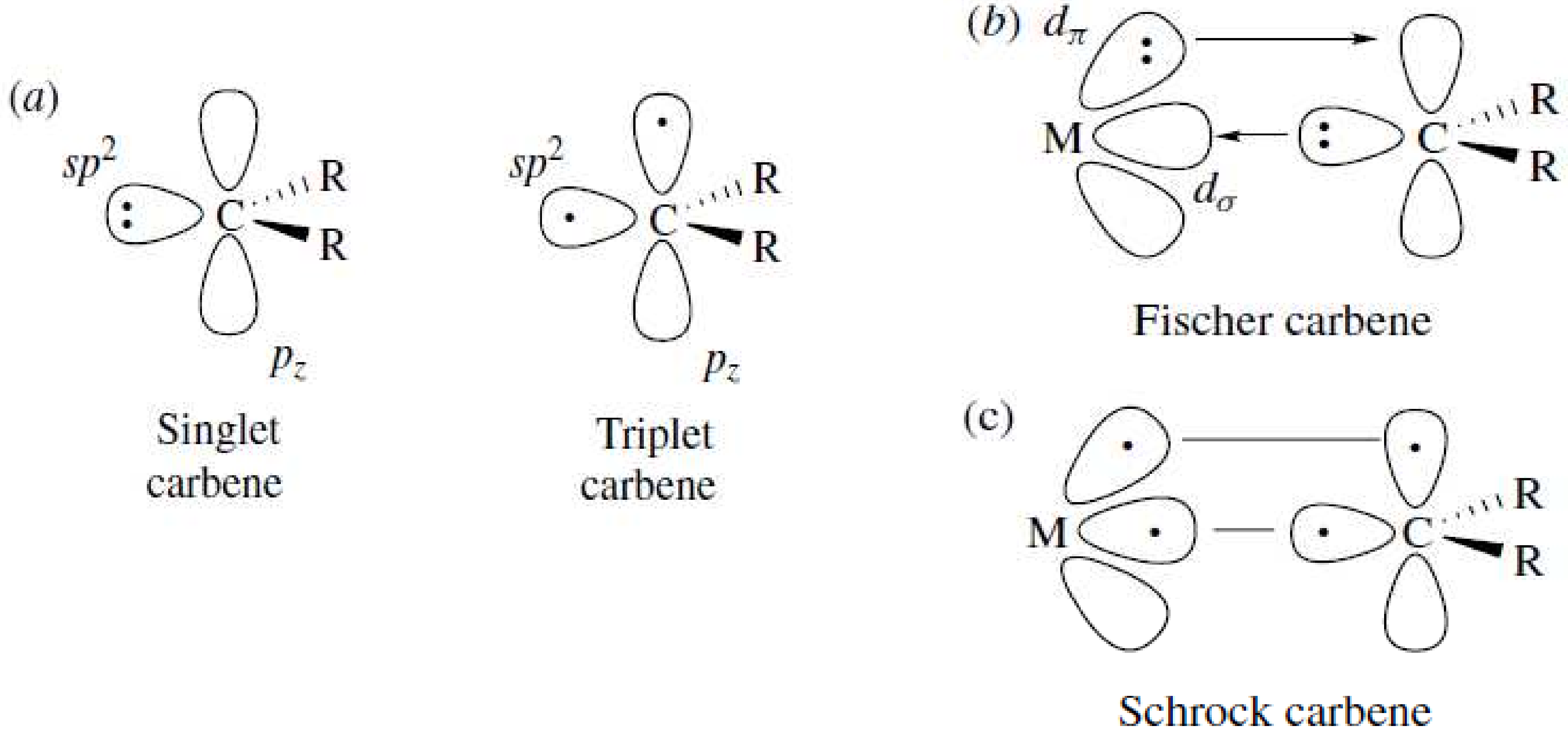
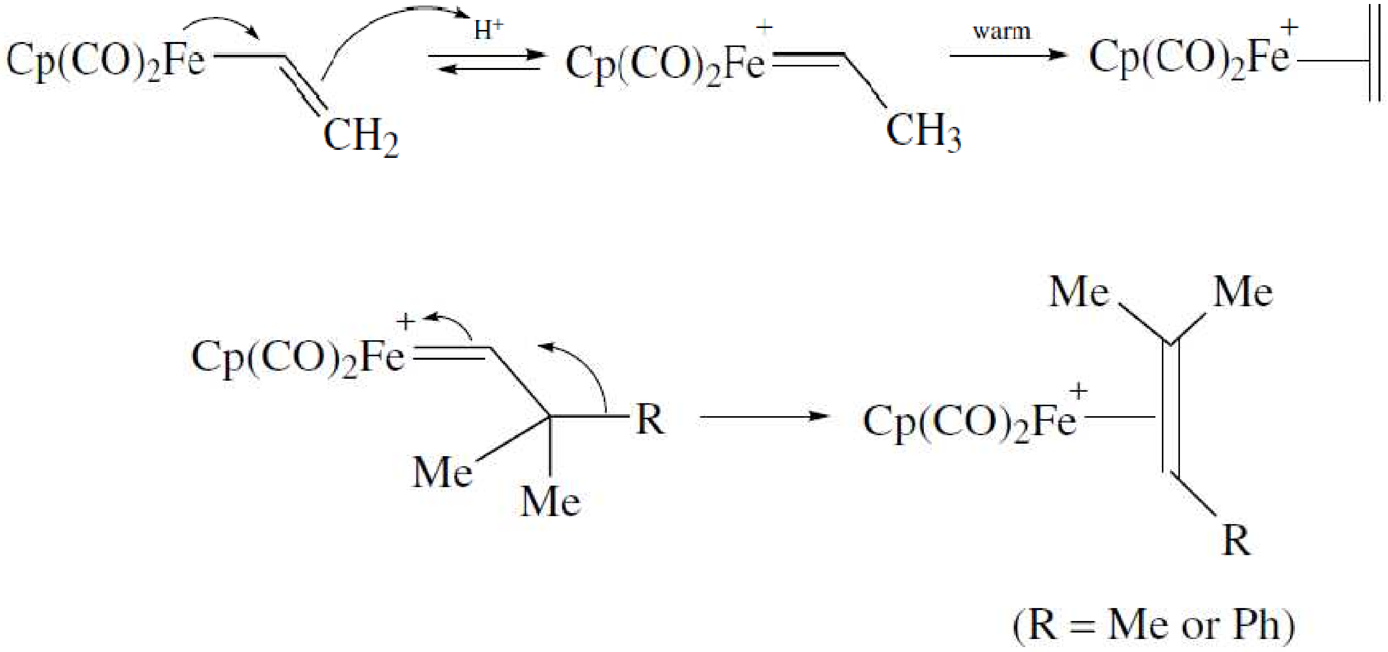


- (a) Singlet and triplet forms of a carbene
- (b) In the Fischer case, direct *C→M donation predominates* and the carbon tends to be positively charged.
- (c) In the Schrock case, *two covalent bonds are formed, each polarized toward the carbon* giving it a negative charge.

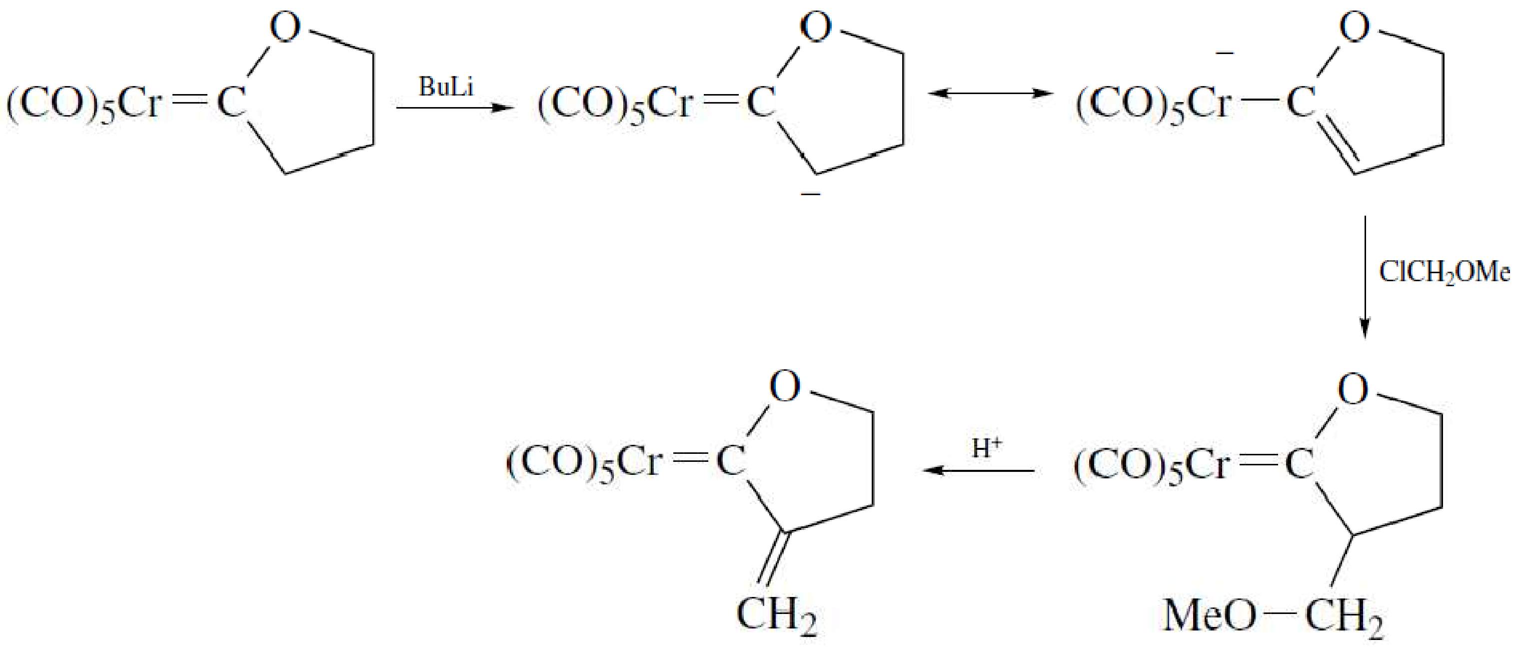
- In the absence of a heteroatom substituent Fischer carbenes are highly reactive and give rise to 1,2 proton or alkyl shifts yielding the thermodynamically more stable metal alkene complex.



