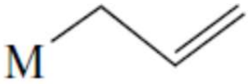
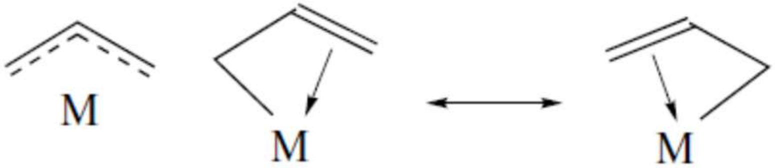
Transition Metal Allyls: Bonding, Syntheses and Reactions

Bonding and Electronic Features

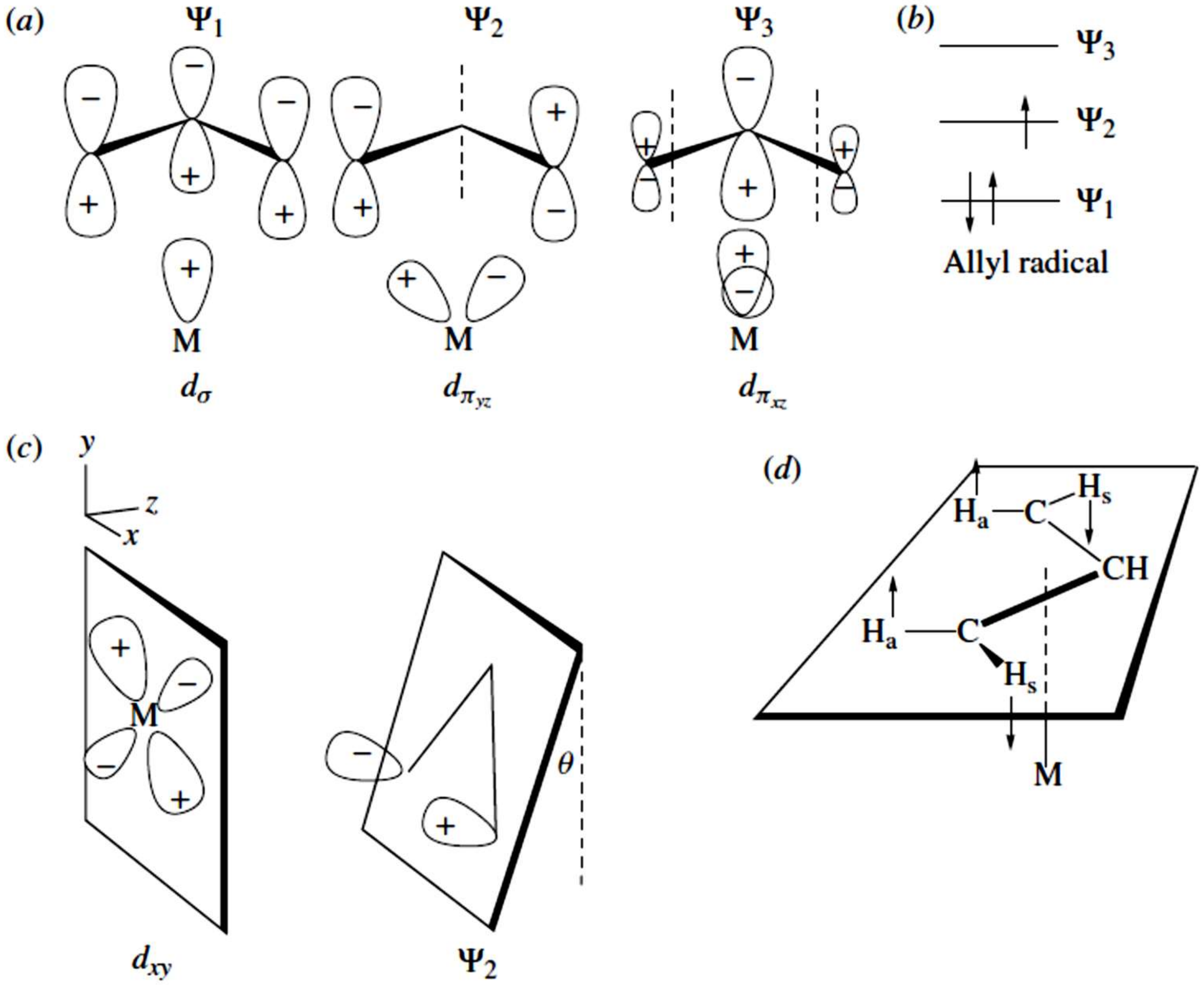
- The allyl group commonly behaves as an actor ligand, coordinate with metals in one of two ways.
- In the monohapto form it is a simple 1e X-type ligand like Me.



