrangement a 2e ligand converts to a 4e ligand set thus a 16e metal fragment is needed to promote the reaction.
- If you notice all of the  $\beta$  C-H bonds are directed away from the metal centre precluding  $\beta$ -elimination.
- Both reactions show resemblance to a  $\beta$  elimination but of a C-C bond instead of a C-H bond.