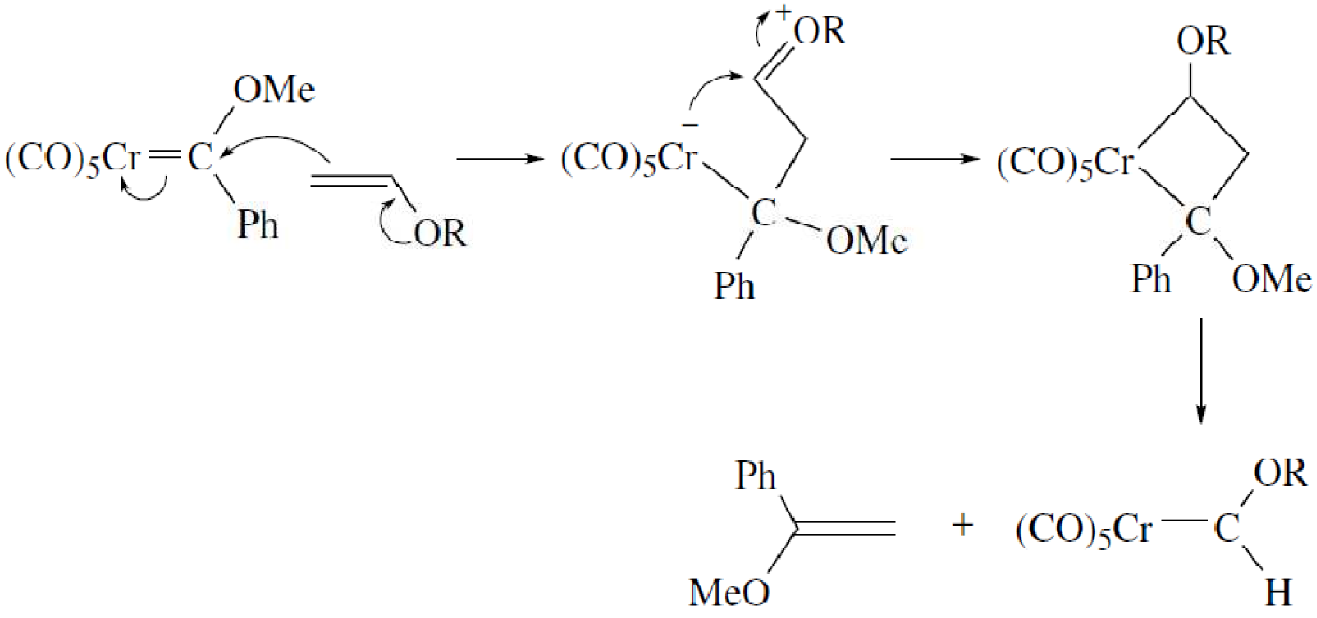
- Rearrangement can be suppressed by using electron rich co-ligands

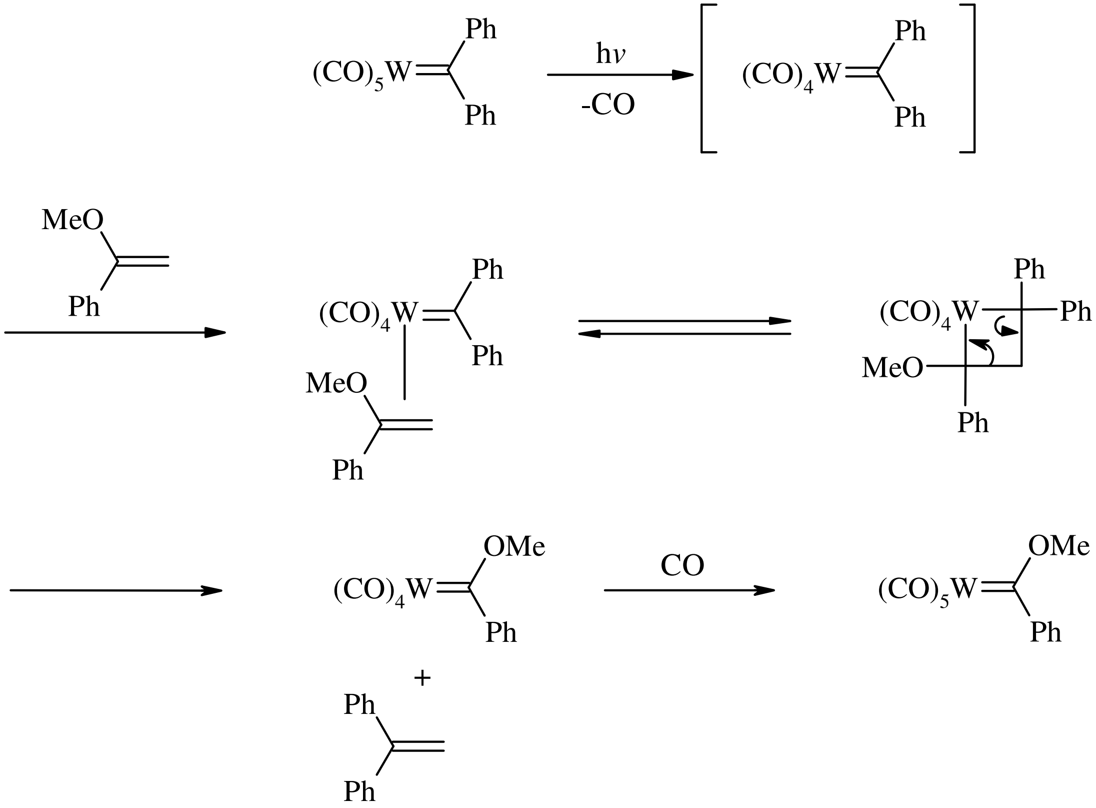
  e.g. [Cp(dppe)Fe=C(H)CMe$_3$]$^+$ does not rearrange due to the basic dppe ligand

- Due to the electrophillic nature of the Fischer carbene C-atom any β–H atoms are acidic and abstracted readily by base.
- The negative charge of the resulting carbanion is delocalized onto the M centre and thus stabilized.
- Further functionalization is possible by reaction with a suitable electrophile

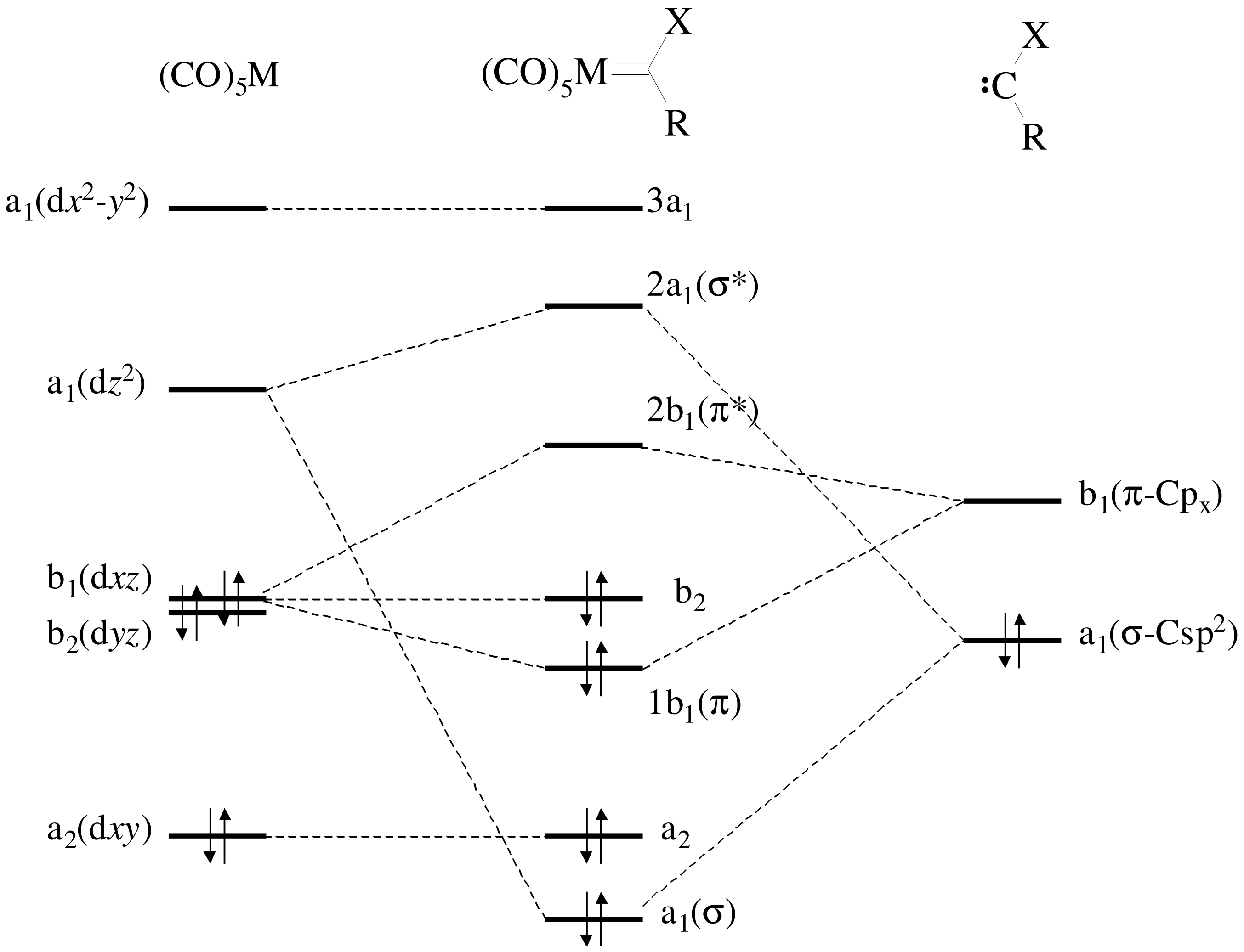


- Addition of unsturated nucleophillic systems such as alkenes or alkynes can lead to the formation of metalacycles
- Metalacycles can break down to give a new carbene and new alkene in a reaction known as alkene metathesis (discussed later)

