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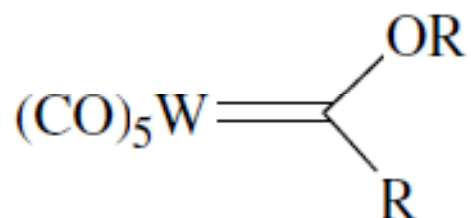
R. R. Schrock, *J. Amer. Chem. Soc.* **1975**, 97, 6578.

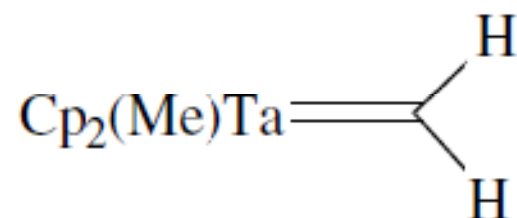R. R. Schrock, *Acc. Chem. Res.* **1979**, 12, 98.

- 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

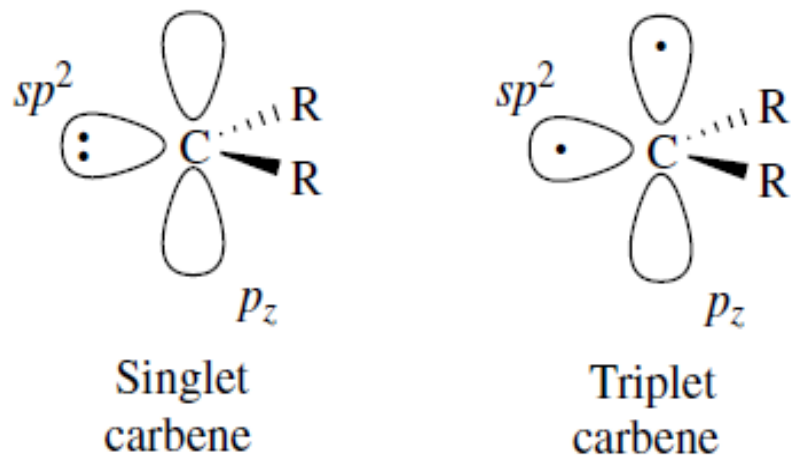| Property	Fischer	Schrock
Nature of carbene carbon	Electrophilic	Nucleophilic
Typical R groups	π Donor (e.g., −OR)	Alkyl, H
Typical metal	Mo(0), Fe(0)	Ta(V), W(VI)
Typical ligands	Good π acceptor (e.g., CO)	Cl, Cp, alkyl
Electron count (covalent model)	2e	2e
Electron count (ionic model)	2e	4e
Oxidation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

$$(CO)_5W=\!\!\!=\!\!\!\begin{array}{c} OR \\ \diagup \\ \diagdown \\ R \end{array} \qquad Cp_2(Me)Ta=\!\!\!=\!\!\!\begin{array}{c} H \\ \diagup \\ \diagdown \\ H \end{array}$$

$$W(0), 18e \qquad\qquad\qquad Ta(V), 18e$$

Property	Fischer	Schrock
Nature of carbene carbon	Electrophilic	Nucleophilic
Typical R groups	π Donor (e.g., $-OR$)	Alkyl, H
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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)

sp^2 R R p_z

Singlet carbene

sp^2 R R p_z

Triplet carbene

(b) d_π

M d_σ C R R

Fischer carbene

(c)

M   C R R
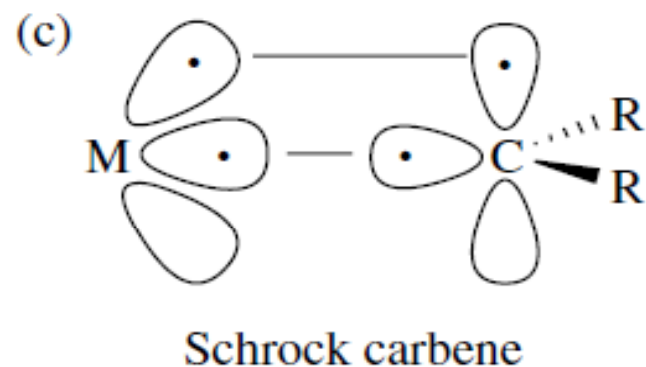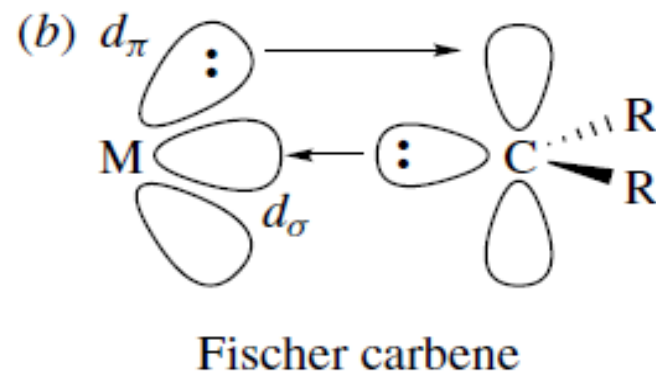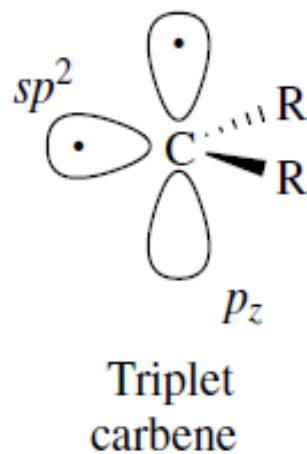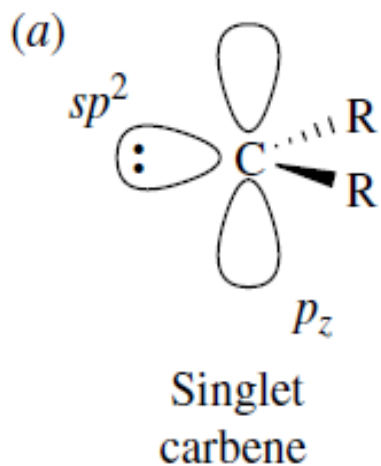
Schrock carbene

- (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.

