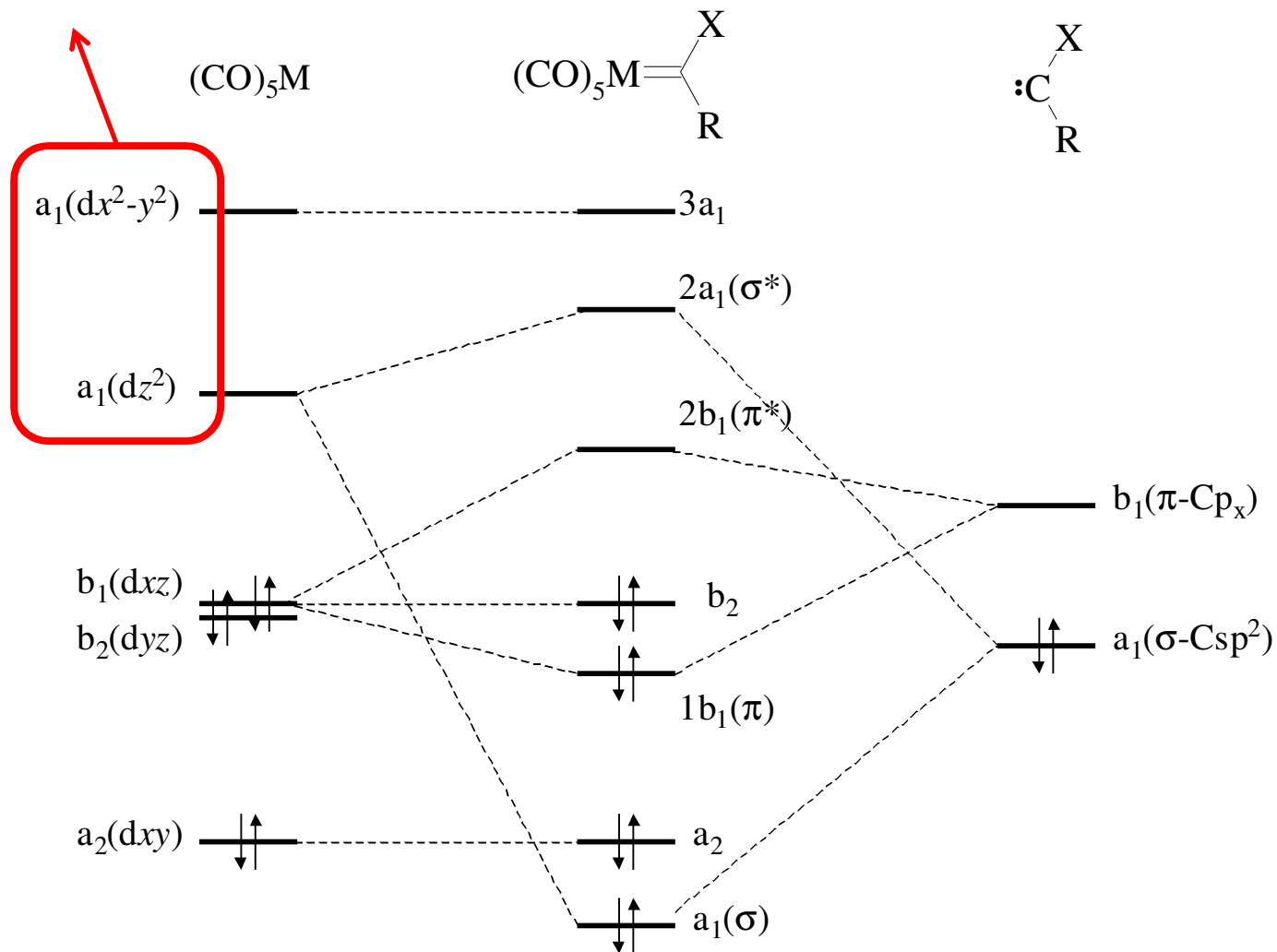
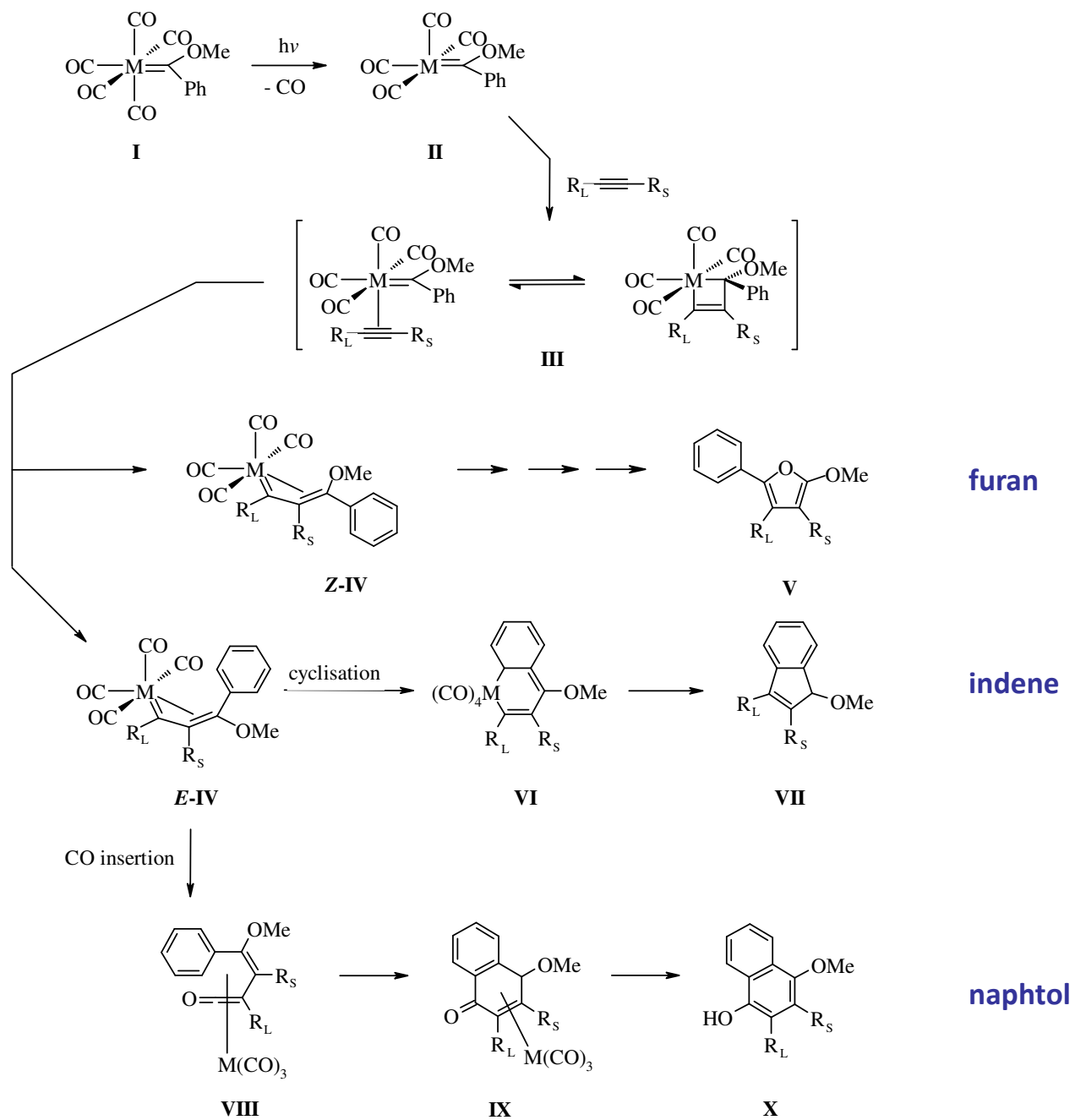


Population can result in CO loss



A schematic MO diagram for Fischer carbenes ($M = Cr, Mo, W$; $X = OR, NR_2$).



