

# Anorganische Strukturen und Reaktionsmechanismen

CHE.367

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## Übersicht

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- Kovalente C-Liganden
  - Alkyl
  - Aryl und Vinyl
  - Alkynyl
  - Cyanide
  - Carbine
  - Allyl, Benzyl, Trimethylenmethan
  - Cyclopentadienyl und Verwandte
- Hydride

## Übersicht

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- Kovalente Heteroatom-Liganden
  - Amide
  - Nitrosyl
  - Polydentate N-Donors
  - $\beta$ -Diketimidinate
  - Alkoxide
  - Boryl
  - Phosphide
  - Silyl
  - Halogenid

# Hydrocarbyle

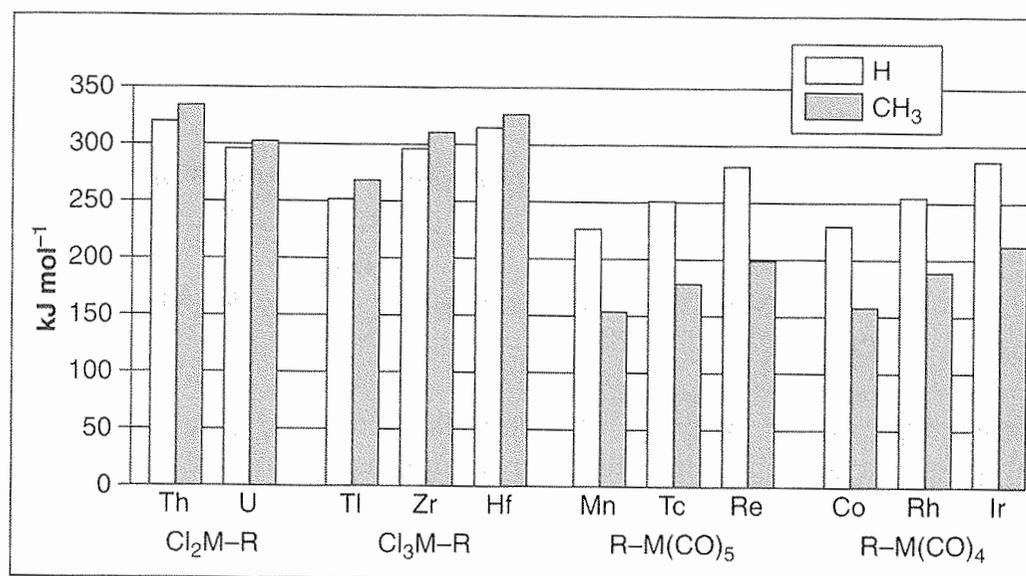
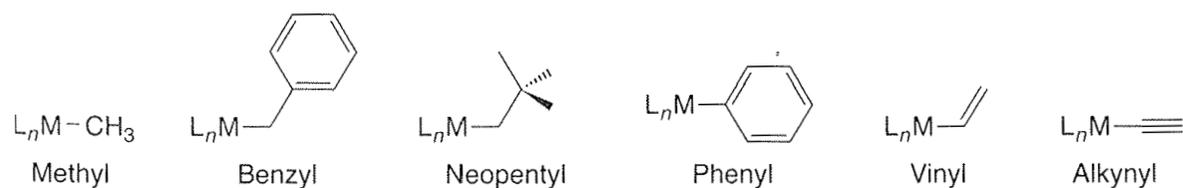


Figure 3.2. Relative strengths of representative M-C bonds. Data from reference 30.

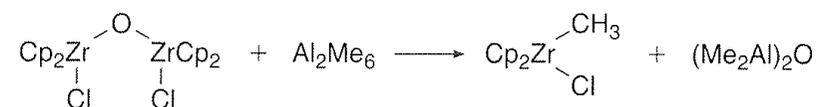
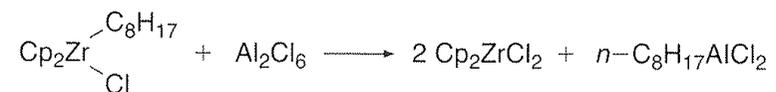
# Alkylkomplexe

