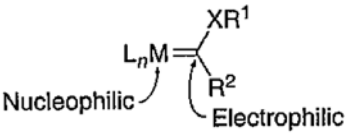
Organometallics Study Seminar
Chapter 13: Metal-Ligand Multiple Bonds

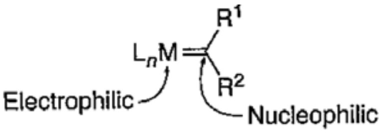
Contents

1. Carbene Complexes

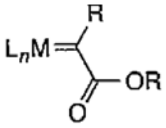
1.1 Classes of Carbene Complexes



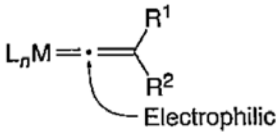
Fischer carbene complexes:
X = O, NR, S
M = low-valent, middle or late transitional metals



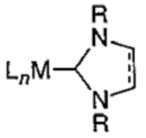
Schrock carbene or Alkylidene complexes:
R^1, R^2 = alkyl or H
M = high-valent carbyl or middle transition metals



Carbenoid complexes:
L_nM = $Rh_2(O_2CR)_4$, N_4Ru, $(N_2O_2)Ru$, or (N, N)Cu

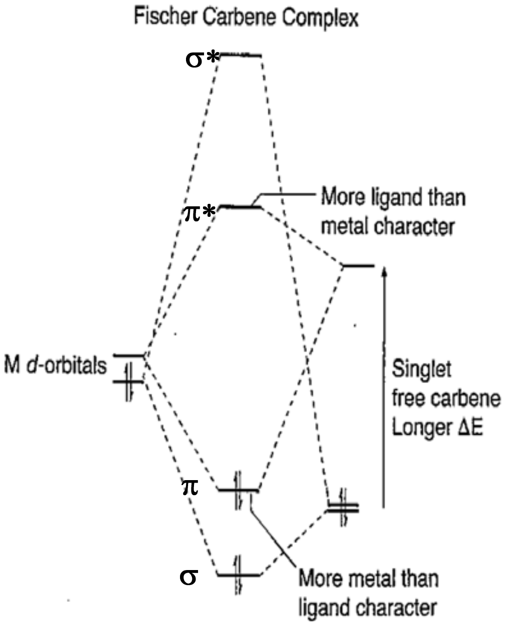


Vinylidene complexes:
R^1, R^2 = H, alkyl or aryl



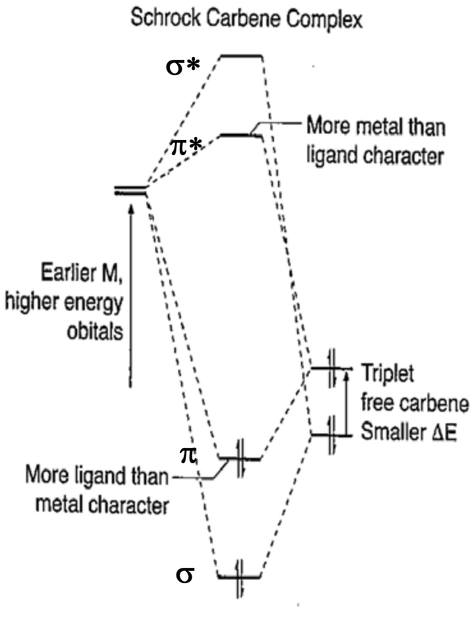
N-Heterocyclic carbene complexes:
R = aryl or alkyl

1.2 Origin of the Electronic Properties of Fisher and Schrock Carbenes



LUMO: ligand character
electrophilic at ligand
HOMO: metal character
nucleophilic at metal

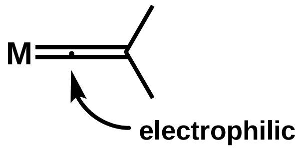
σ-bond: polarize toward the carbon
π-bond: polarize toward the metal



LUMO: metal character
electrophilic at metal
HOMO: ligand character
nucleophilic at ligand

σ-bond: polarize toward the carbon
π-bond: polarize toward the carbon

vinylidene complex



:CCH_2
singlet state is more stable by 42kcal/mol.

M: low oxidation state

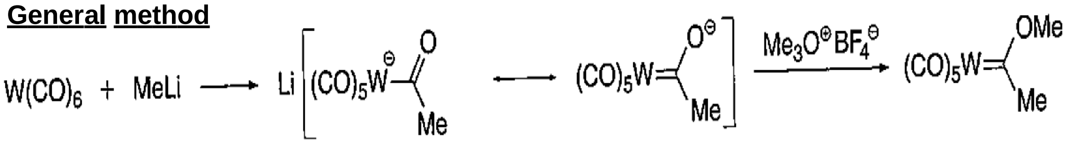
⇩

Fisher type carbene

1.3 Synthesis of Carbene Complexes

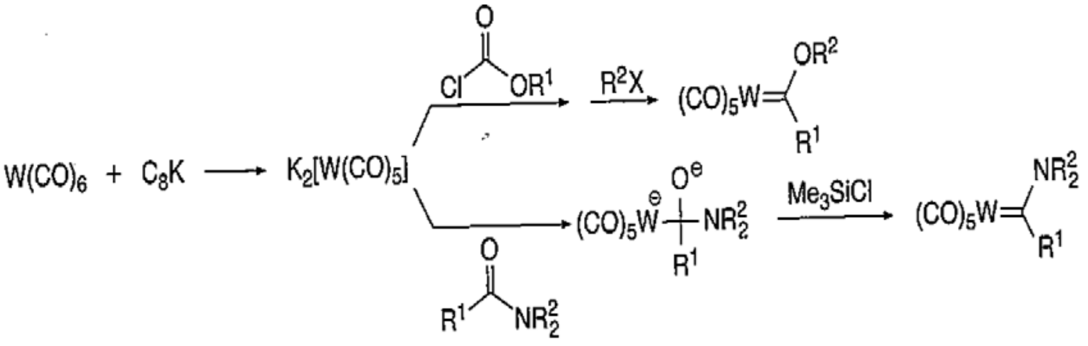
Fisher carbene complexes

General method



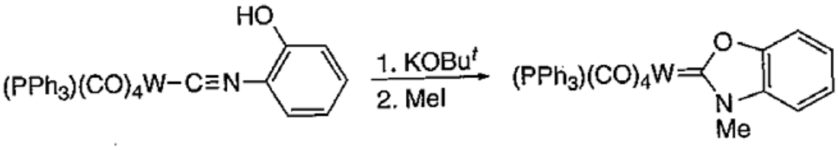
(13.1)

Metal dianion



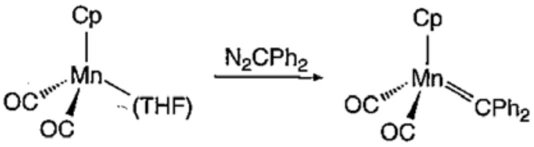
(13.2)

Isocyanide complex



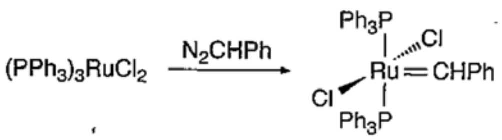
(13.3)

