Anorganische Strukturen und Reaktionsmechanismen

CHE.367

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Übersicht

- Nucleophiler Angriff auf auf koordinierte Liganden
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  - Angriff auf Carbene
  - Angriff auf Alkyle
  - Angriff auf η^2-ungesättigte
  - Angriff auf Polyhaptoliganden
- Electrophiler Angriff auf auf koordinierte Liganden
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  - Electrophile Modifikation von Liganden

Übersicht

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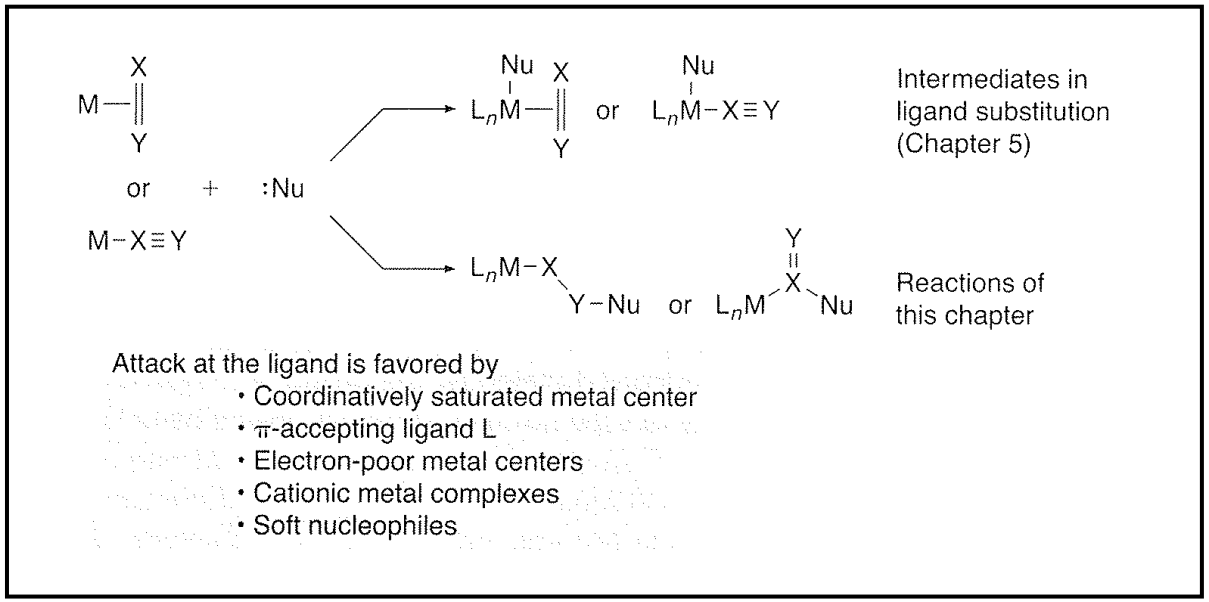
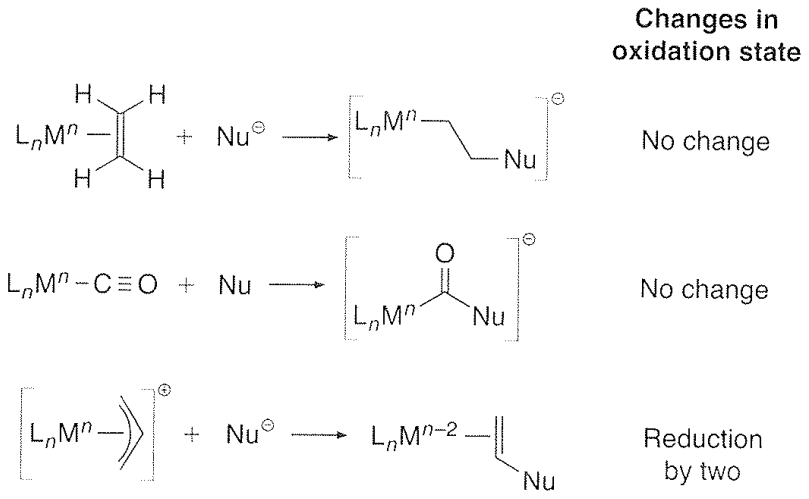
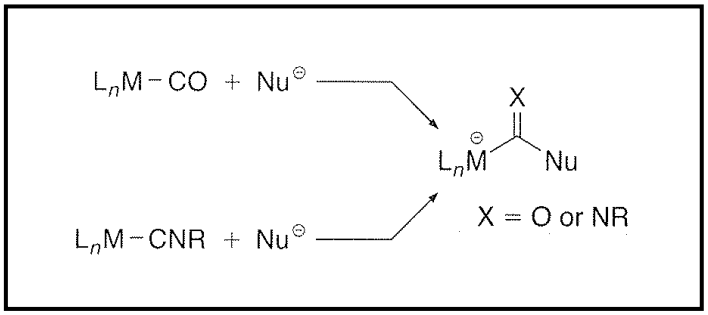
    - Bindung
    - Synthese
    - Reaktivität
  - Silylenkomplexe
  - Metall-Heteroatom Mehrfachbindungen

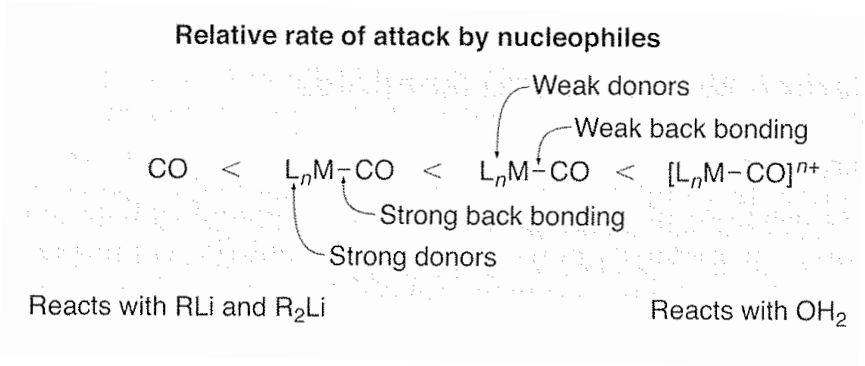
Nucleophiler Angriff





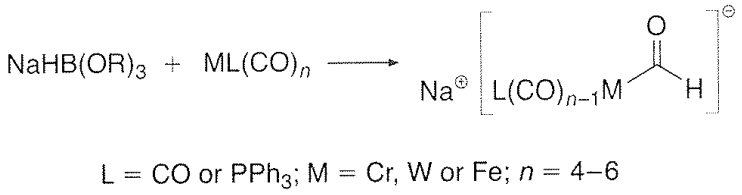
Nucleophiler Angriff auf CO und Isonitril

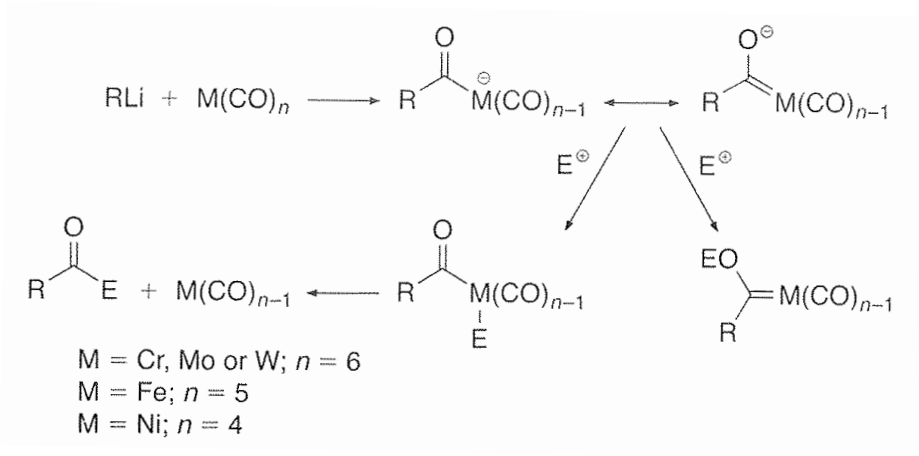


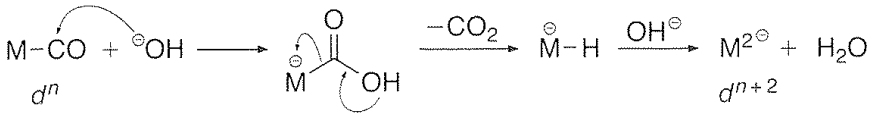


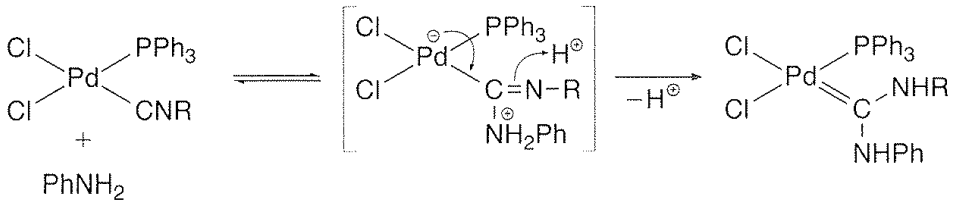
Effect of coordination, ancillary ligands, and charge on the rate of nucleophilic attack on CO.