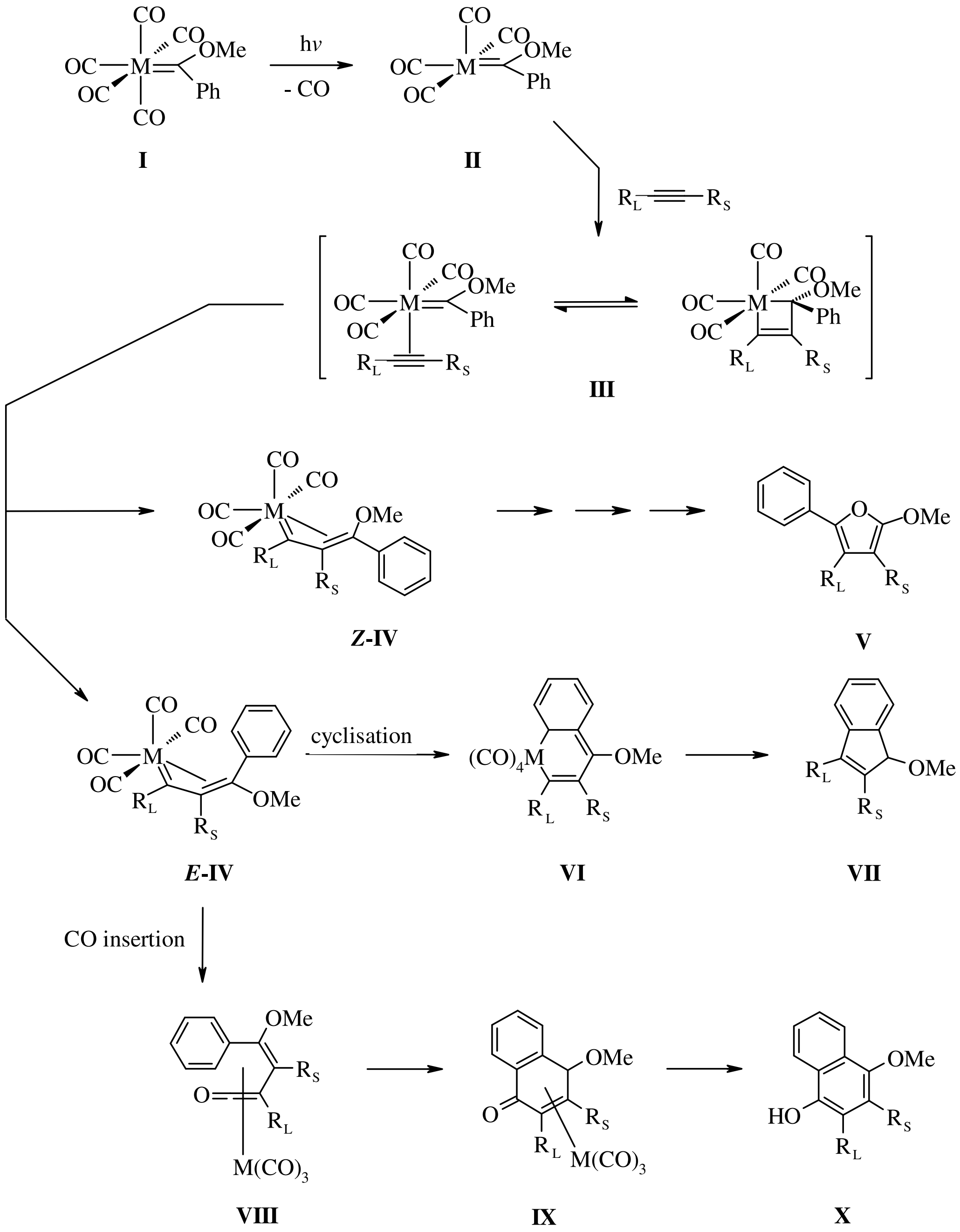




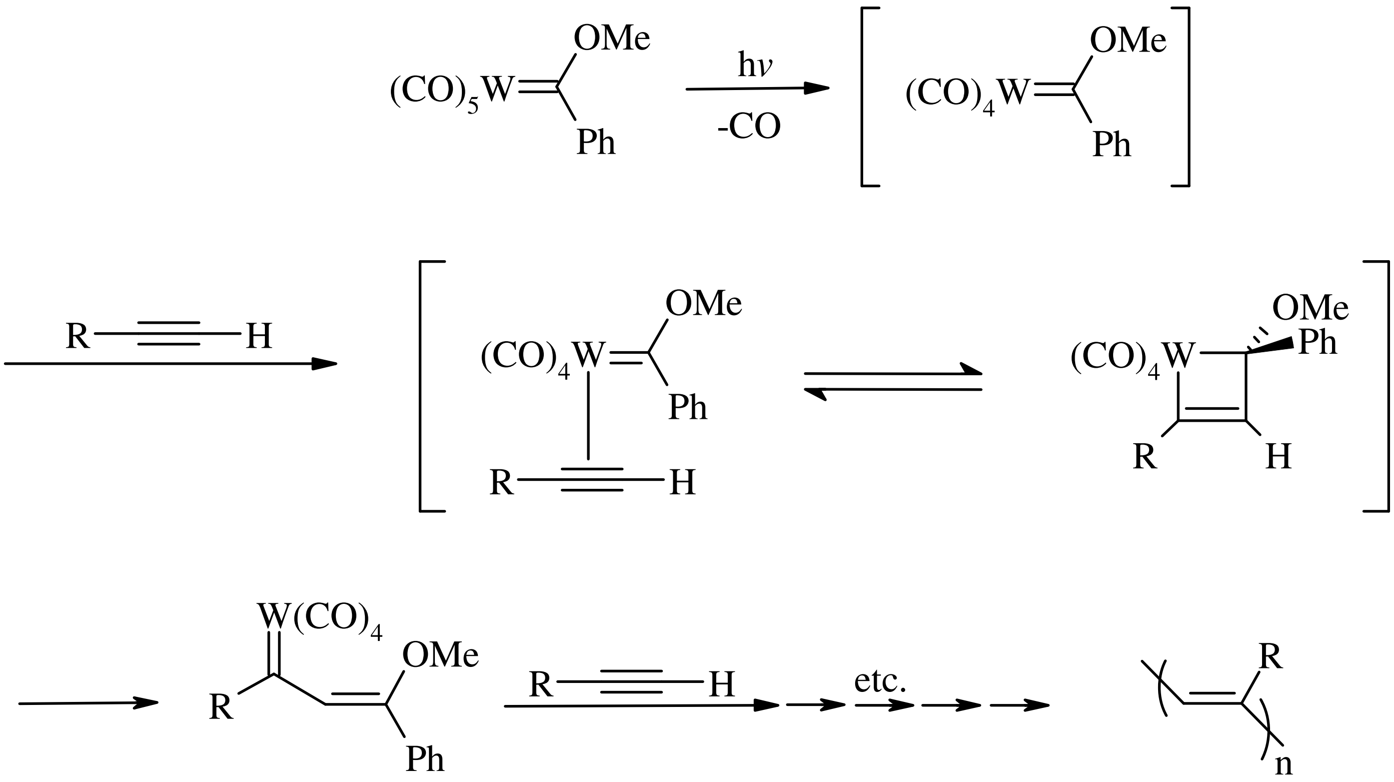
- Photoinduced metathesis was observed upon population of the high-energy LF state.
- Population of the $dx^2\text{-}y^2$ e_g^* metal orbital, which is anti-bonding with respect to an equatorial CO ligand allows direct access to the *cis*-alkene/alkyne complex required for metallacyclobutane formation.
- Irradiation of the MLCT band at 485 nm did not result in metathesis.