- In the trihapto form, it acts as a 3e LX enyl ligand. This bonding mode can exist in two canonical forms.



- Intermediate cases between monohapto and trihapto forms (η^2-allyls) are also known.



The electronic structure of the allyl ligand and some features of metal-allyl bonding. Nodes are shown as dotted lines in (a)

Figure (a) in the previous slide display that of the three molecular orbitals of the allyl fragment.

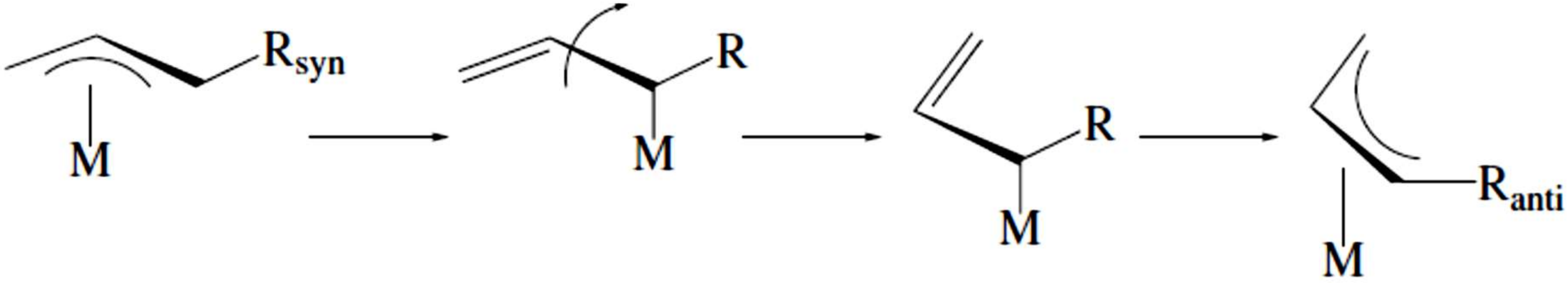
- ψ_1 can interact with a suitable metal d_σ orbital
- ψ_2 with an M(dπ) orbital on the metal;
- Ψ_3 is not a frontier orbital and so probably of lesser importance.

As the number of nodes increases, the MOs of the free ligand become less stable (b).

Two peculiarities of the structures of η^3-allyl complexes can be understood on this picture.

- First, the plane of the allyl is canted at an angle θ with respect to the coordination polyhedron around the metal, as shown in Fig. c; θ is usually 5°–10°.
- The reason is that the interaction between ψ_2 and the d_{xy} orbital on the metal is improved if the allyl group moves in this way, as can be seen in Fig. c.
- The structures also show that 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 as shown by the arrows in Fig. d.
- This allows the p orbital on these carbons to point more directly toward the metal, thus further improving the overlap. Note the nomenclature of the allyl substituents, which are syn or anti with respect to the central CH.

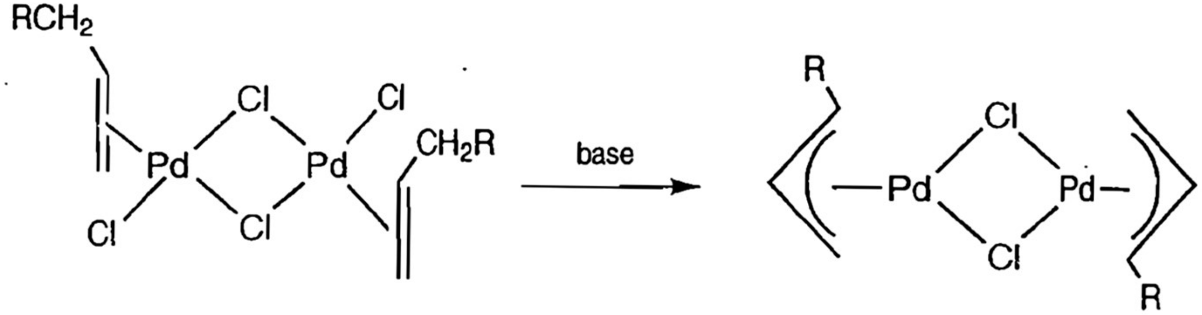
The η^3-allyl group often shows exchange of the syn and anti substituents. One mechanism goes through an η^1-allyl intermediate. This kind of exchange can affect the appearance of the ^{1}H NMR spectrum and also means that an allyl complex of a given stereochemistry may rearrange with time.