Diazoalkane



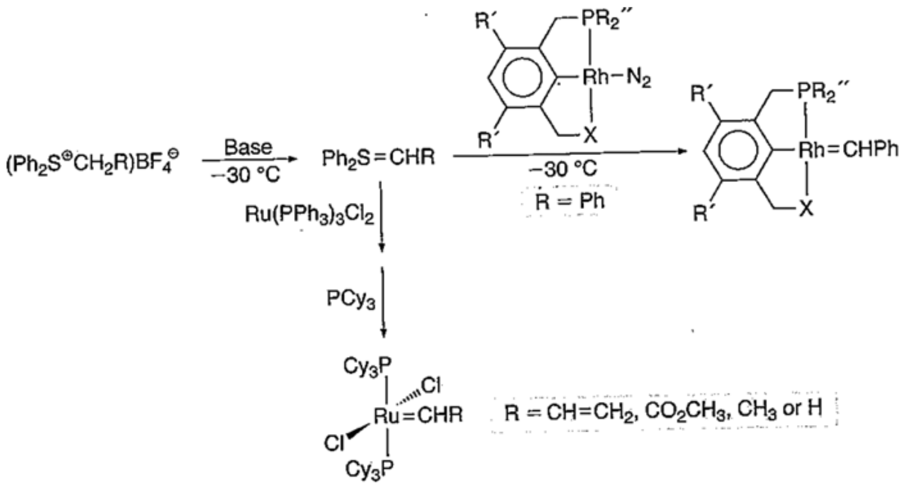
(13.4a)

cf) rhozium-carbene complex



(13.4b)

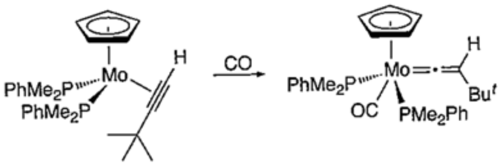
Surfur ylide



Scheme 13.1

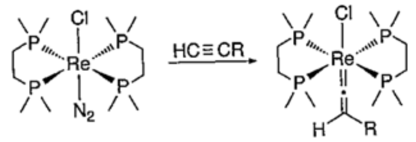
Vinylidene carbene complexes

Alkyne complexes

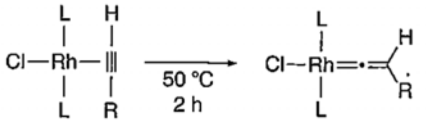


(13.6)

alkyne: 4e donor (without CO)
→ 18 e complex
alkyne: 2e donor (with CO)
→ vinylidenetautomer is more stable on this relatively electron-rich, low-valent metal fragment



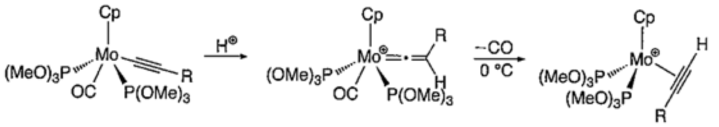
(13.7)



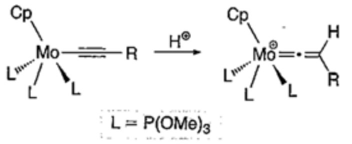
(13.9)

In all cases, these vinylidene complexes contain transition metals in relatively low oxidation state.

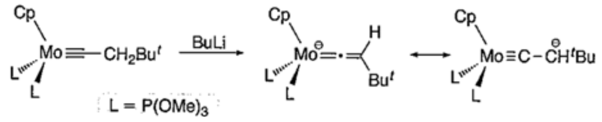
Metal-acetylide complexes



(13.10) **Vinylidene complex is thermodynamically unstable.**



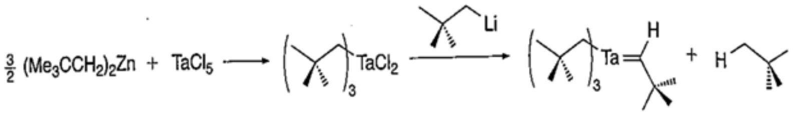
(13.11) **Vinylidene complex is stable with more electron-rich ligand.**



(13.12)

Alkylidene complexes

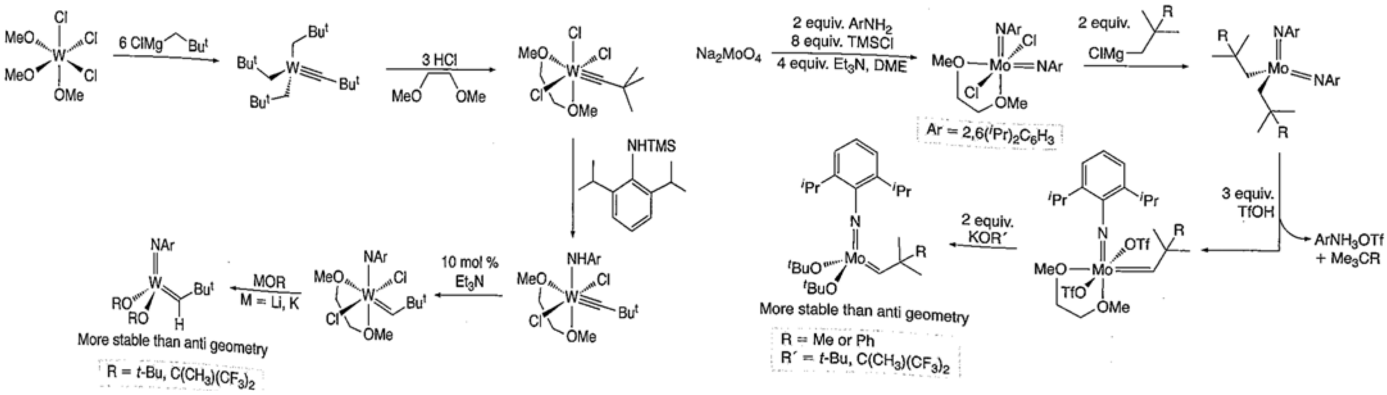
General procedure (synthesis of first Schrock carbene)



(13.13)

α-hydrogen elimination from a high-valent, early metal , dialkyl complex

Schrock alkylidene catalysts

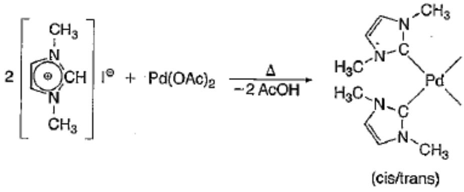


active catalyst for olefin metathesis (reactivity: Mo > W)

Tebbe's reagent

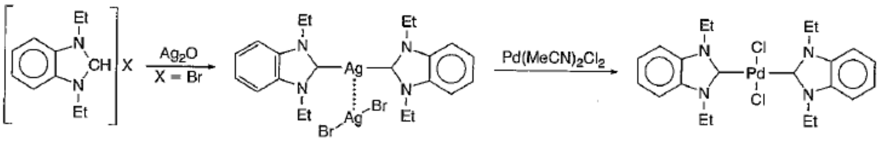
1.4 Synthesis of *N*-heterocyclic carbene complexes

Synthesis of N-heterocyclic carbene complexes

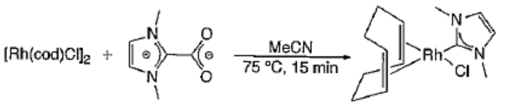


(13.14)