## Transmetallierung

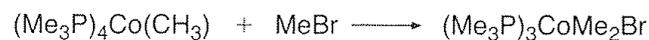
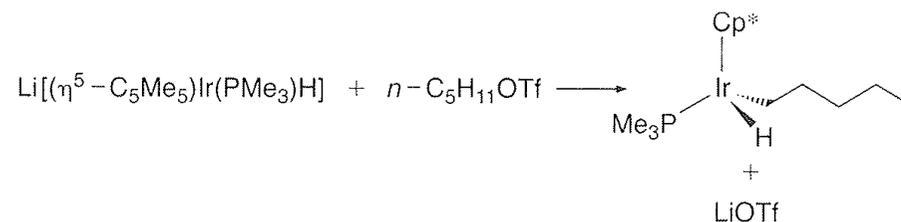
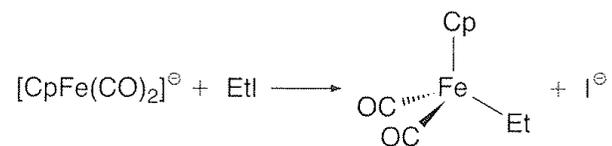


M = Li, Mg, Zn, Al

M' = transition metal

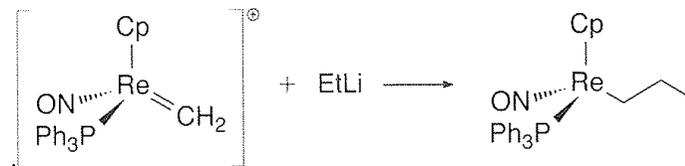
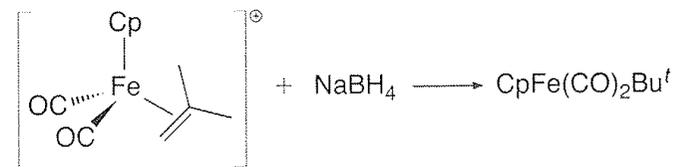
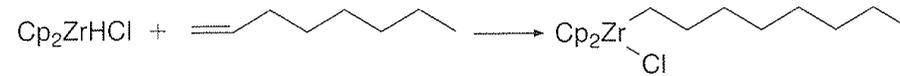


## Alkylierung/Oxidative Addition

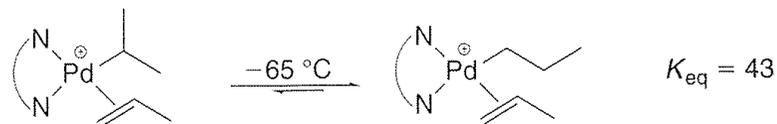
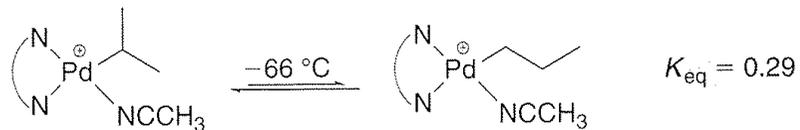
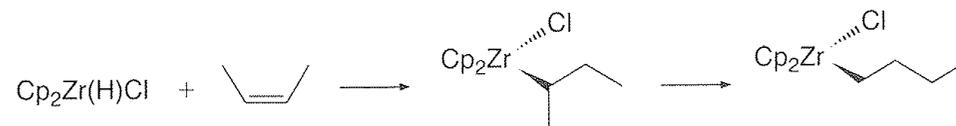
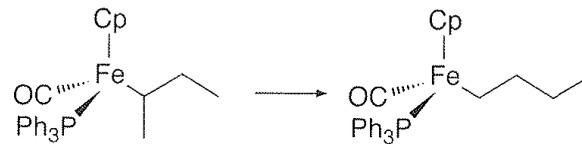
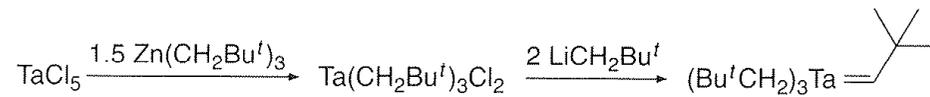


