Metal Carbenes

- The concept of a double bond between transition metals and carbon constitutes one of the most important elements in the field of organometallic chemistry
- The notion of a metal–carbon double bond was first brought forward by Fischer and Maasbol in 1964 with the synthesis of $(CO)_5W{=}C(Ph)(OMe)$
- Soon after the discovery of Fischer type complexes their chemistry was systematically explored and they have been since well established as valuable species in organic synthesis as well as in catalytic processes
- Schrock later prepared a number of tantalum complexes including $(Np)_3Ta{=}CH(CMe_3)$ and $(\eta^5\text{-}Cp)_2MeTa{=}CH_2$

E.O. Fischer, A. Maasbol, *Angew. Chem.* **1964**, 76, 645.

K. H. Dotz, *Angew. Chem. Int. Ed. Engl.* **1984**, 23, 587.

W. D. Wulff, ‘*Metal-Carbene Cycloadditions*’ in ‘*Comprehensive Organic Synthesis*’, Wiley-Interscience:New York, **1988**.

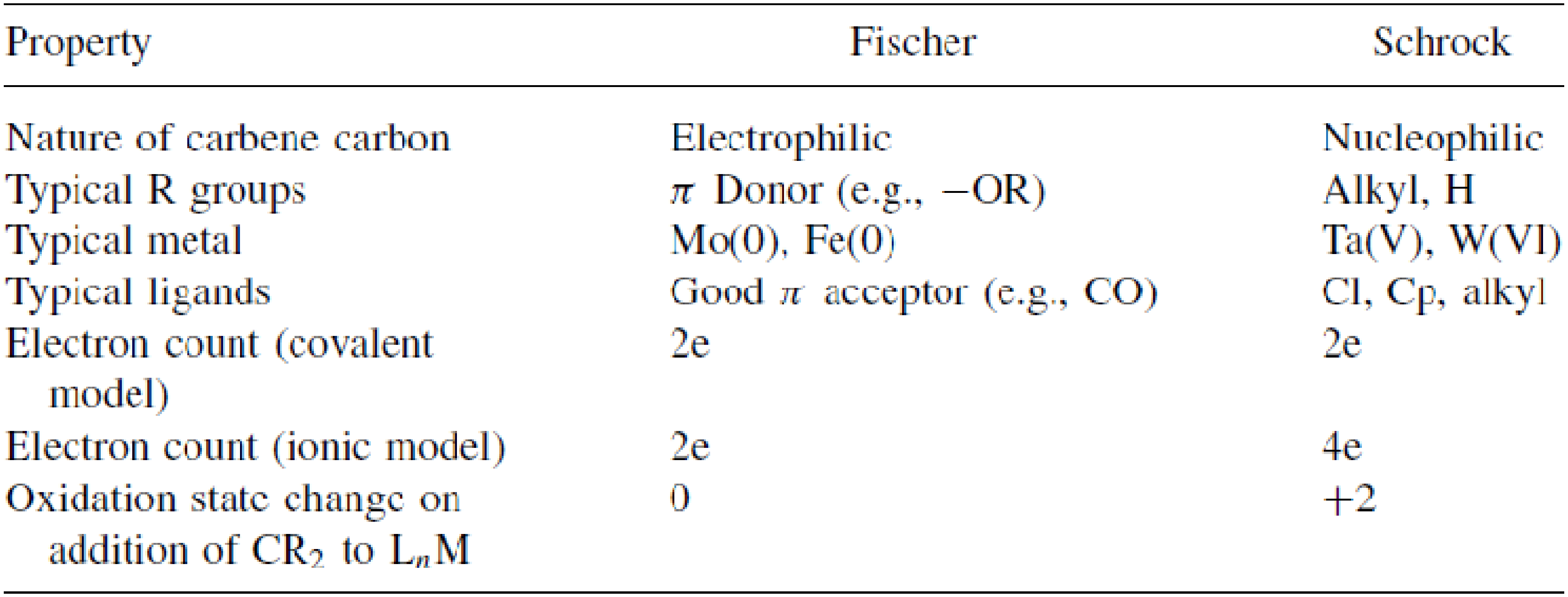
L. S. Hegedus, ‘*Transition Metals in the Synthesis of Complex Organic Molecules*’, **1994**, University Science Books.

R. R. Schrock, *J. Amer. Chem. Soc.* **1975**, 97, 6578.

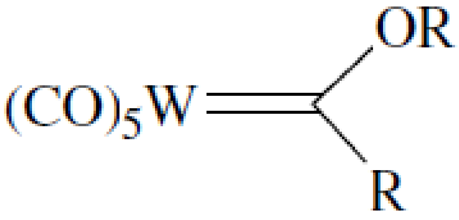
R. R. Schrock, *Acc. Chem. Res.* **1979**, 12, 98.

- Two different patterns of reactivity emerged during the development of these systems resulting in their classification as Fischer and Schrock type carbenes.
- Each represents a different formulation of the bonding of the CR_2 group to the metal and real cases fall somewhere between the two.

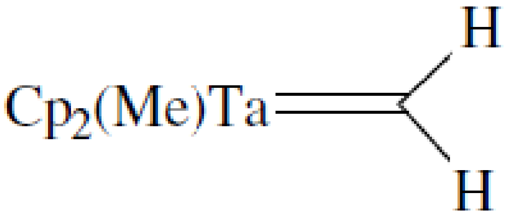
Fischer type vs. Schrock type carbene complexes



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

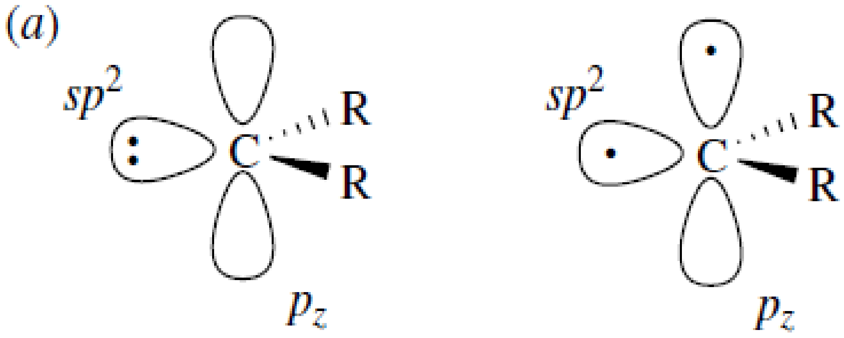


W(0), 18e



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

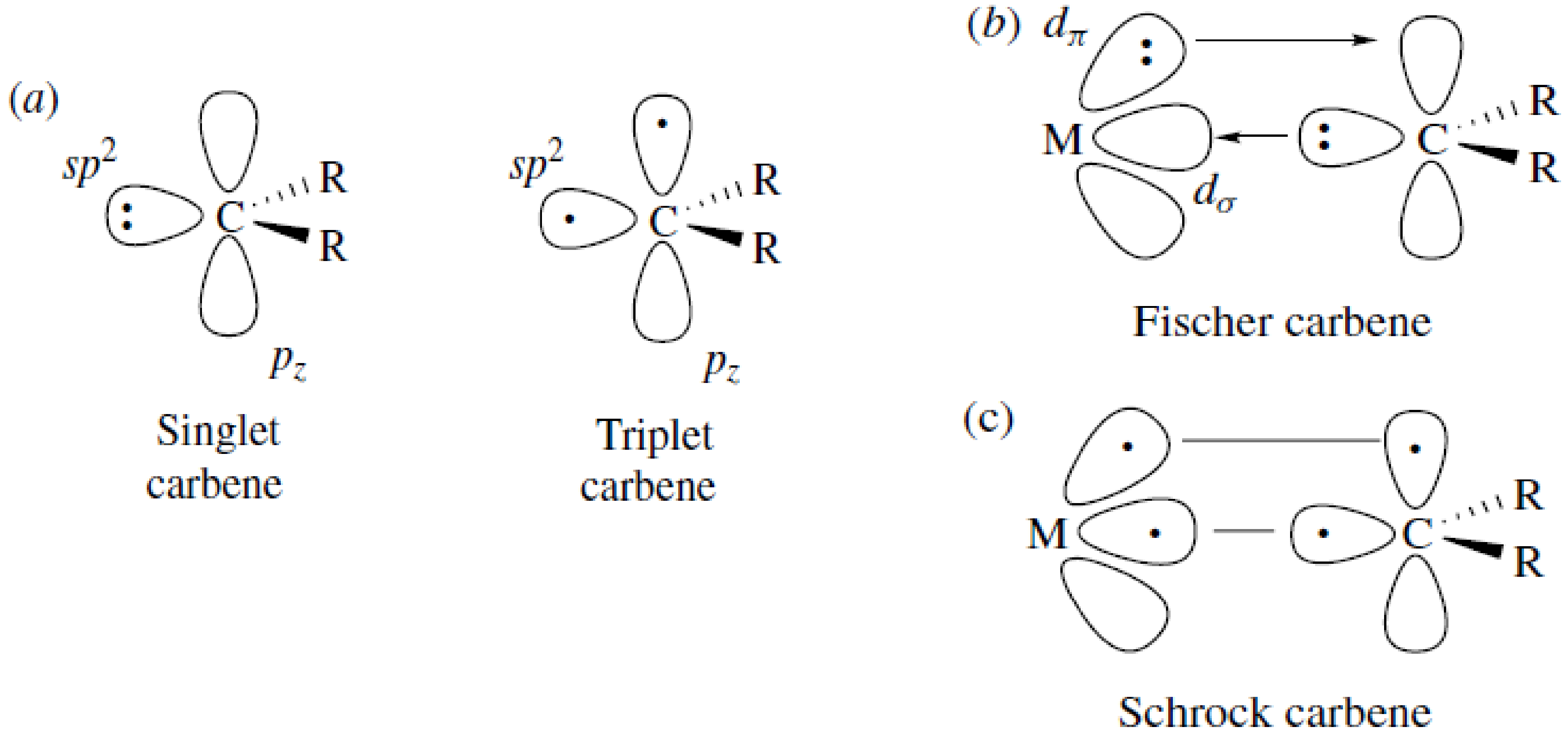


Singlet carbene

Triplet carbene

- Free carbene CH_2 has two distinct *spin isomers:* singlet and triplet

  – not resonance forms (sinlget ↔ triplet resonance forbidden)
- Singlet and triplet forms have different H-C-H angles
- In the singlet state 2e^- are paired up in the sp_2 orbital leaving the p_z orbital unoccupied
- In the triplet state both the sp_2 and p orbitals are singly occupied



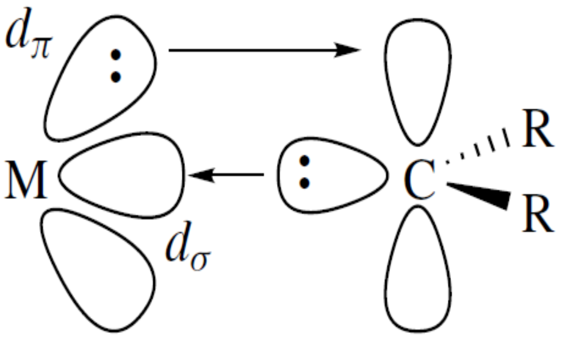
- (a) Singlet and triplet forms of a carbene
- (b) In the Fischer case, direct C→M donation predominates and the carbon tends to be positively charged.
- (c) In the Schrock case, two covalent bonds are formed, each polarized toward the carbon giving it a negative charge.