  - 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
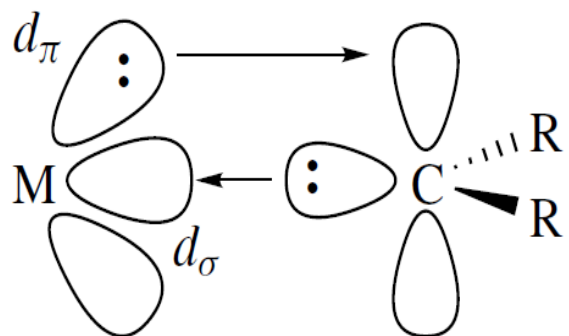
- Reactivity of the carbene carbon is controlled by the bonding

- 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**

a   b   c

X=O, N, S

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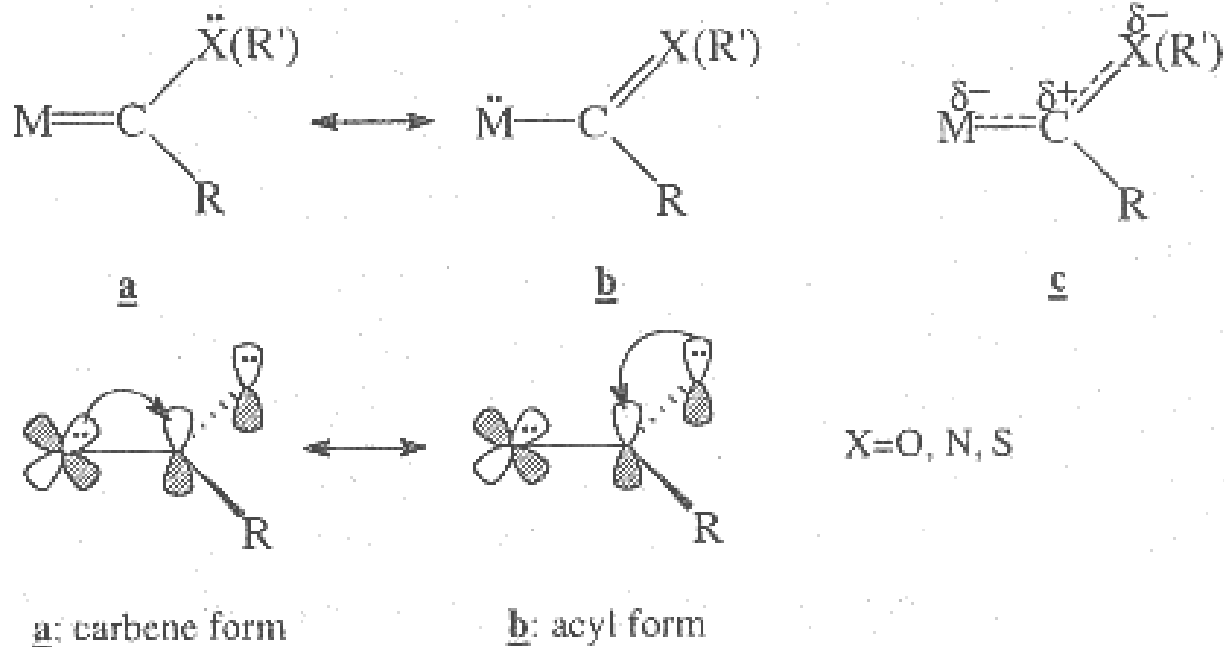
- the π-bond character of Fischer type carbene complexes is best represented by a M-C-X **three-centred four–electron bond** with the π-electron density mainly located at either the $M(d_{xz})$ orbital of M or the p orbital of the heteroatom 'X' in the carbene ligand.
- In reality the true M=C bond order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

Synthesis, Structures, and Electrochemistry of Group 6 Aminocarbenes with a P-Chelating 1′-(Diphenylphosphino)ferrocenyl Substituent

Luděk Meca,[†] Dalimil Dvořák,[†] Jiří Ludvík,[‡] Ivana Císařová,[§] and Petr Štěpnička*,[§]

2
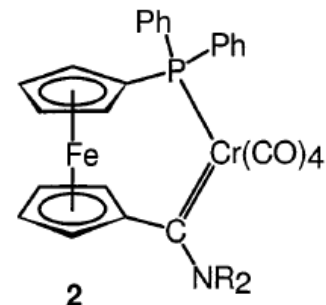
R = morpholin-4-yl

Table 2. Selected Bond Distances (Å) and Angles (deg) for 2b[a]

|			
Fe−Cg(1)	1.6448(8)	Fe−Cg(2)	1.6391(8)
Cr−P	2.4092(6)	Cr−C(28)	1.848(2)
P−C(6)	1.809(2)	C(28)−O(2)	1.157(2)
P−C(16)	1.833(2)	Cr−C(29)	1.890(2)
P−C(22)	1.842(2)	C(29)−O(3)	1.155(2)
Cr−C(11)	2.139(2)	Cr−C(30)	1.888(2)
C(1)−C(11)	1.500(2)	C(30)−O(4)	1.151(2)
C(11)−N	1.325(2)	Cr−C(31)	1.854(2)
N−C(12)	1.475(2)	C(31)−O(5)	1.155(2)
N−C(15)	1.491(2)	C(12)−C(13)	1.515(3)
O(1)−C(13)	1.428(2)	C(14)−C(15)	1.515(3)
O(1)−C(14)	1.424(2)		
Cp(1)−Cp(2)	2.1(1)	C(11)−N−C(12)	124.6(2)
P−Cr−C(11)	90.15(5)	C(11)−N−C(15)	127.4(2)
C(6)−P−C(16)	103.97(8)	C(12)−N−C(15)	109.0(1)
C(6)−P−C(22)	100.75(8)	N−C(12)−C(13)	109.5(2)
C(16)−P−C(22)	99.50(8)	N−C(15)−C(14)	108.8(2)
C(1)−C(11)−N	111.0(1)	C(13)−O(1)−C(14)	110.1(1)