# Alkylkomplexe

## Weiter Methoden

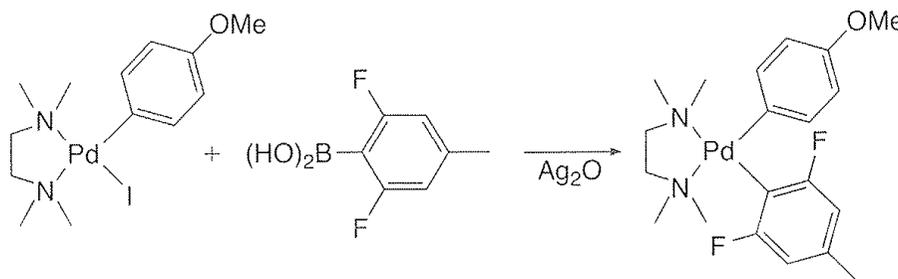
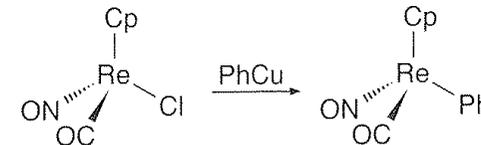
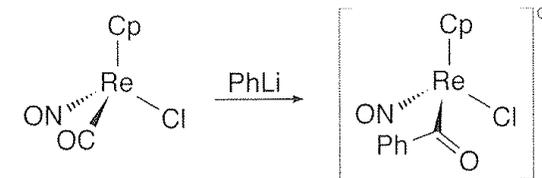
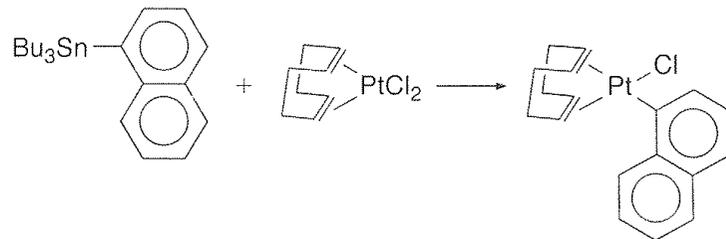
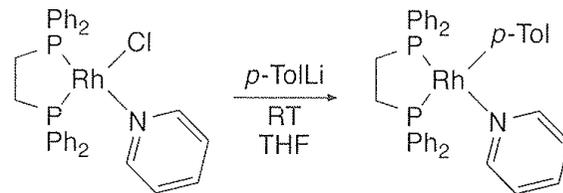


# Alkylkomplexe Reaktivität

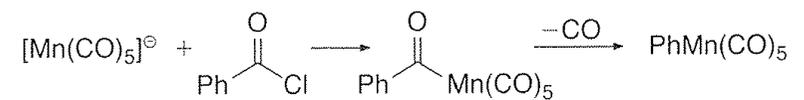
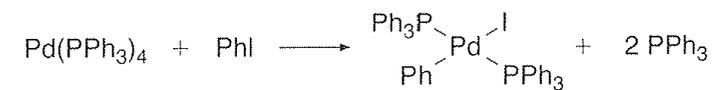