The metal-carbene-alkyne adduct methylphenylacetylene decompose by a mechanism first proposed by Dotz et al. to form indenyl ethers and naphthol derivatives (previous slide).

- The process is initiated, thermally or photochemically, by the dissociation of CO from complex **I** to produce the coordinatively unsaturated carbene complex **II**.
- Intermediate **II** is trapped by methylphenylacetylene present in solution, which binds the metal in such a way that the bulkier substituent R_L (Ph in this case) is placed parallel to the axial CO ligand to avoid unfavourable steric interactions with the carbene ligand in complex **III**. This steric effect is ultimately responsible for the regiochemistry observed in the final products
- The alkyne then undergoes insertion into the metal-carbon double bond to afford the η^3 -metallatrienes **E-IV** and **Z-IV**.
- Only the *E*-isomer undergoes cyclization with the double bond giving rise to the indene (**VII**) and naphthol (**X**) products.
- The *Z*-isomer undergoes CO insertion and reductive elimination to form the furan derivative **V**.
- Dotz and co-workers have shown that $(CO)_5Cr=C(OMe)Ph$ gives solely naphthol derivatives as opposed to the indene derivative which is predominantly formed by the tungsten analogue.^{7(a)} One explanation for this is that the tungsten complex is less likely to undergo CO insertion due to the greater W-CO bond strength (178 kJmol^{-1}) compared to that of the Cr-CO bond (108 kJmol^{-1}). H. Fischer, J. Muhlemeier, R. Markl, K. H. Dotz, *Chem. Ber.* **1982**, 115, 1355.

(a) K. H. Dotz, R. Dietz, *Chem. Ber.* **1978**, 111, 2517.

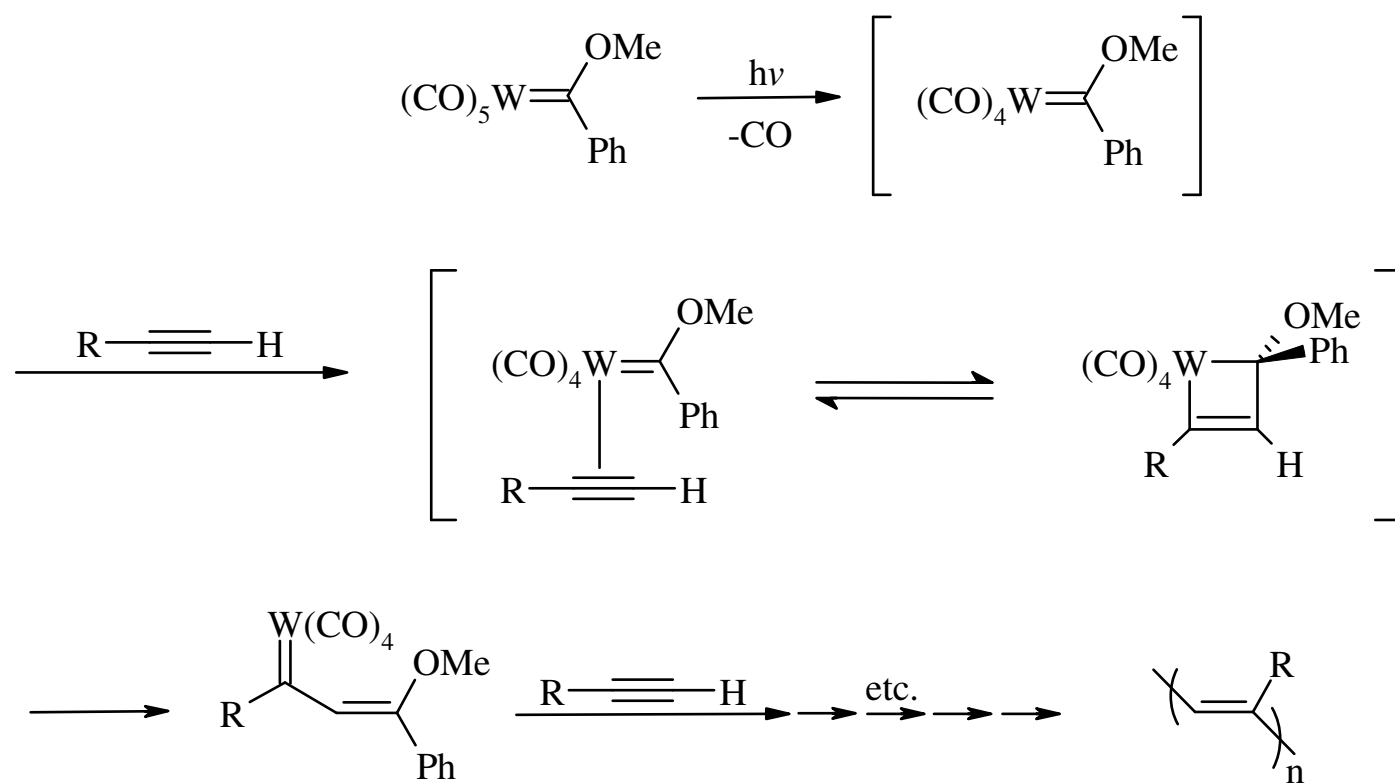
(b) K. H. Dotz, I. Pruskil, *Chem. Ber.* **1980**, 113, 2876.

(c) W. D. Wulff, P. C. Tang, J. S. McCallum, *J. Am. Chem. Soc.* **1981**, 103, 7677.

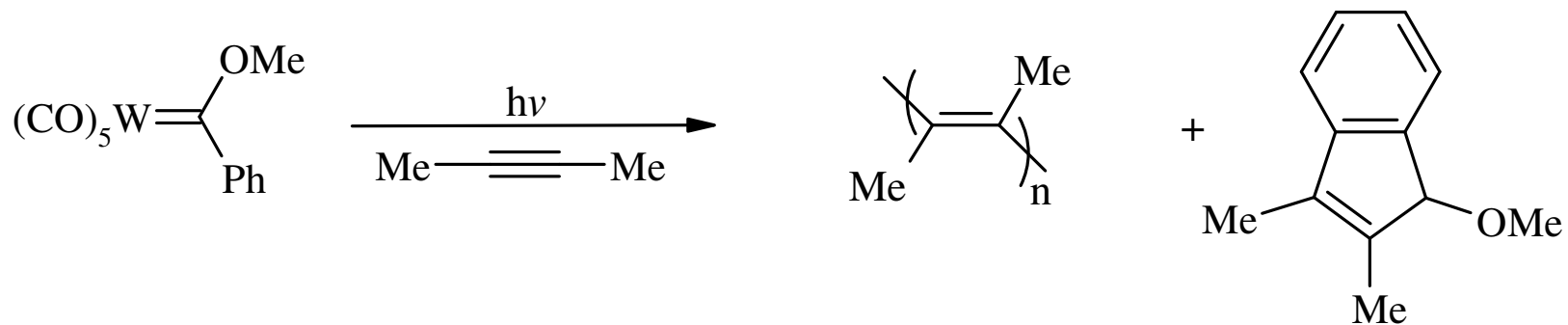
(d) K. H. Dotz, J. Muhlemeier, U. Schubert, O. Orama, *J. Organomet. Chem.* **1983**, 247, 187.

(e) J. S. McCallum, F. A. Kunng, S. R. Gilbertson, W. D. Wulff, *Organometallics* **1988**, 7, 2346.