[a] Definitions of the ring planes: Cp(1), C(1−5); Cp(2), C(6−10). Cg(1) and Cg(2) are the respective ring centroids.
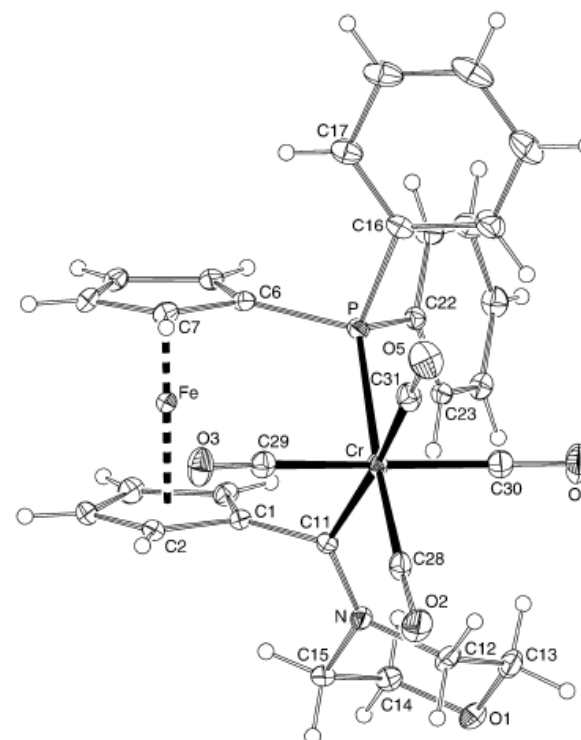
Figure 3. View of the molecular structure of **2b**. Thermal motion ellipsoids are drawn at the 30% probability level.

- 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 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.
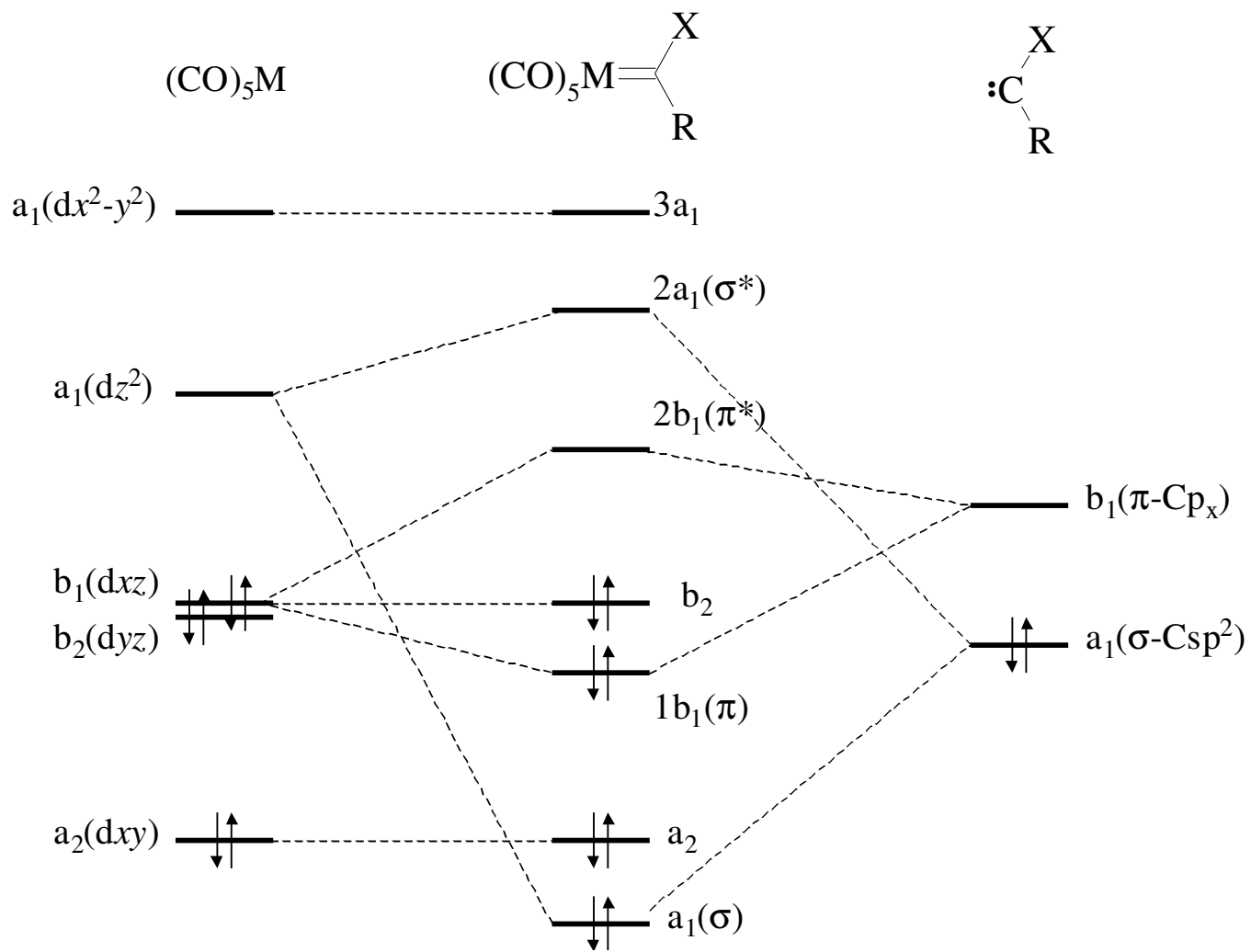
A schematic MO diagram for Fischer carbenes (M = Cr, Mo, W; X = OR, NR$_2$).

Electronic Structure of Alkoxychromium(0) Carbene Complexes: A Joint TD-DFT/Experimental Study

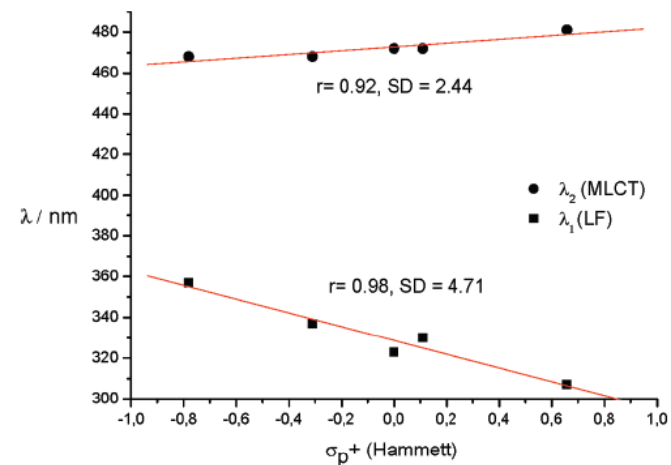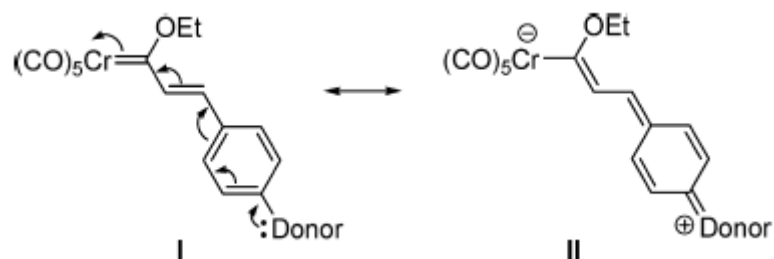Marta L. Lage, Israel Fernández,* María J. Mancheño, and Miguel A. Sierra*