# Arylkomplexe

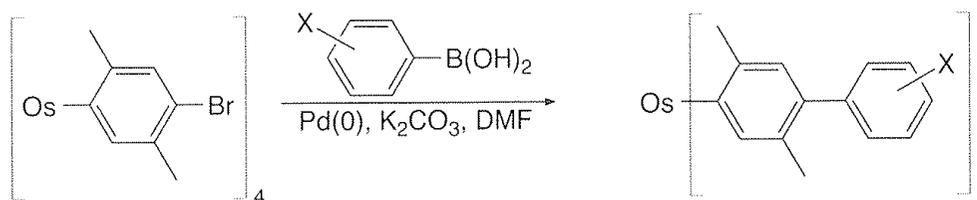
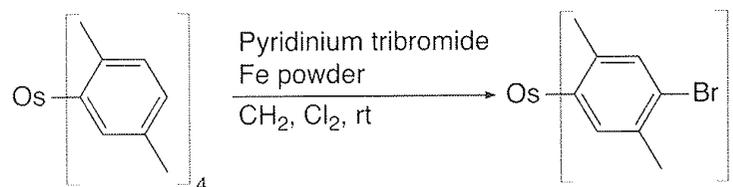
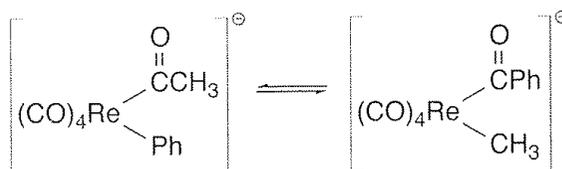
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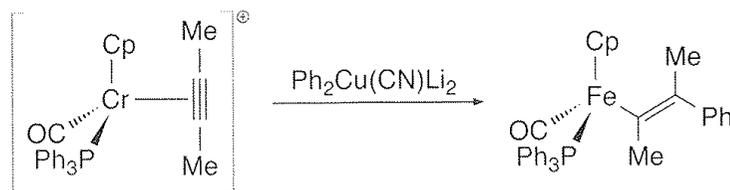
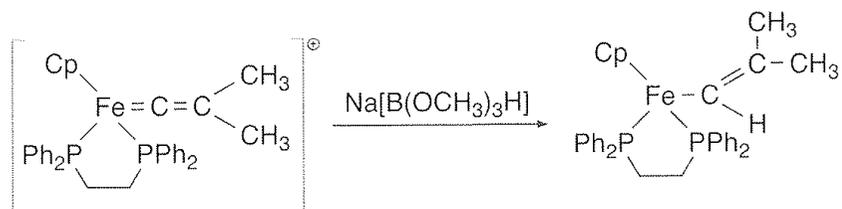
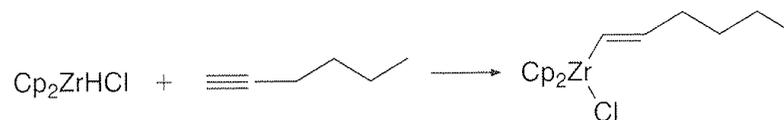
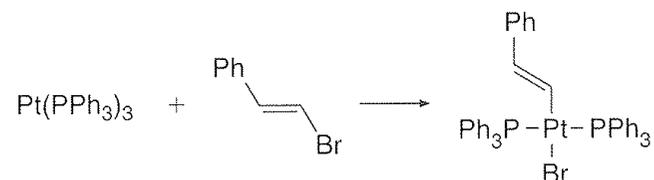
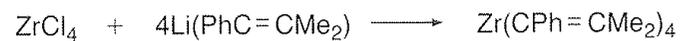
## Oxidative Addition



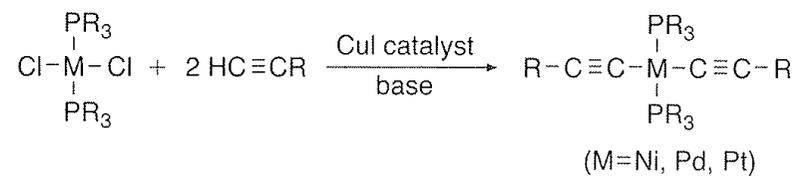
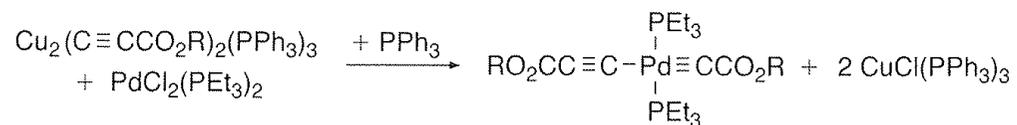
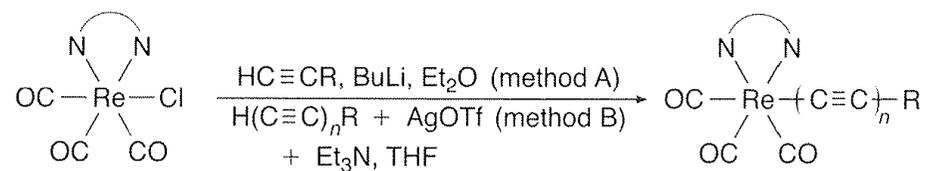
# Arylkomplexe: Reaktivität