imidazolium salt with a complex containing a basic ligand

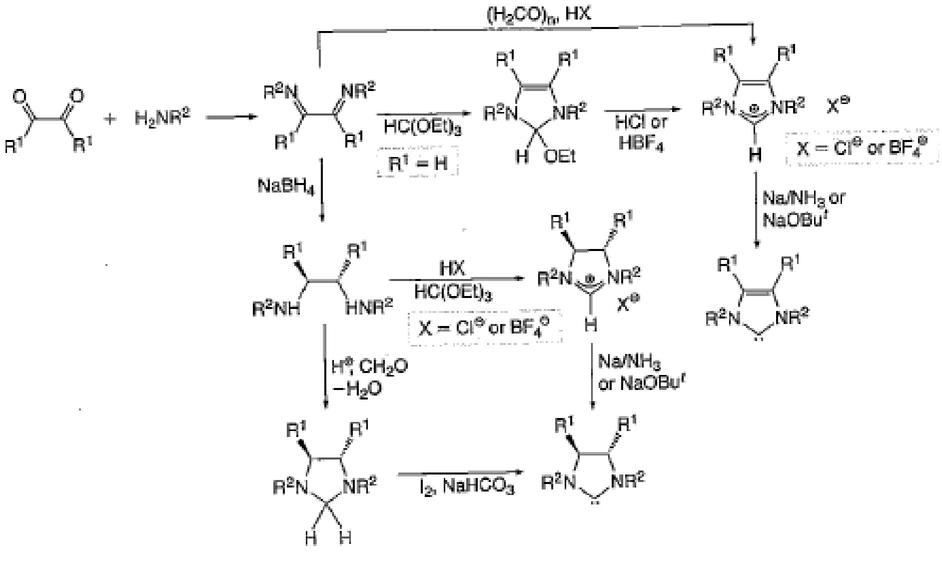


(13.15) **transfer from silver carbene**



(13.16) **imidazolium-2-carboxylate**

Synthesis of free carbene



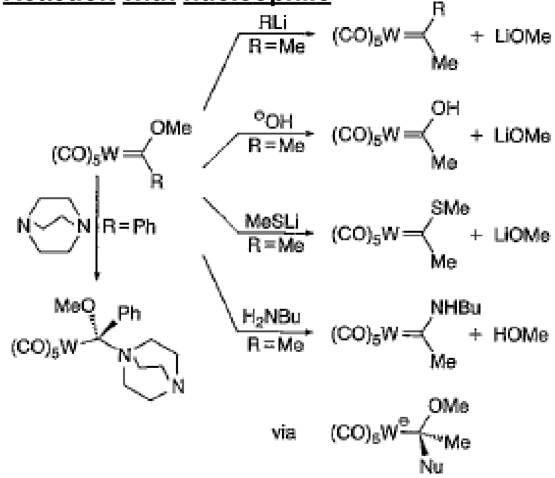
Scheme 13.6

These carbene are stable at monomeric species when the substituents at nitrogen are large enough to prevent dimerization (t-Bu, Ad, di-ortho-substituted aryl groups).

1.5 Reactivity of carbene complexes

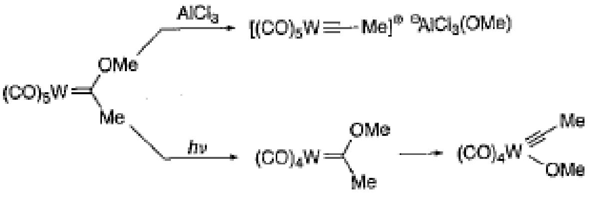
Fisher carbene complexes: related to the reaction chemistry of organic ester

Reaction with nucleophile



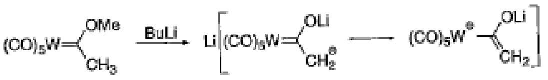
Scheme 13.7

Conversion to carbyne complexes

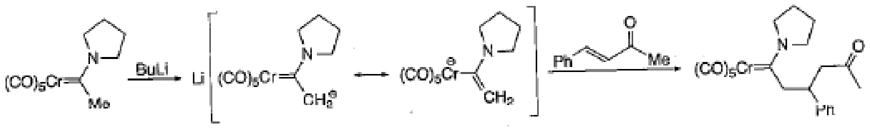


Scheme 13.8

Reactions related to those of enolates

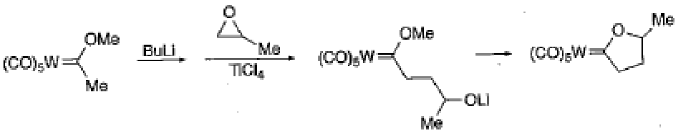


(13.18)



(13.19)

(13.20)

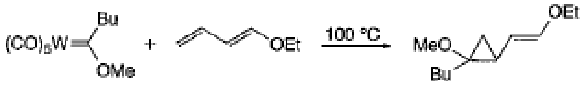


(13.21)

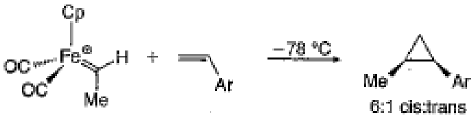
Fisher carbene complexes react like enolates when treated with base.

Cyclopropanations

(13.22)

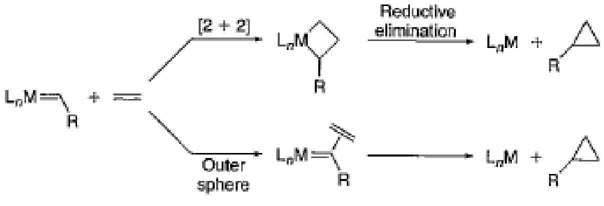


(13.23)



(13.24)

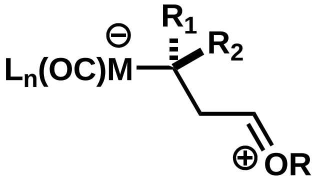
mechanism **Both pathways are possible.**



Scheme 13.9

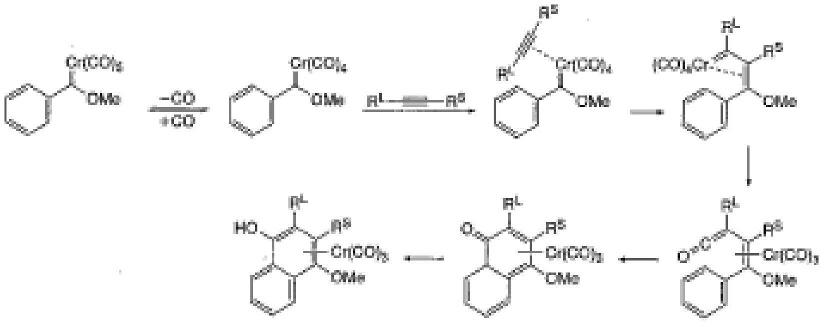
cyclopropanation + olefin methathesis

→ metallacycle intermediate



zwitterionic intermediate

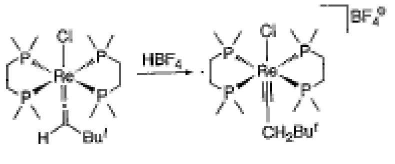
Annulations: The Dotz reaction



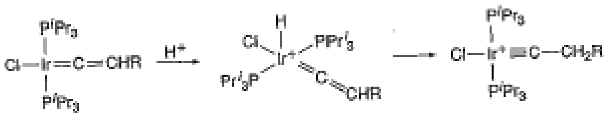
Scheme 13.12

Vinylidene complexes: similarity to Fisher carbenecomplexes

Basicity of β-carbon

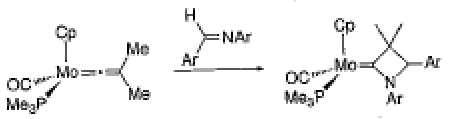


(13.26)



(13.27)

[2+2] reaction

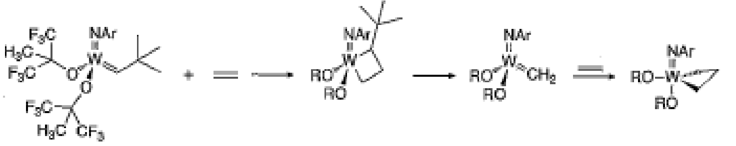


(13.28)

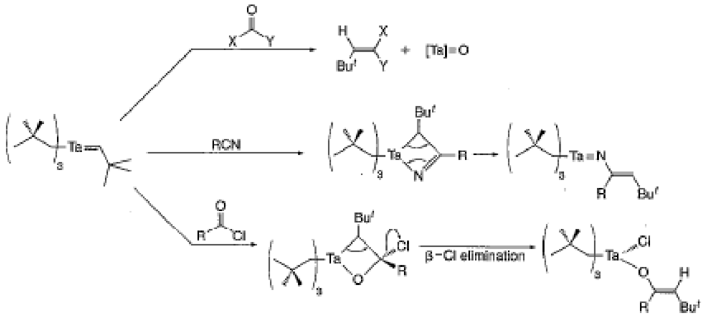
stepwise: nucleophilic attack, ring closure