- Taylor and Hall used ab-initio calculations to differentiate between the electronic structures of Fischer and Schrock type carbene complexes.
- Calculations on a variety of free carbenes indicated that heteroatom and phenyl substituents preferentially stabilize a singlet ground state, whereas alkyl and hydride substituents stabilized a triplet ground state at the carbene carbon.
- Carbenes are both thermodynamically and kinetically unstable therefore forming very strong metal-carbene bonds disfavoring dissociation

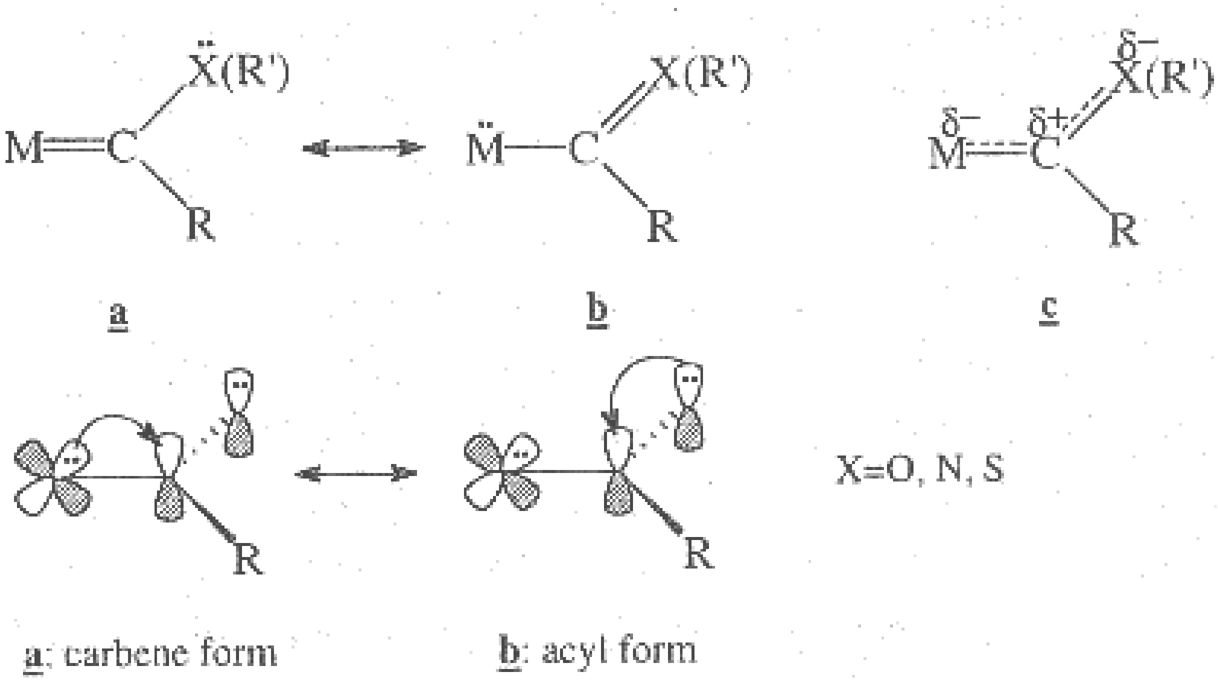
  e.g. just as pramagnetic triplet :CH_2 can dimerize to form diamagnetic $H_2C=CH_2$, it also binds to a triplet L_nM fragment to give a diamagnetic $L_nM=CH_2$ complex.

T. E. Taylor, M. B. Hall, *J. Amer. Chem. Soc.* **1984**, 106, 1576-1584.

Fischer Carbenes



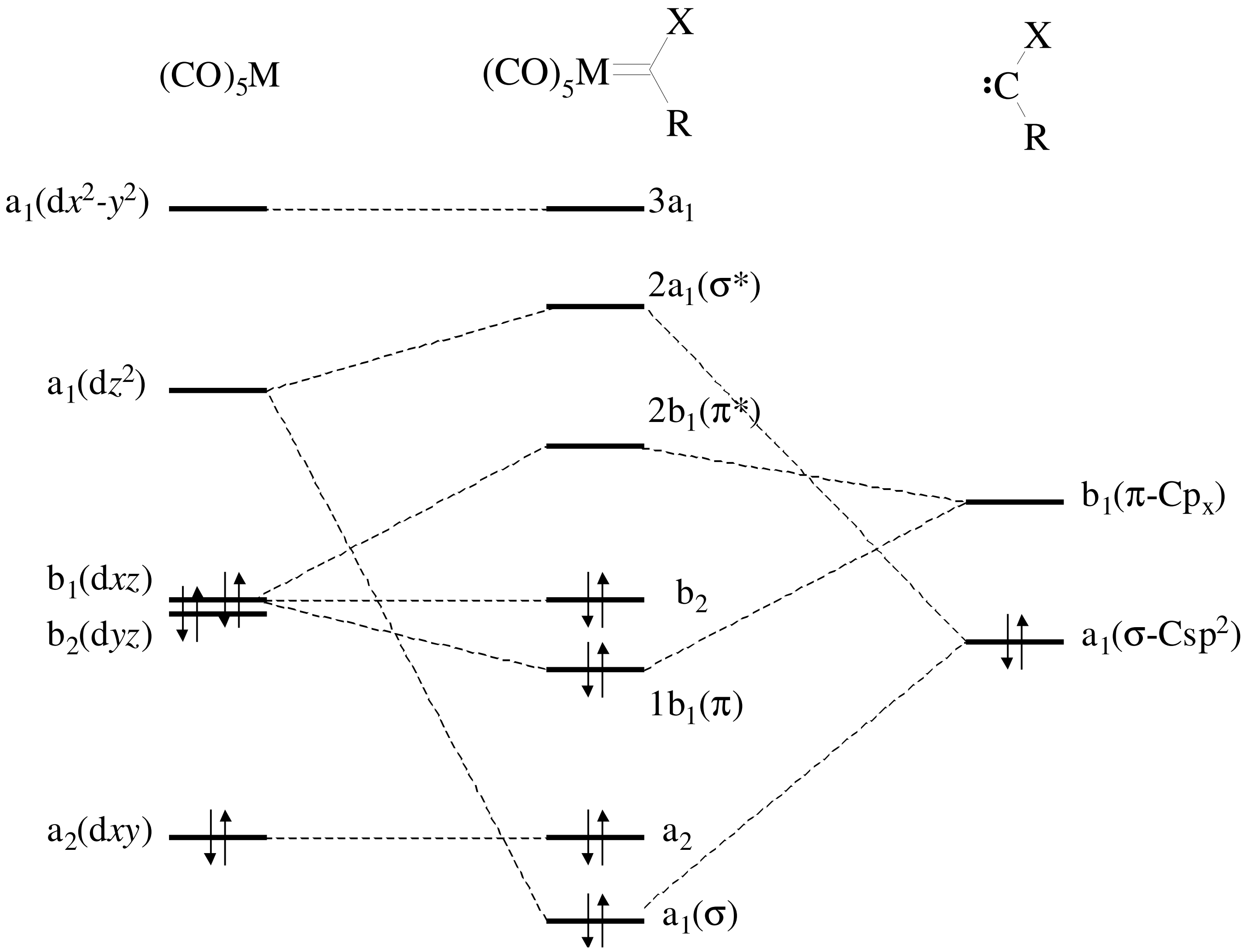
- Reactivity of the carbene carbon is controlled by the bonding
- A Fischer carbene is predominantly a σ-donor via the lone pair, but the empty π orbital on carbon is also a weak acceptor for π back donation from the M(d_π) orbitals.
- This leaves an electrophillic carbon because direct C⟶M donation is only partly compensated by M⟶C back donation.
- The late transition metals, being more electronegative, have stabilized M(d_p) orbitals resulting in weak M⟶C π back donation.
- Thus Fischer carbene ligands are classed as 2e donors with electrophilic character



- the π-bond character of Fischer type carbene complexes is best represented by a M-C-X three-centred four–electron bond with the π-electron density mainly located at either the M(d_{xz}) orbital of M or the *p* orbital of the heteroatom 'X' in the carbene ligand.
- In reality the true M=C bond order is much less than 2, as observed by x-ray crystallography, favouring the acyl form.

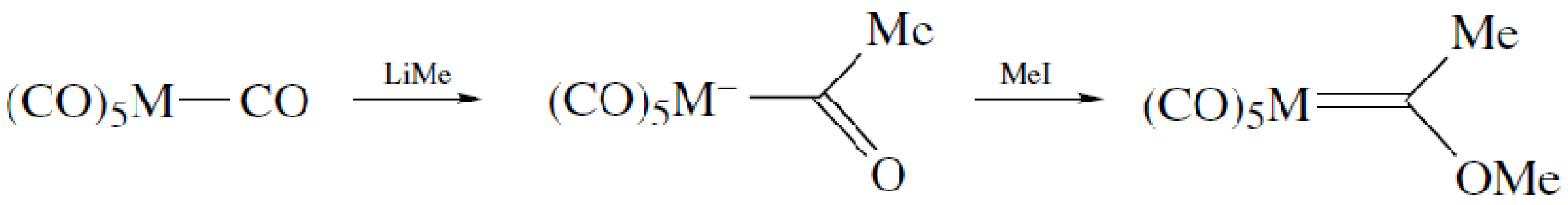
- Through theoretical studies on Fischer type carbene complexes the MOs of the $(CO)_5M$ (M=Cr, W) fragment are correlated to the MOs of the carbene fragment.
- Fong and Cooper reported a simplified MO diagram for Fischer carbenes where they assumed C_{2v} local symmetry for the carbene moiety.
- The pentacarbonyl fragment is of C_{4v} symmetry, which results in a splitting of the *d* orbitals into b_2, a_2, a_1 and b_1 states.
- The important feature of the ordering of the occupied levels is that the $b_2(d_{yz})$ metal based orbital is calculated to be the HOMO.
- The $b_1(d_{xz})$ and $b_2(d_{yz})$ orbitals are less stabilised by π-acceptor interactions with the carbonyl ligands than the $a_2(d_{xy})$ orbital, and the $b_1(d_{xz})$ orbital will have a stabilising π-interaction with the $C(p_x)$ orbital on the carbene carbon which will bring it below the energy of the $b_2(d_{yz})$ orbital.
- The LUMO is assigned to the $2b_1(\pi^*)$ orbital, which is primarily ligand $C(p_x)$ in character, as the lowest allowed absorption in these complexes shows strong metal-to-ligand-charge-transfer (MLCT) characteristics.