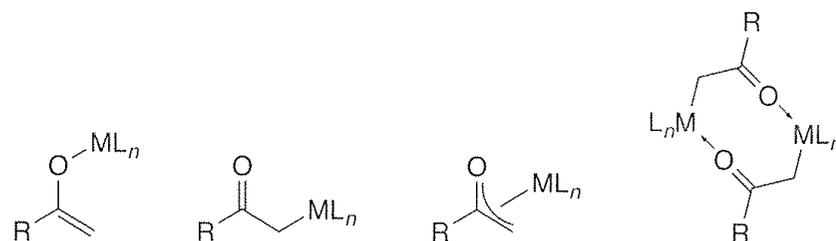
# Vinylkomplexe



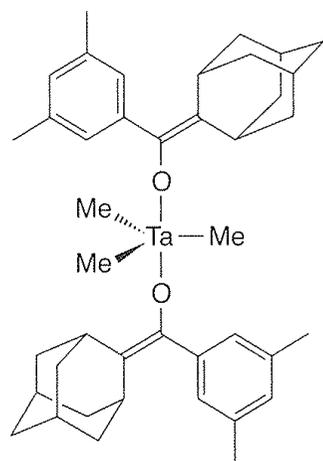
# Alkynylkomplexe



# Enolatkomplexe



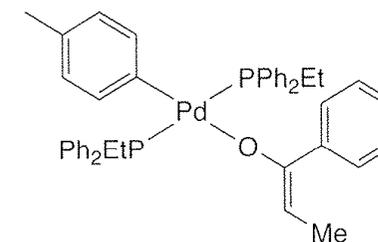
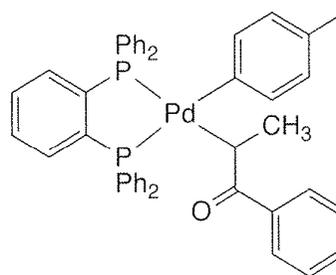
Binding modes of transition metal enolate complexes.



Early metals

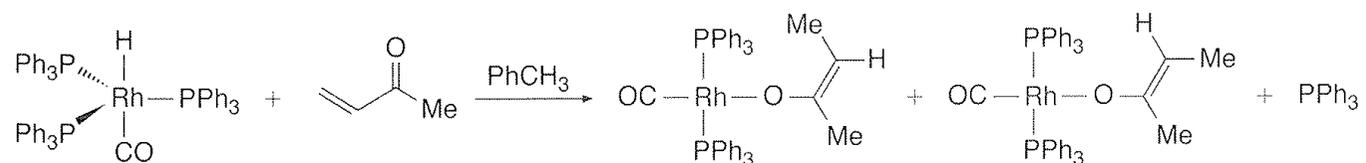
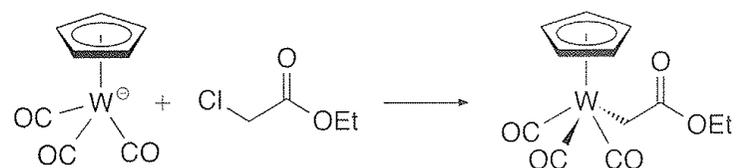
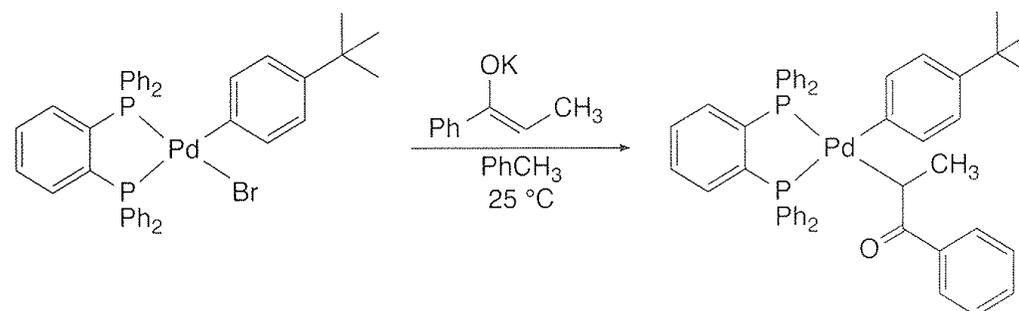
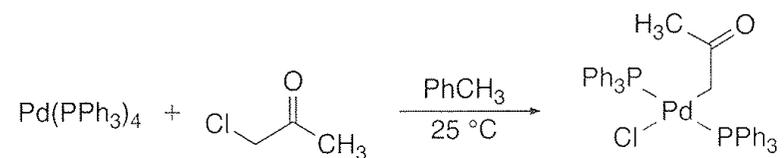