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

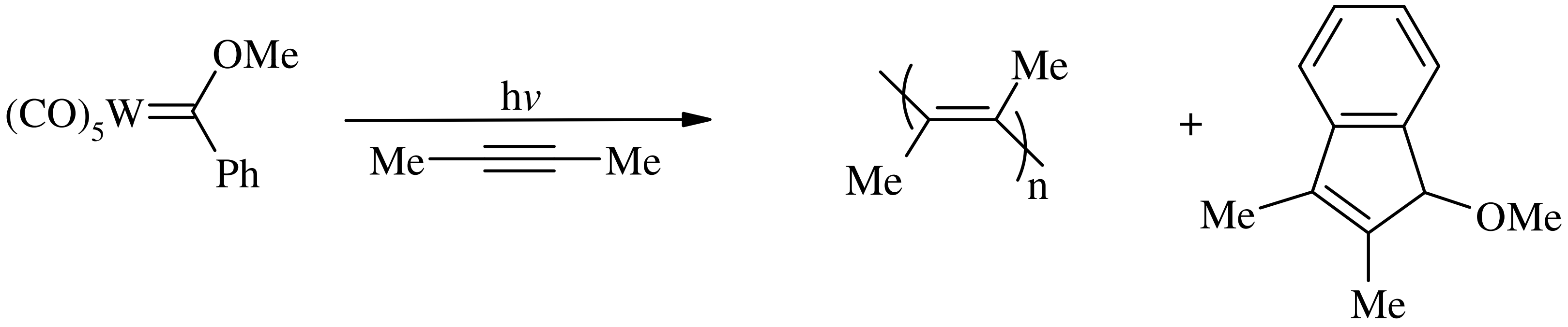

hν
- CO
I
II
III
Z-IV
V
E-IV
cyclisation
VI
VII
CO insertion
VIII
IX
X

- 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



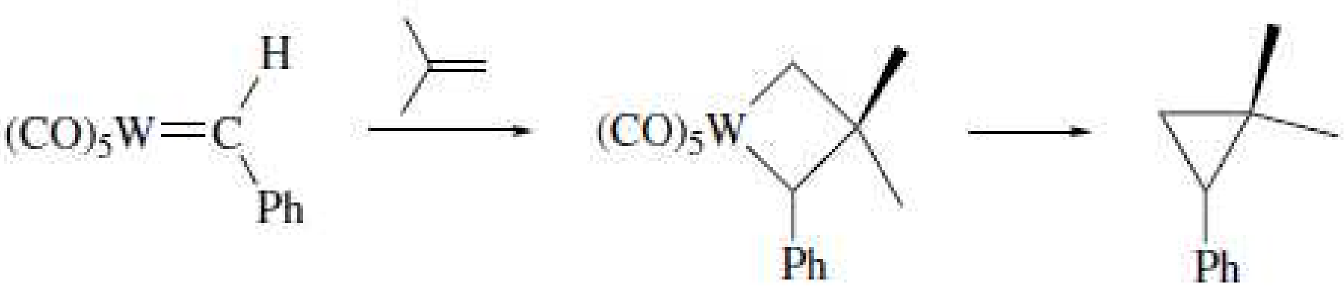
T. J. Katz, S. J. Lee, *J. Am. Chem. Soc.* **1980**, 102, 422.

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



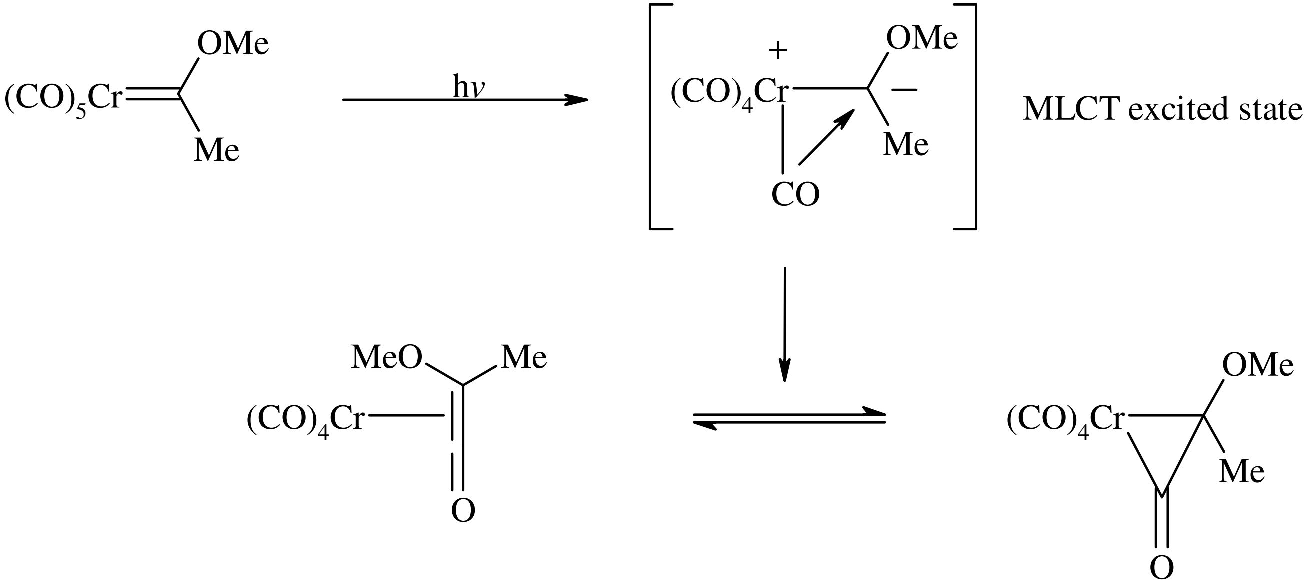
H. C. Foley, L. M. Strubinger, T. S. Targos, G. L. Geoffroy, *J. Am. Chem. Soc.* **1983**, 105, 3064

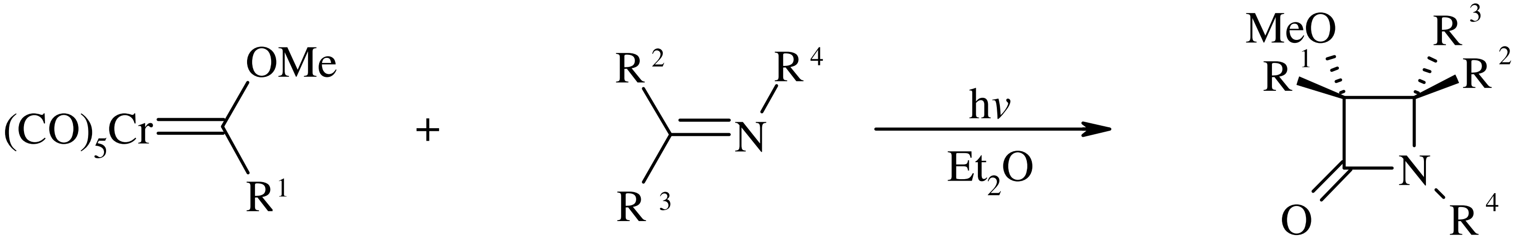
- The cyclopropanation of alkenes with Fischer-carbenes under thermal conditions is also a well known reaction.
- Metalacycles break down to give cyclopropanes via reductive elimination
- Olefin metathesis and cyclopropanation only occurs when the carbene and alkene moieties are coplanar when forming 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

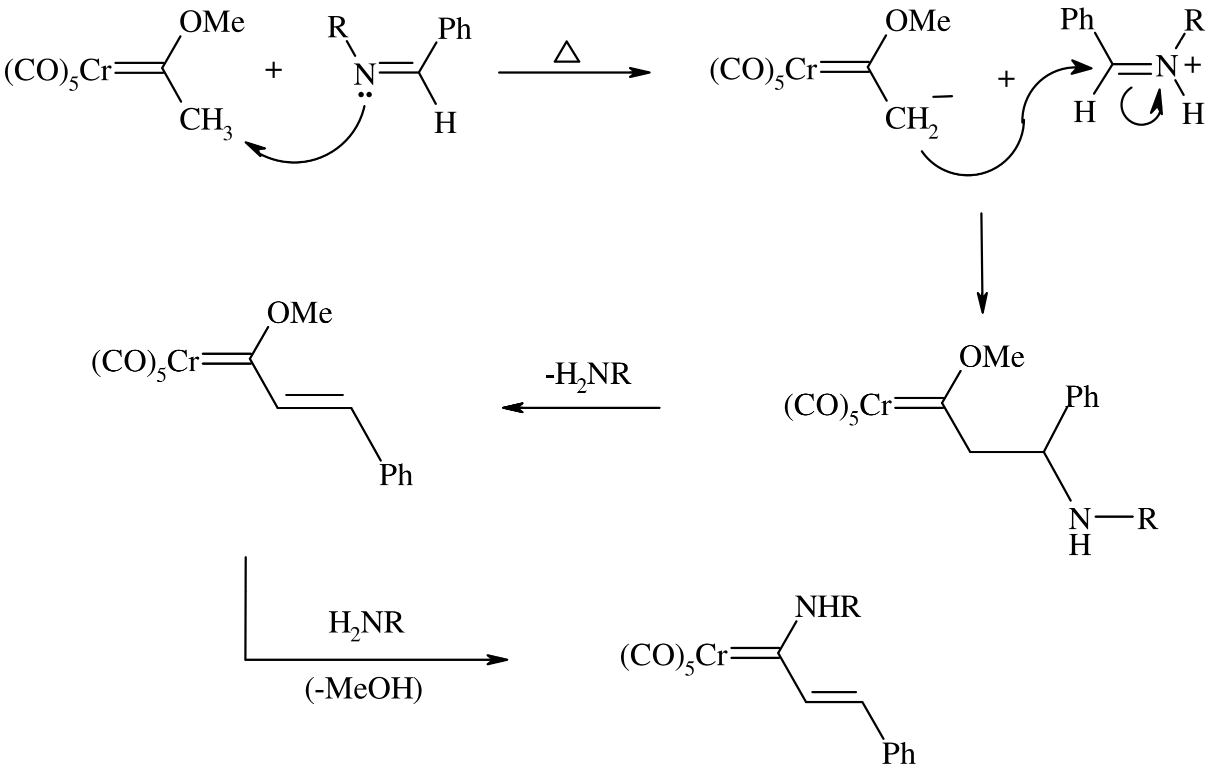
- Fischer-carbenes have been converted photochemically to a range of compounds, e.g. amino-acids, β-lactams from imines, β-lactones from aldehydes, cyclobutanones from alkenes.
- These reactions are all photochemically driven by MLCT excitation of the carbene complex forming a metal-ketene transient 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 (CO)5Cr=C(OMe)Me.
- This reaction was stereospecific, producing only one diastereomer of the product.