Syntheses

- From an alkenes

$$\mathrm{Mo(dpe)_2(\eta^2\text{-propene}) \rightleftharpoons Mo(dpe)_2(\eta^3\text{-allyl})H}$$



- From an allyl compound by nucleophilic attack on metals

$$\mathrm{CH_2{=}CHCH_2SnMe_3 + Mn(CO)_5Br \xrightarrow{reflux} (\eta^3\text{-}CH_2CHCH_2)Mn(CO)_4}$$

- From an allyl compound by electrophilic attack on metals

$$\begin{tikzcd}
\mathrm{CH_2{=}CHCH_2Cl + Mn(CO)_5^-} \arrow[r] & \mathrm{(\eta^1\text{-}CH_2{=}CHCH_2)Mn(CO)_5} \arrow[d, "\Delta"] \\
& \mathrm{(\eta^3\text{-}CH_2CHCH_2)Mn(CO)_4}
\end{tikzcd}$$

For allyl systems the metal often attacks at the least hindered terminal CH_2 group

Synthesis continued

- From diene complexes

$$(\eta^2\text{-CH}_2\text{=CH–CH=CH}_2)\text{Fe(CO)}_3 \xrightarrow{\text{HCl}} (\eta^3\text{-CH}_2\text{CHCHMe})\text{Fe(CO)}_3\text{Cl}$$

This reaction demonstrates an electrophilic attack on a diene complex

$$\text{Cp}_2\text{TiCl} \xrightarrow[-\text{propene}]{i\text{-PrMgBr}} \{\text{Cp}_2\text{TiH}\} \xrightarrow{\text{butadiene}} \text{Cp}_2\text{Ti}(\eta^3\text{-MeCHCHCHMe})$$

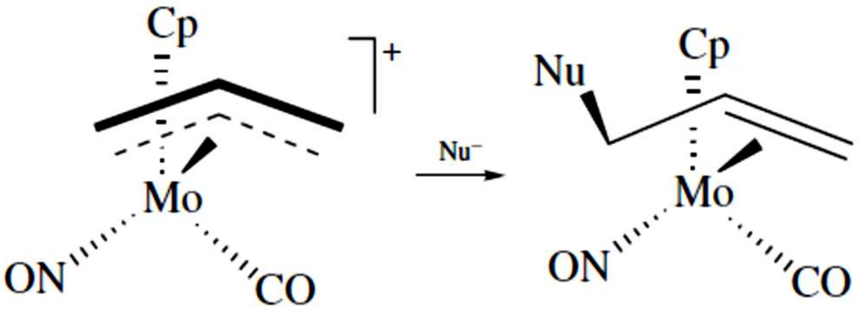
This reaction shows that when one C=C group of a diene undergoes insertion into a M−H bond, the hydrogen tends to attach itself to the terminal carbon of the conjugated chain. This leaves a methylallyl group, which can become η^3 if a vacant site is available.

$$[\text{PtH(acetone)(PR}_3)_2]^+ + \text{CH}_2\text{=C=CH}_2 \longrightarrow [(\eta^3\text{-allyl})\text{Pt(PR}_3)_2]^+$$

allenes insert into an M−H bond to put the hydride on the central carbon and generate an allyl group

Reactions

With Nucleophiles



With Electrophiles

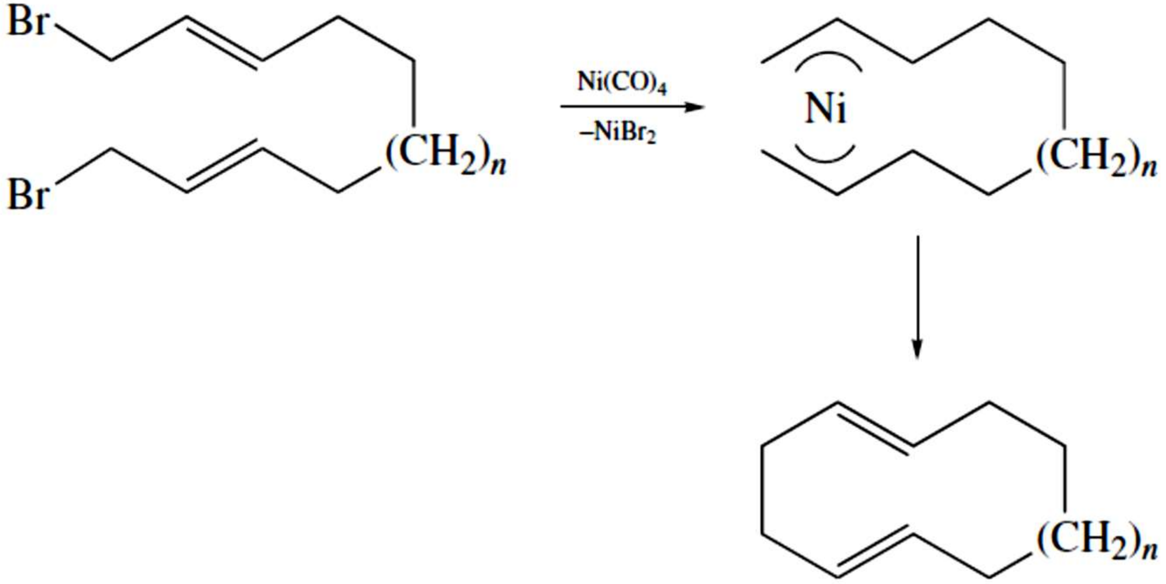
$$Cp(CO)_2FeCH_2CH{=}CH_2 + E^+ \longrightarrow [Cp(CO)_2Fe(CH_2{=}CHCH_2E)]^+$$