Nucleophiler Angriff auf CO und Isonitril

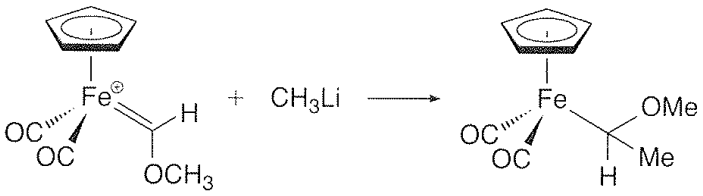


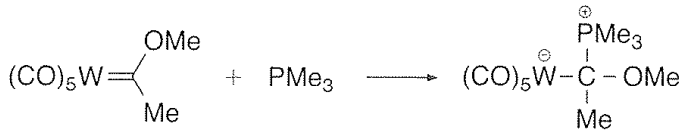


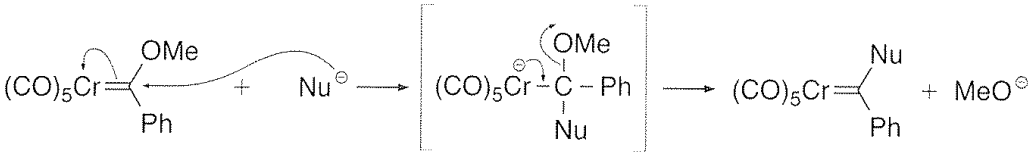




Nucleophiler Angriff auf Carbene

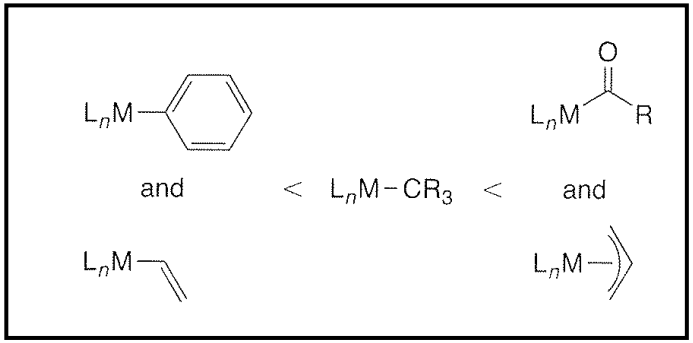


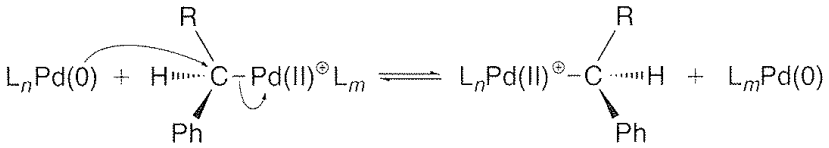


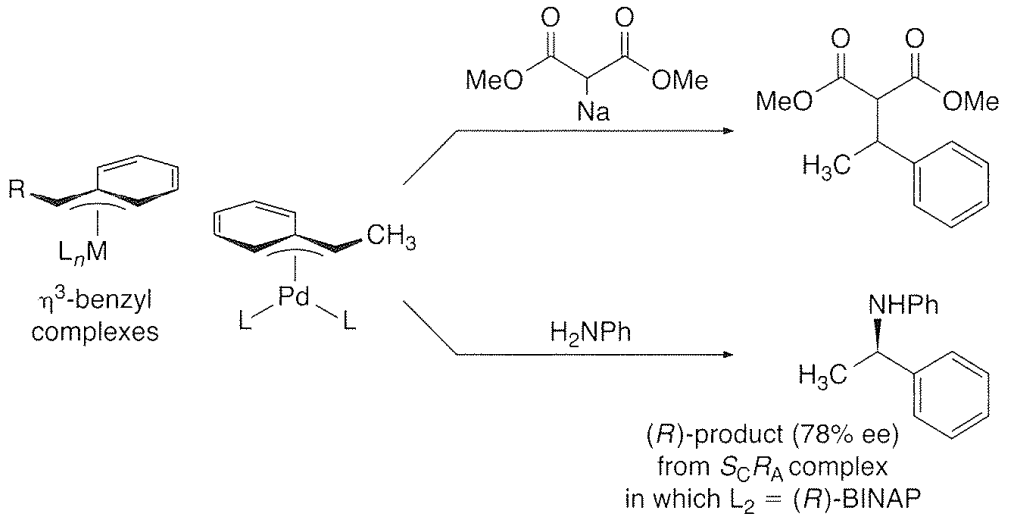


Nu = $RS^{\ominus}$, R_2NH, or PhLi

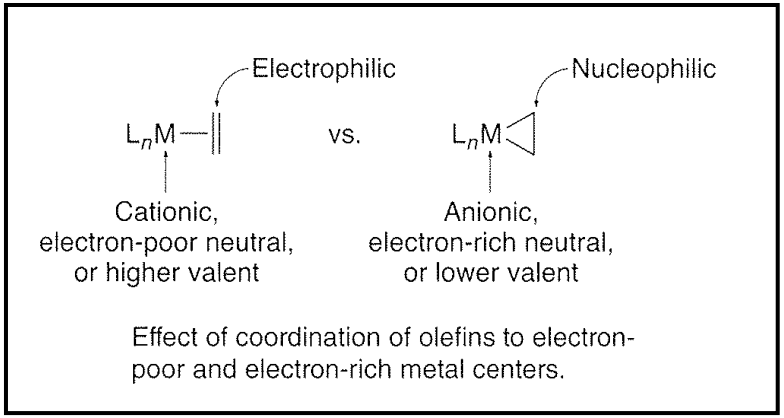
Nucleophiler Angriff auf σ-gebundene Liganden



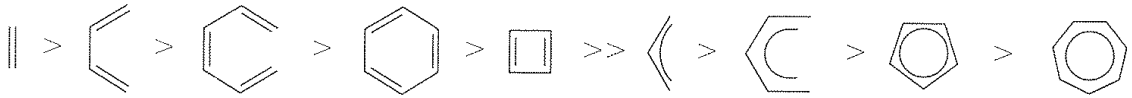




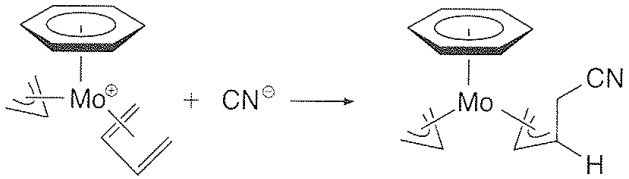
Nucleophiler Angriff auf η^2-ungesättigte Liganden



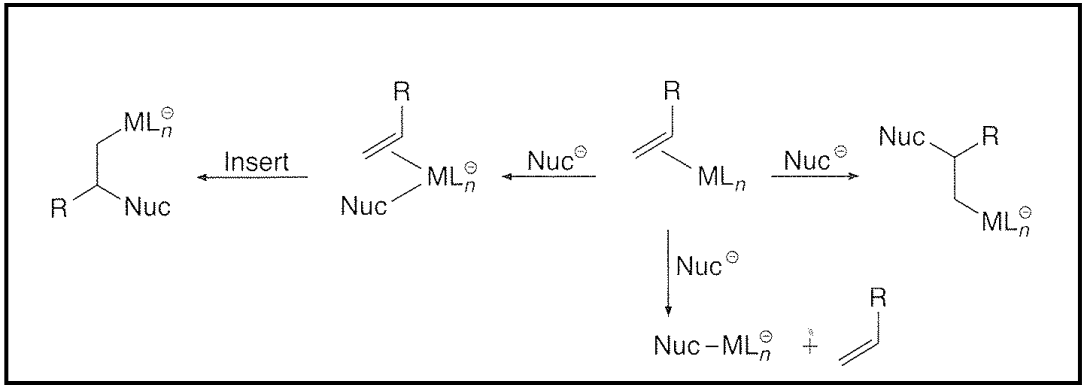
Effect of coordination of olefins to electron-poor and electron-rich metal centers.

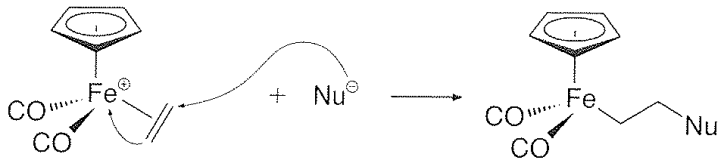


Order of reactivity of π-ligands according to the Davies–Green–Mingos rules.