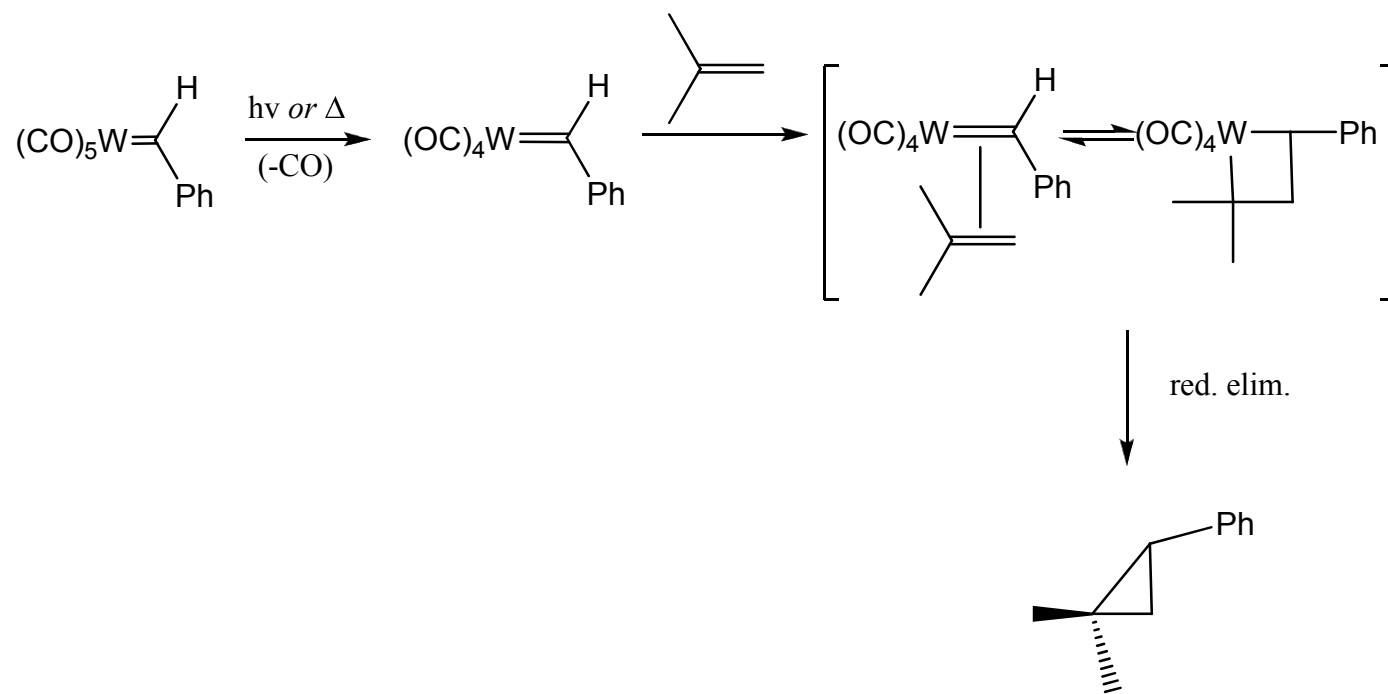
- Terminal alkynes, phenylacetylene and *n*-butylacetylene, both result in the production of polyacetylenes.
- Katz proposed that these metal-carbene-alkyne complexes undergo reaction as shown below



- Polyacetylene formation from terminal alkynes and indene/naphthol formation from internal alkynes suggests that there is some steric control involved in the reaction mechanism with increased steric hindrance favouring production of indenenes and naphthols.
- Dimethylacetylene was shown to have mixed reactivity supporting the latter proposal.

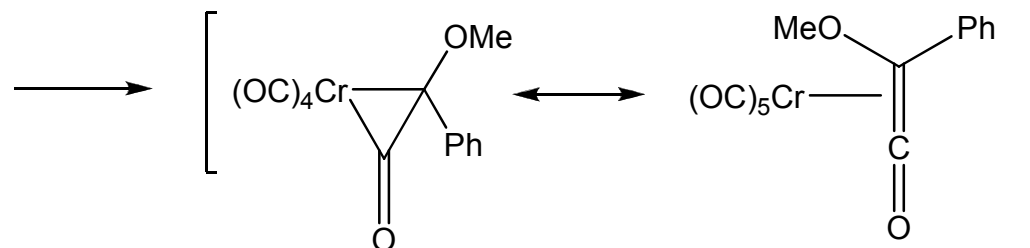
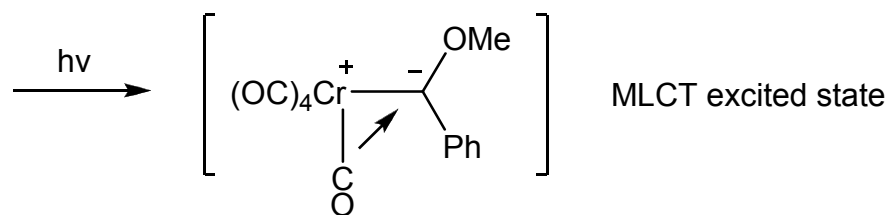
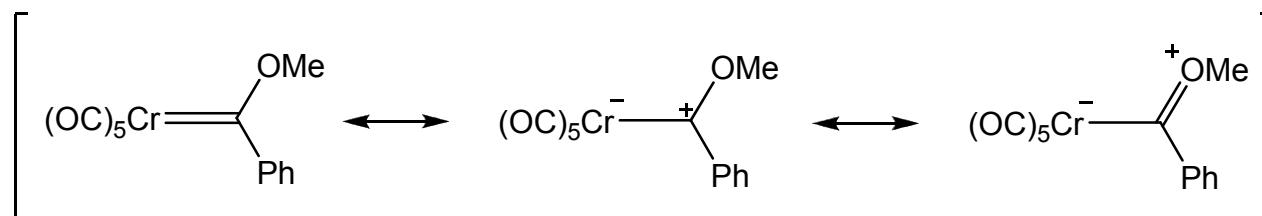


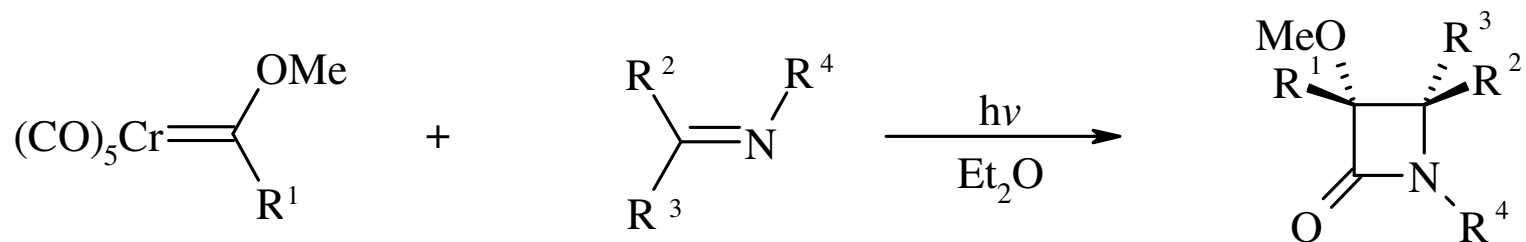
- The cyclopropanation of alkenes with Fischer-carbenes under thermal conditions is also a well known reaction.
- Metalacycles break down to give cyclopropanes via reductive elimination
- Olefin metathesis and cyclopropanation only occurs when the carbene and alkene moieties are coplanar when forming the metallacyclobutane intermediate (whether metathesis or cyclopropanation occurs is dependent on the electronic nature of the alkene and of the metal-carbene involved).