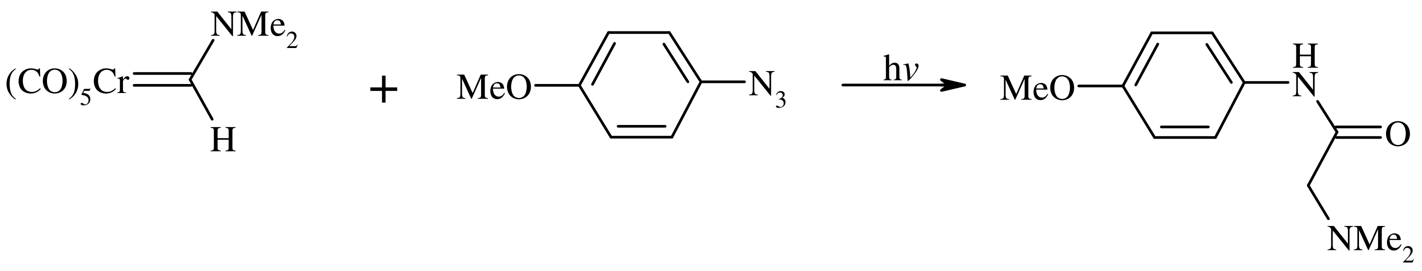
M. A. McGuire, L. S. Hegedus, *J. Am. Chem. Soc.* **1982**, 104, 5538.



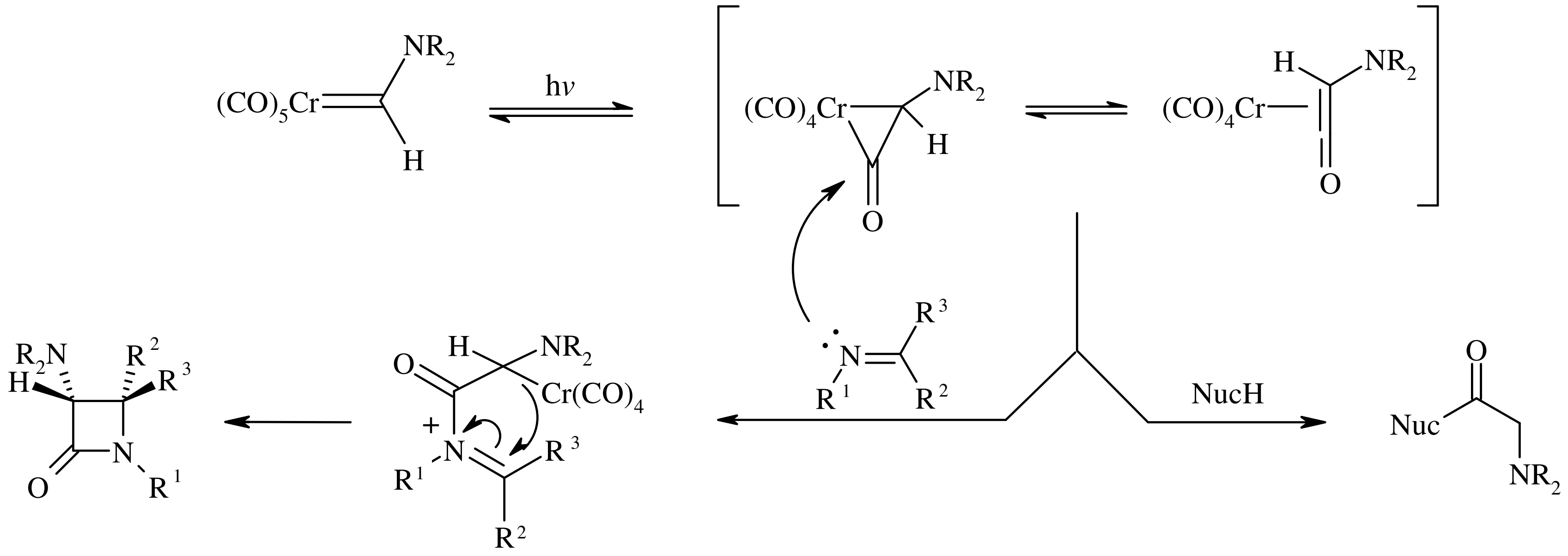
- In contrast, under thermal conditions the chemistry of the α-carbon dominates, producing new carbene complexes

L. S. Hegedus, M. A. McGuire, L. M. Schultze, C. Yijun, O. P. Anderson, *J. Am. Chem. Soc.* **1984**, 106, 2680.

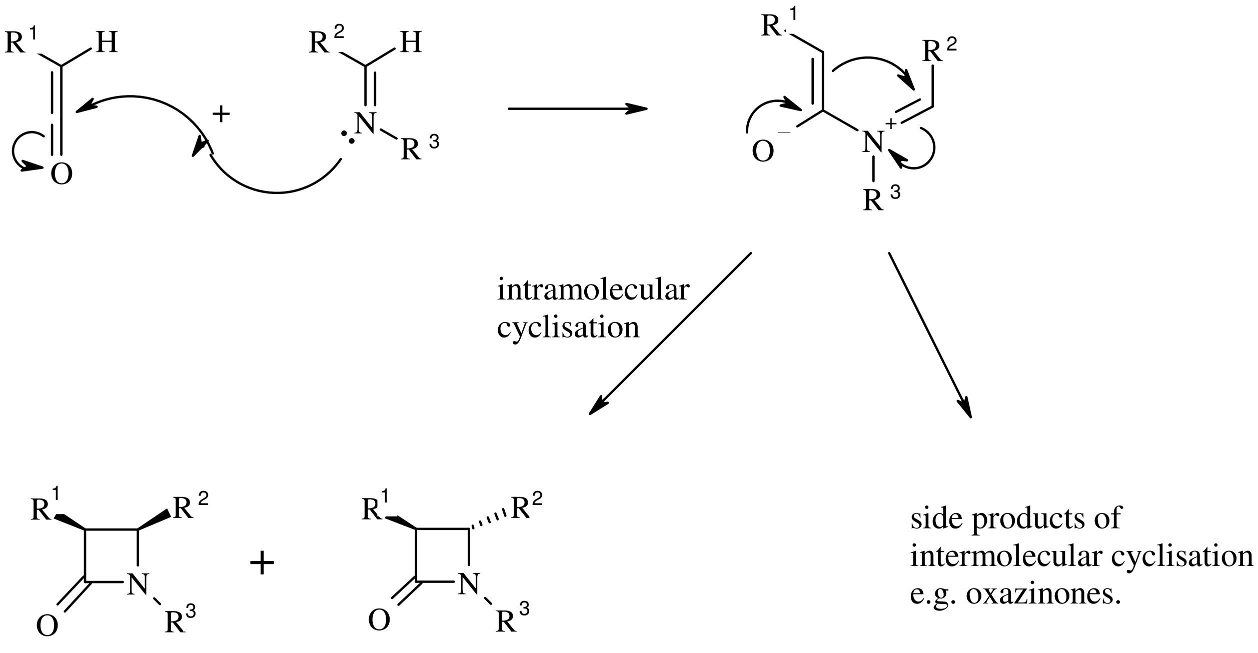
- Initially photoinduced CO loss from the chromium carbene complex was believed to be the primary photoprocess in β-lactam formation.
- However, β-lactam formation is not observed thermally.
- Also, high yields of β-lactam products are observed when the photochemical reaction is carried out under high pressures of CO.
- Strong evidence for the intermediacy of chromium-ketene complexes was observed by Hegedus when in an attempt to carry out a 1,3-cycloaddition of *p*-methoxyphenyl azide to the amino carbene $(CO)_5Cr{=}C(NMe_2)H$ the unexpected glycinamide was produced.



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



- The reactions involved in glycinamide and b-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 nucleophillic attack on a ketene.
- The formation of ketene intermediates is typically inferred from subsequent reactions as its high reactivity and unstability make it extremely difficult to observe.



intramolecular cyclisation

side products of intermolecular cyclisation e.g. oxazinones.

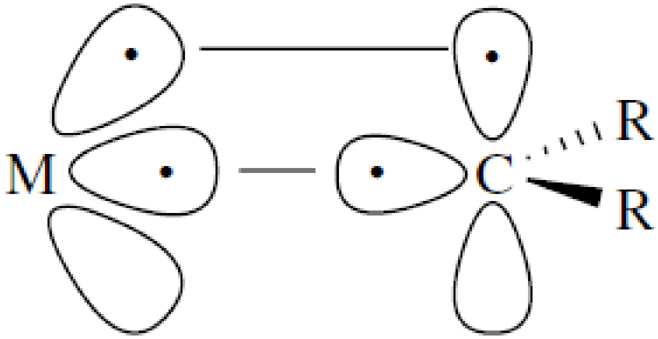
β-lactam isomers

- The Cr ketene complex does not undergo typical free-ketene cycloaddition reactions with olefins, as it is only reactive towards nucleophillic reagents.
- The reaction of free ketenes with imines to form β-lactams proceeds via a dipolar, non-concerted pathway.
- This reaction occurs via nucleophillic attack of the imine at the ketene carbonyl producing a zwitterionic intermediate, which undergoes a conrotatory ring closure to form the β-lactam.
- Free ketenes are generated in situ from acid halides and trimethylamine.

- Lower yields are often observed in the reaction of free ketenes with imines due to intermolecular reaction of the zwitterionic intermediate with further ketene rather than intramolecular cyclisation to form a β-lactam ring.
- Intermolecular reactions are prevented in chromium ketene intermediates by the presence of the metal moiety, which results in higer yields for b-lactam formation, as well as stereospecifity.