M = Zr or Ti  
R = Et or Me

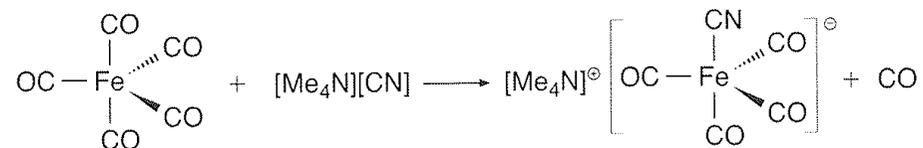
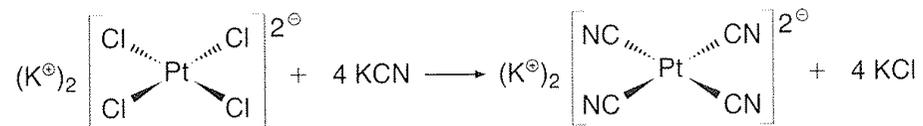
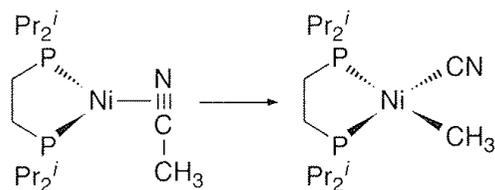
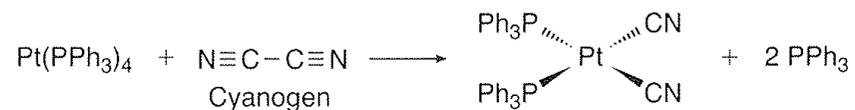
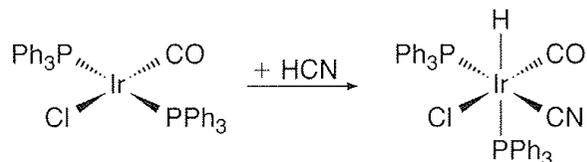


The effect of the trans ligand on C- vs. O-binding modes of palladium enolates.

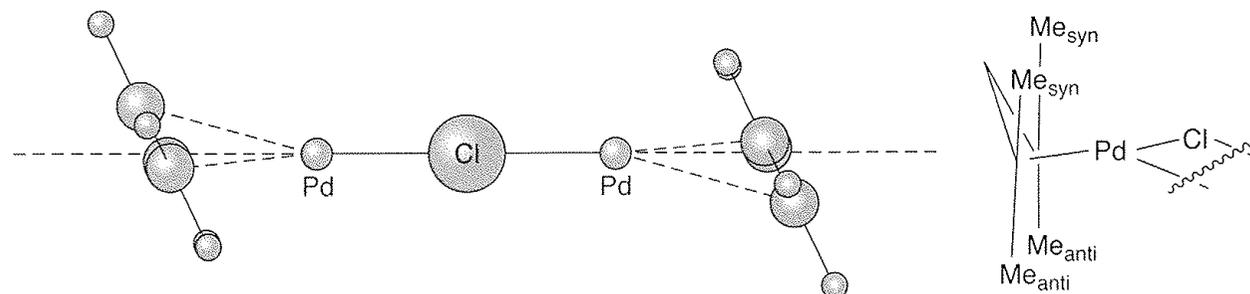
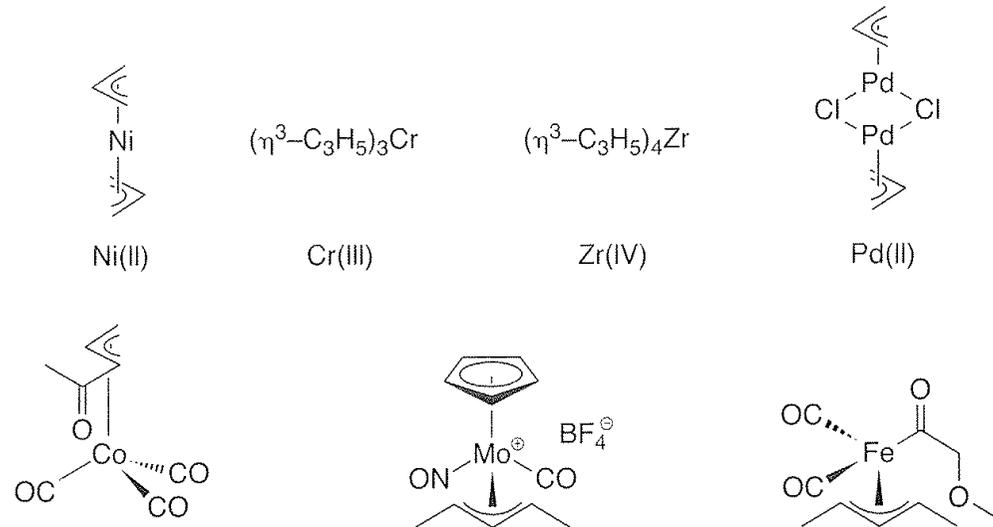
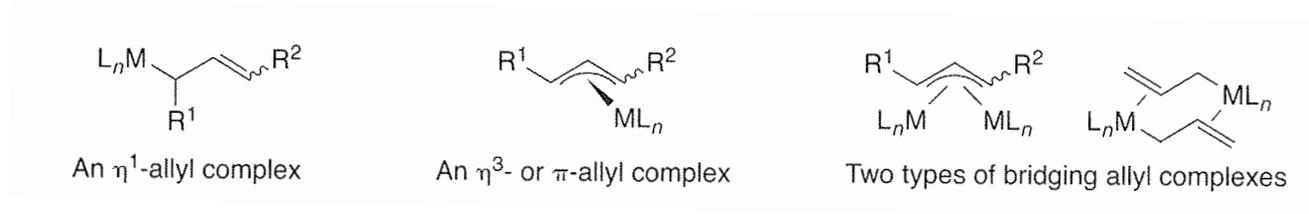
# Enolatkomplexe: Synthese