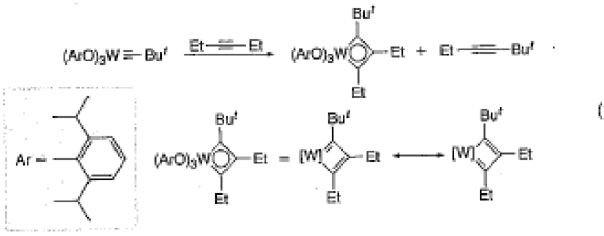
Alkylidene and alkylidyne complexes

Examples [2+2]



(13.29)

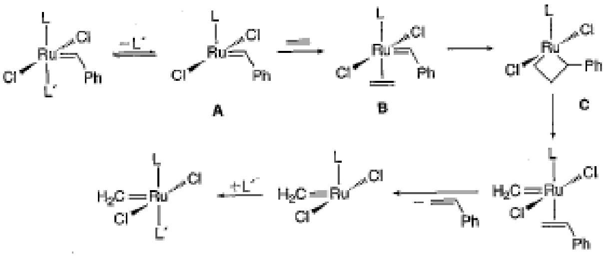




(13.30)

Scheme 13.14

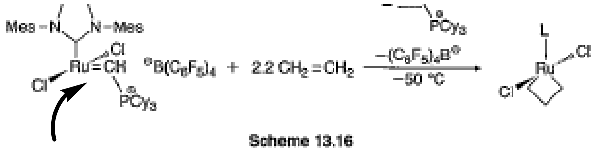
Mechanism



Scheme 13.15

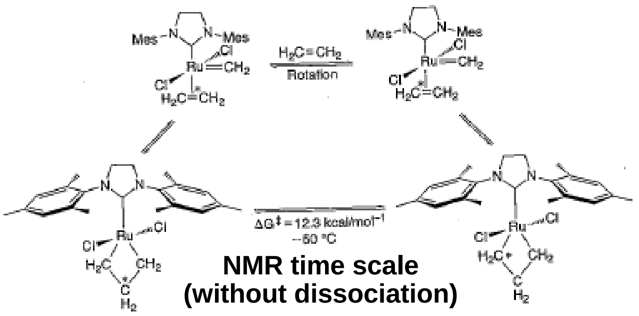
(Schrock-type carbene complexes also undergo the [2+2] reaction.)

Direct detection of ruthenacyclobutane intermediate



Scheme 13.16

open coordination site



NMR time scale (without dissociation)

Scheme 13.17

Factor of the reaction speed

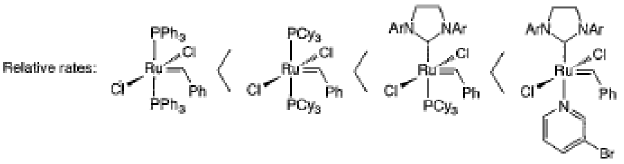
16e 14e

For L = PCy3

L'	k_1	k_{-1}/k_2
PCy_3	0.26	15,300
	0.0031	1.25

dissociation of ligand

reassociation of ligand

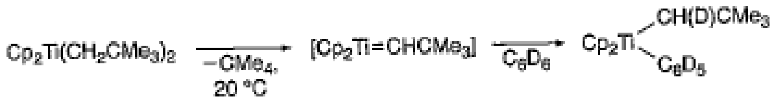


Scheme 13.18

Formal [2+2] reactions with C-H σ-bond

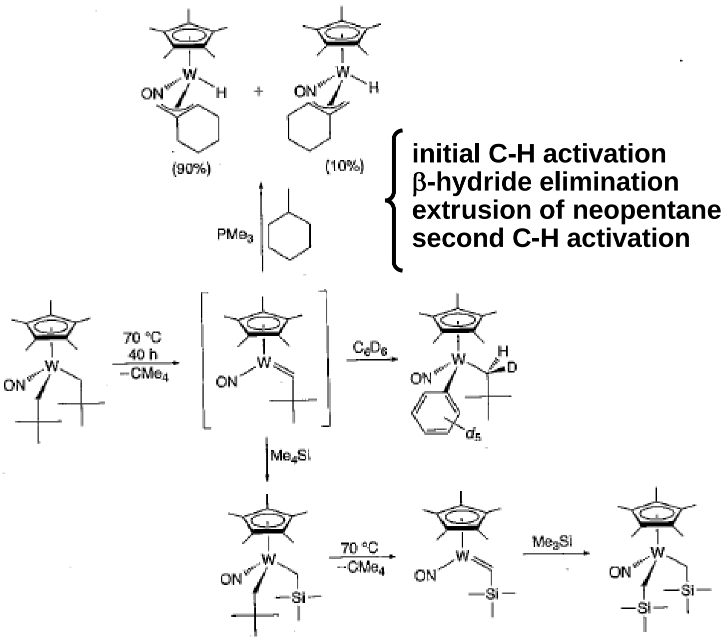
opposite of the α-eliminations that forms alkylidene complexes

less common



$$Cp_2Ti(CH_2CMe_3)_2 \xrightarrow[-CMe_4,\ 20\,^{\circ}C]{} [Cp_2Ti{=}CHCMe_3] \xrightarrow[C_6D_6]{} Cp_2Ti(CH(D)CMe_3)(C_6D_5)$$

reactive intermediate



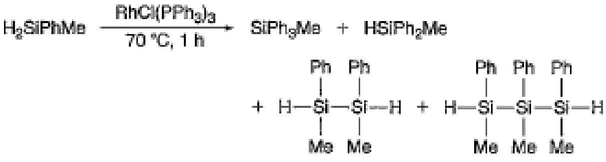
initial C-H activation
β-hydride elimination
extrusion of neopentane
second C-H activation

2. Silylene Complexes

2.1 Overview of Silylene Complexes

In general, multiple bonds to silicon and other second-row main group elements are less stable than multiple bonds to carbon, oxygen and nitrogen.
ex) Si=O, M=Si: unstable

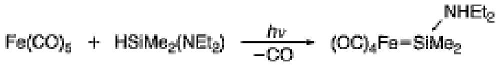
$$Si_2Me_5H \xrightarrow[90\ °C,\ 18\ h]{trans\text{-}PtCl_2(PEt_3)_2} Si_nMe_{2n+1}H \quad n = 1\text{–}6 \qquad (13.33)$$



$$H_2SiPhMe \xrightarrow[70\ °C,\ 1\ h]{RhCl(PPh_3)_3} SiPh_3Me + HSiPh_2Me + H{-}SiPhMe{-}SiPhMe{-}H + H{-}SiPhMe{-}SiPhMe{-}SiPhMe{-}H$$

(13.34)

via metal-silylene intermediate

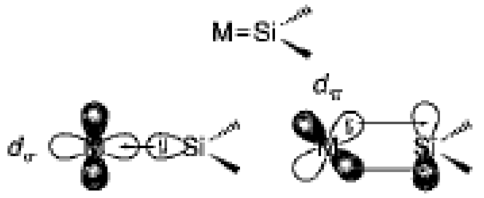


$$Fe(CO)_5 + HSiMe_2(NEt_2) \xrightarrow[-CO]{h\nu} (OC)_4Fe{=}SiMe_2(NHEt_2)$$

(13.35) **metal-silylene complex is stabilized by coordination of a Lewis base.**

2.2 Bonding of Silylene Complexes

Orbital interaction: same as carbene complex

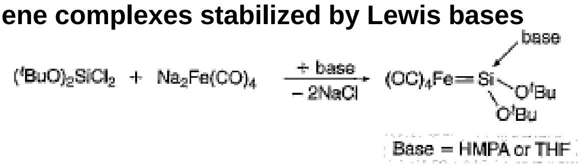


Back donation from the metal d-orbital to silicon: weaker than that of carbene complex

⟶ silicon remains Lewis acidic, and the silylene complexes are often stabilized by Lewis bases.