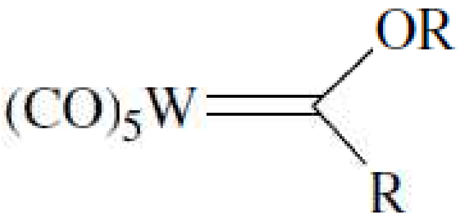
C. Borel, L. S. Hegedus, J. Krebs, Y. Satoh, *J. Am. Chem. Soc.* **1987**, 109, 1101.

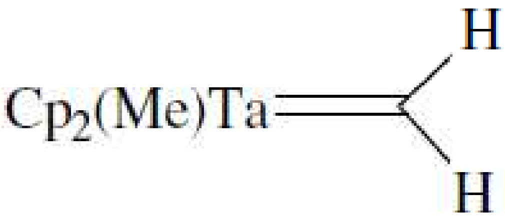
Schrock Carbenes



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 nucleophillic 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

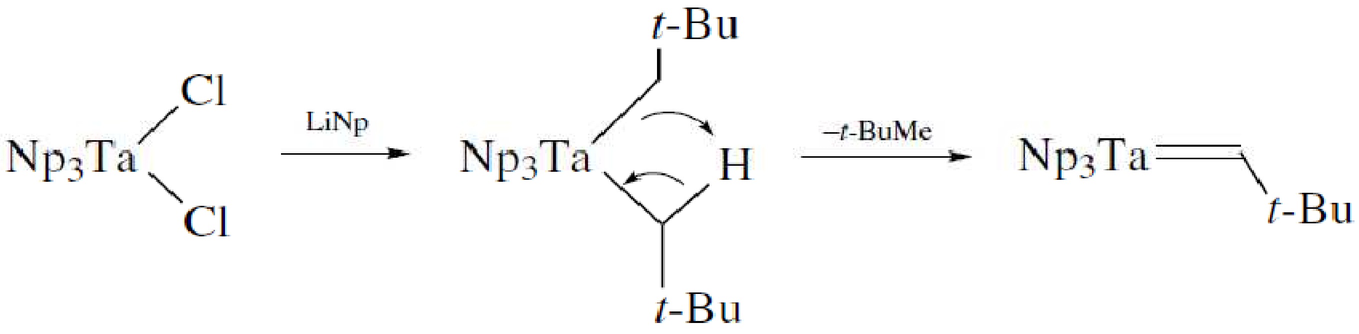
If we consider the Schrock carbene as a Fischer carbene with strongly enhanced M→C p-back bonding, the 2 electrons originally in $M(d_\pi)$ transfer to the $C(p_z)$ orbital, oxidizing the metal by 2 units and giving a CR_2^{2-} ligand.

- The more electropositive early transition metal complexes have less stable $M(d_\pi)$ 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 X_2-type character.

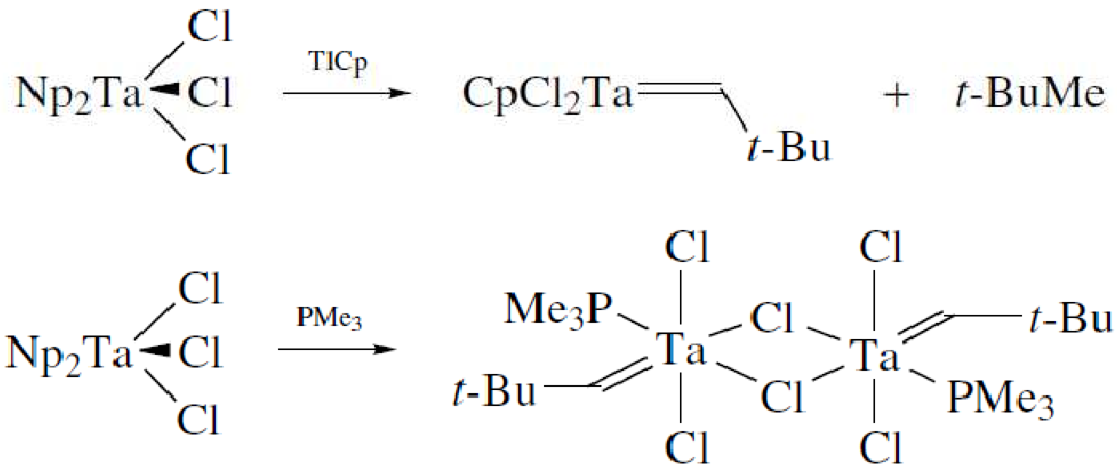
Schrock carbene synthesis

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

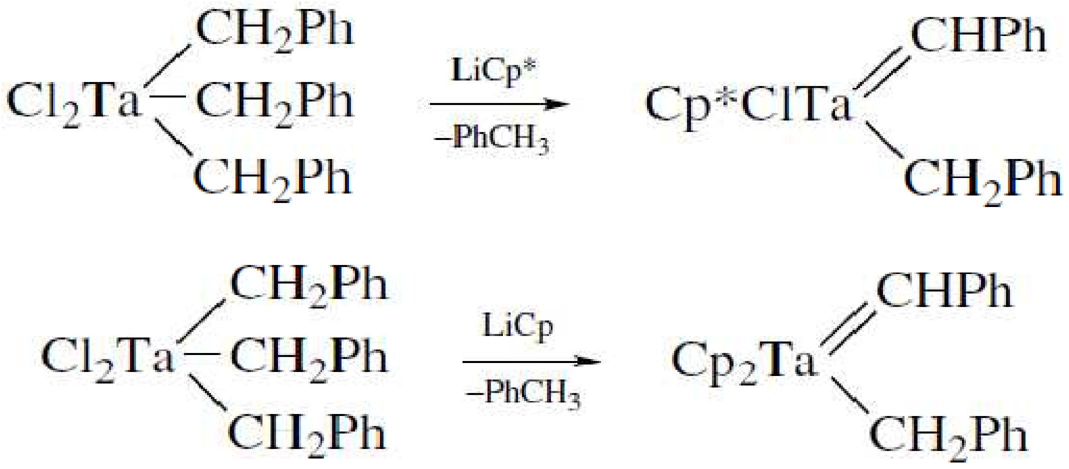


Np = neopentyl ($Me_3CCH_2^-$)

- This reaction is believed to involve an a-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}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 a-proton abstraction liberating toluene to produce corresoponding 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 it's α-elimination carbene product due to the low steric requirements of the Me group

$$\mathrm{TaMe_3Cl_2} \xrightarrow{\mathrm{LiCp}} \mathrm{CpTaMe_3Cl} \xrightarrow{\mathrm{LiCp}} \mathrm{Cp_2TaMe_3}$$

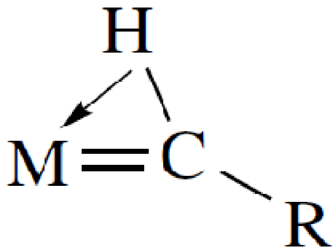
- Synthesis of the methylene complex requires electrophillic Me^- abstraction followed by addition of strong base

$$\mathrm{Cp_2TaMe_3} \xrightarrow{\mathrm{Ph_3C^+}} \mathrm{Cp_2TaMe_2}^+ \xrightarrow{\mathrm{base}} \mathrm{Cp_2Ta({=}CH_2)Me}$$

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

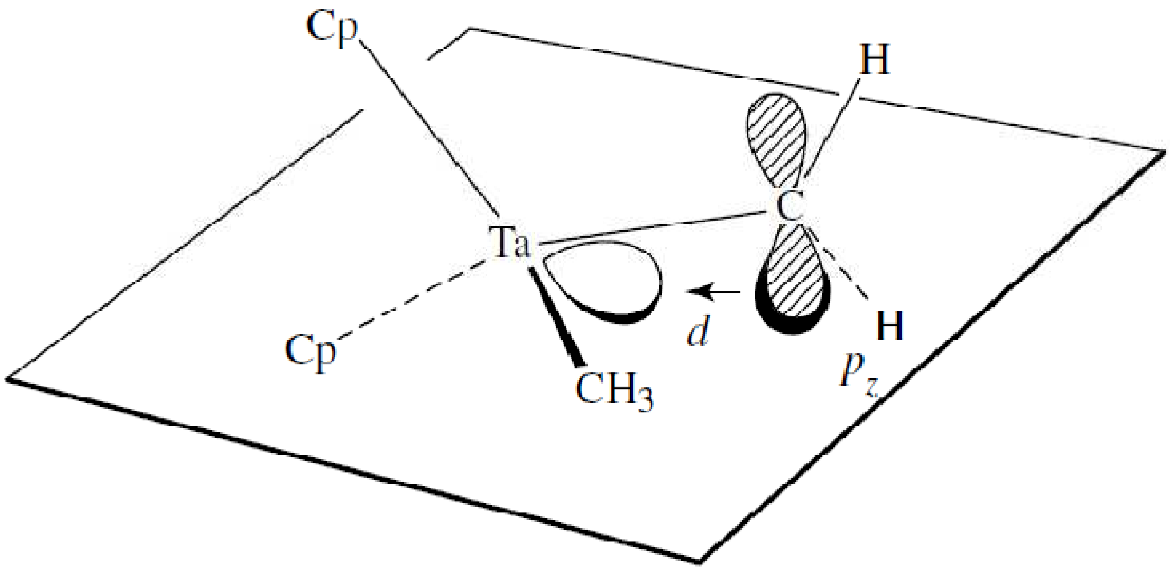
Schrock carbene characterization

- 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



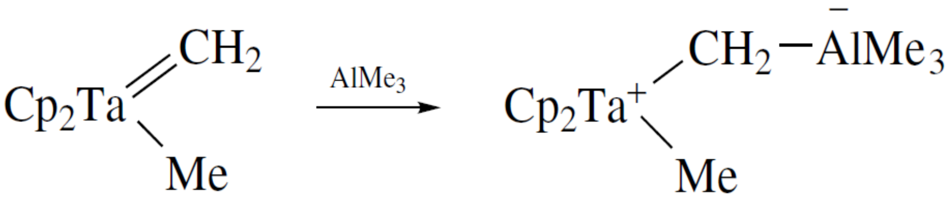
- Agostic interactions result in high field proton shifts (-2σ) and reduced *J*(C,H) coupling, as well as lower frequency C-H stretches in the IR spectra.
- M-C-R angle can increase up to 175° with the M-C-H angle decreasing to *ca.* 80°

- The $Cp_2Ta(=CH_2)Me$ complex has been characterized by x-ray crystallography
- For $Cp_2Ta(=CH_2)Me$ the Ta-C bond lies in the mirror plane with the 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.