L. K. Fong, N. J. Cooper, *J. Amer. Chem. Soc.* **1984**, 106, 2595-2599.

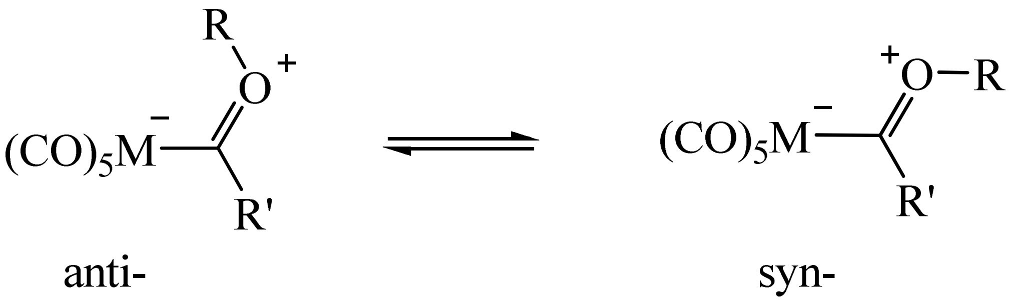


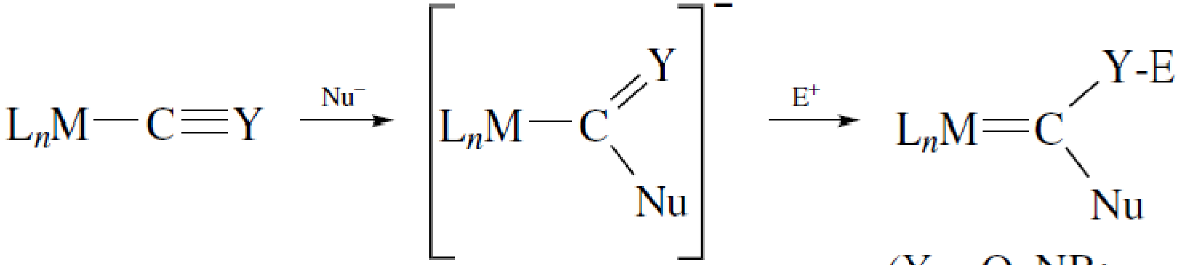
A schematic MO diagram for Fischer carbenes (M = Cr, Mo, W; X = OR, NR_2).

Fischer carbene synthesis



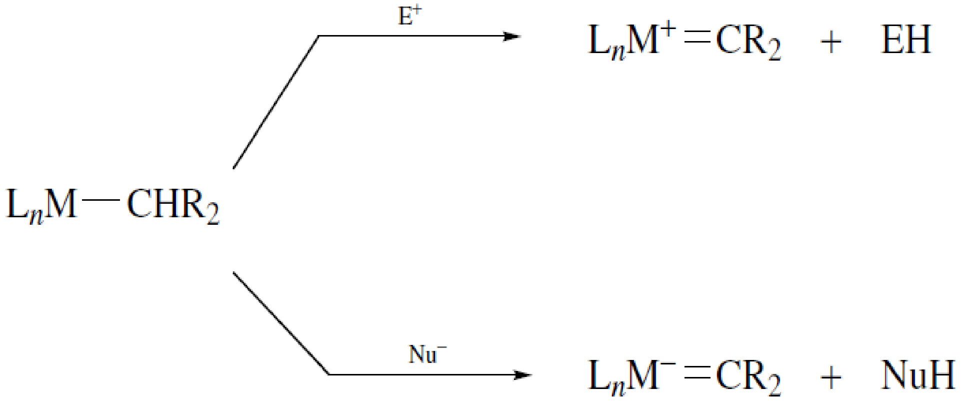
- Alkyl lithium attack at metal carbonyl followed by alkylation.
- Dominant zwitterionic resonance form in heteroatom stabilized Fischer carbenes
- Therefore rotation is restricted about C-X bond resulting in *syn* and *anti* isomers for alkoxy deriavtives typically observable via low temperature ^{1}H NMR spectroscopy.





(Y = O, NR;
Nu = OMe^-, NR_2^-, LiMe)

- Acyl intermdiate is treated with an electrophile to give the Fischer carbene



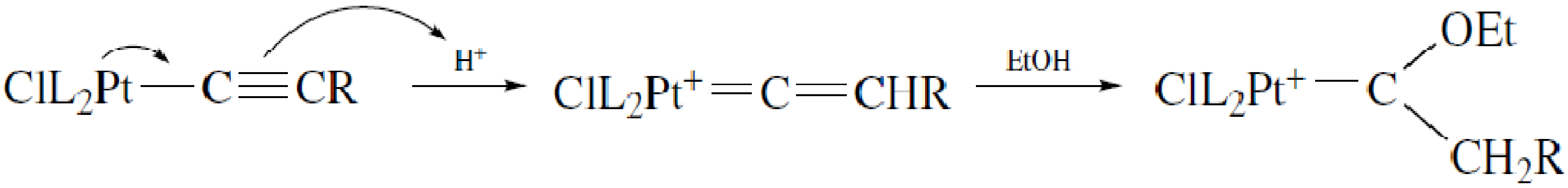
$$L_nM + CH_2N_2 \longrightarrow L_nMCH_2 + N_2$$

- Alternatively, Hydride (H^-) is abstracted from the a position of a metal-alkyl
  (H^+ abstraction results in Schrock type carbene)

- Isonitrile complexes are very sensitive to nucleophillic attack, and a wide range of bisheteroatom-stabilized carbenes can be obtained:

$$[(MeNC)_4Pt]^{2+} + 4MeNH_2 \longrightarrow [Pt\{=C(NHMe)_2\}_4]^{2+}$$

- Acetylides make for suitable bases due to their canonical vinylidene form and undergo nucleophillic attack by alcohols in-situ to generate the heteroatom stabilized Fishcer carbene complex.

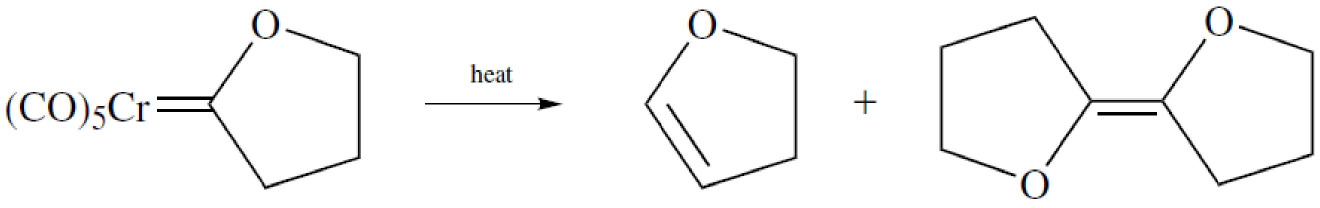


- Electrophillic abstraction from metal alkyl complexes is another possible route.
- The following example is driven by Si-F bond formation

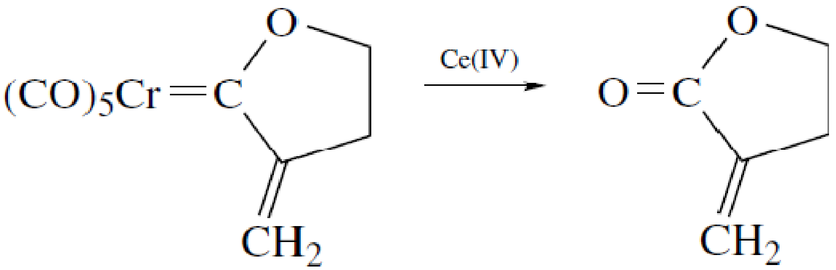
$$\mathrm{Cl(CO)(MeCN)L_2RuCF_3 + Me_3SiCl \longrightarrow Cl_2(CO)L_2Ru{=}CF_2 + Me_3SiF}$$

Fischer carbene reactions

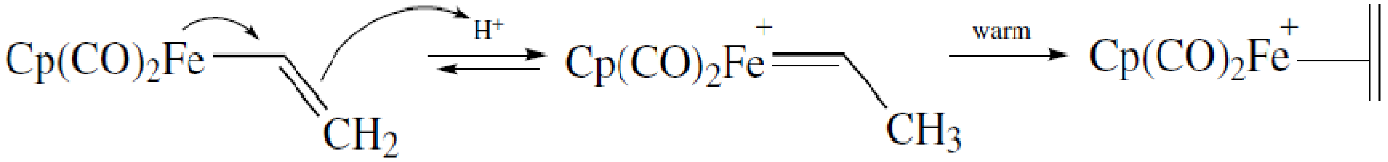
- Thermal decomposition of Fishcer carbenes gives rise to a set of alkene products: rearranged monomer and the dimer.

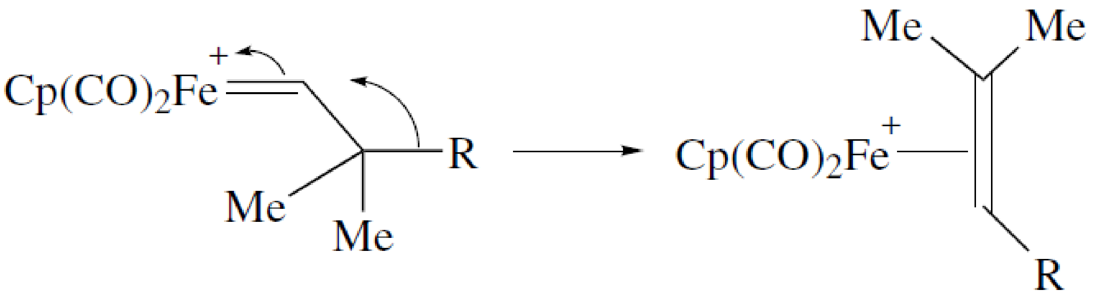


- Oxidative cleavage of the M-C bond using Ce^{IV}, pyridine-*N*-oxide, DMSO or even simply O_2 usually gives rise to the ketone derivative.