Metal-ketene formation

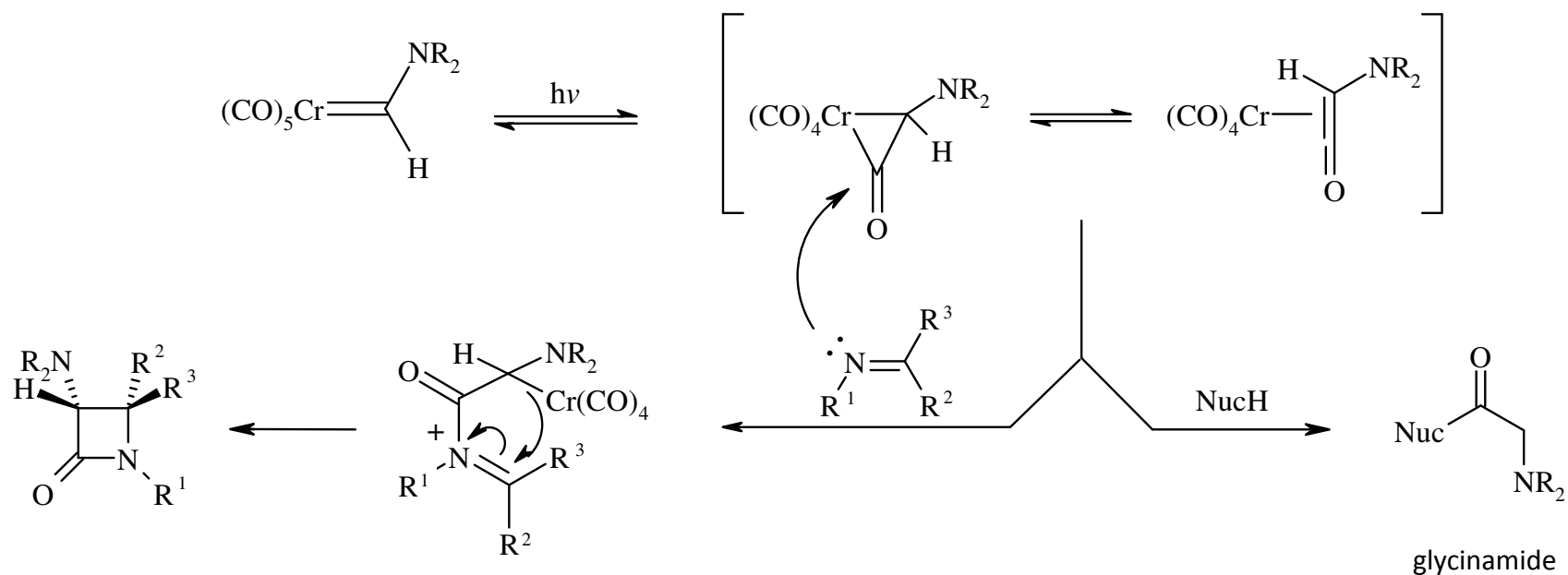
- Fischer-carbenes have been converted photochemically to a range of compounds, e.g. amino-acids, β -lactams from imines, β -lactones from aldehydes, cyclobutanones from alkenes.
- These reactions are all photochemically driven by MLCT excitation of the carbene complex forming a metal-ketene transient formed by insertion of one of the equatorial carbonyl ligands into the metal-carbene bond





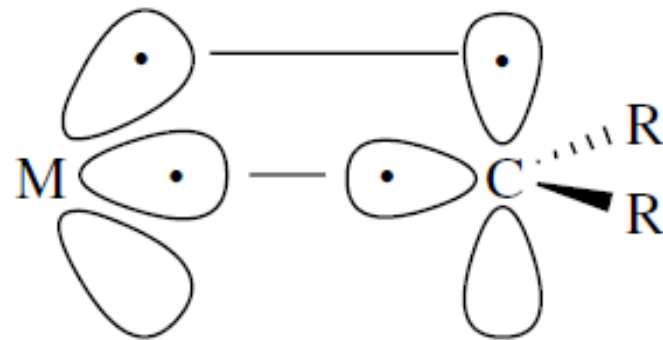
- The formation of ketene intermediates upon irradiation of chromium carbene complexes was first postulated by Hegedus and McGuire when they reported the synthesis of β -lactams by the photolysis of ether solutions containing various imines and the chromium carbene complex $(\text{CO})_5\text{Cr}=\text{C}(\text{OMe})\text{Me}$.
- This reaction was stereospecific, producing only one diastereomer of the product.

M. A. McGuire, L. S. Hegedus, *J. Am. Chem. Soc.* **1982**, 104, 5538.



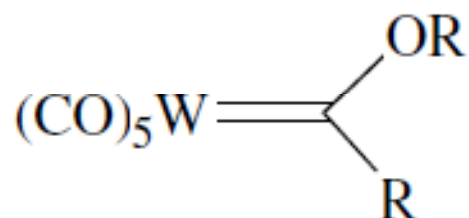
- The reactions involved in glycinamide and β -lactam formation are similar in that the products formed all consist of the carbene carbon, one CO ligand and the nucleophile.
- Although there is no direct evidence of ketene formation both classes of compounds are potentially derived from nucleophilic attack on a ketene.
- The formation of ketene intermediates is typically inferred from subsequent reactions as its high reactivity and instability make it extremely difficult to observe.

Schrock Carbenes

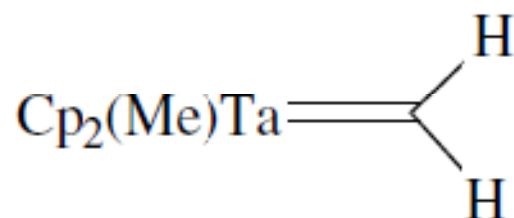


Schrock carbene

- A Schrock carbene forms two covalent bonds via unpaired electrons.
- Each M-C bond is polarized towards the carbene carbon because C is more electronegative than M, leading to a nucleophilic carbene carbon



W(0), 18e



Ta(V), 18e

Property	Fischer	Schrock
Nature of carbene carbon	Electrophilic	Nucleophilic
Typical R groups	π Donor (e.g., -OR)	Alkyl, H
Typical metal	Mo(0), Fe(0)	Ta(V), W(VI)
Typical ligands	Good π acceptor (e.g., CO)	Cl, Cp, alkyl
Electron count (covalent model)	2e	2e
Electron count (ionic model)	2e	4e
Oxidation state change on addition of CR_2 to L_nM	0	+2

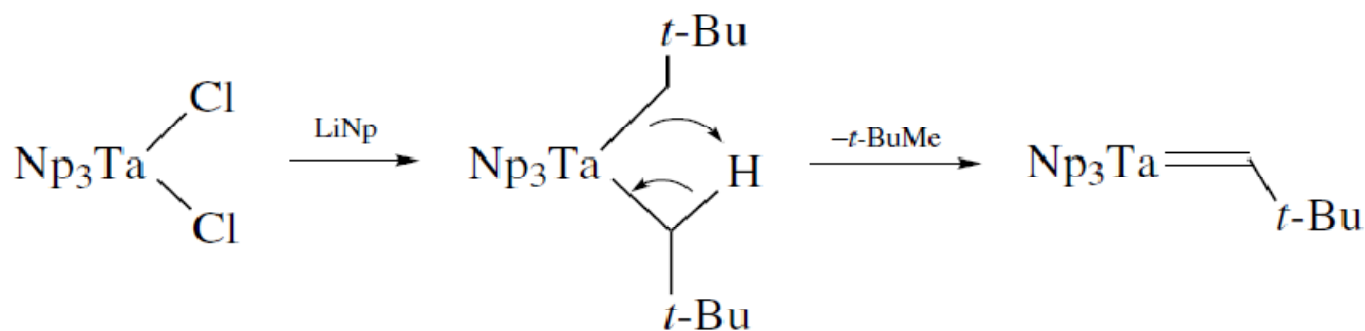
If we consider the Schrock carbene as a Fischer carbene with strongly enhanced M→C p-back bonding, the 2 electrons originally in M(d_{π}) transfer to the C(p_z) orbital, oxidizing the metal by 2 units and giving a CR₂²⁻ ligand.