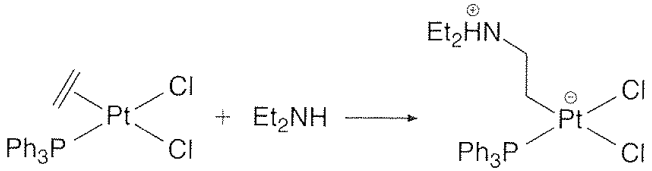


Nucleophiler Angriff auf η^2-ungesättigte Liganden

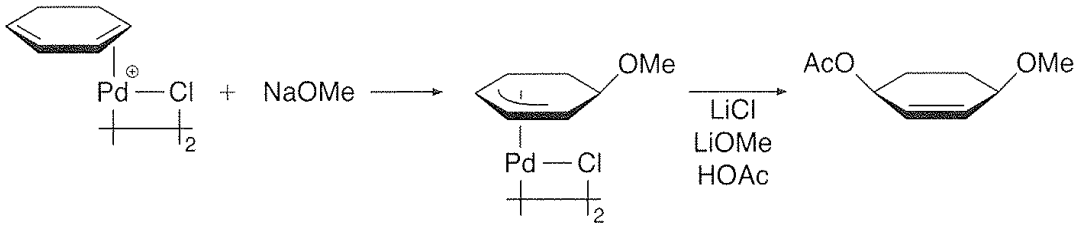


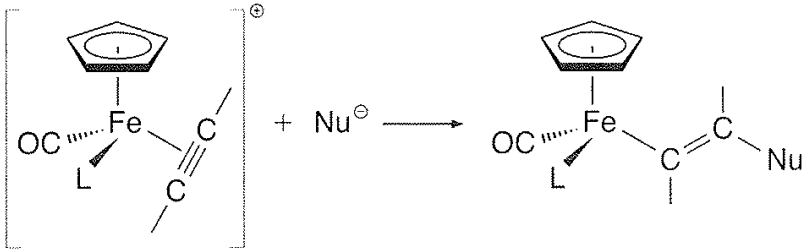


Nu$^{\ominus}$ or Nu = MeO$^{\ominus}$, ^{t}BuS$^{\ominus}$, Ph_3P, $(EtO)_3P$, R_2NH, $^{\ominus}CH_2NO_2$, $^{\ominus}CH(COMe)(CO_2Me)$
$^{\ominus}CH(CO_2Me)_2$, $^{\ominus}CH(CN)(CO_2Me)$, $R_2N-CH=C$ and $LiCuMe_2$



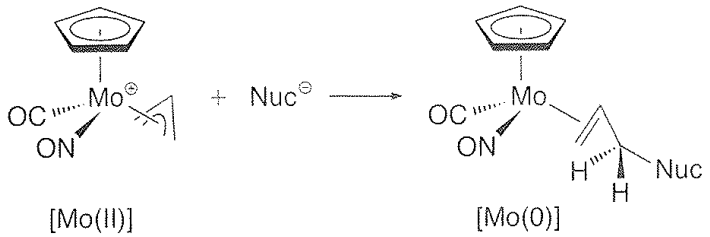
Nucleophiler Angriff auf η^2-ungesättigte Liganden

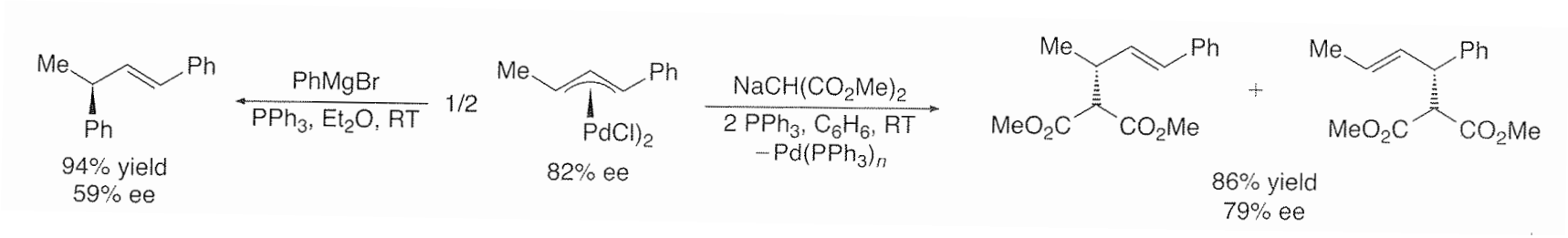


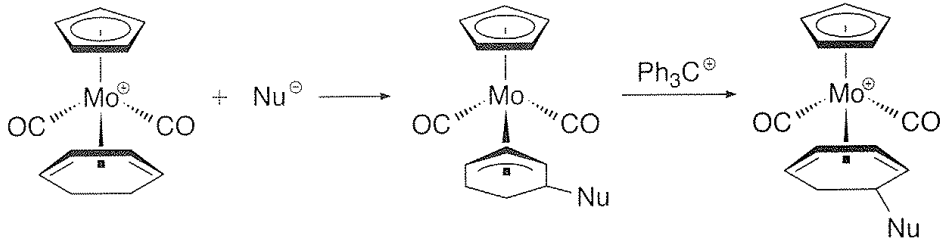


$Nu^{\ominus}$ = $PhS,^{\ominus}CN,^{\ominus}CH^{\ominus}(CO_2Et)_2$, $Ph^{\ominus}$, $Me^{\ominus}$, $H_2C{=}CH^{\ominus}$, or $MeC{\equiv}C^{\ominus}$ from $R_2Cu(CN)Li_2$
L = PPh_3 or $P(OPh)_3$

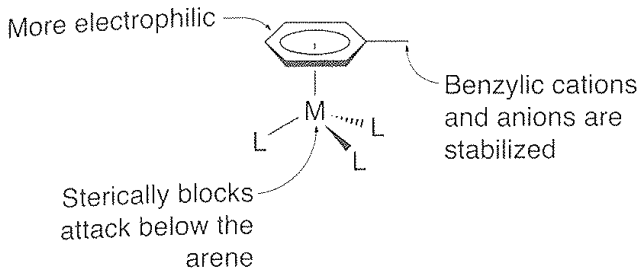
Nucleophiler Angriff auf Polyhaptoliganden