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



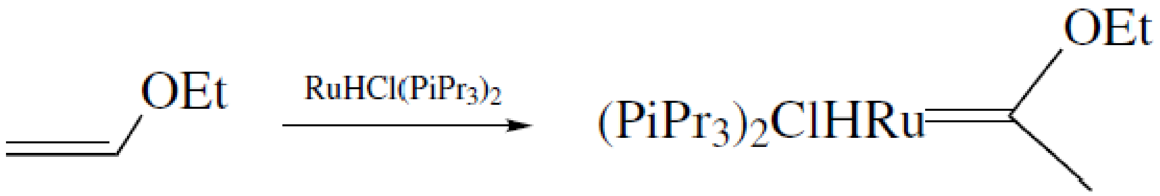


(R = Me or Ph)

- 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

- Upon sufficient stabilization the alkene can rearrange to the metal-carbene complex



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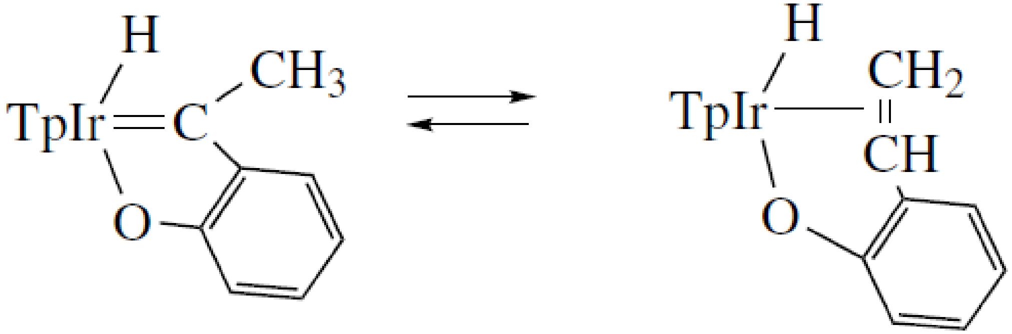
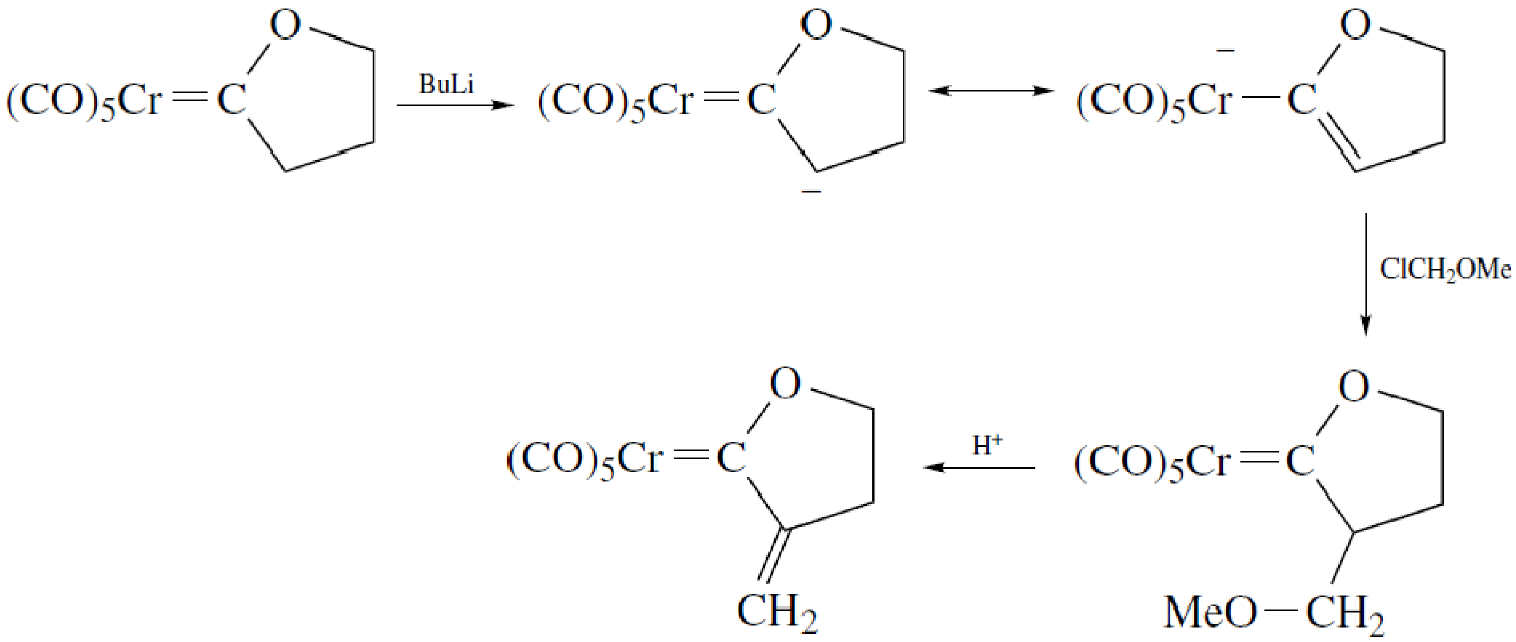
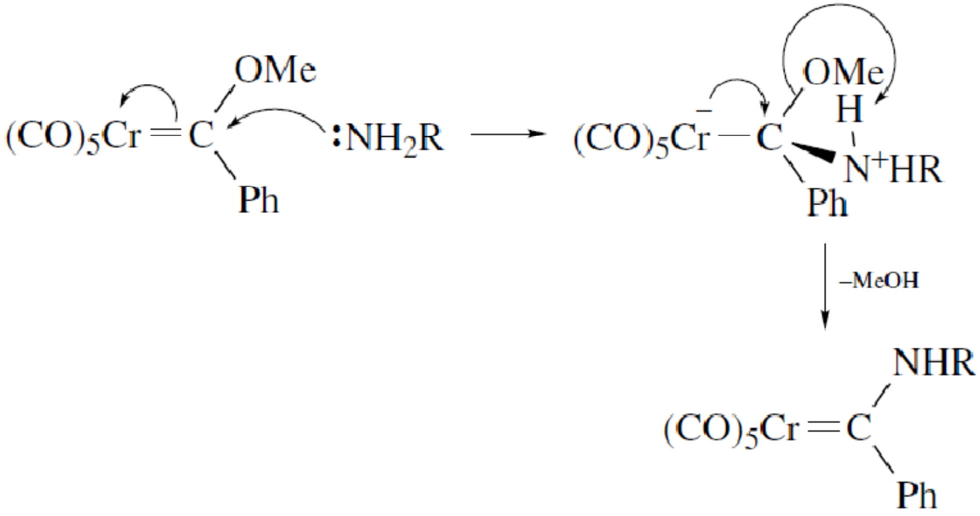


- Due to the electrophillic nature of the Fischer carbene C-atom any β–H atoms are acidic and abstracted readily by base.
- The negative charge of the resulting carbanion is delocalized onto the M centre and thus stabilized.
- Further functionalization is possible by reaction with a suitable electrophile