$(E^+ = HgCl^+, Me^+, RCO^+, H^+, Br^+)$

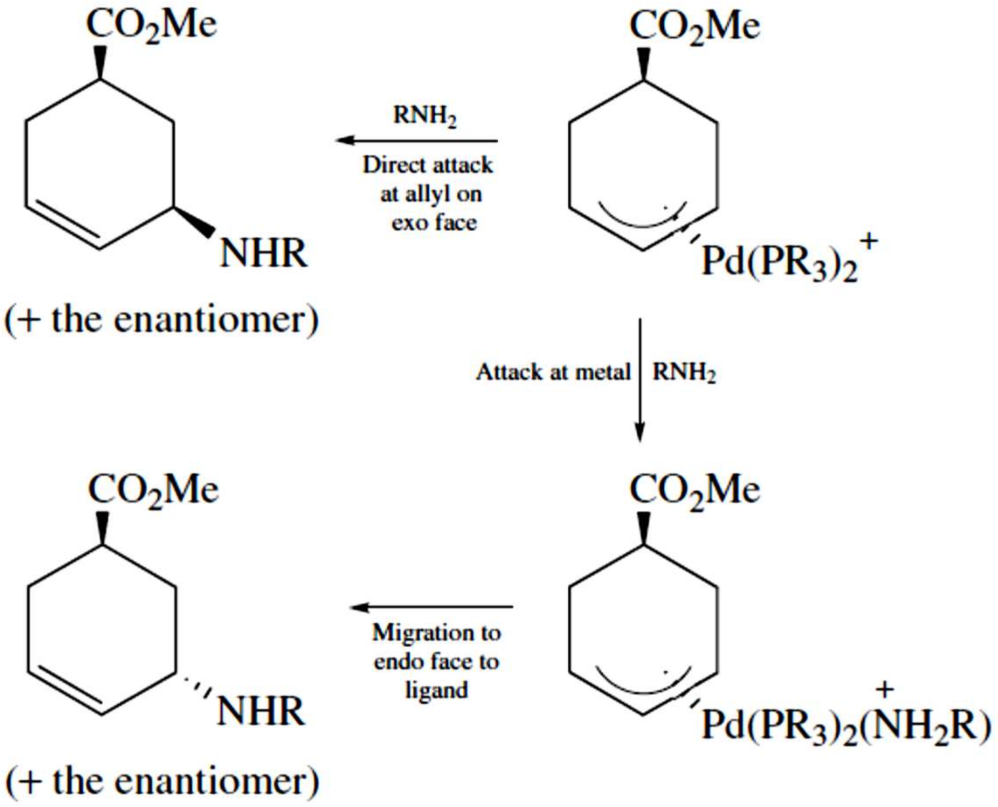
By insertion

$$(\eta^3\text{-allyl})_2Ni \xrightarrow{CO_2} (\eta^3\text{-allyl})NiOCOCH_2CH{=}CH_2$$

Reductive Elimination



Nucleophilic attack at one of the terminal carbons of the allyl group most often takes place from the face of the allyl away from the metal. This happens when the nucleophile attacks directly. On the other hand, cases are known in which the nucleophile first attacks the metal and only then is transferred to the allyl group. The latter route can only take place when a vacant site is made available at the metal. An example of a system that gives products of both stereochemistries is shown below



References

- **Basic Organometallic Chemistry: Concepts, Syntheses and Applications by B. D. Gupta and Anil J. Elias**
- **The Organometallic Chemistry of the Transition Metals by R. H. Crabtree**