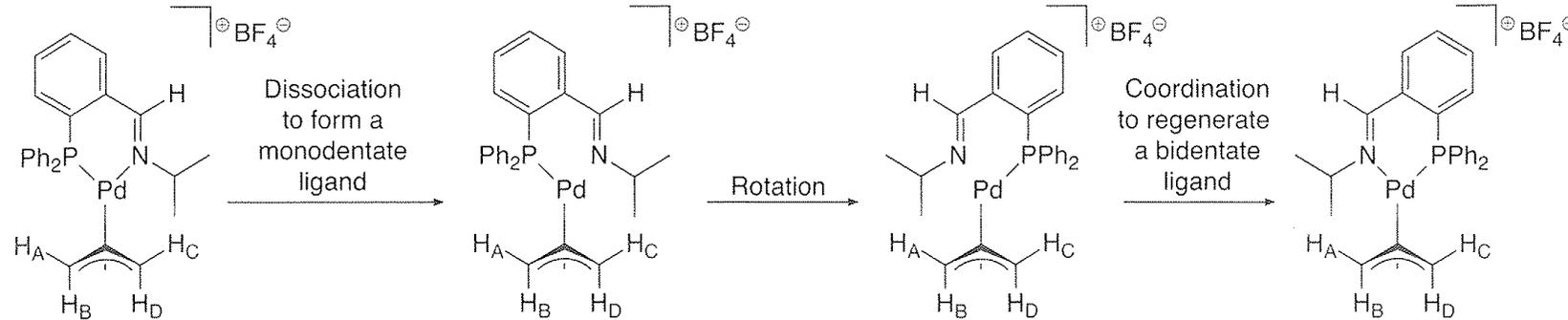
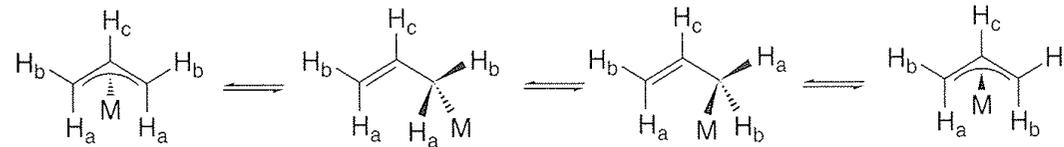
# Cyanidkomplexe: Synthese