2.3 Examples of Isolated Silylene Complexes

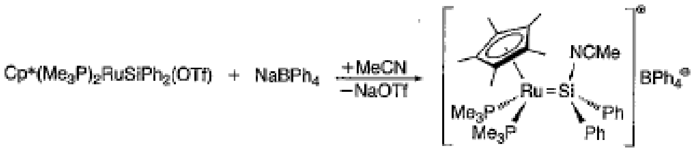
Silylene complexes stabilized by Lewis bases



$$({}^tBuO)_2SiCl_2 + Na_2Fe(CO)_4 \xrightarrow[-\,2NaCl]{+\,base} (OC)_4Fe{=}Si(base)(O^tBu)_2$$

Base = HMPA or THF

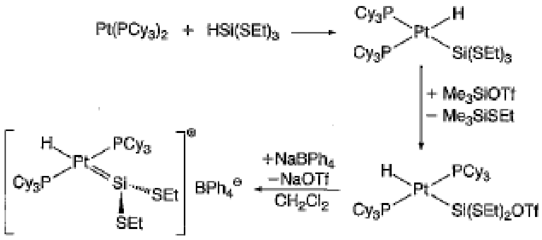
(13.36) **elimination of a salt**



$$Cp^*(Me_3P)_2RuSiPh_2(OTf) + NaBPh_4 \xrightarrow[-NaOTf]{+MeCN} [Cp^*(Me_3P)_2Ru{=}SiPh_2(NCMe)]^{\oplus}BPh_4^{\ominus}$$

(13.37) **abstraction of triflate**

Base-free silylene complexes



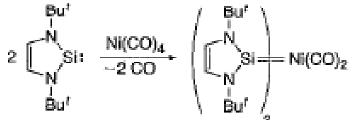
(13.38)

soft π-donating thiolate substituenets on silicon

⟶ stabilization of silicon center

Preparation of silylene complexes

Free silylene

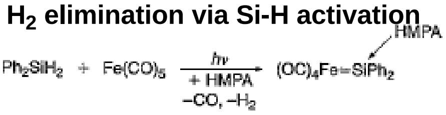


(13.39)

Photo extrusion of silylene

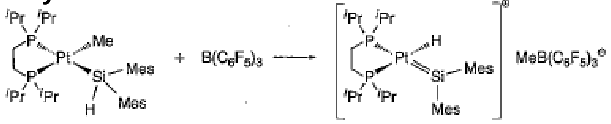
$Pt(PCy_3)_2 + (Me_3Si)_2SiMes_2 \xrightarrow[-(Me_3Si)_2]{h\nu} Pt(Cy_3P)_2{=}SiMes_2$ (13.40)

H_2 elimination via Si-H activation



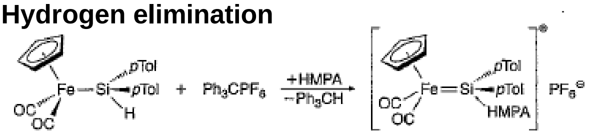
$Ph_2SiH_2 + Fe(CO)_5 \xrightarrow[+\,HMPA,\ -CO,\ -H_2]{h\nu} (OC)_4Fe{=}\overset{HMPA}{SiPh_2}$ (13.41)

Alkyl elimination

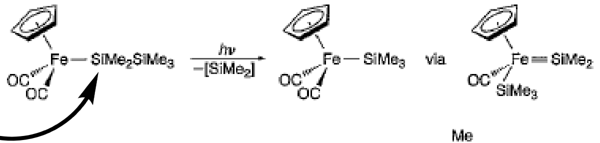


(13.42)

Hydrogen elimination



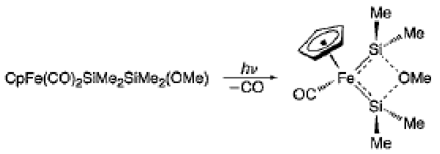
(13.43)



(13.44)

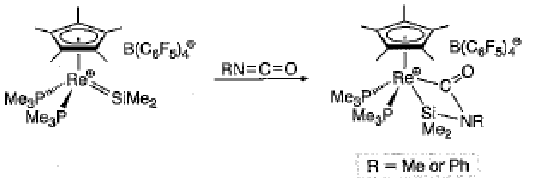
dissociation of CO, silyl migration

dissociation of CO, Si-Si bond cleavage ⟶

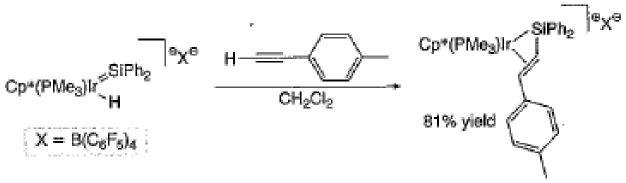


(13.45)

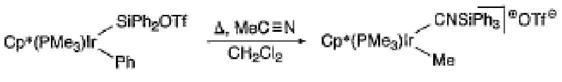
2.4 Reactivity of Silylene Complexes



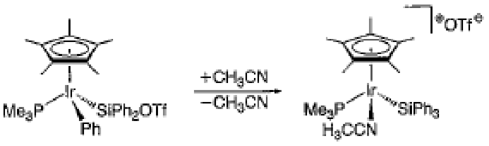
(13.46) **[2+2] addition with isocyanate**



(13.47) **alkyne insertion**



(13.48) **migration of Ph to silylene unit, C-C cleavage of the nitrile, insertion of the cyano group into M-Si bond**



(13.49) **generation of an aryliridium silylene intermediate**

3. Metal-Heteroatom Multiple Bonds

3.1 Scope of the Section

3.2 Overview

3.3 Bonding of Oxo and Imido Complexes

Formal charge

dianionic
cf) carbene: neutral
6e donor

Qualitative molecular orbital diagram

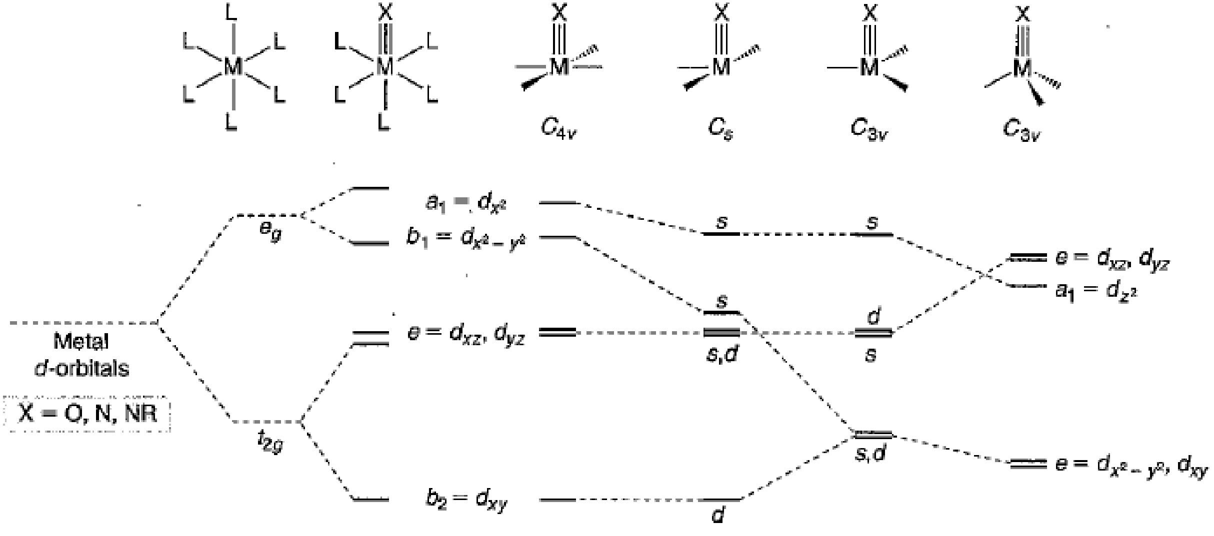
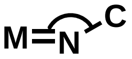


Figure 13.9.
Qualitative molecular orbital diagrams of oxo, nitrido, and linear imido complexes of various geometries. Adapted with permission from Figure 4 of Mayer, J. M., Thorn, D. L., Tulip, T. H. *J. Am. Chem. Soc.* **1985**, *107*, 7454.