- The more electropositive early transition metal complexes have less stable M(d_{π}) orbitals, i.e. easier to oxidize. For example d^2 metals are especially strong p-donors.
- The system can thus be visualized as a metal stabilized carbanion acting as both a σ and π donor to the metal hence its X₂-type character

(will define X₂ later)

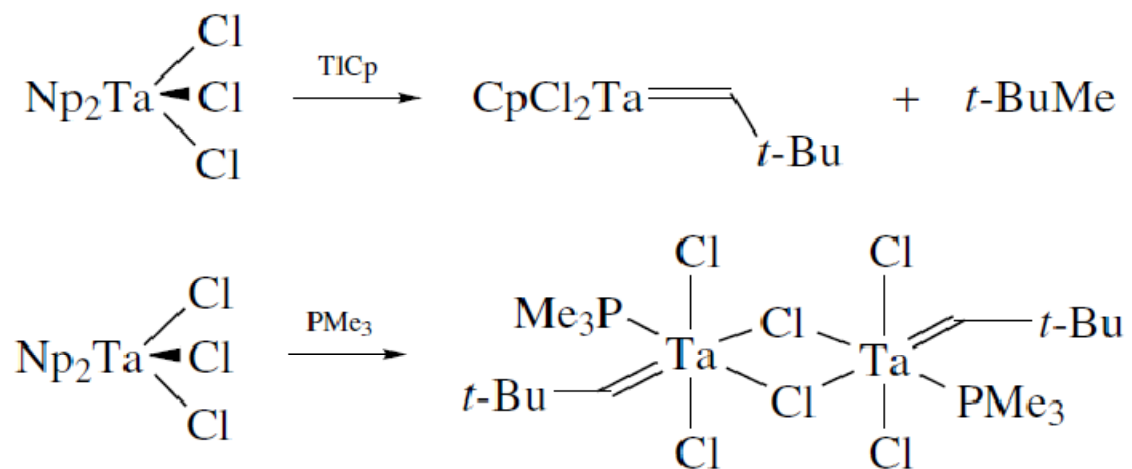
Schrock carbene synthesis

- High valent metal alkyls of the early transition metals can undergo proton abstraction at the a carbon to give nucleophilic Schrock carbenes

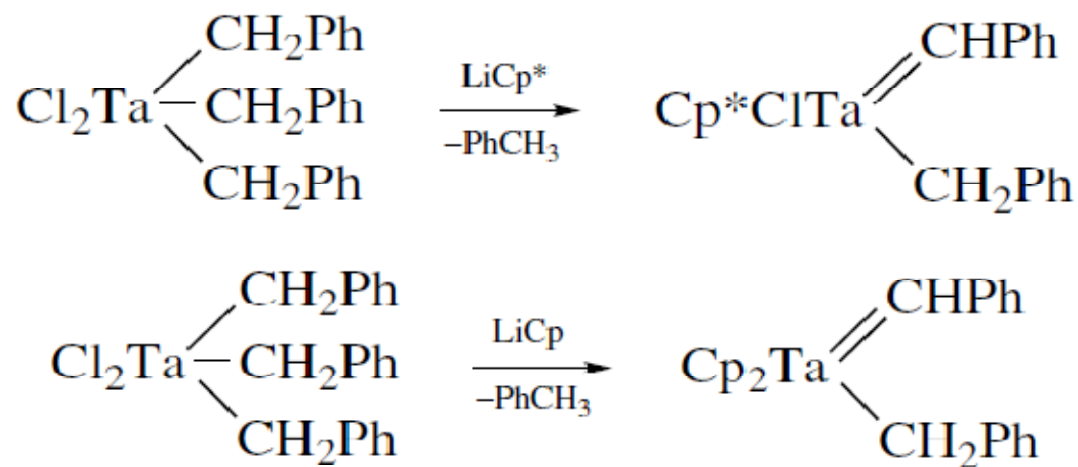


Np = neopentyl ($\text{Me}_3\text{CCH}_2^-$)

- This reaction is believed to involve an α -proton abstraction (possibly agostic) by a neighbouring Np ligand liberating t-BuMe .



- One requirement of this α -abstraction reaction is that the *molecule must be sterically crowded*.
- For example, simple substitution of Cl in Np_2TaCl_3 with the bulky Cp or PMe_3 ligands induces α -abstraction and $t\text{-BuMe}$ elimination producing the corresponding Schrock carbene complex.

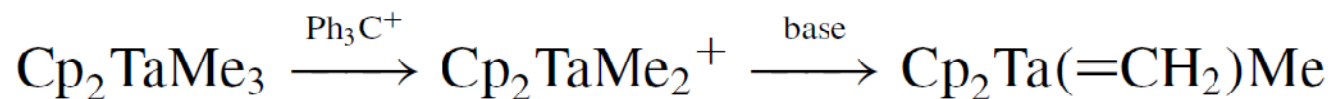


- On replacing the Np ligand with the benzyl ligand a more sterically demanding ligand set is required to induce α -proton abstraction liberating toluene to produce corresponding Schrock carbene complex.
- Typically 2 Cp rings can be used or even pentamethylcyclopentadiene (Cp^{*})

- The Me group does not undergo α -proton abstraction
- Cp_2TaMe_3 is thermodynamically more stable than its α -elimination carbene product due to the low steric requirements of the Me group



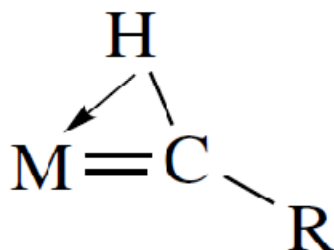
- Synthesis of the methylene complex requires electrophilic Me^- abstraction followed by addition of strong base



Question: Why are methylene complexes stable as Schrock carbenes but not so as Fischer carbenes?

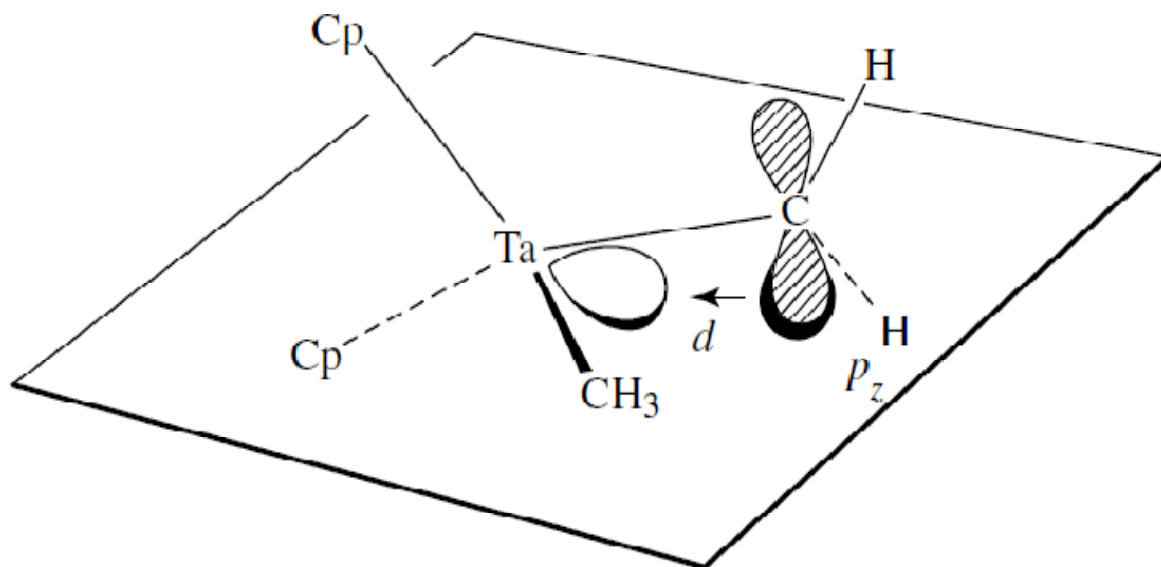
Schrock carbene characterization

- Schrock carbene complexes of high oxidation state early transition metals commonly have agostic interactions
- This shortens the M=C bond and lengthens the C-H bond