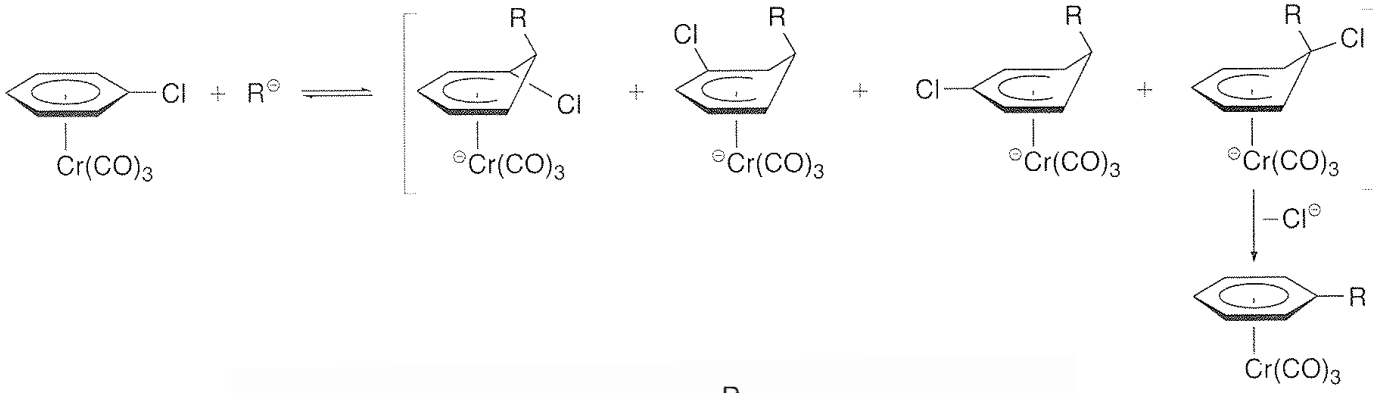


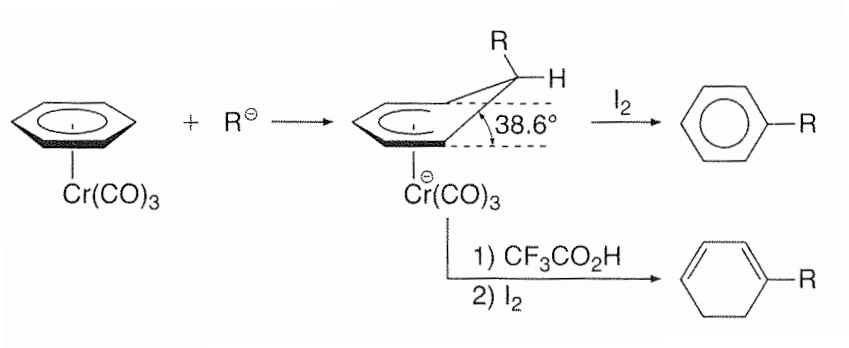




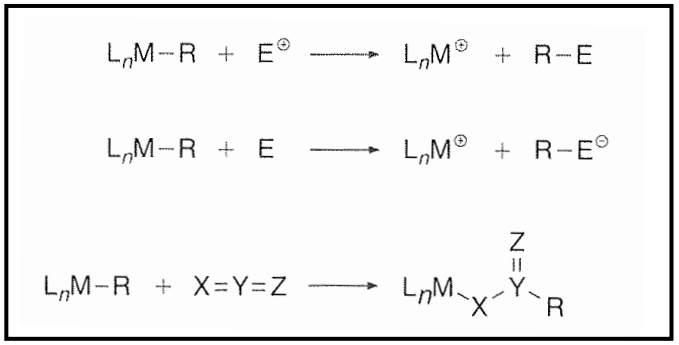
Nucleophiler Angriff auf Arenliganden

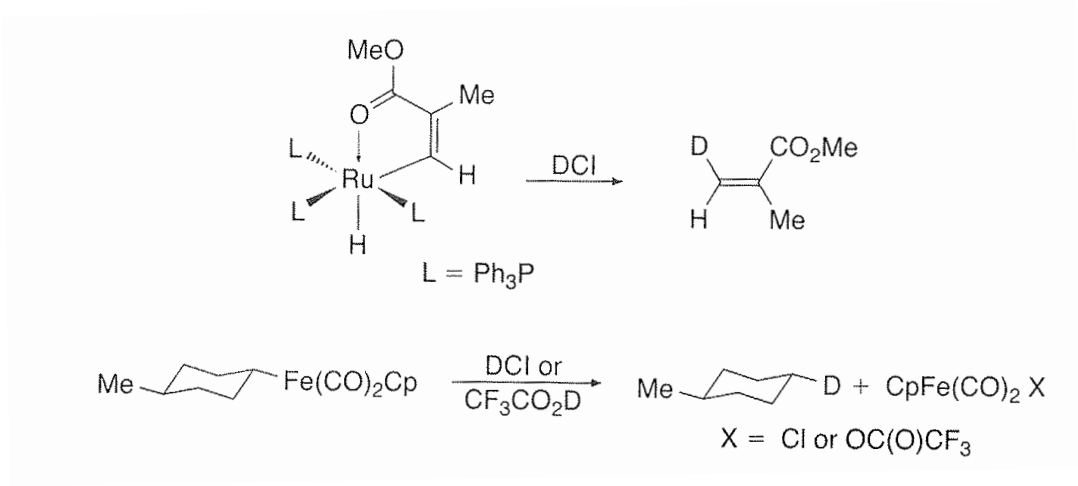


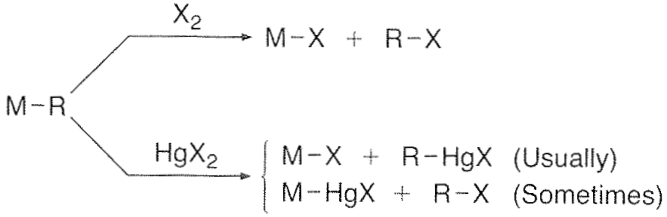




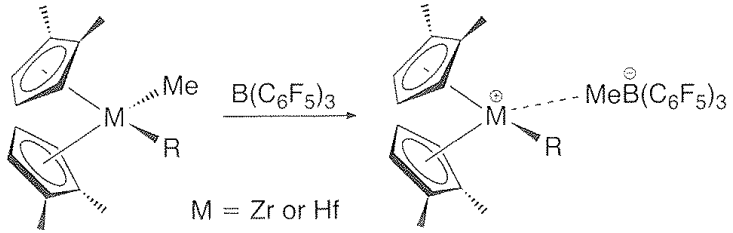
Electrophiler Angriff







Electrophiler Angriff

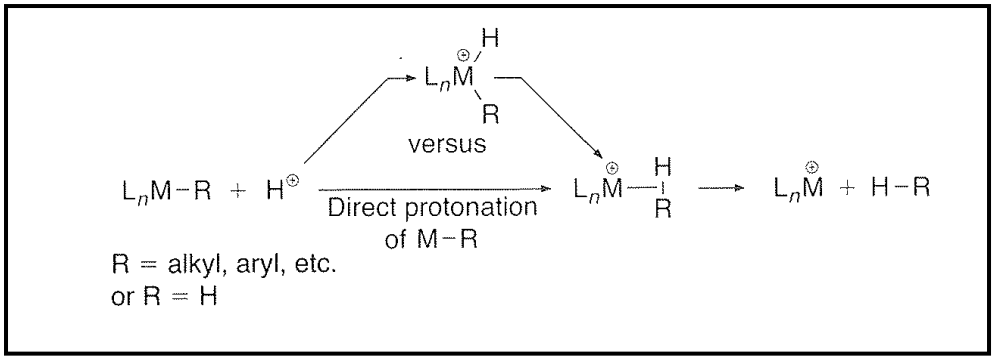


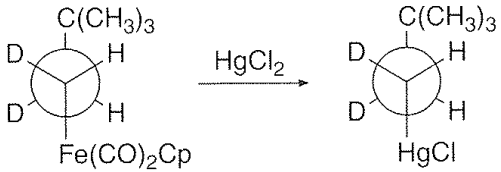
M	R	ΔH_{form}[a] (kcal/mol)
Zr	Me	−24.6(0.8)[b]
Zr	CH_2TMS	−22.6(1.0)
Zr	$CH(TMS)_2$	−59.2(1.4)
Hf	Me	−20.8(0.5)[b]
Hf	CH_2TMS	−31.1(1.6)

[a] Values are determined by titration calorimetry.

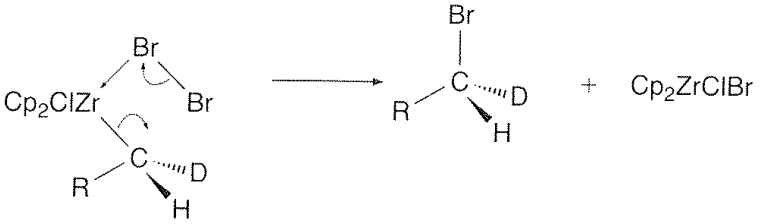
[b] From Deck, P. A.; Beswick, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 1772.

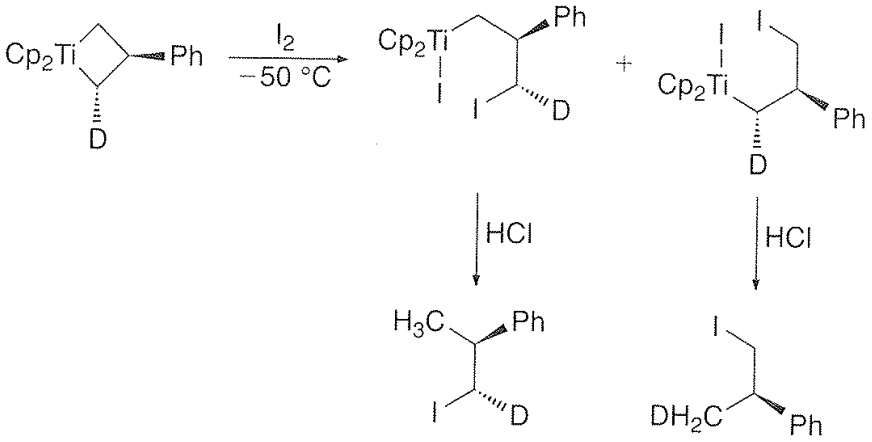
Electrophiler Angriff: Protonierung



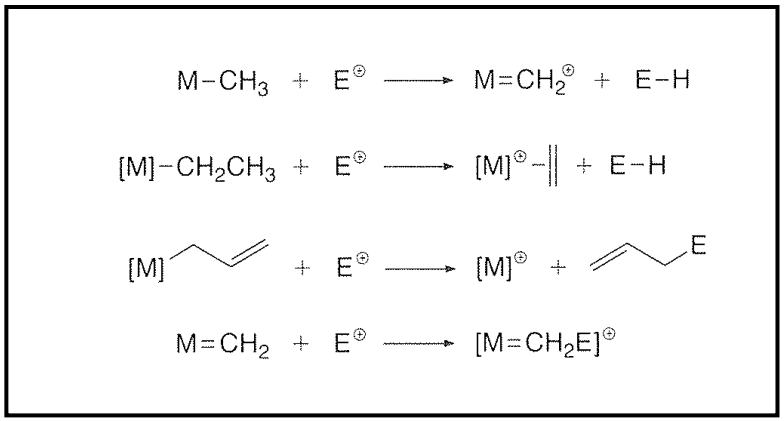


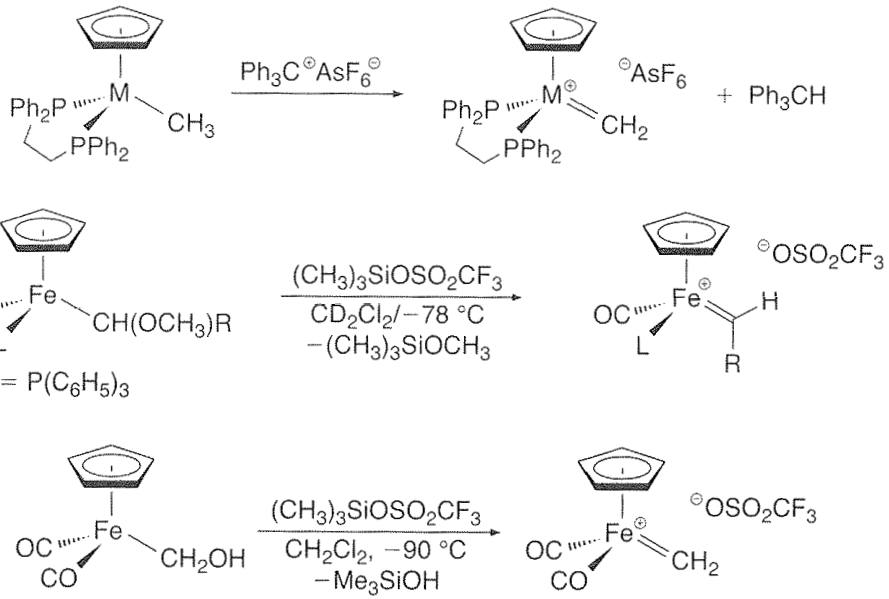
Electrophiler Angriff: ohne d-Elektronen