Figure 4. Plot of the wavelengths of absorption maxima of the LF band (squares) and MLCT band (circles) versus the σ_p^+ values for **2a−e**.
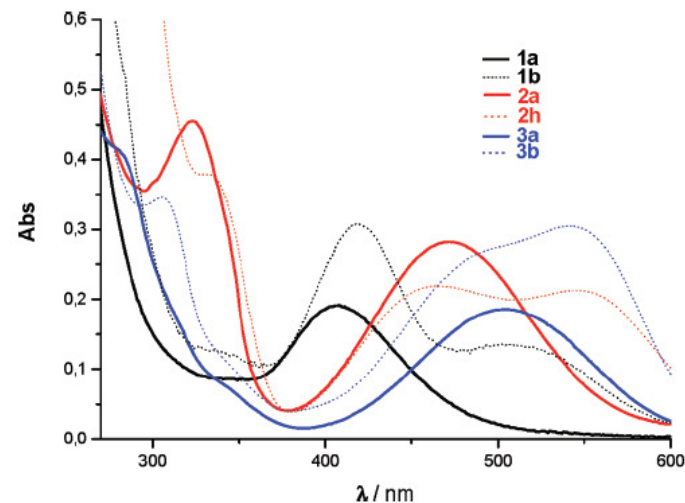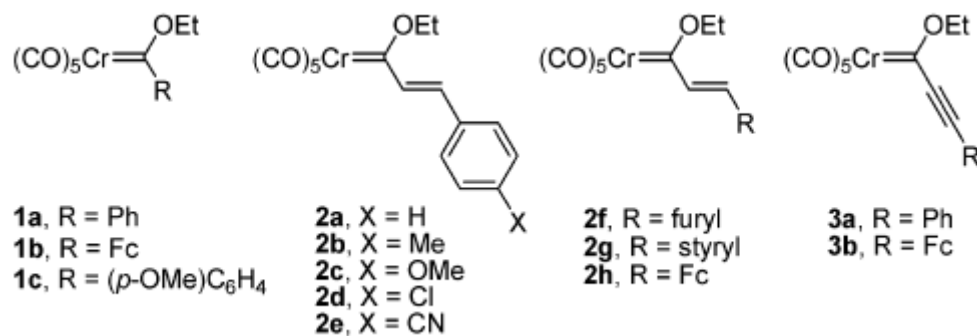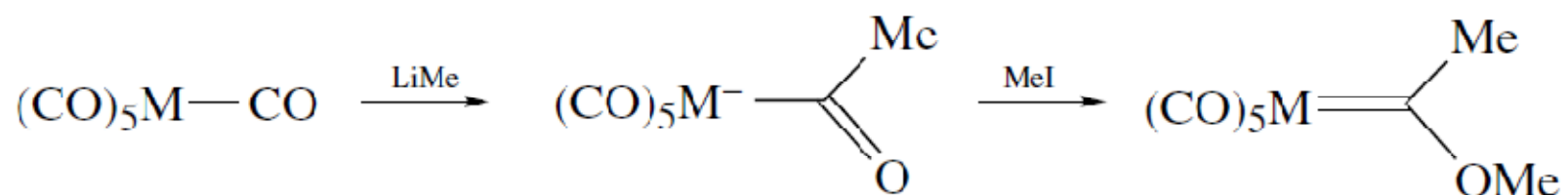
1a, R = Ph
1b, R = Fc
1c, R = (p-OMe)C₆H₄

2a, X = H
2b, X = Me
2c, X = OMe
2d, X = Cl
2e, X = CN

2f, R = furyl
2g, R = styryl
2h, R = Fc

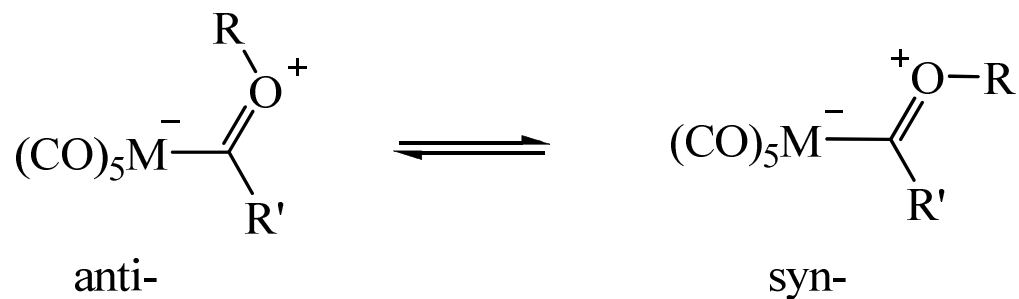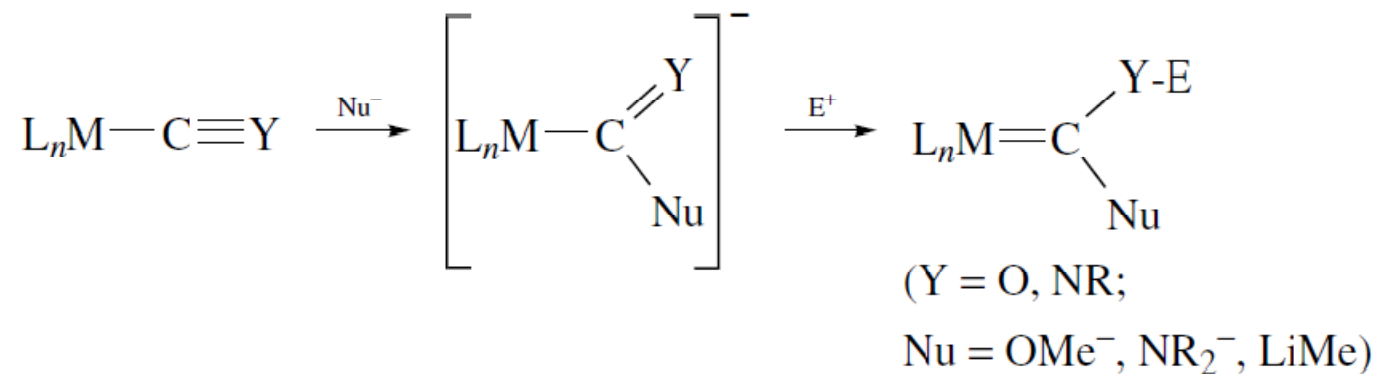3a, R = Ph
3b, R = Fc