C_{4v} symmetry: π-bonding of the O or N with the M leads to splitting the degenerated e_g and t_{2g}.
octahedral: d_{xz}, d_{yz} orbitals are π-antibonding.

complexes possessing more than two *d*-electrons must contain these electrons in a *d*-orbital that overlaps with the filled π-orbitals on the oxo, nitride, or linear imido complexes.

Bond angle between M, N and C

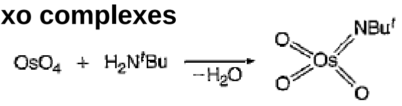


Analysis implies that linear imido compounds would have a larger degree of π-donation than bent imido compounds. (most of the complexes are linear)

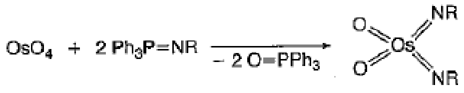
3.4 Synthesis of Metal-Imido and Metal-Oxo Complexes

Metal-imido complex

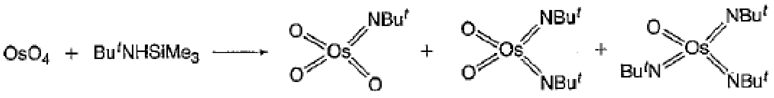
From metal-oxo complexes



(13.50)



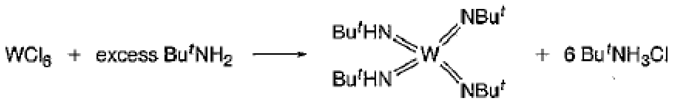
(13.51)



(13.52)

α-elimination

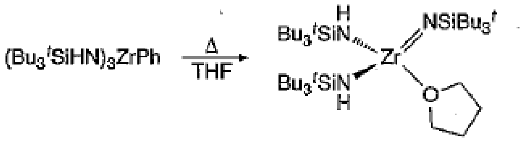
$Cp^*TaMe_3Cl + LiNHBu^t \longrightarrow [Cp^*TaMe_3(NHBu^t)] \longrightarrow Cp^*Ta(NBu^t)Me_2 + CH_4$ (13.54)



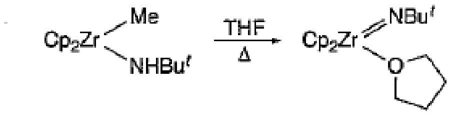
(13.55)

$\frac{1}{2}[Cp^*IrCl_2]_2 + 2\,LiNHBu^t \longrightarrow Cp^*Ir{=}NBu^t + H_2NBu^t$ (13.56)

elimination of ligand

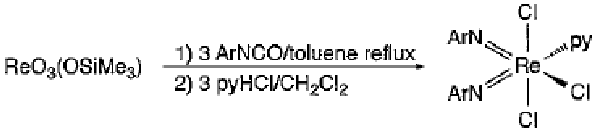


(13.57)

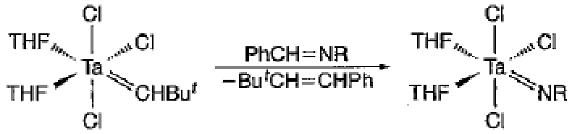


(13.58)

metathesis

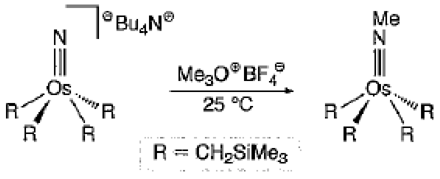


(13.59)

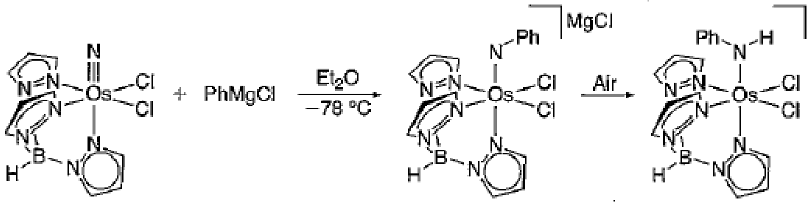


(13.60)

alkylation of nitrogen



(13.61) **Electron-rich nitrido: alkylation with electrophile**



(13.62) **Electron-poor nitrido: alkylation with nucleophile**

transfer of imide group

$Cp_2V + Me_3SiN_3 \longrightarrow Cp_2V{=}NSiMe_3$ (13.63a)

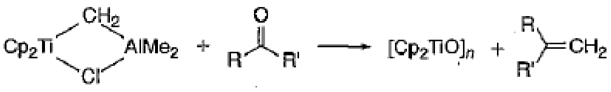
$Cp^*_2V + PhN_3 \longrightarrow Cp^*_2V{=}NPh$ (13.63b)

unsaturated transition metal azide complex,
N_2 elimination

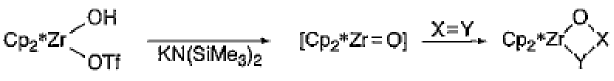
Metal-oxo complex

parallel to imido complexes

$Cp_2NbCl + O_2 \longrightarrow Cp_2NbCl(O)$ (13.64) **oxidation of a lower valent metal**



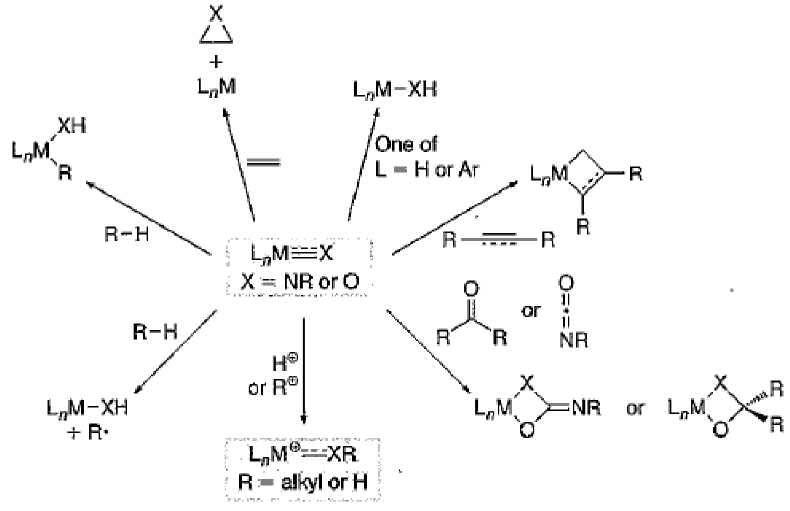
(13.65) **metathesis**



(13.66) **α-elimination**

oxidative addition... etc

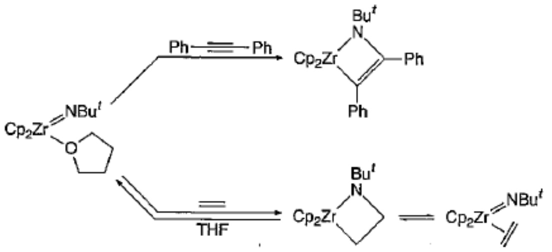
3.5 Reaction of Imido and Oxo Compounds



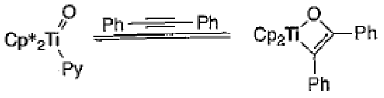
Scheme 13.20

[2+2] and [3+2] cycloaddition

[2+2]