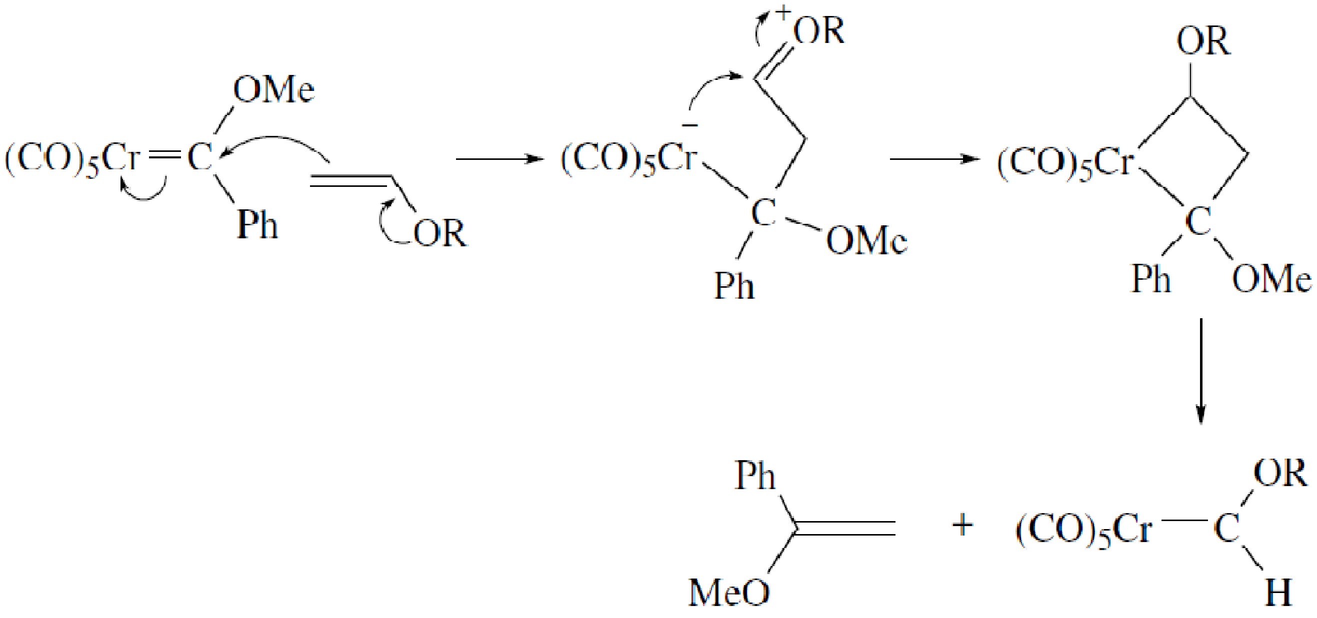


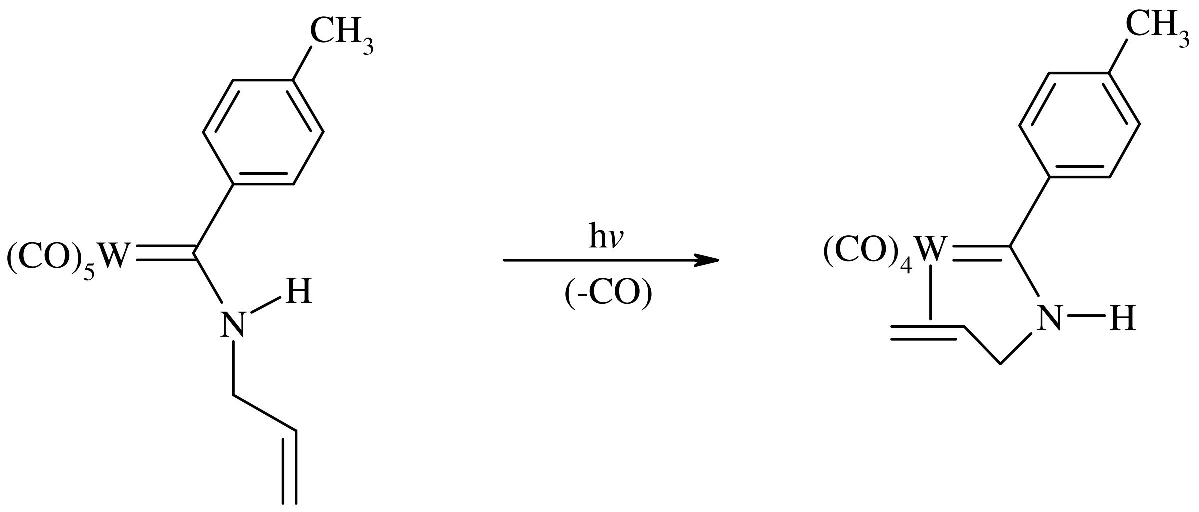
- Fischer carbenes readily undergo nucleophillic attack at the carbene carbon
- Attack of amines can give a zwitterionic intermediate which produces the amino carbene with loss of the corresponding alcohol



- This reaction is comparable to that of amide formation via ketone aminolysis if we replace $(CO)_5M$ with C=O.

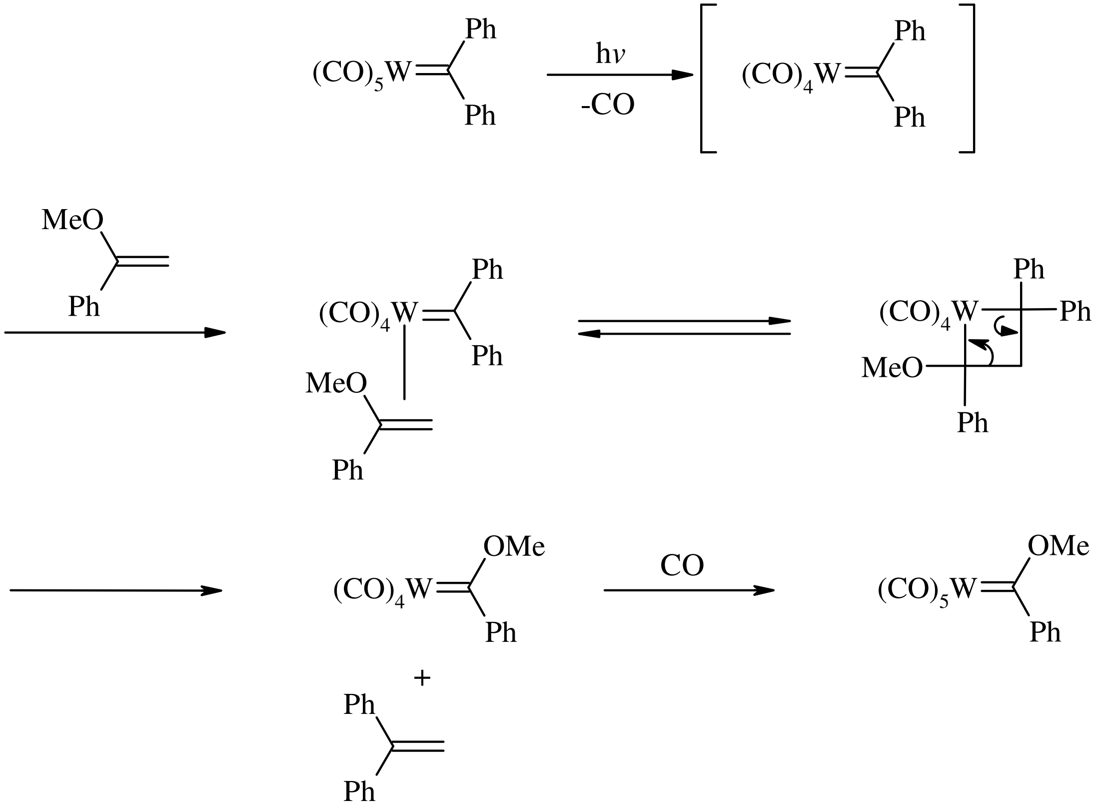
- Addition of unsturated nucleophillic systems such as alkenes or alkynes can lead to the formation of metalacycles
- Metalacycles can break down to give a new carbene and new alkene in a reaction known as alkene metathesis (discussed later)



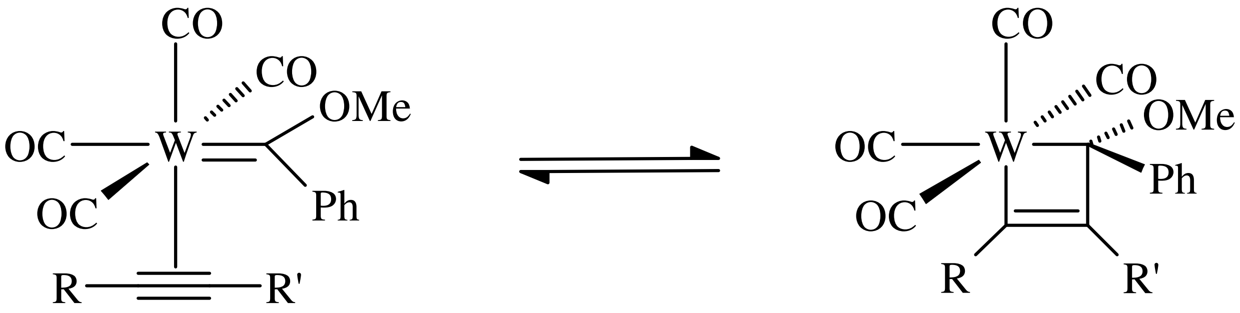


- Casey et al. have reported the photoinduced CO loss and preparation of a tetracarbonyl tungsten-carbene-alkene chelated complex.
- This was the first reported case of a stable metal-carbene-alkene complex and was early evidence that these complexes as well as metallacyclobutanes could be key intermediates in metal catalysed reactions such as olefin metathesis, cyclopropanation and benzannulation.

C. P. Casey, A. J. Shusterman, N. W. Vollendorf, K. J. Haller, *J. Amer. Chem.* **1982**, 104, 2417.



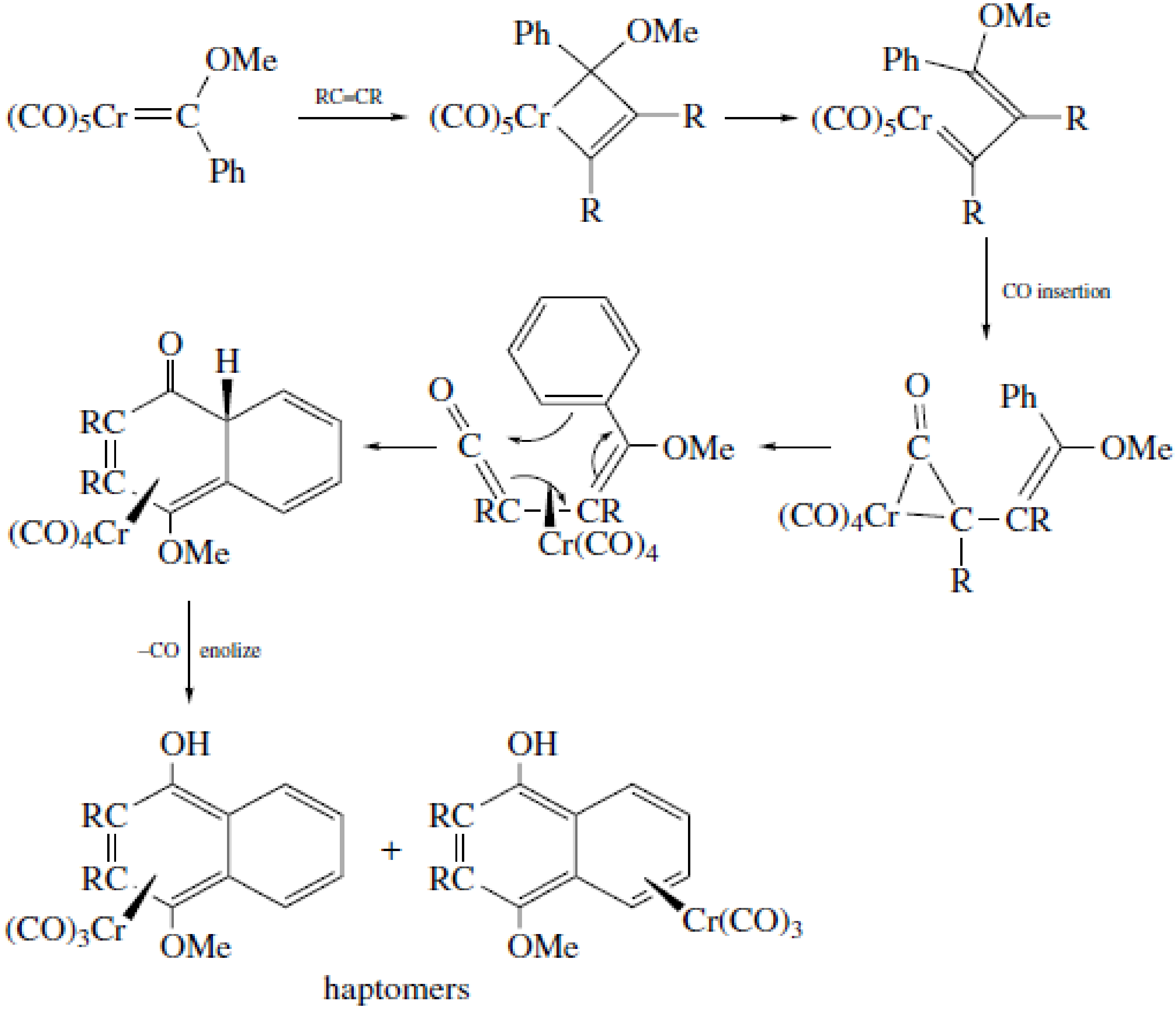
- Photoinduced metathesis was observed upon population of the high-energy LF state.
- Population of the $dx^2\text{-}y^2$ metal orbital, which is anti-bonding with respect to an equatorial CO ligand allows direct access to the *cis*-alkene/alkyne complex required for metallacyclobutane formation.
- Irradiation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