Figure 6. Room-temperature UV−vis spectra of **1a,b**, **2a,h**, and **3a,b** in hexane (in all cases the concentration of sample is ca. 1×10^{-5} mol/L).

Fischer carbene synthesis

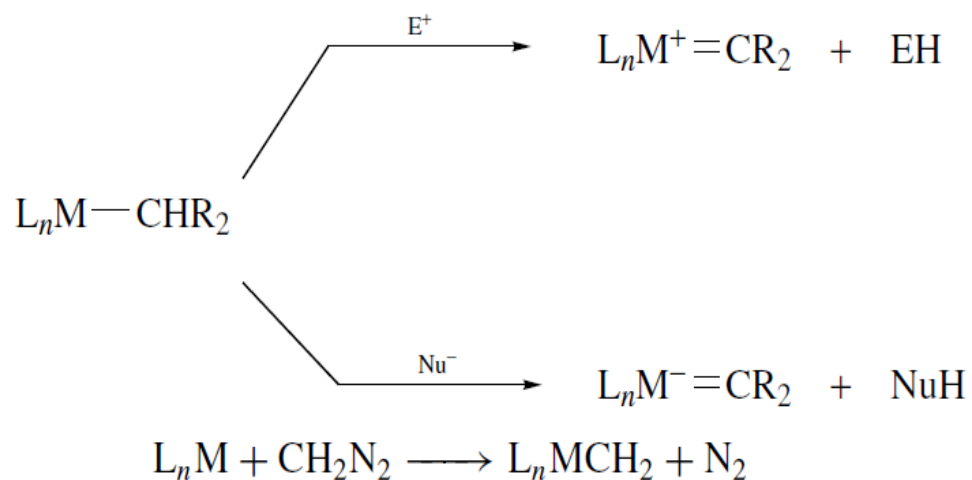- Alkyl lithium attack at metal carbonyl followed by alkylation.

- 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.

- Can also be observed by laser flash photolysis by transient UV-vis absorption.

$$L_nM-C\equiv Y \xrightarrow{\ Nu^-\ } \left[L_nM-C \overset{\displaystyle Y}{\underset{\displaystyle Nu}{\diagup\!\!\!\diagdown}} \right]^{-} \xrightarrow{\ E^+\ } L_nM=C \overset{\displaystyle Y\text{-}E}{\underset{\displaystyle Nu}{\diagup\diagdown}}$$

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

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

$$L_nM-CHR_2 \quad \begin{cases} \xrightarrow{\ E^+\ } & L_nM^+=CR_2 \ + \ EH \\[2em] \xrightarrow{\ Nu^-\ } & L_nM^-=CR_2 \ + \ NuH \end{cases}$$

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

- Alternatively, Hydride (H$^-$) is abstracted from the a position of a metal-alkyl

  (proton 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:

$$[(MeNC)_4Pt]^{2+} + 4MeNH_2 \longrightarrow [Pt\{=C(NHMe)_2\}_4]^{2+}$$
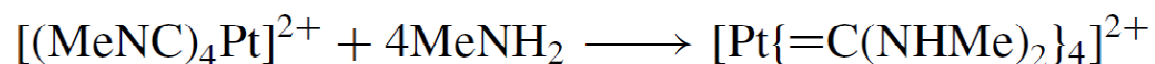
- Acetylides make for suitable bases due to their canonical vinylidene form and undergo nucleophillic attack by alcohols in-situ to generate the heteroatom stabilized Fishcer carbene complex.
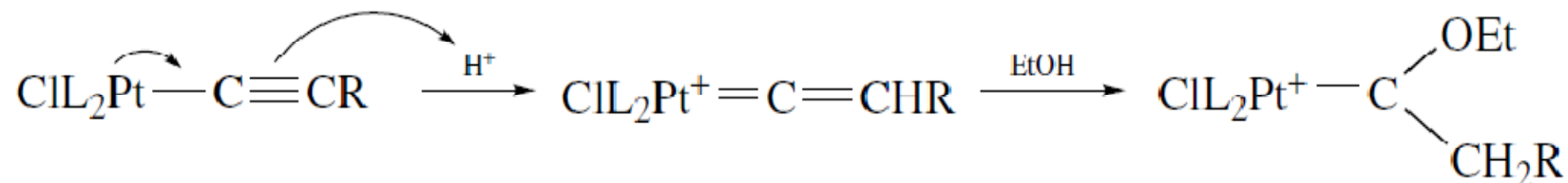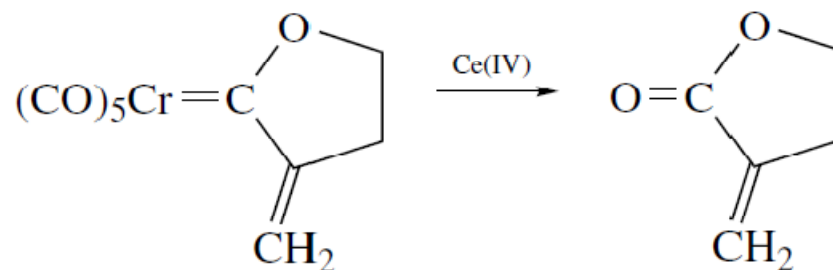
Fischer carbene reactions