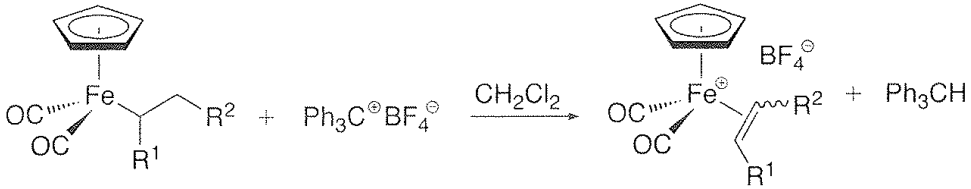


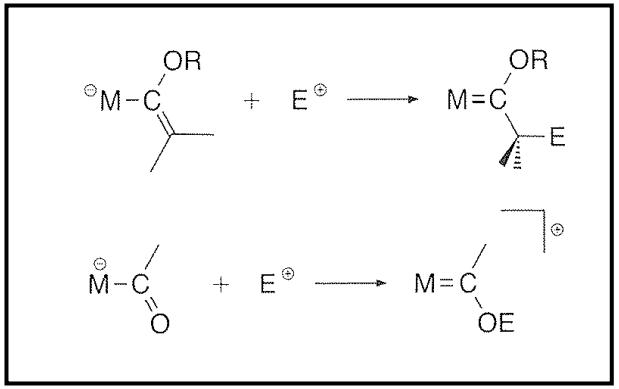
Electrophile Modifikation von Liganden

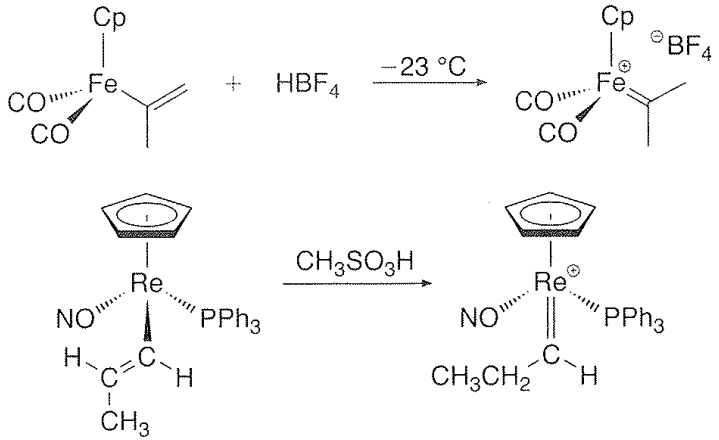




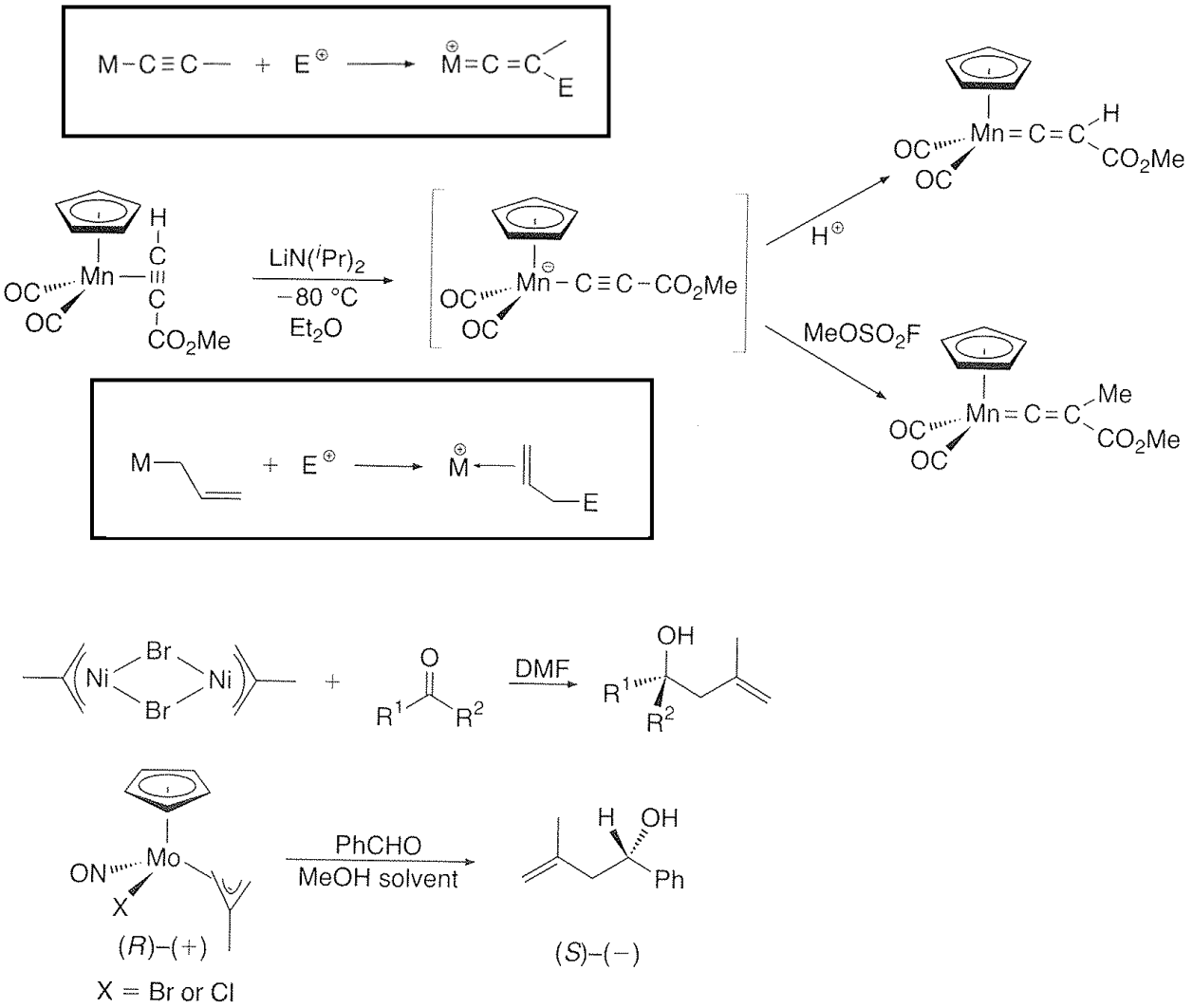
Electrophile Modifikation von Liganden



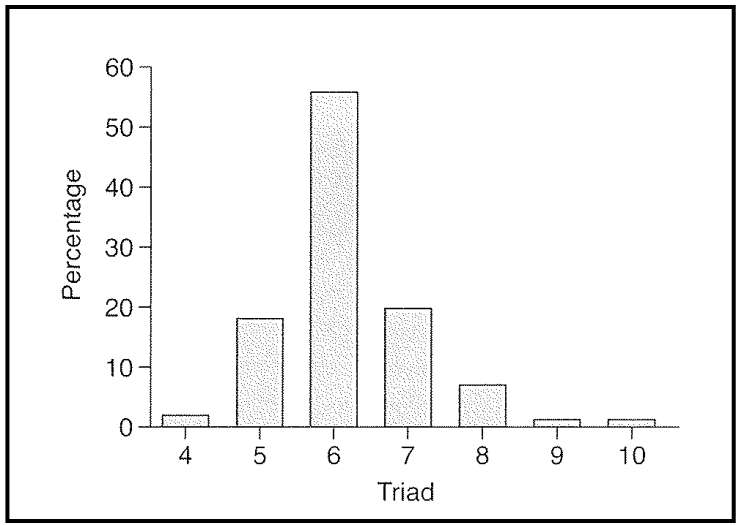




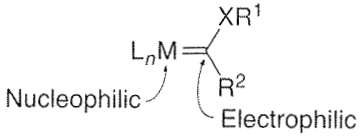
Electrophile Modifikation von Liganden



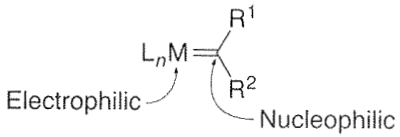
Metall-Ligand Mehrfachbindungen



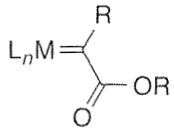
Occurrence of complexes with metal–ligand multiple bonds by triad. Data from the Cambridge Structural Database in 2000. Adapted with permission from Cundari, T. R. *Chem. Rev.* **2000**, *100*, 807.