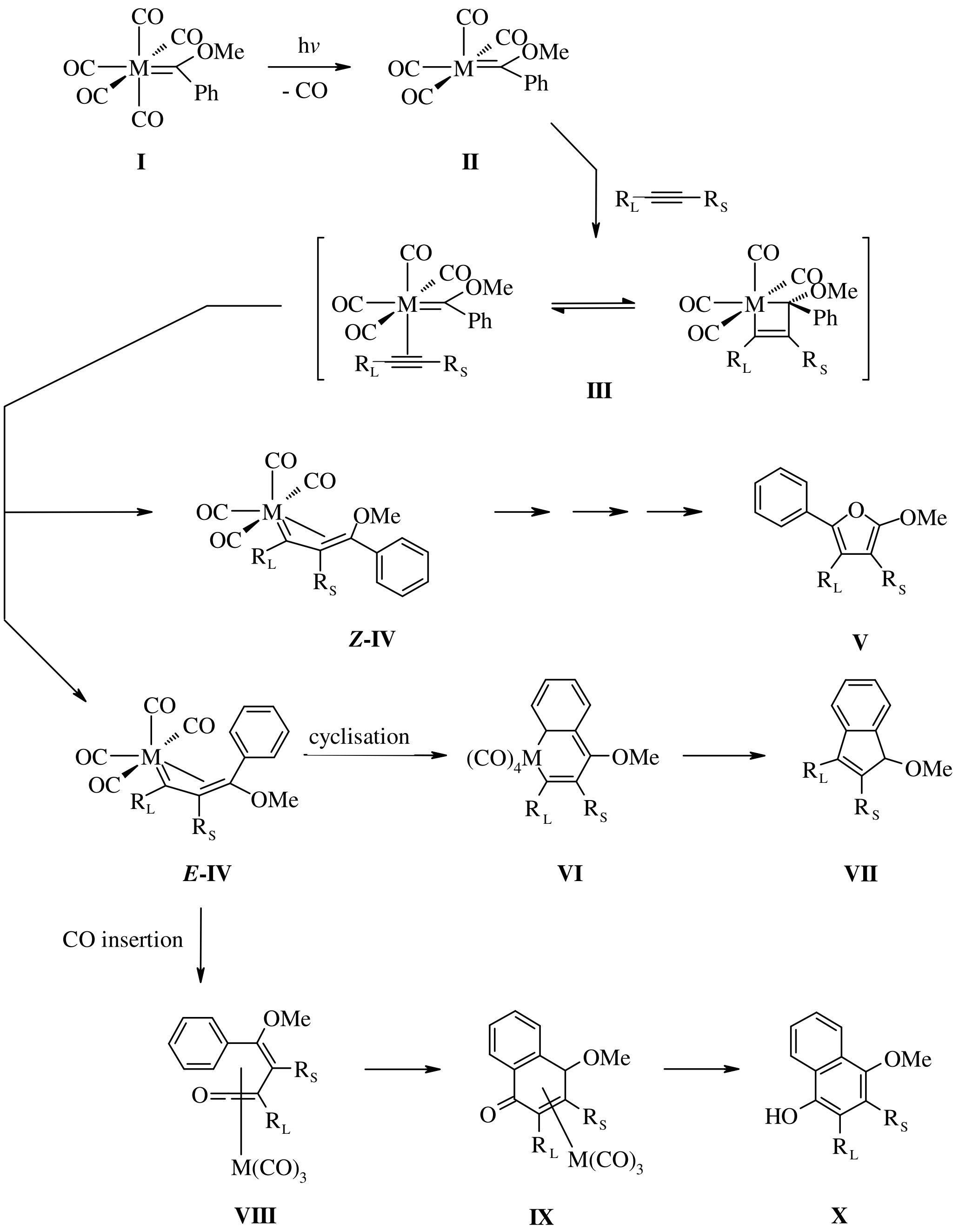


- The alkyne-carbene complexes later synthesized by Foley et al. have considerable metallacyclobutene character, however, due to their instability in solution at ambient temperatures their exact structure could not be confirmed.
- These complexes decompose at room temperature via the proposed metallacyclobutene intermediate to give products that depend markedly upon the steric nature of the alkyne.
- The metal-carbene-alkyne adducts decompose by a mechanism first proposed by Dotz et al. to form indenyl ethers and naphthol derivatives.

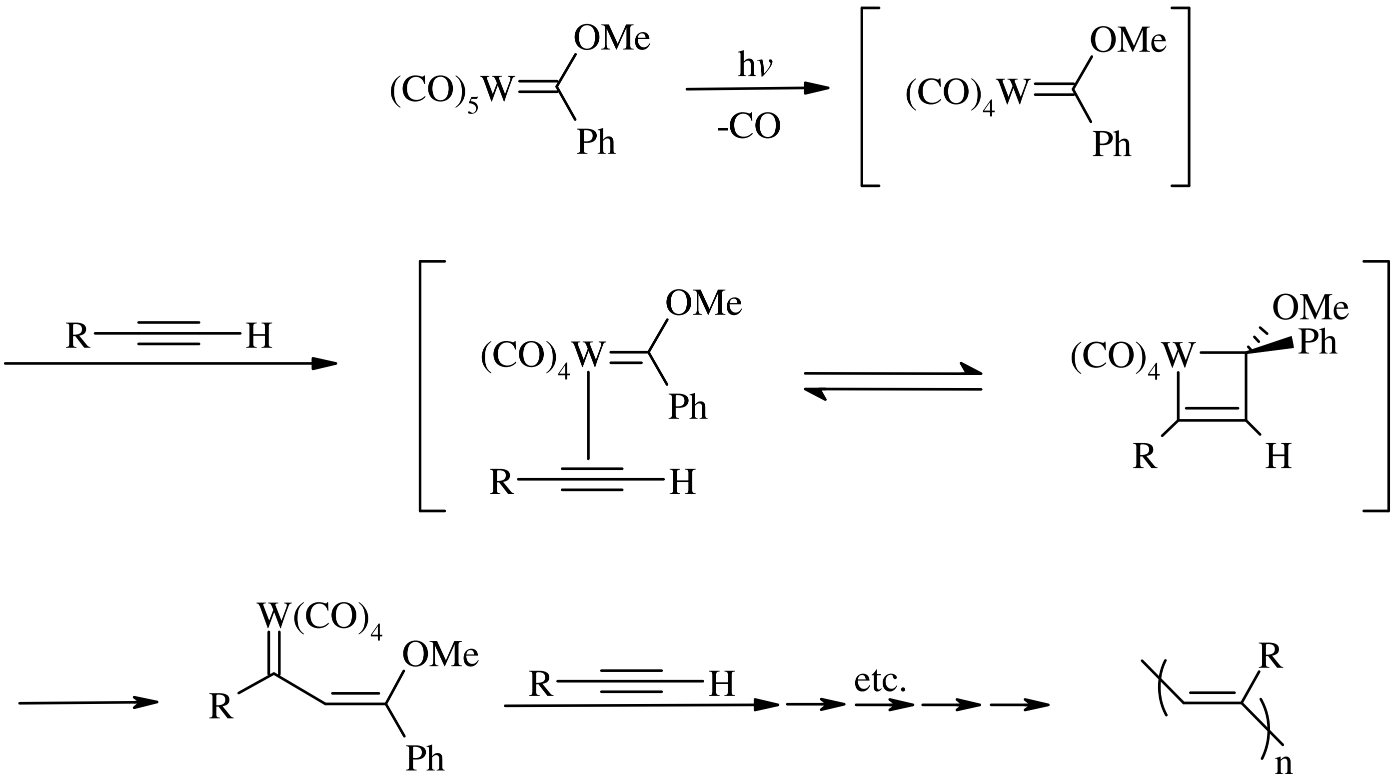
H. C. Foley, L. M. Strubinger, T. S. Targos, G. L. Geoffroy, *J. Am. Chem. Soc.* **1983**, 105, 3064.

Dötz Benzannulation Reaction



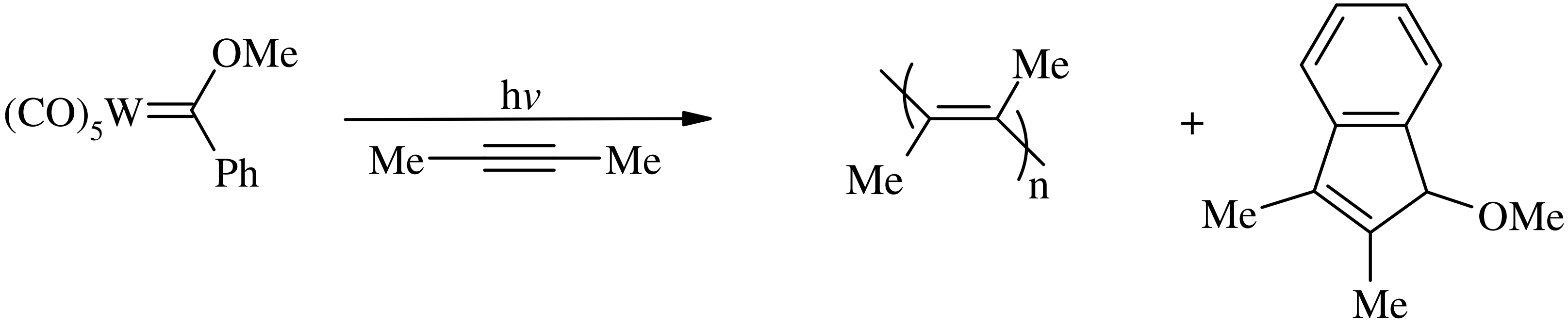

I
hν
- CO
II
R_L—≡—R_S
III
Z-IV
V
E-IV
cyclisation
VI
VII
CO insertion
VIII
IX
X

- 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



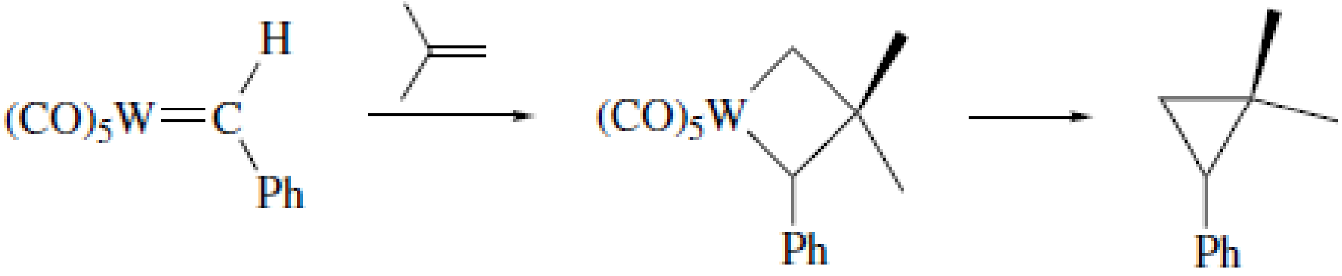
T. J. Katz, S. J. Lee, *J. Am. Chem. Soc.* **1980**, 102, 422.