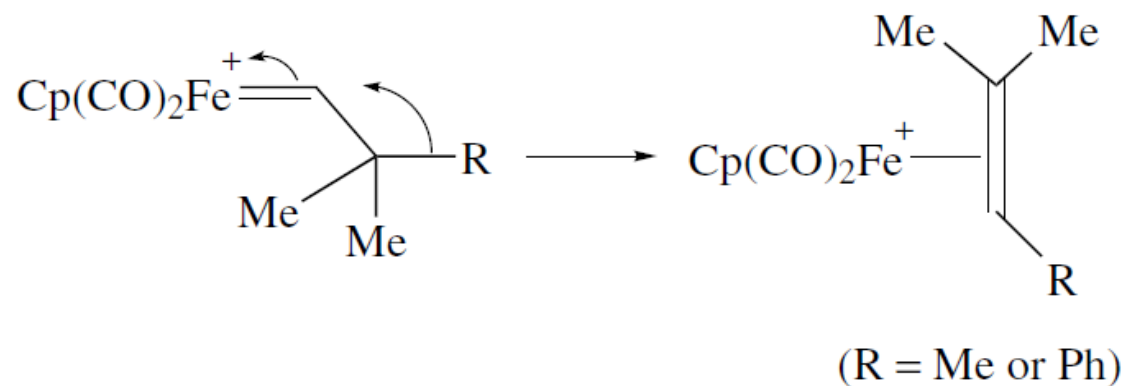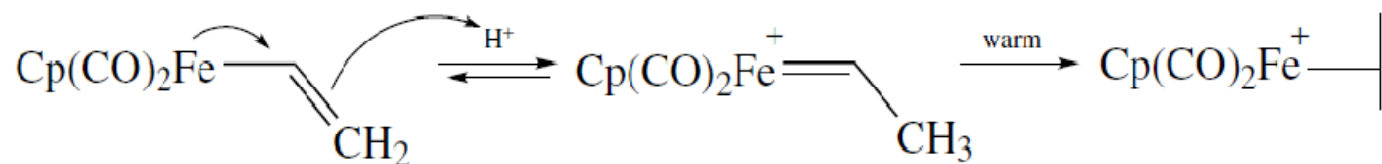- Thermal decomposition of Fishcer carbenes gives rise to a set of alkene products: rearranged monomer and the dimer.
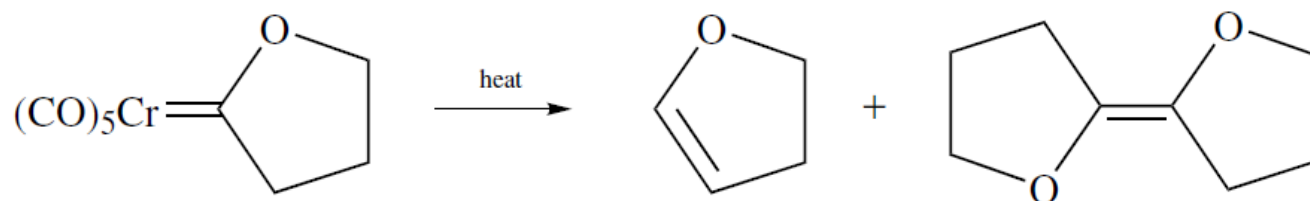
- Oxidative cleavage of the M-C bond using Ce^{IV}, pyridine-N-oxide, DMSO or even simply O_2 usually gives rise to the ketone derivative.

- 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.

$$Cp(CO)_2Fe-\!\!\!\diagdown\!\!\!\diagup_{CH_2} \xrightleftharpoons{H^+} Cp(CO)_2\overset{+}{Fe}=\!\!\!\diagdown\!\!\!\diagup_{CH_3} \xrightarrow{warm} Cp(CO)_2\overset{+}{Fe}-\!\!\!\parallel$$

$$Cp(CO)_2\overset{+}{Fe}=\!\!\!\diagup\!\!\!\diagdown\!\!\underset{Me}{\overset{}{\diagdown}}\!\!\underset{Me}{\diagup}\!\!-R \longrightarrow Cp(CO)_2\overset{+}{Fe}-\!\!\!\parallel\!\!\underset{R}{\overset{Me\diagdown\diagup Me}{}}$$

(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

- Due to the electrophillic nature of the Fischer carbene C-atom any $\beta-H$ 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
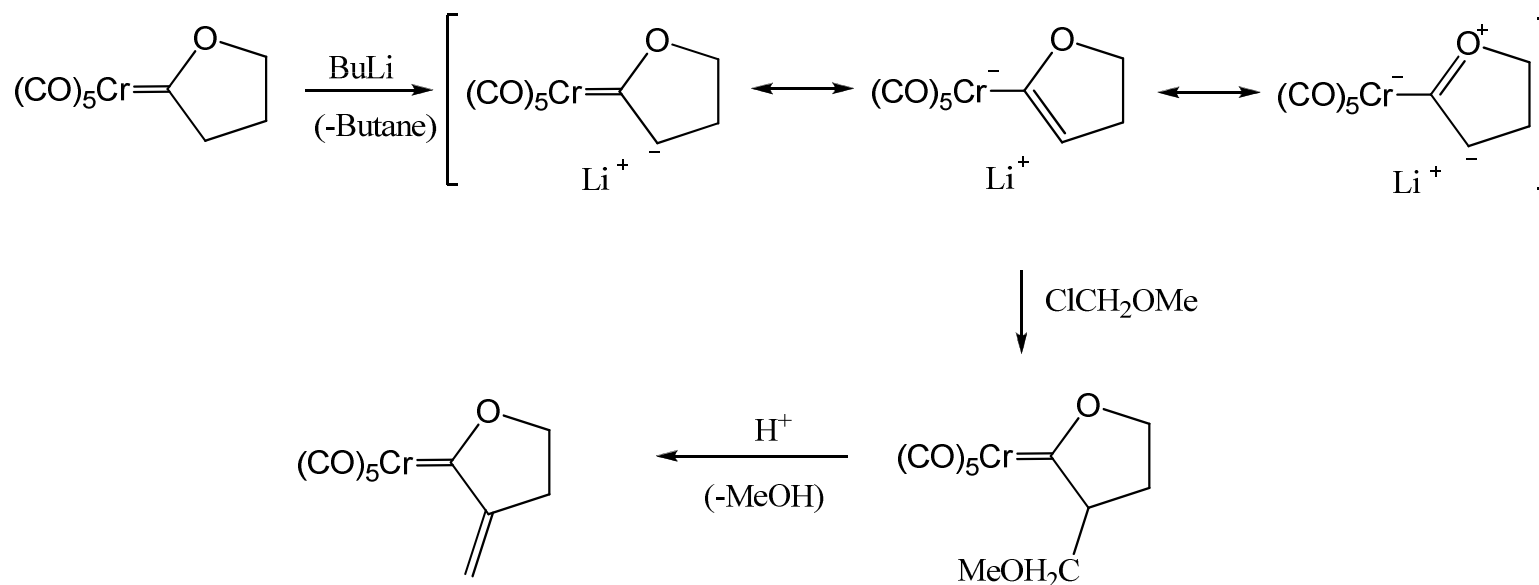
- Fischer carbenes readily undergo nucleophillic attack at the carbene carbon