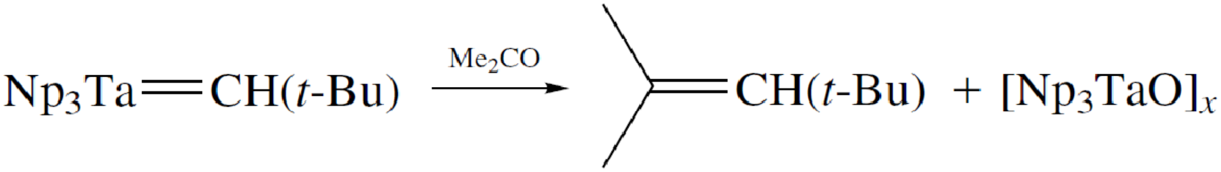


Schrock carbene reactions

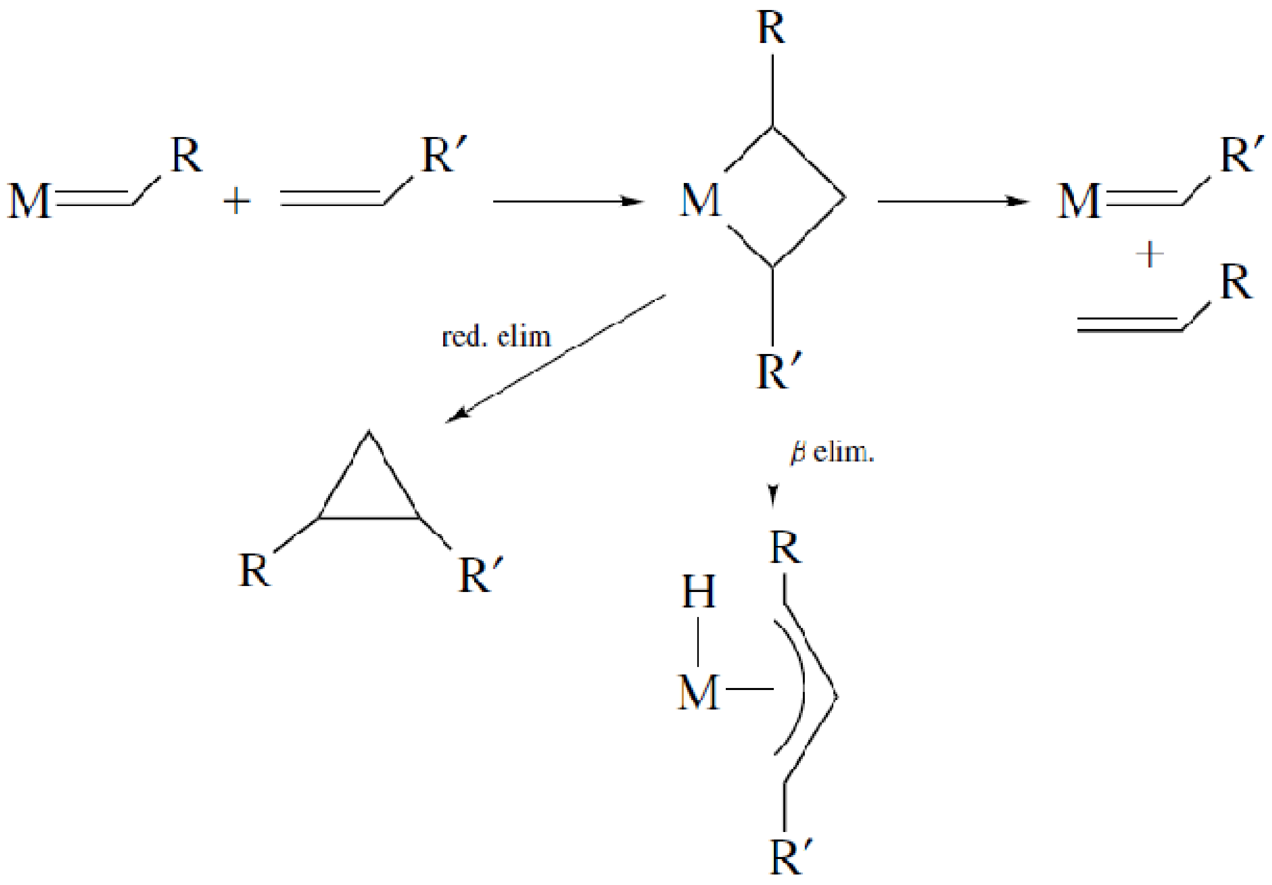
- Their nucleophillic character allows them to form adducts with Lewis acids



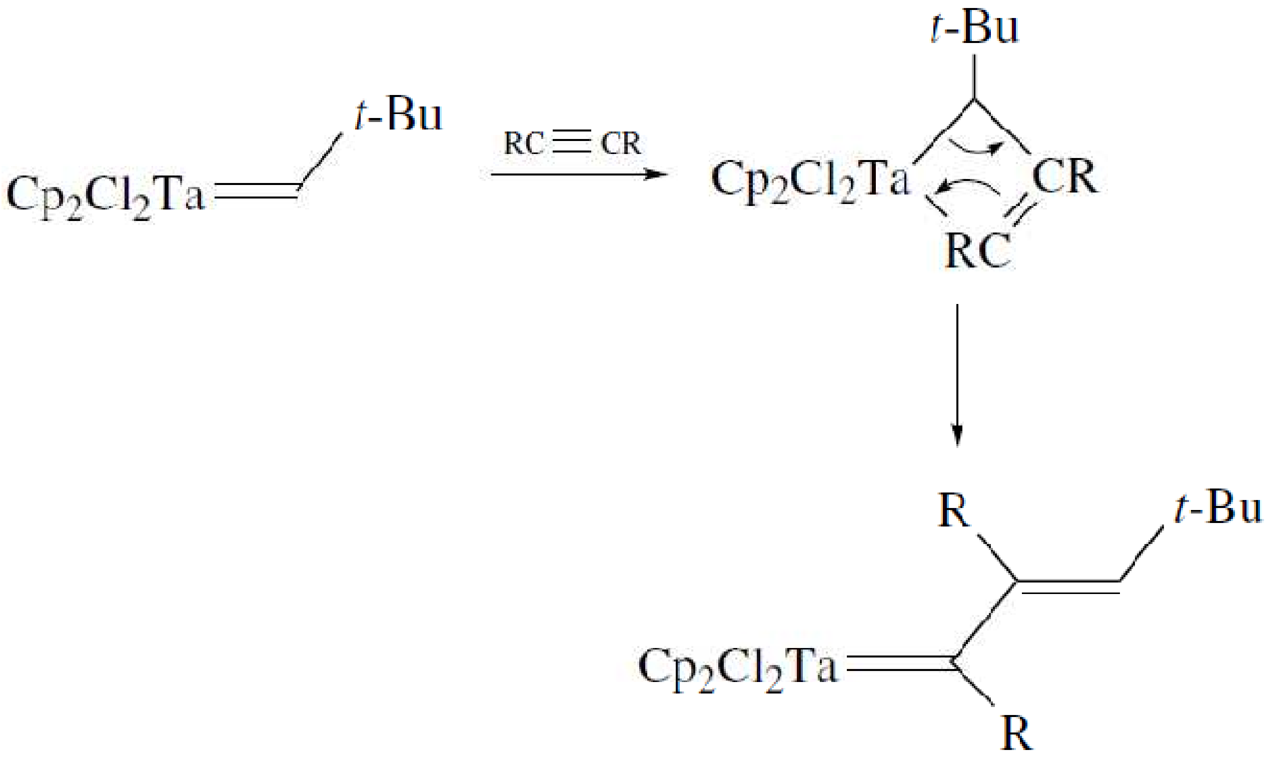
- They react with ketones in a similar fashion as Wittig ($Ph_3P{=}CH_2$) reagents



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

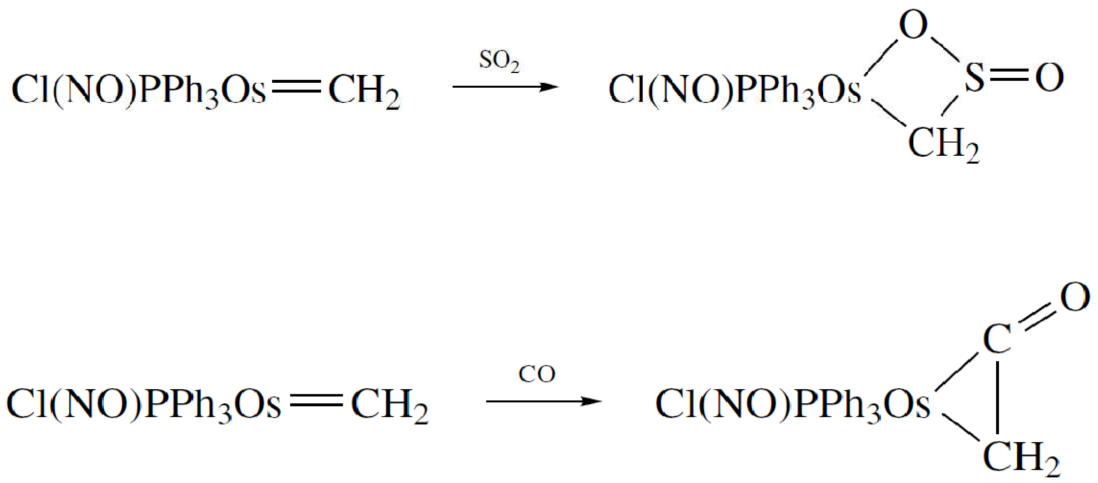


- Schrock type complexes react with alkynes to form metalacyclobutenes which can rearrange to form the π-extended carbene-ene systems