- 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.

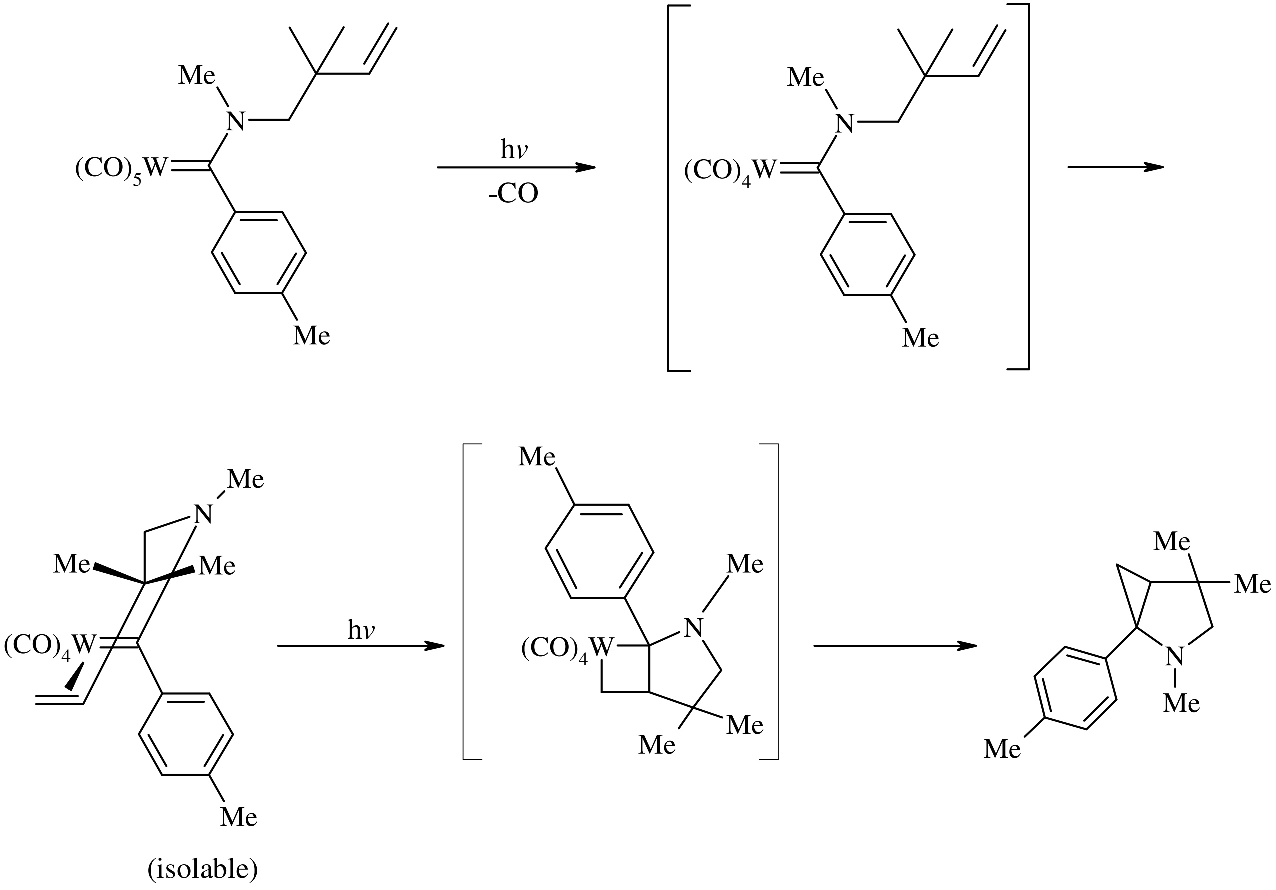


H. C. Foley, L. M. Strubinger, T. S. Targos, G. L. Geoffroy, *J. Am. Chem. Soc.* **1983**, 105, 3064

- 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).



- Casey et al. confirmed the intermediacy of a metallacyclobutane in cyclopropane formation, and CO loss as the primary photochemical process in its formation.
- A chelated tungsten-carbene-alkene complex was isolated after photoinduced CO loss and a cyclopropane product was formed on continued photolysis of the isolated species



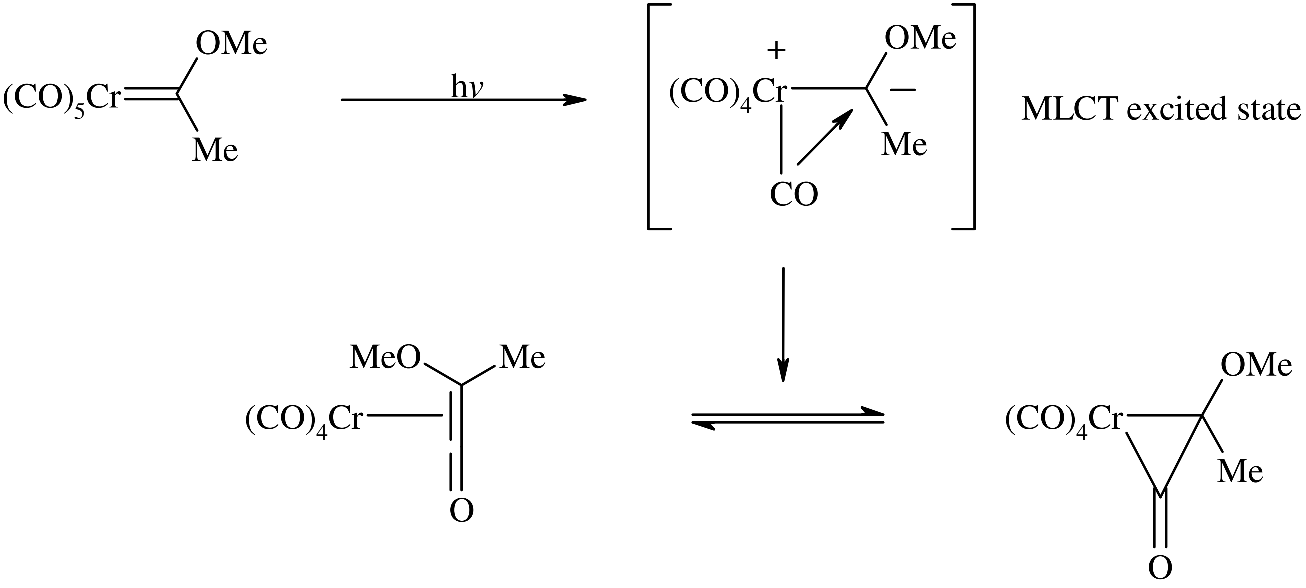
C. P. Casey, N. W. Vollendorf, K. J. Haller, *J. Am. Chem. Soc.* **1984**, 106, 3754

- Irradiation of the isolated species (previous slide) into its MLCT band is thought to decrease the bond order of the W-C and the C-N bonds thus increasing the conformational mobility required for metallacyclobutane formation.
- No olefin metathesis products were observed as they would have required the concurrent formation of the unstable $(CO)_5W{=}CH_2$ complex, which is unfavoured.
- By placing a methoxy group on the alkene moiety of a similar catalyst, it has been shown that metathesis can also occur, under certain conditions, with concurrent formation of the relatively stable $(CO)_5W{=}C(OMe)H$ complex.

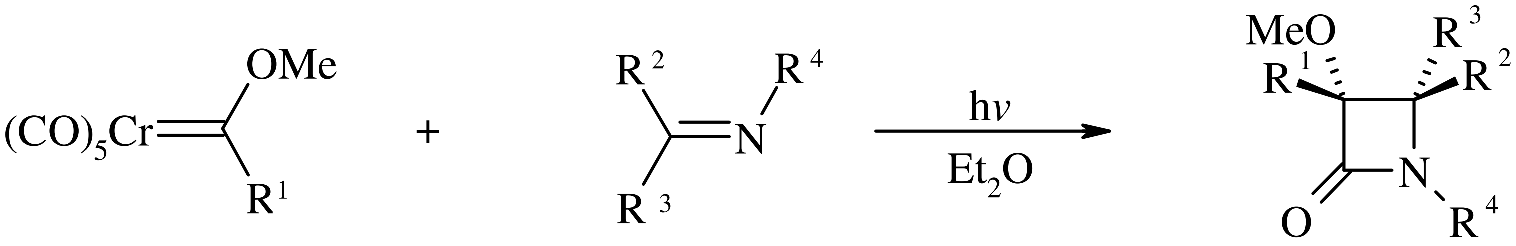
C. P. Casey, N. L. Hornung, W. P. Kosar, *J. Am. Chem. Soc.* **1987**, 109, 4908.