- Attack of amines can give a zwitterionic intermediate which produces the amino carbene with loss of the corresponding alcohol

$$(CO)_5Cr = C \overset{OMe}{\underset{Ph}{\big|}} \quad :NH_2R \longrightarrow (CO)_5\overset{-}{Cr} - C \overset{OMe}{\underset{Ph}{\big\langle}} \overset{H}{\underset{N^+HR}{\big|}}$$

$$\downarrow -MeOH$$

$$(CO)_5Cr = C \overset{NHR}{\underset{Ph}{\big\langle}}$$
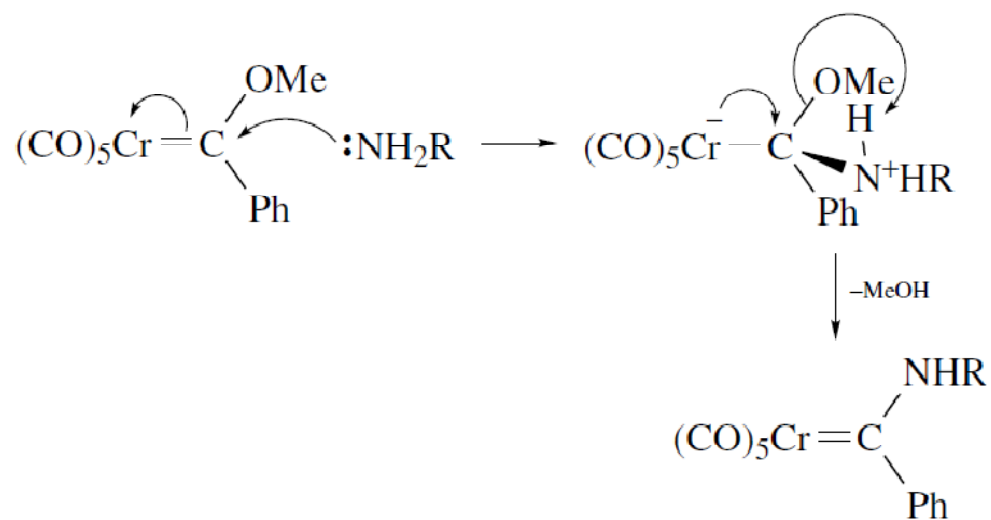
- This reaction is comparable to that of amide formation via ketone aminolysis if we replace $(CO)_5M$ with C=O.

- 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)
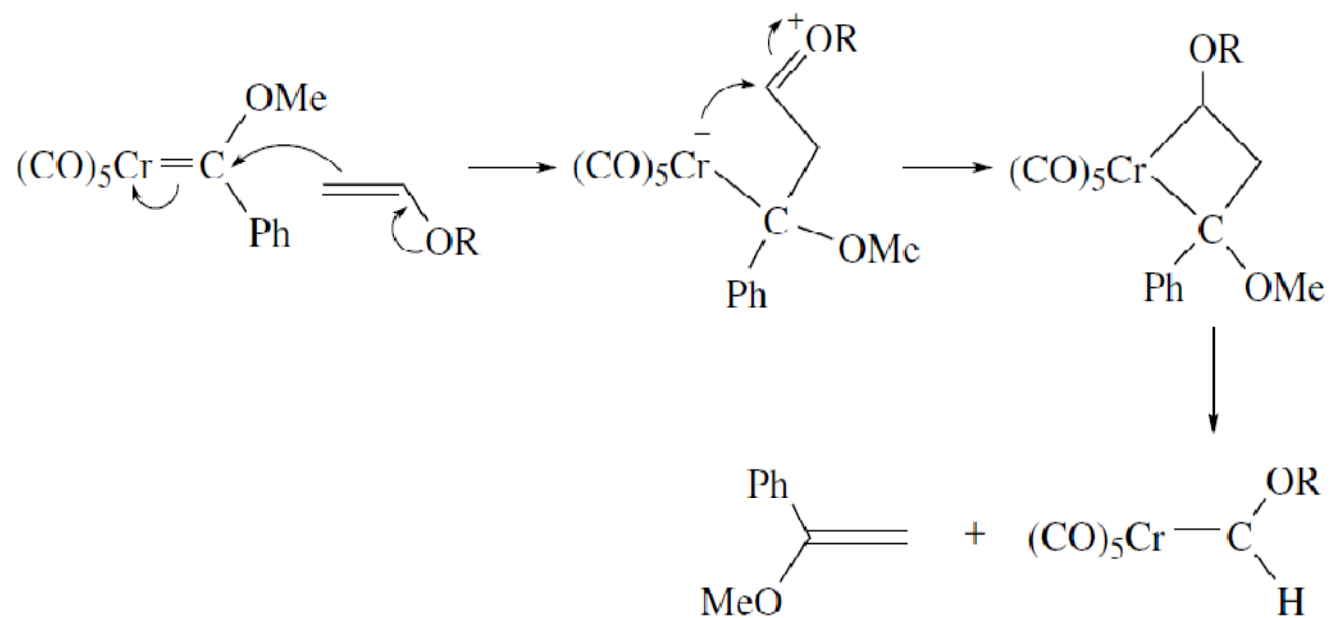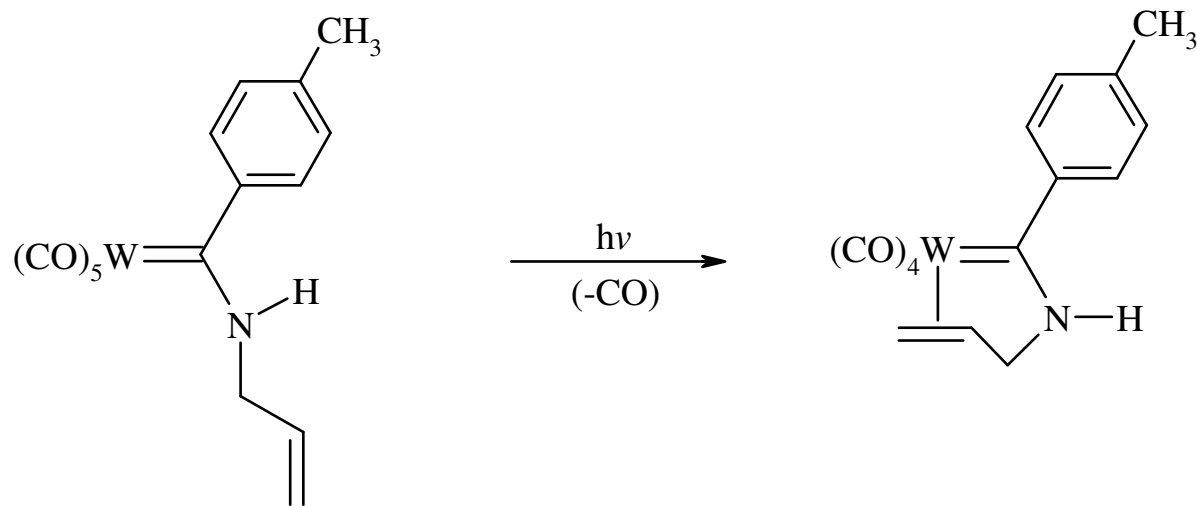
- Casey et al. have reported the photoinduced CO loss and preparation of a tetracarbonyl tungsten-carbene-alkene chelated complex.