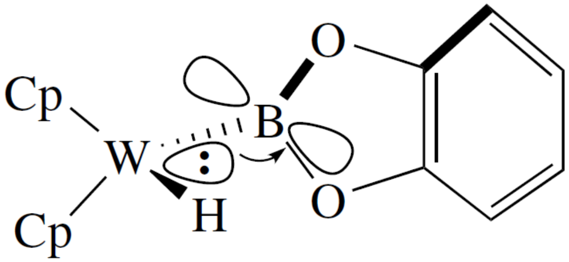


Intermediate Fischer-Schrock cases

- $Cl(NO)PPh_3Os(=CH_2)$ 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.

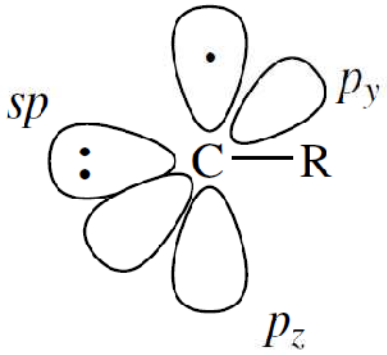


- The boryl group BR_2^- is isoelectronic with the carbene group
- Several metal-boryl complexes have now been reported, e.g. RhHCl(B{Cat})($Ph_3P)_2$ which is formed via oxidative addition of H-B(Cat) to Wilkinson’s catalyst
- In the solid state it has been shown for Cp_2WH(B{Cat}) how electronic factors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

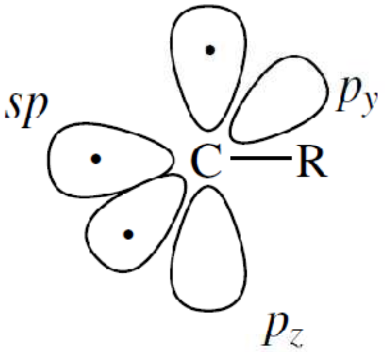


Metal Carbynes

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

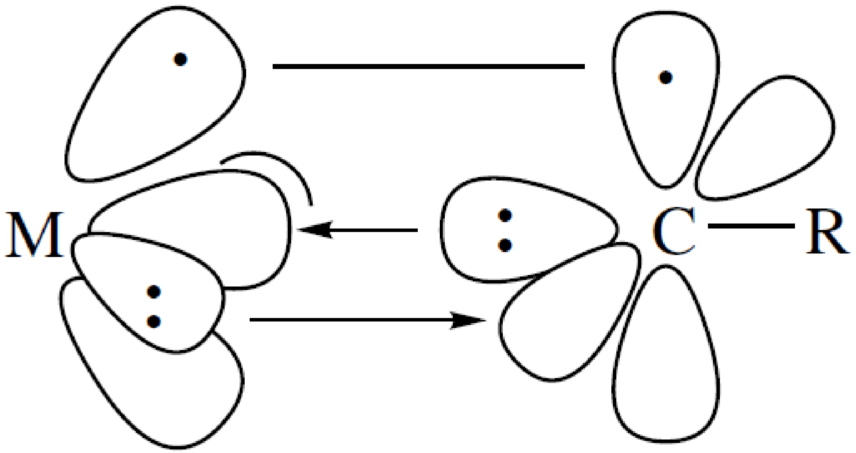


Doublet carbyne



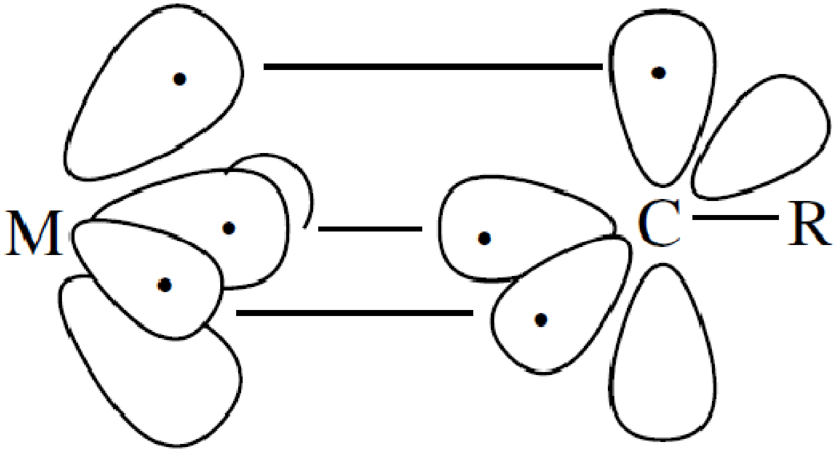
Quartet carbyne

- The carbyne ligand is linear
- Carbyne carbon is *sp* hybridized
- The M≡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→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.

$$\mathrm{L(CO)_4M{=}C(OMe)Me + 2BX_3 \longrightarrow [L(CO)_4M{\equiv}CMe]^+BX_4^-}$$

$$\mathrm{+\ BX_2(OMe) \longrightarrow X(CO)_4M{\equiv}CMe}$$

- The high *trans* effect of the carbyne ligand resulted in replacement of a CO ligand with a halide
- If L = PPh_3 (a stronger field ligand) the cationic species is the final product

$$\mathrm{Br(CO)_4W{\equiv}CMe \xrightarrow{Br_2,\ dme} Br_3(dme)W{\equiv}CMe}$$

$$\mathrm{(dme = MeOCH_2CH_2OMe).}$$

- 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 a-CH

$$\mathrm{CpCl_2Ta{=}CHR} \xrightarrow{\text{(i) } \mathrm{PMe_3}\text{, (ii) } \mathrm{Ph_3P{=}CH_2}} \mathrm{CpCl(PMe_3)Ta{\equiv}CR}$$

- Intramolecular oxidative addition of a bound Schrock carbene

  (a elimination)

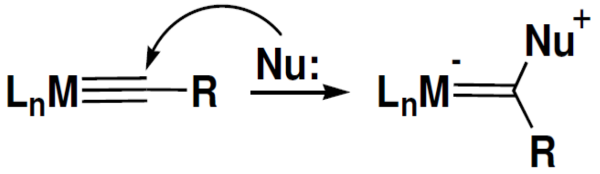
$$\mathrm{Cp^{*}Br_2Ta{=}CH}t\text{-}\mathrm{Bu} \xrightarrow{\text{(i) dmpe, (ii) Na/Hg}} \mathrm{Cp^{*}(dmpe)HTa{\equiv}C}t\text{-}\mathrm{Bu}$$

- Metathesis of tertiary butoxide (^{t}BuO) complexes

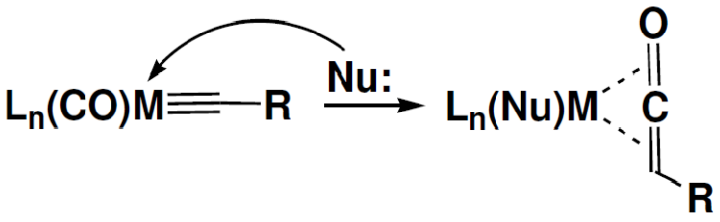
  (triple bi-nuclear oxidative addition, i.e. +III change in oxidation state)

$$(t\text{-}\mathrm{BuO})_3\mathrm{W{\equiv}W(O}t\text{-}\mathrm{Bu})_3 + t\text{-}\mathrm{BuC{\equiv}C}t\mathrm{Bu} \longrightarrow 2(t\text{-}\mathrm{BuO})_3\mathrm{W{\equiv}C}t\text{-}\mathrm{Bu}$$

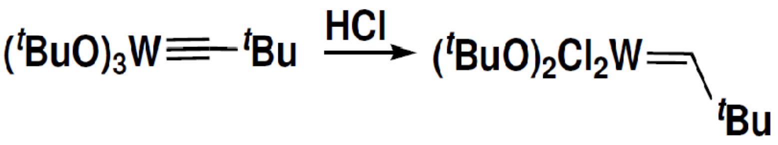
- Fischer carbynes are electrophillic and thus prone to nucleophillic attack
- Nucleophiles such as PMe_3, pyridine, alkyl lithiums, and isonitriles react with Fischer carbynes to give the corresponding Fischer carbene complex.



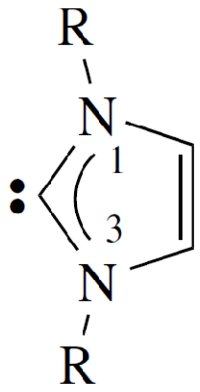
- Alternatively the nucleophile may attack the metal centre producing a ketenyl complex



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



N-Heterocyclic Carbenes (NHC's)



- In contrast to Fischer and Schrock type carbenes NHC's are extremely stable, inert ligands when complexed
- Like phosphine ligands they are electronically and sterically tunable
- Also, like phosphines they are very good σ-donors and promote a wide variety of catalytic reactions