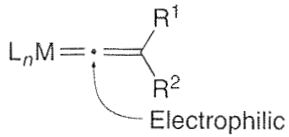
Fischer carbene complexes:
X = O, NR, S
M = low-valent, middle or late transitional metals



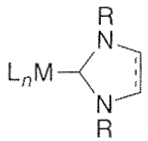
Schrock carbene or Alkylidene complexes:
R^1, R^2 = alkyl or H
M = high-valent carbyl or middle transition metals



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

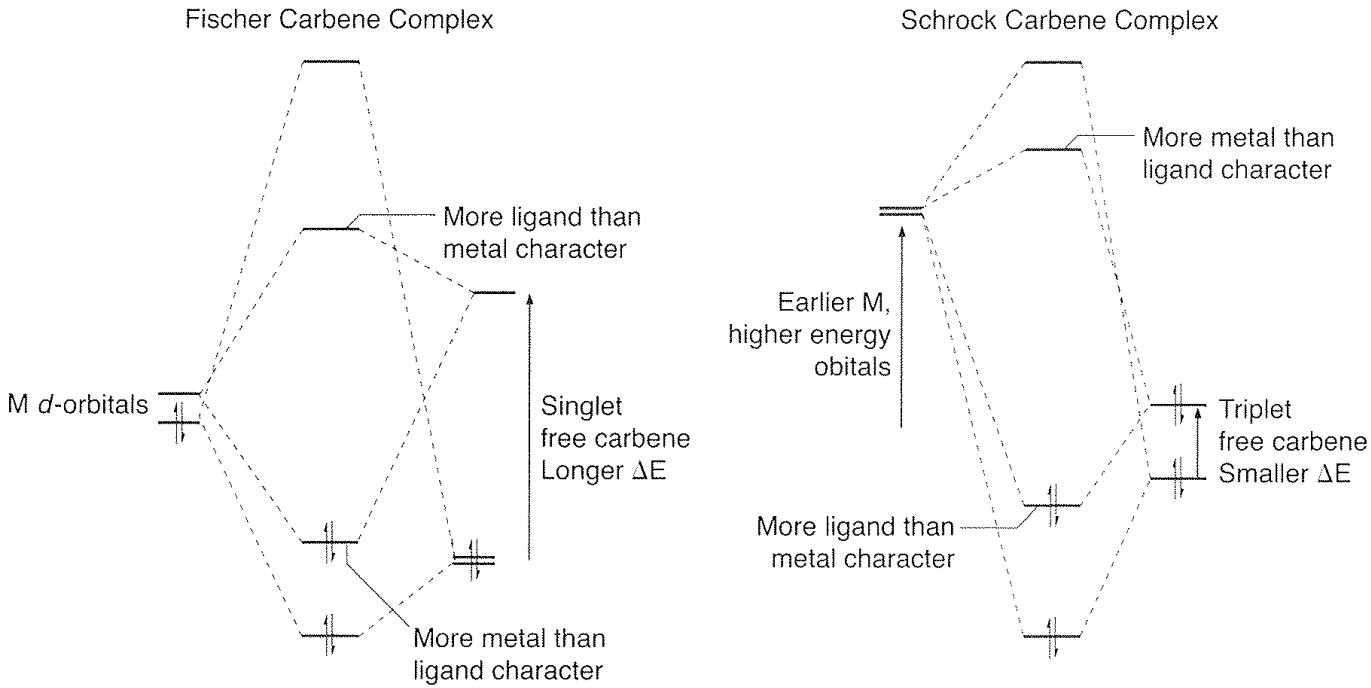


Vinylidene complexes:
R^1, R^2 = H, alkyl or aryl

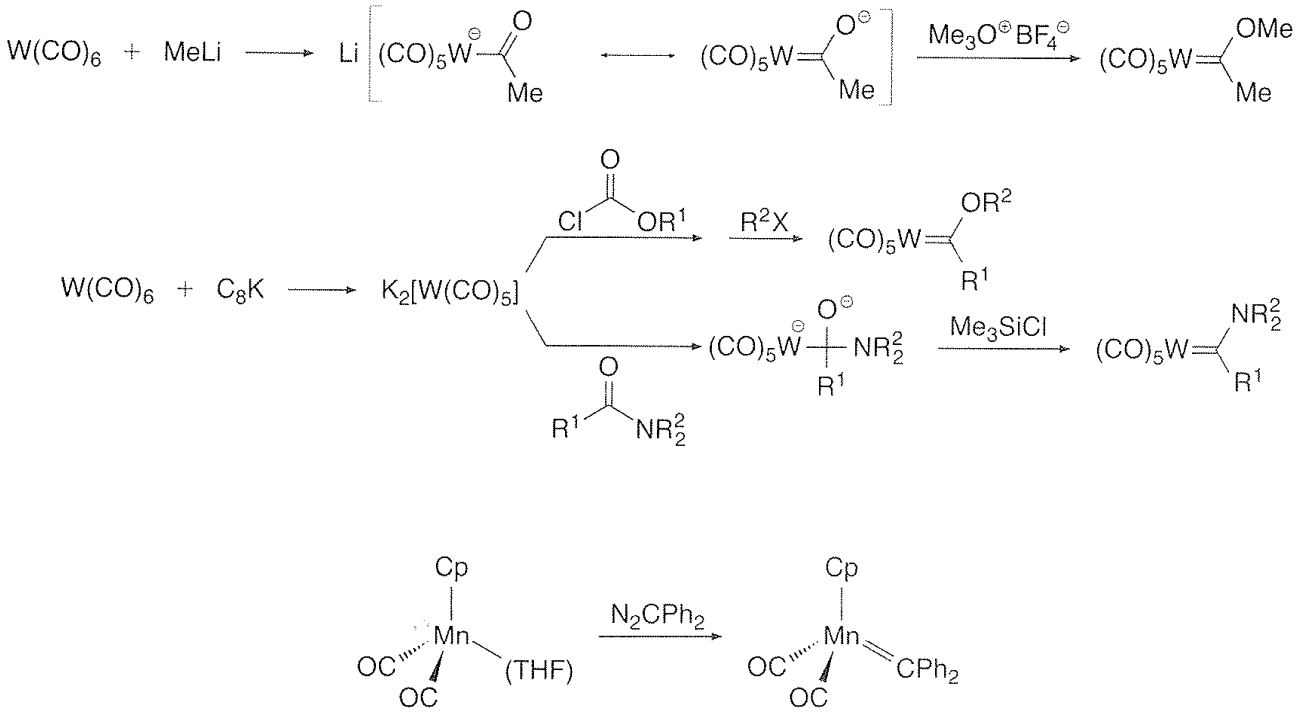


N-Heterocyclic carbene complexes:
R = aryl or alkyl

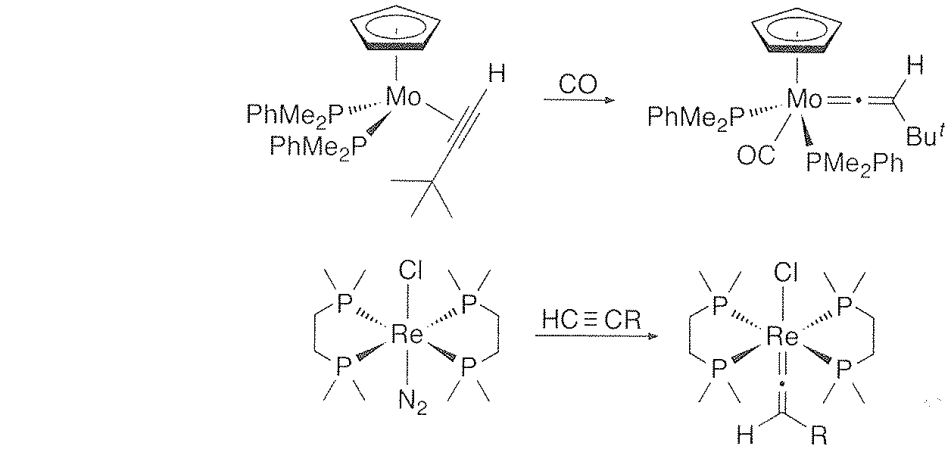
Carben-Komplexe: Fischer vs Schrock

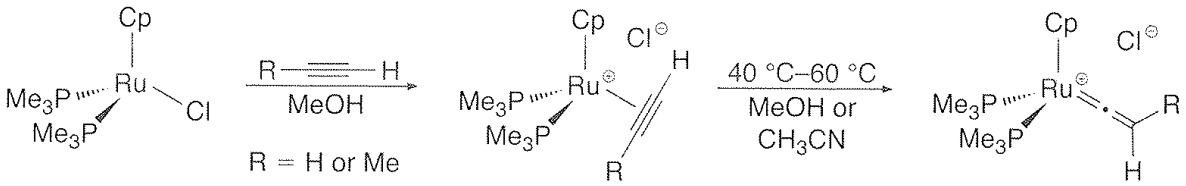