- 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.
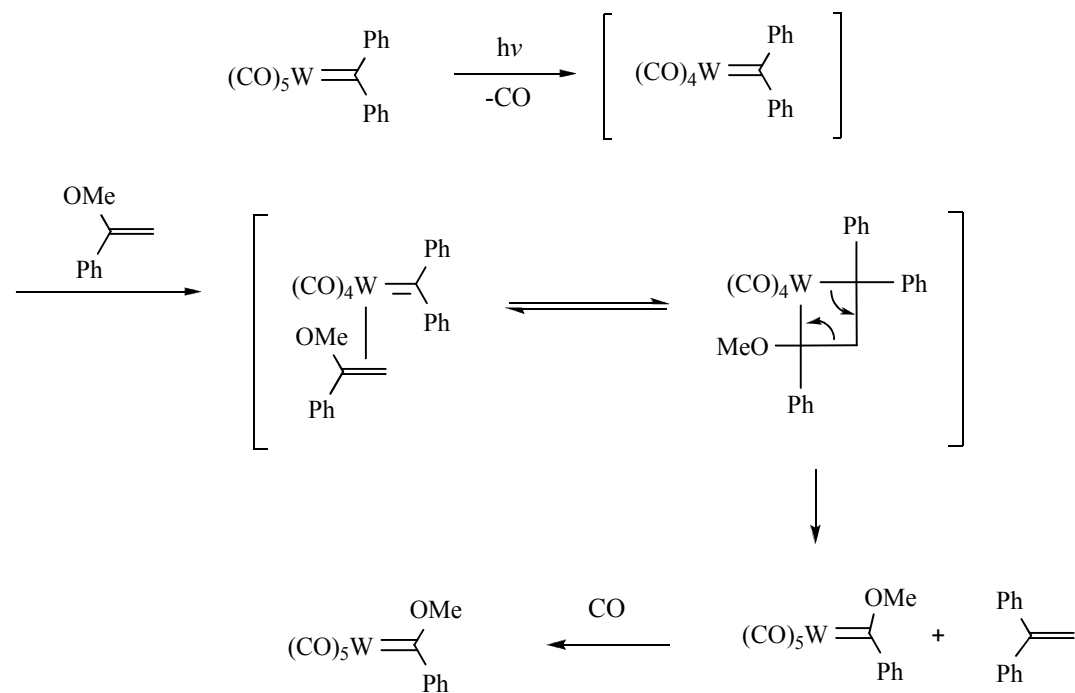
- Photoinduced metathesis was observed upon population of the high-energy LF state.

- Population of the dx^2-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.
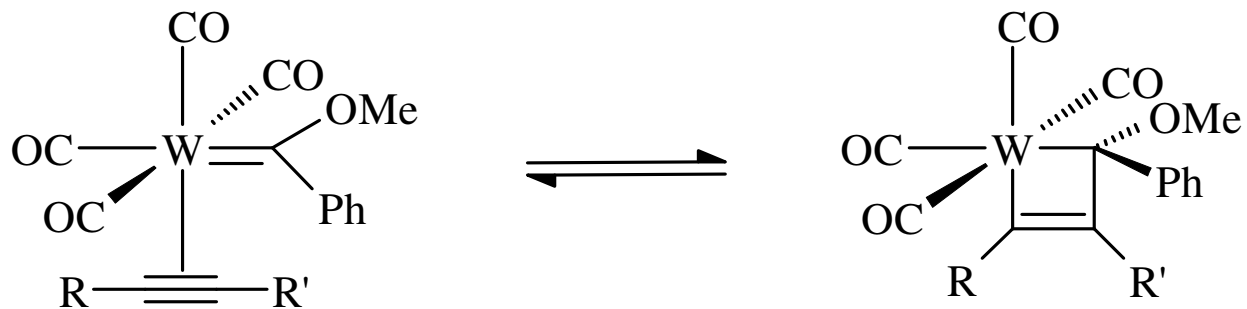
- The alkyne-carbene complexes later synthesized by Foley et al. have considerable metallacyclobutene character, however, due to their instability in solution at ambient temperatures their exact structure could not be confirmed.

- 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 $\xrightarrow{\begin{array}{c} h\nu \\ -CO \end{array}}$ II

$R_L \equiv\!\!\!\equiv R_S$

III

Z-IV $\longrightarrow \longrightarrow \longrightarrow$ V

E-IV $\xrightarrow{\text{cyclisation}}$ VI $\longrightarrow$ VII

CO insertion

VIII $\longrightarrow$ IX $\longrightarrow$ X