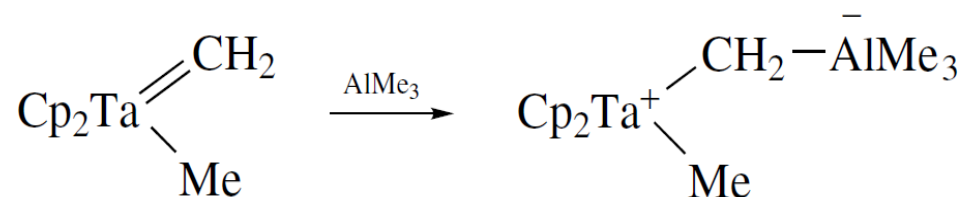
- Agostic interactions result in high field proton shifts (-2σ) and reduced $J(\text{C,H})$ coupling, as well as lower frequency C-H stretches in the IR spectra.
- M-C-R angle can increase up to 175° with the M-C-H angle decreasing to *ca.* 80°

- The $\text{Cp}_2\text{Ta}(=\text{CH}_2)\text{Me}$ complex has been characterized by x-ray crystallography
- For $\text{Cp}_2\text{Ta}(=\text{CH}_2)\text{Me}$ the Ta-C bond lies in the mirror plane with the $\text{M}(d_{xz})$ and p_z orbitals.
- The C-H bonds are almost orthogonal to this plane (88°) in close proximity of the Cp ligands.
- This represents an example of where electronic factors are more dominant than steric factors in determining the lowest energy conformation of a complex.

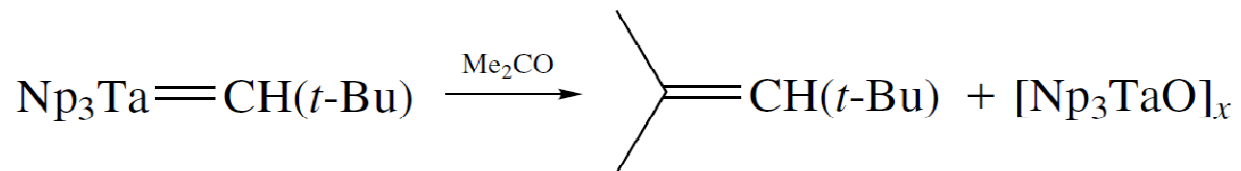


Schrock carbene reactions

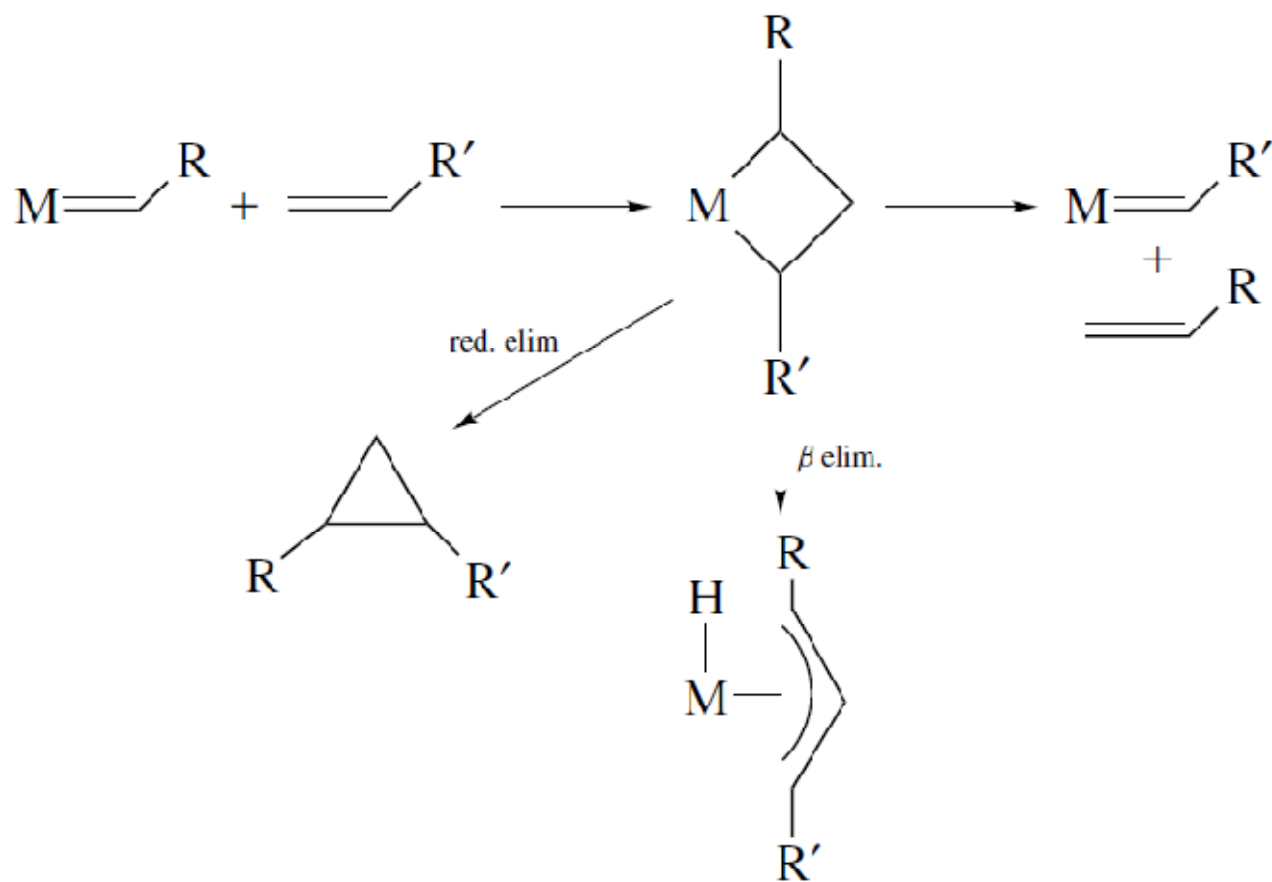
- Their nucleophilic character allows them to form adducts with Lewis acids