Carben-Komplexe: Synthese Fischer

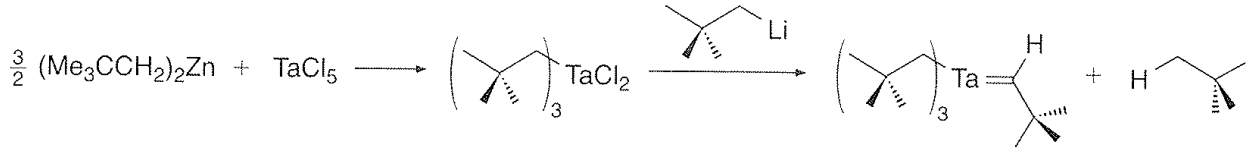


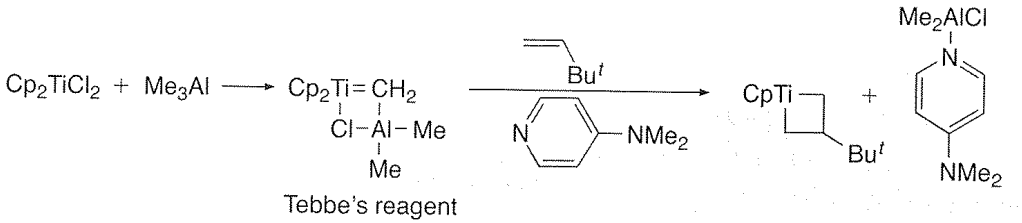
Carben-Komplexe: Synthese Vinyliden

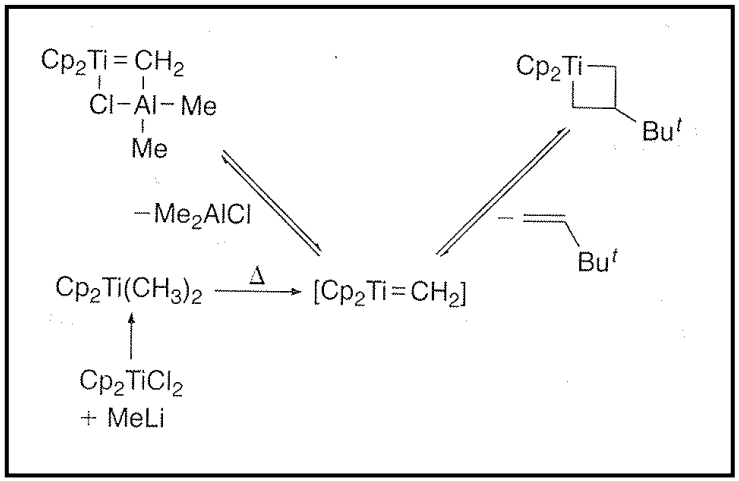




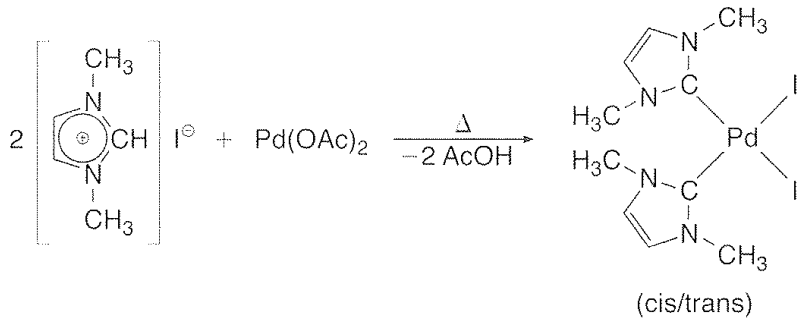
Carben-Komplexe: Synthese Schrock

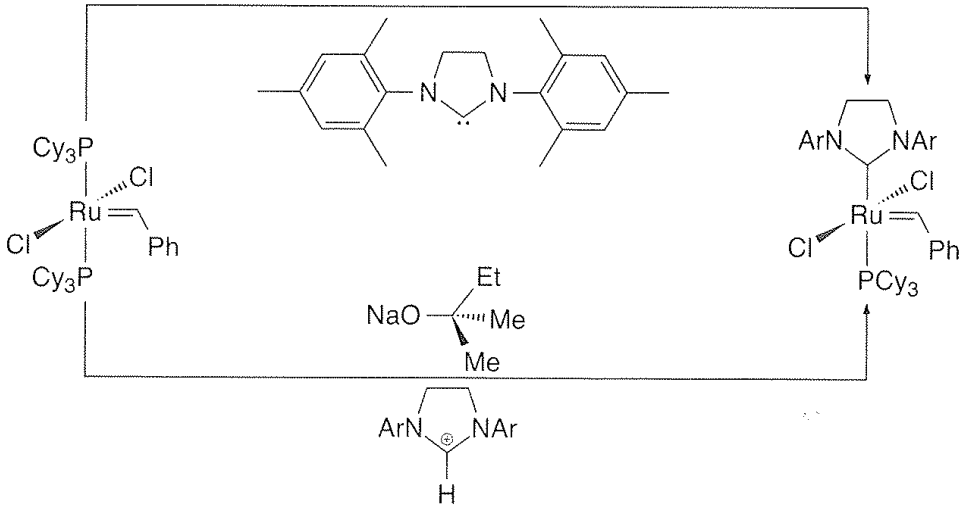




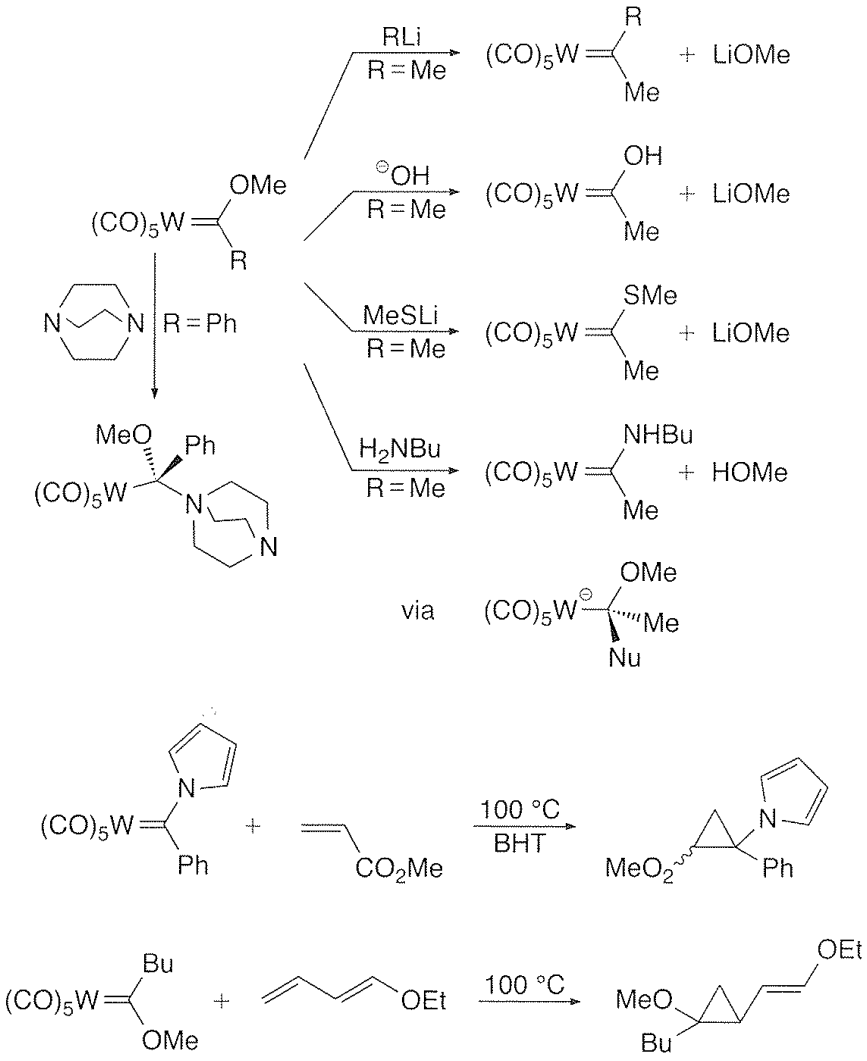


Carben-Komplexe: Synthese NHC

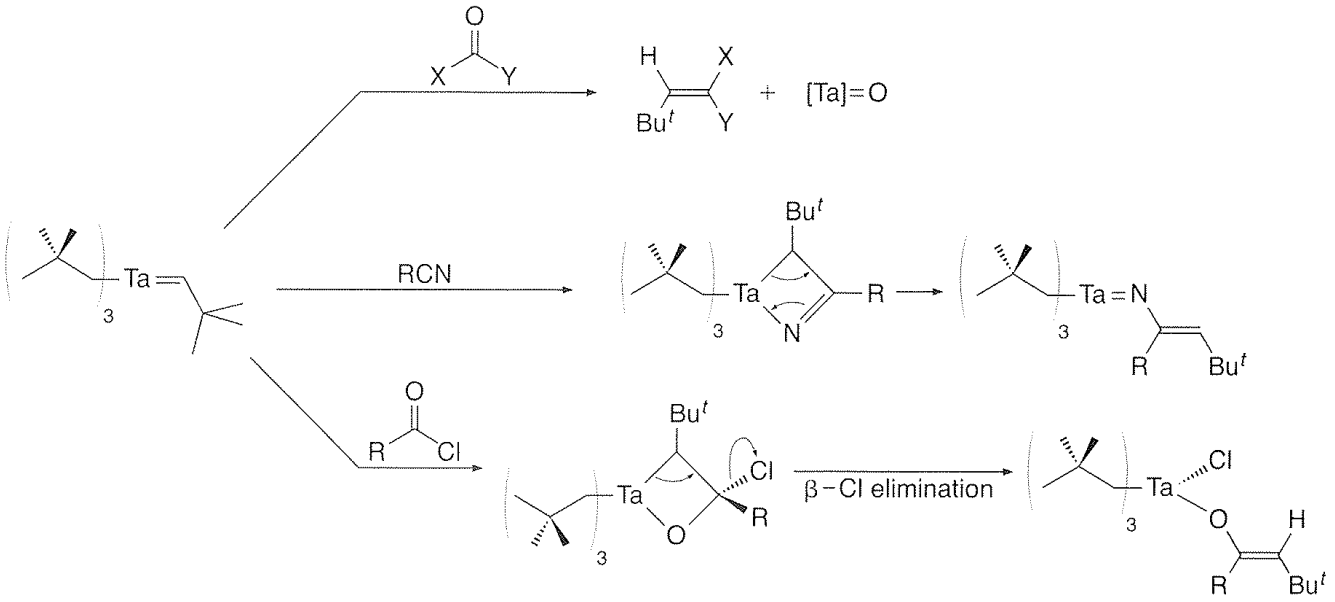


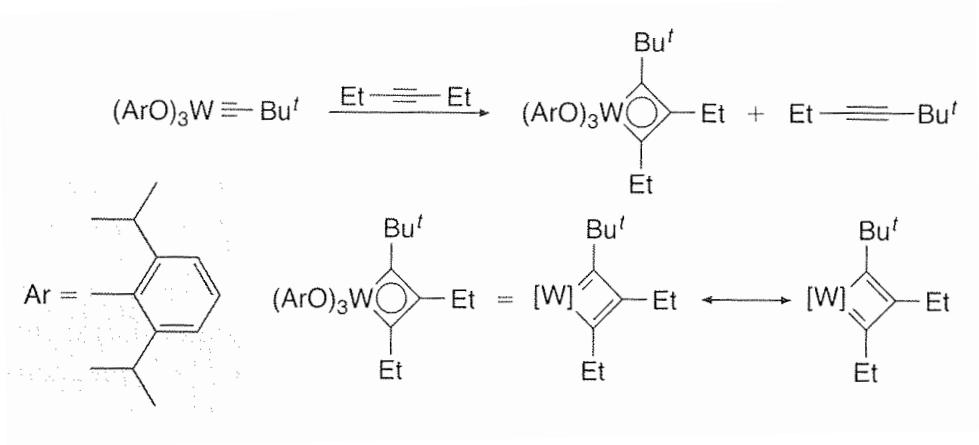


Carben-Komplexe: Reaktivität Fischer

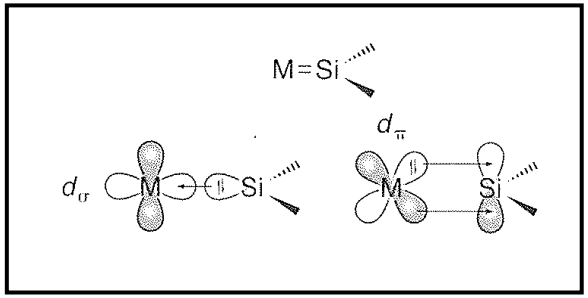


Carben-Komplexe: Reaktivität Schrock





Silylen-Komplexe



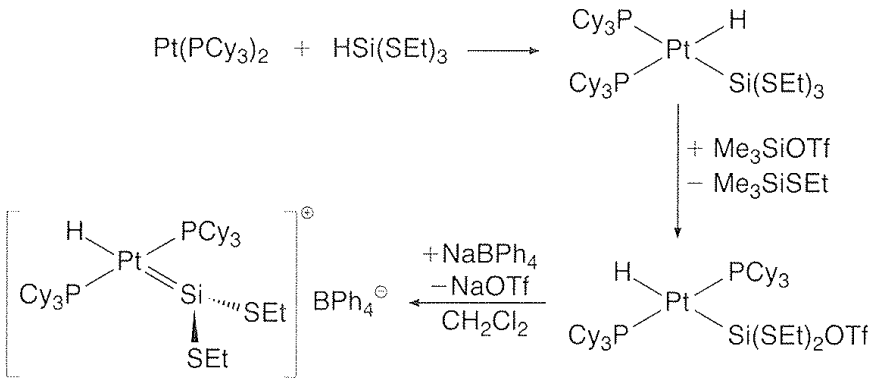