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

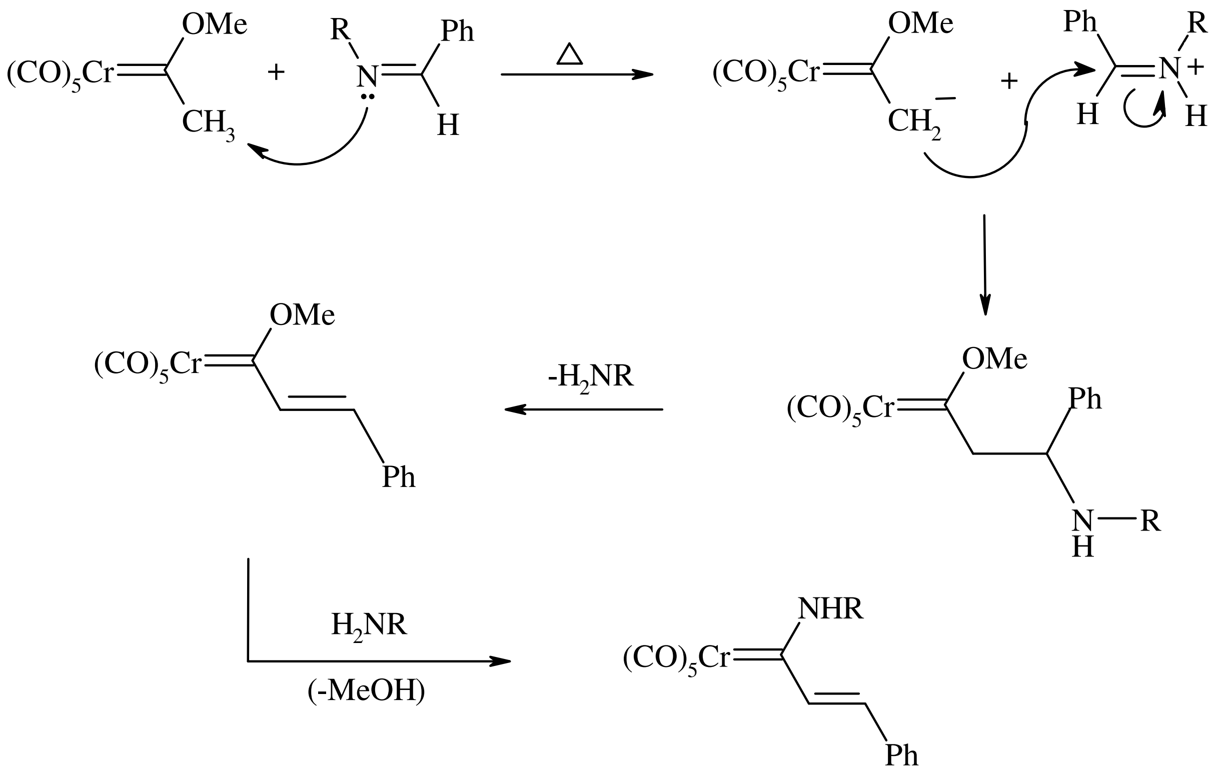


MLCT excited state



- 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.

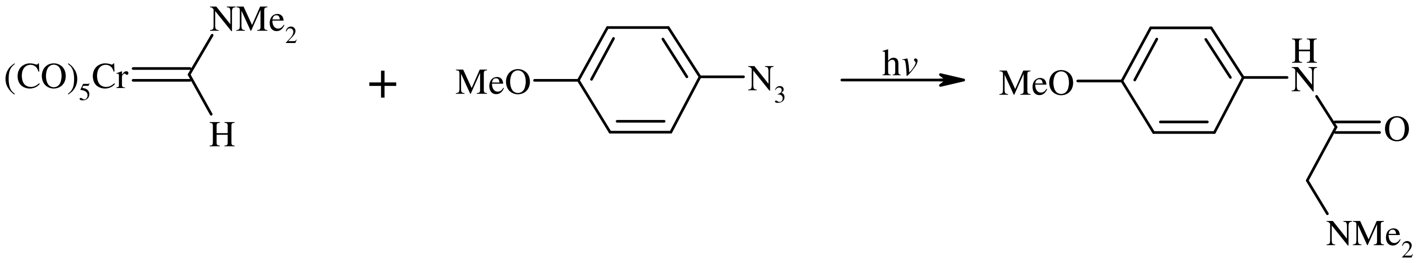
M. A. McGuire, L. S. Hegedus, *J. Am. Chem. Soc.* **1982**, 104, 5538.



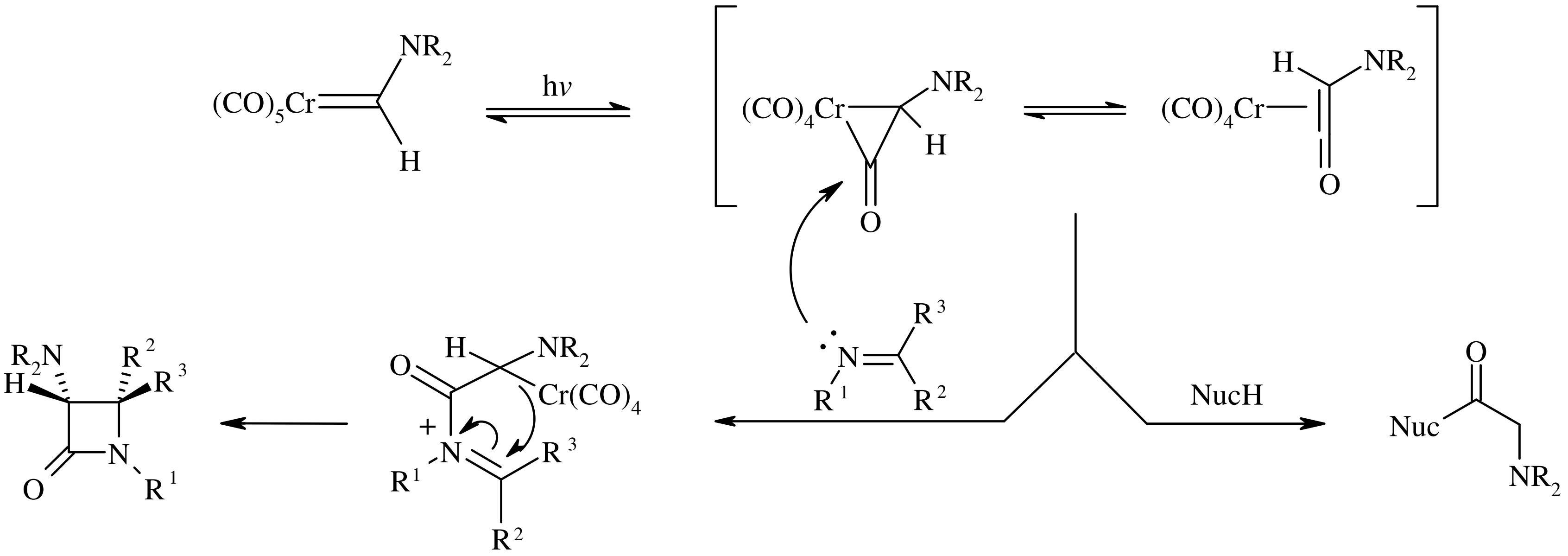
- In contrast, under thermal conditions the chemistry of the α-carbon dominates, producing new carbene complexes

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

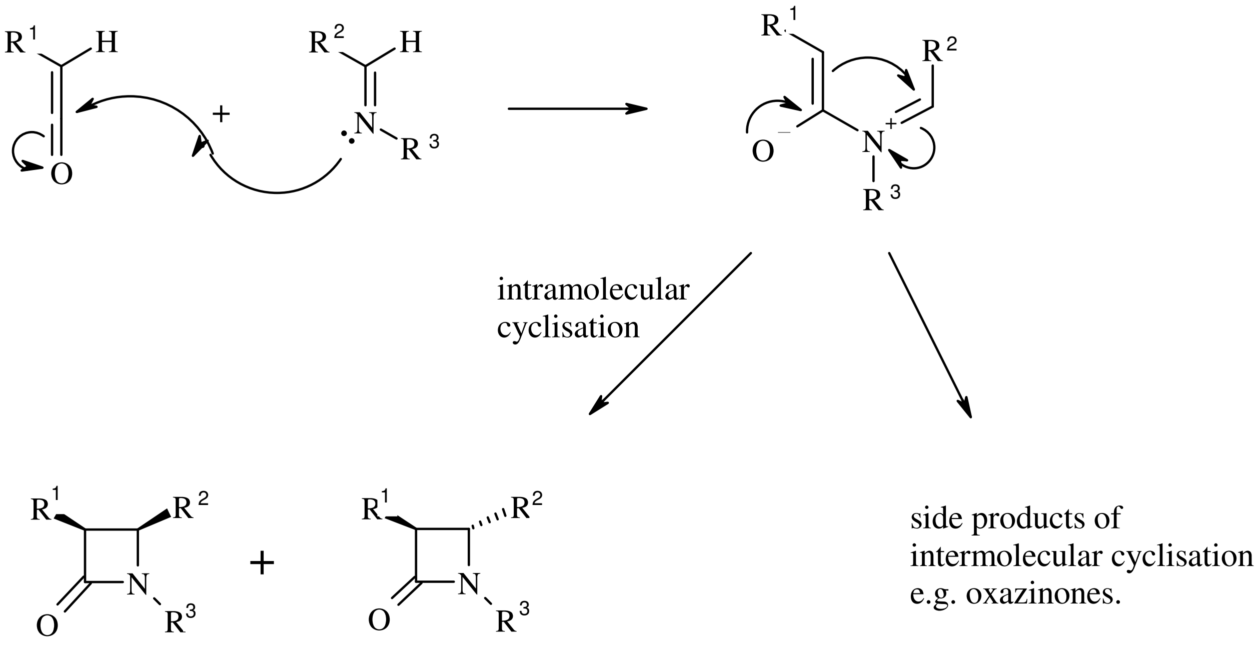
- Initially photoinduced CO loss from the chromium carbene complex was believed to be the primary photoprocess in β-lactam formation.
- However, β-lactam formation is not observed thermally.
- Also, high yields of β-lactam products are observed when the photochemical reaction is carried out under high 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.

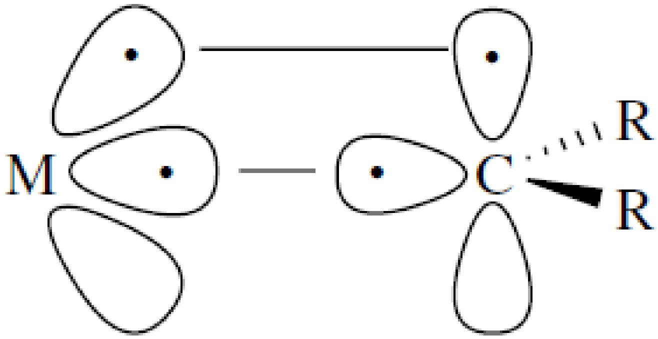
β-lactam isomers

- 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 b-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 b-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 b-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 acting as an X_2-type ligand.
- Each M-C bond is polarized towards the carbene carbon because C is more electronegative than M, leading to a nucleophillic carbene carbon