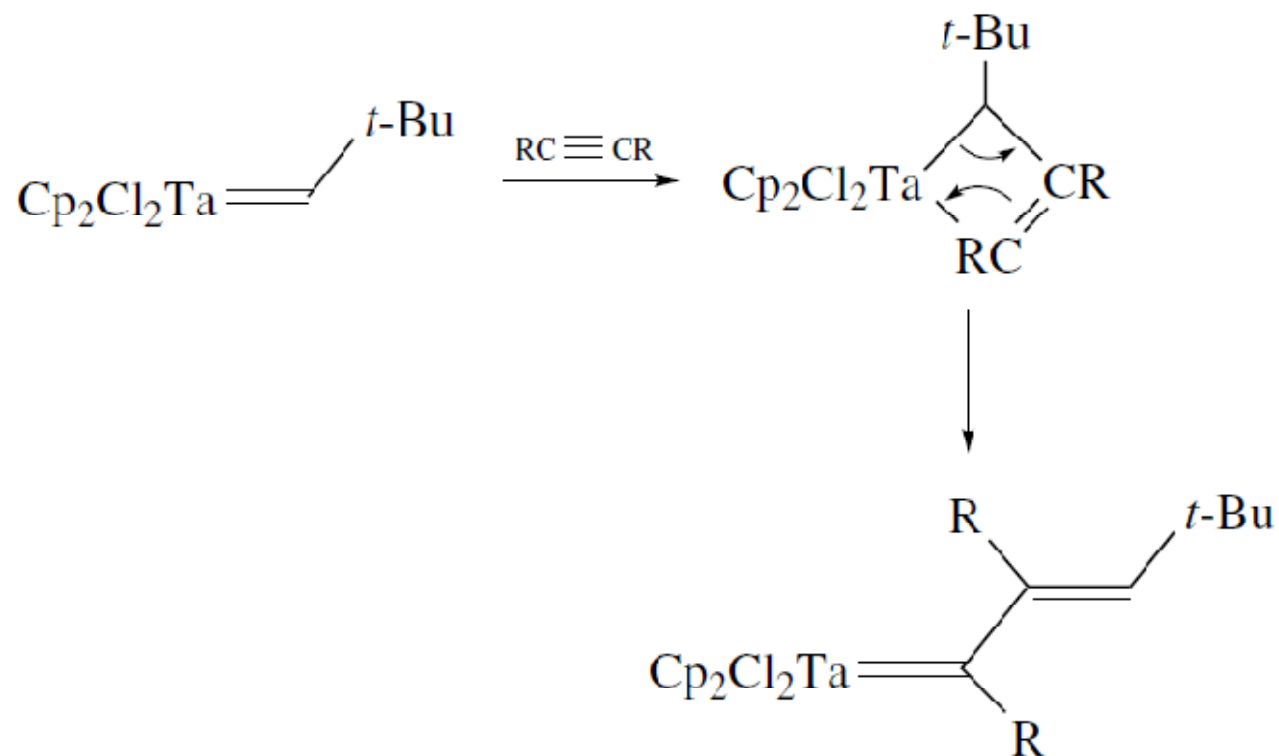
- They react with ketones in a similar fashion as Wittig ($\text{Ph}_3\text{P}=\text{CH}_2$) reagents



- Similar to Fischer carbenes Schrock type complexes also react with alkenes and alkynes to form metallocycles

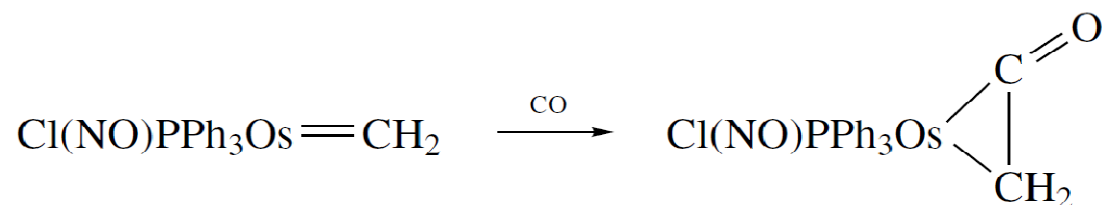
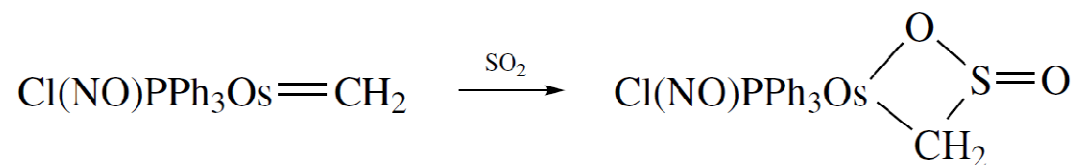


- Schrock type complexes react with alkynes to form metalacyclobutenes which can rearrange to form the π -extended carbene-ene systems

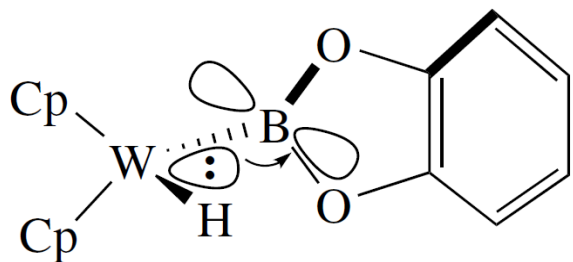


Intermediate Fischer-Schrock cases

- $\text{Cl}(\text{NO})\text{PPh}_3\text{Os}(\text{=CH}_2)$ shows both Fischer and Schrock type reactivity
- Reacts with electrophiles (SO_2) and nucleophiles (CO)
- Contains both π -donor (Cl) as well as π -acceptor (NO) ligands
- The carbene carbon does not have any π -donor ligands
- Using the ionic model here we can consider Os as +2 or +4 depending on how we classify the ligand.

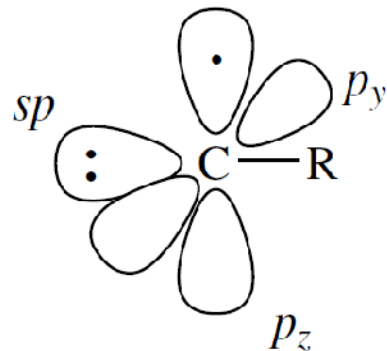


- The boryl group BR_2^- is isoelectronic with the carbene group
- Several metal-boryl complexes have now been reported, e.g. $RhHCl(B\{Cat\})(Ph_3P)_2$ which is formed via oxidative addition of $H-B\{Cat\}$ to Wilkinson's catalyst
- In the solid state it has been shown for $Cp_2WH(B\{Cat\})$ how electronic factors are again important for metal-multiple bond systems
- In a condensed phase, however, boryl systems show free rotation about the M-B bond indicating a weaker bond than metal-carbene systems

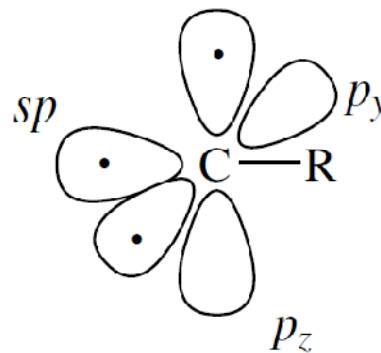


Metal Carbynes

- Have similar bonding formulations as per Fischer and Schrock carbenes
- The free carbyne can be of doublet (Fischer) or quartet (Schrock) multiplicity