$$(^t\mathrm{BuO})_2\mathrm{SiCl}_2 + \mathrm{Na}_2\mathrm{Fe(CO)}_4 \xrightarrow[-\,2\mathrm{NaCl}]{+\,\text{base}} (\mathrm{OC})_4\mathrm{Fe}{=}\mathrm{Si}(\mathrm{O}^t\mathrm{Bu})_2$$

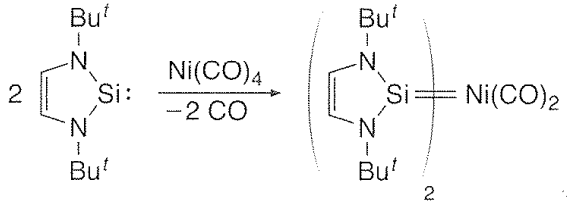
base

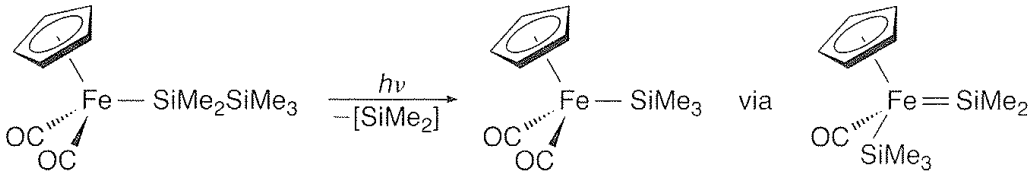
Base = HMPA or THF

$$\mathrm{Cp^*(Me_3P)_2RuSiPh_2(OTf)} + \mathrm{NaBPh_4} \xrightarrow[-\,\mathrm{NaOTf}]{+\,\mathrm{MeCN}} [\mathrm{Cp^*(Me_3P)_2Ru{=}Si(NCMe)Ph_2}]^{\oplus}\,\mathrm{BPh_4}^{\ominus}$$

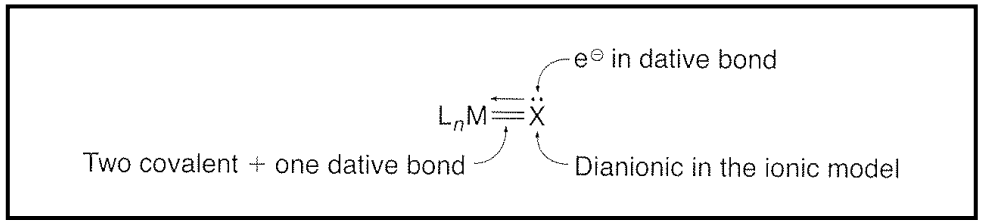
Silylen-Komplexe

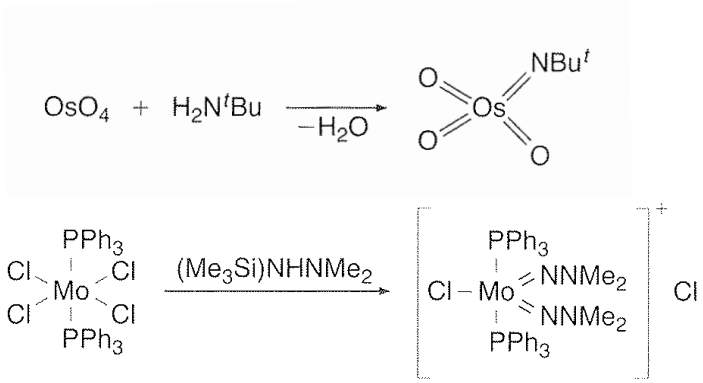


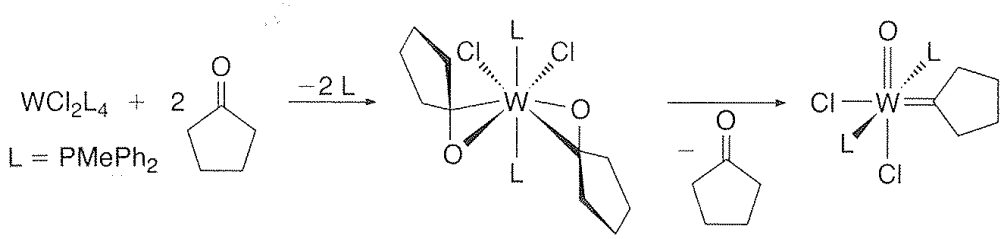




Oxo und Imido-Komplexe







Oxo und Imido-Komplexe: Reaktivität