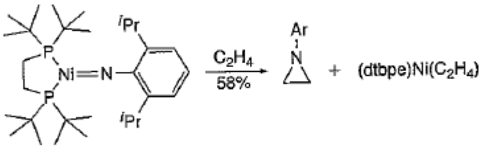
(13.68)



(13.73)

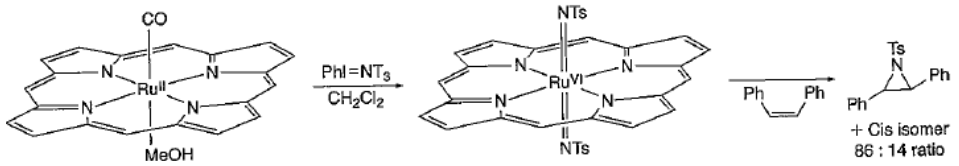
(early metal oxo complex: only one example)

alkyne: thermodynamically favorable
alkene: reversible



(13.74)

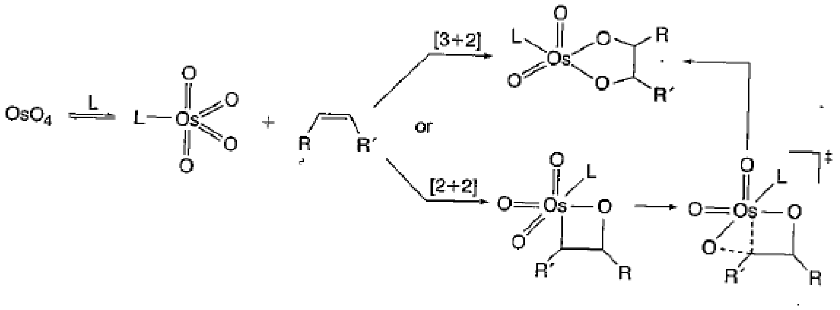
[2+2], reductive elimination



(13.75)

direct reaction

[3+2]



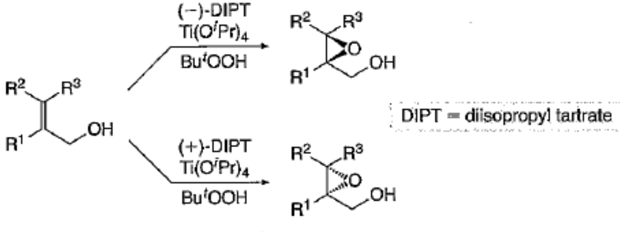
Scheme 13.21

computational study:
barrier [2+2] > [3+3]

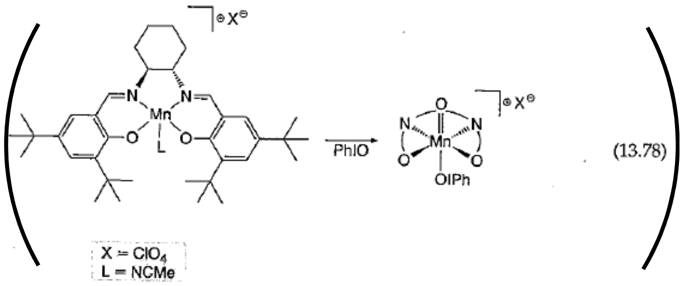
^{13}C istope effct:
similar magnitudes for both carbons of the olefine

Atom transfer of oxo and imide groups to olefins

Sharpless asymmetric dyhydroxylation

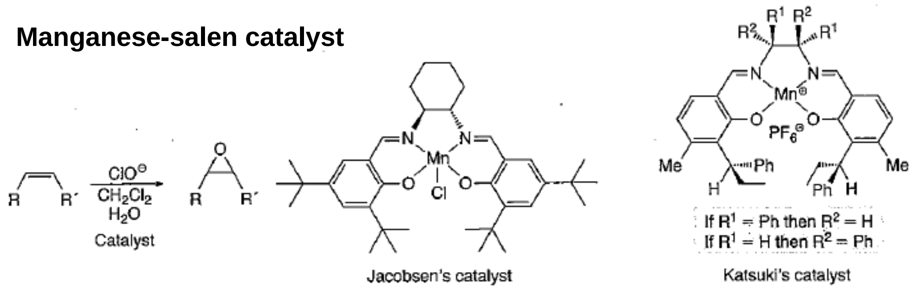


Scheme 13.22



(13.78)

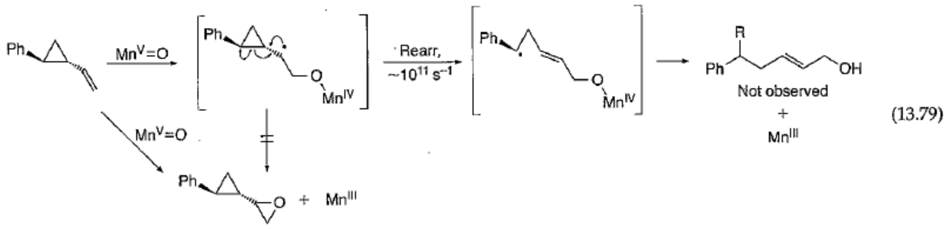
Manganese-salen catalyst



Scheme 13.23

via metal oxo complex

Mechanism of epoxydation of olefin

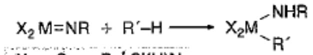


(13.79)

non-radical concerted process

Reactions with C-H bonds

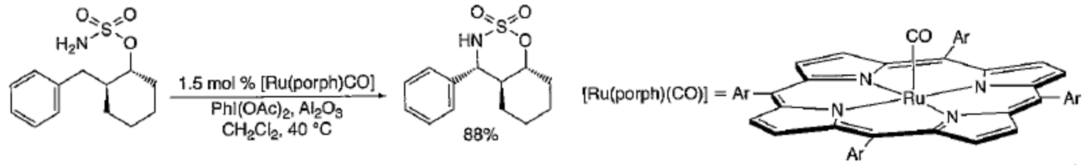
[2+2] reactions with C-H σ-bond



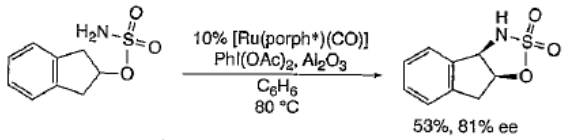
$$X_2M{=}NR + R'{-}H \longrightarrow X_2M(NHR)(R')$$

X = Cp or Bu$^t_3$Si(H)N
M = Ti, Zr, or W
R = Bu^t, Ar, or SiBu$^t_3$
R′ = alkyl or aryl

(13.80) See Chapter 6

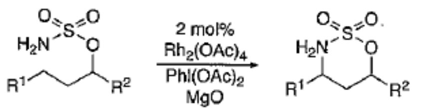


(13.81)



(13.82)

direct interaction of imide group with C-H σ-bond

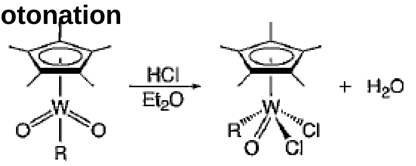


(13.83)

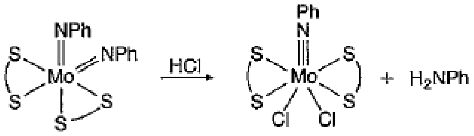
$L_nM{=}O + R{-}H \longrightarrow L_nM{-}OH + R\bullet \longrightarrow L_nM + ROH$ (13.84)

Reaction with electrophiles

protonation

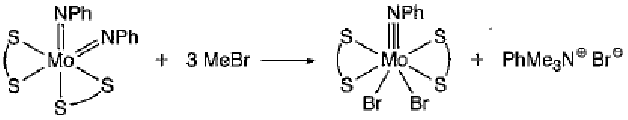


(13.85)