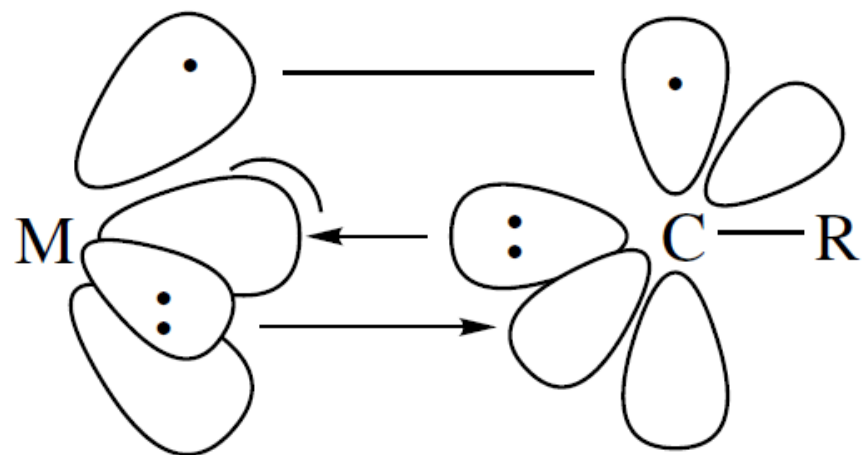


Doublet
carbyne



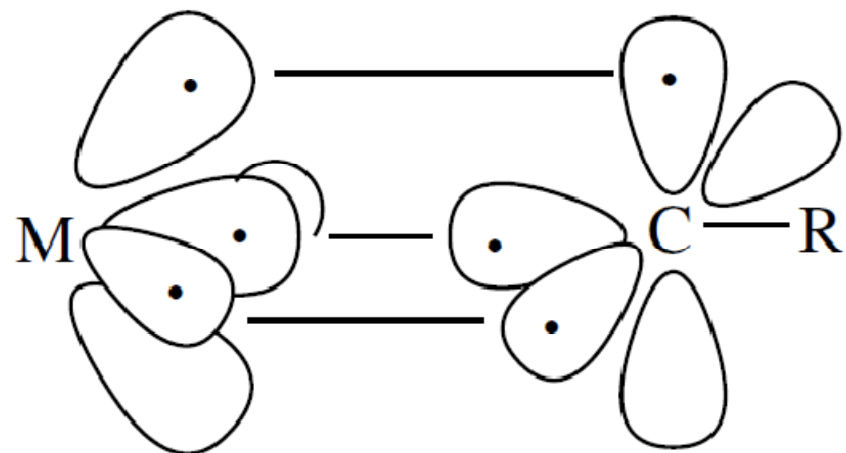
Quartet
carbyne

- The carbyne ligand is linear
- Carbyne carbon is sp hybridized
- The $M\equiv C$ bond is very short (1.65 – 1.90 Å)
- Characteristic low-field ^{13}C NMR resonance in the range +250 to +400 ppm



Fischer carbyne

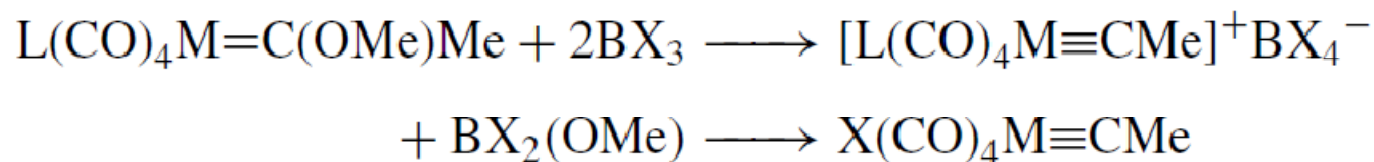
- A doublet (Fischer) carbyne is sp hybridized
- Contains one filled sp orbital capable of donating $2e^-$ to a metal centre
- Contains one singly occupied p orbital capable forming an additional π bond
- The remaining empty p orbital is capable of $M \rightarrow C$ π back donation
- $3e^-$ donor covalent model / $4e^-$ donor ionic model



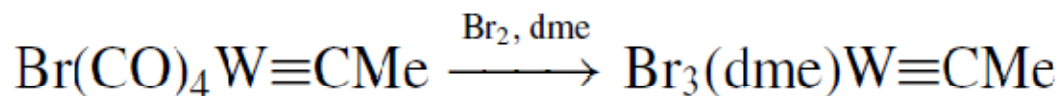
Schrock carbyne

- A quartet (Schrock) carbyne is also sp hybridized
- Contains three singly occupied orbitals (one sp and two p) capable of forming three covalent M-C bonds (one s and two p bonds)
- This class of ligand is X_3 -type
- $3e^-$ ligand in covalent model (or $6e^-$ ionic model)

- Fischer first prepared metal carbyne complexes by the electrophilic abstraction of methoxy from a methoxy methyl Fischer carbene.



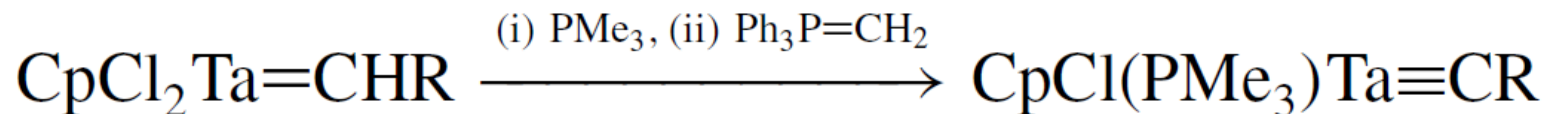
- The high *trans* effect of the carbyne ligand resulted in replacement of a CO ligand with a halide
- If L = PPh₃ (a stronger field ligand) the cationic species is the final product



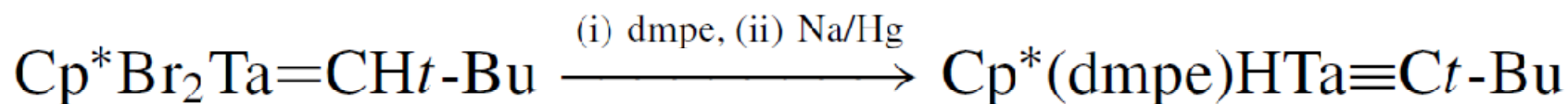
(dme = MeOCH₂CH₂OMe).

- In particular cases careful oxidation of a Fischer carbyne by replacement of its CO ligands can result in a Schrock carbyne

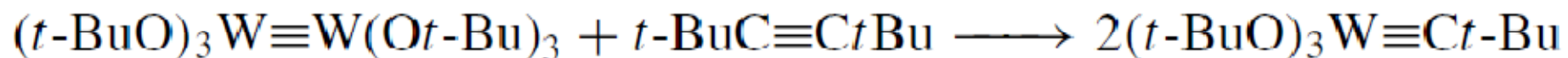
- In a more general approach, Schrock carbynes can be prepared by deprotonation of an α -CH



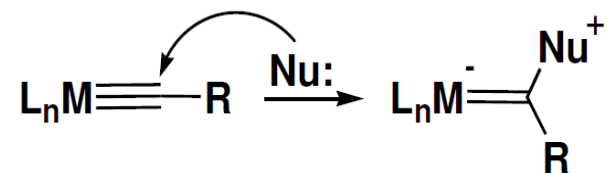
- Intramolecular oxidative addition of a bound Schrock carbene
(α elimination)



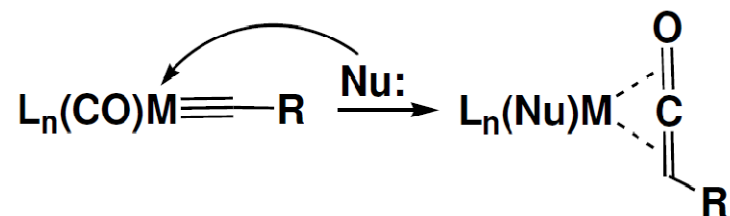
- Metathesis of tertiary butoxide ($t\text{-BuO}$) complexes
(triple bi-nuclear oxidative addition, i.e. +III change in oxidation state)



- Fischer carbynes are electrophilic and thus prone to nucleophilic attack
- Nucleophiles such as PMe_3 , pyridine, alkyl lithiums, and isonitriles react with Fischer carbynes to give the corresponding Fischer carbene complex.



- Alternatively the nucleophile may attack the metal centre producing a ketenyl complex



- In contrast, Schrock carbynes are nucleophilic and prone to attack by electrophiles