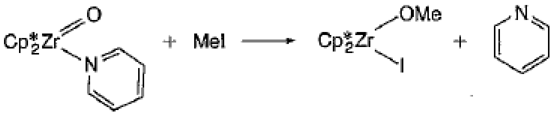


(13.86)

organic electrophiles

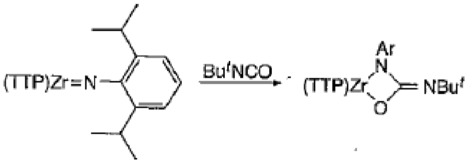


(13.87)



(13.88)

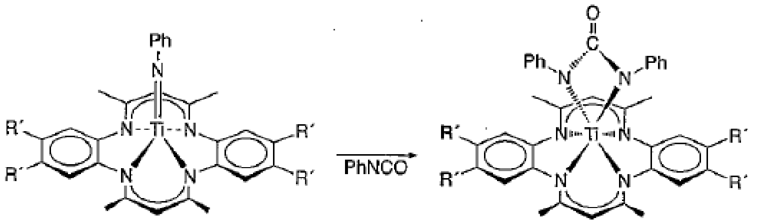
polar C=X bond



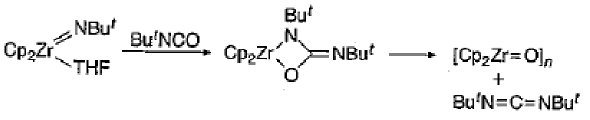
(13.90)

TTP = *meso*-5,10,15,20-tetra-*p*-tolyporphyrinato dianion

Metallacycle was isolated or characterized by NMR.



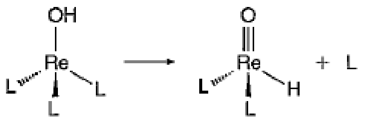
(13.91)



(13.92)

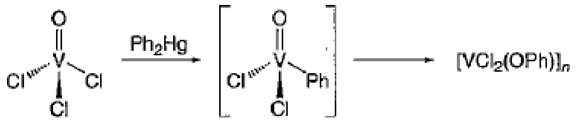
Migration of alkyl and hydride groups from M to O or N

proton transfer



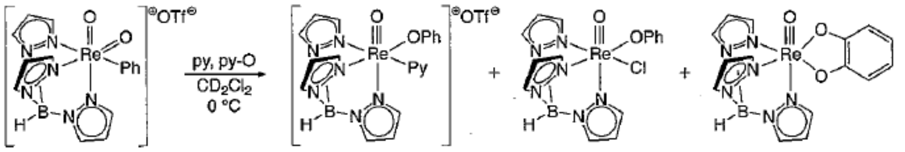
(13.93)

L = Et—≡—Et

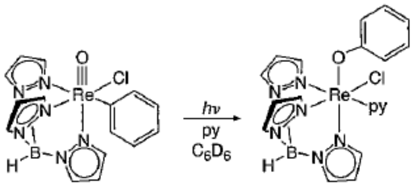


(13.94)

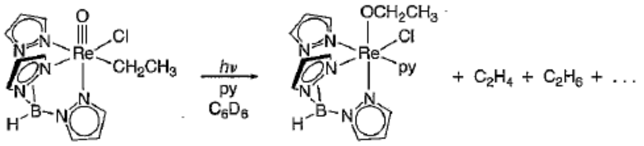
aryl transfer



(13.95)



(13.96)



(13.97)

Catalytic reactions of imido and metal-oxo compounds through organometallic intermediates

olefin metathesis/ alkene and alkyne hydroamination

3.6 Nitrido ligands

Bonding of nitrido ligands

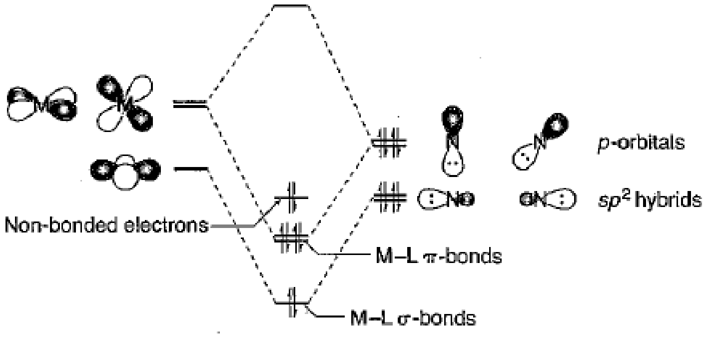


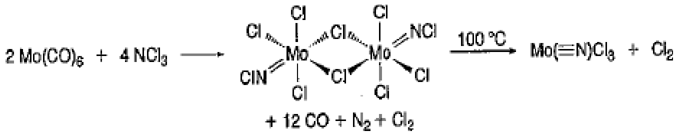
Figure 13.13.
Qualitative orbital diagram of the interaction between a transition metal fragment and a nitrido ligand.

trianionic
one σ-bond, two π-bond
strong π-donor ligand

Structural and spectral features

X-ray crystallography, IR, NMR

Synthesis of metal-nitrido complexes



(13.99)

$$trans\text{-}[Ru(O)_2X_4]^{2-} + HX + NaN_3 + CsX \longrightarrow Cs_2[Ru(\equiv N)X_5] \qquad (13.100)$$

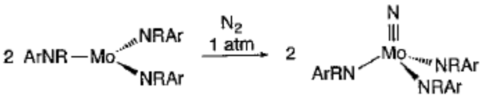
(X = Cl or Br)

$$MoCl_4(py)_2 + 4\,(CH_3)_3SiN_3 \longrightarrow Mo(\equiv N)(N_3)_3py + N_2 + py + 3\,(CH_3)_3SiCl \qquad (13.101)$$

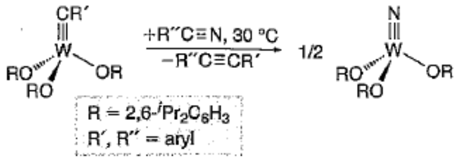
$$NaReO_4 + PR_3 + N_2H_4 \cdot 2\,HCl \xrightarrow{EtOH} [Re(\equiv N)Cl_2(PR_3)_n] \qquad (13.102)$$

$PR_3 = PMe_2Ph$

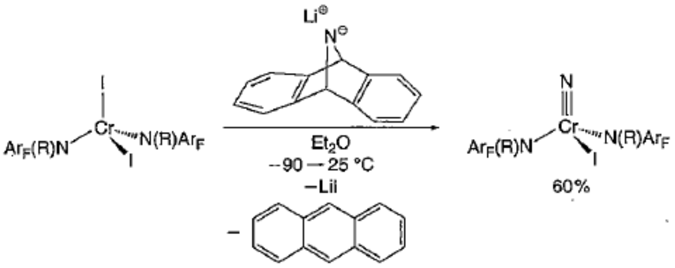
metathesis and atom transfer processes



(13.103)



(13.104)

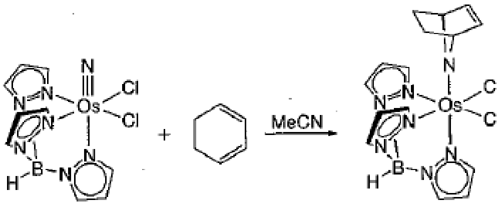


(13.105)

Reactions of metal-nitrido complexes

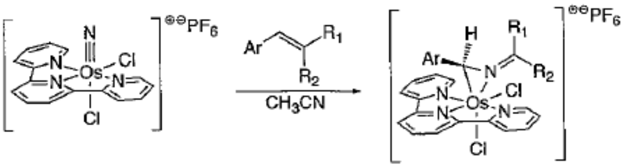
The uncoordinated lone pair on nitrogen can act as a nucleophile, as a lewis base, or as abridge to form μ-nitrido complexes.

[4+1] cycloaddition



(13.106)

cleavage of C-C double bond



(13.107)