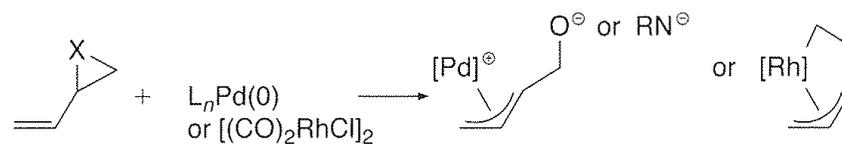
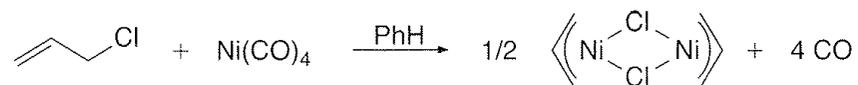
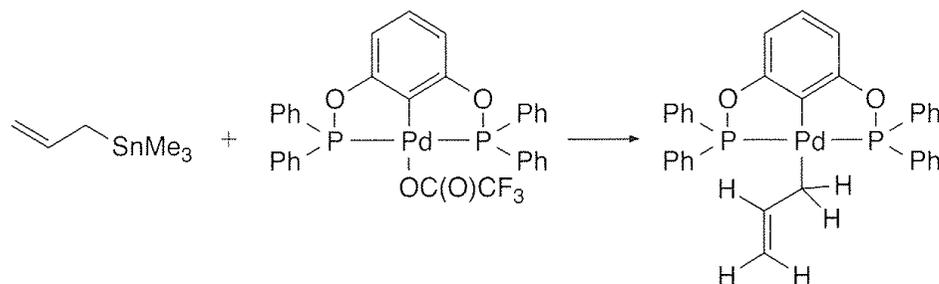
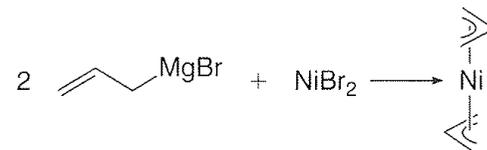
# Allylkomplexe



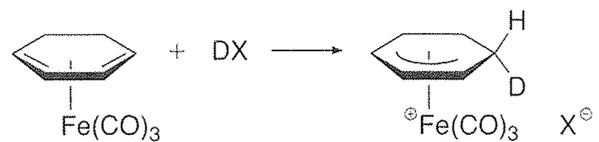
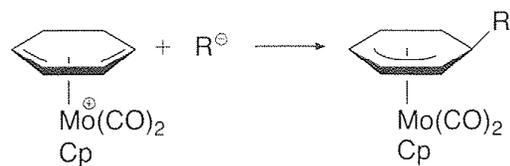
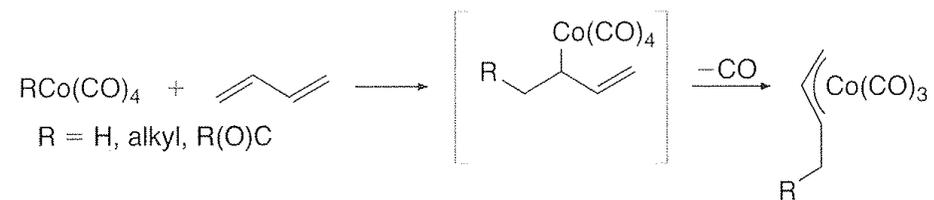
# Allylkomplexe: Dynamik



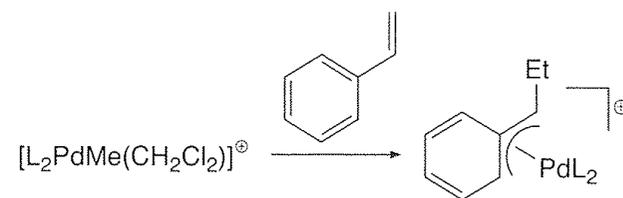
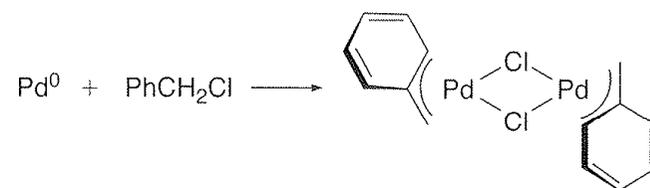
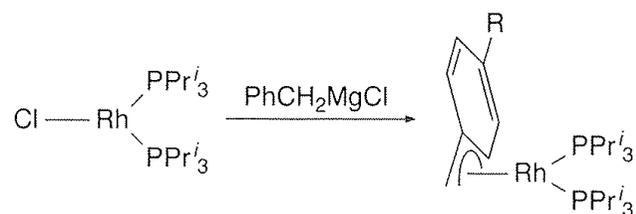
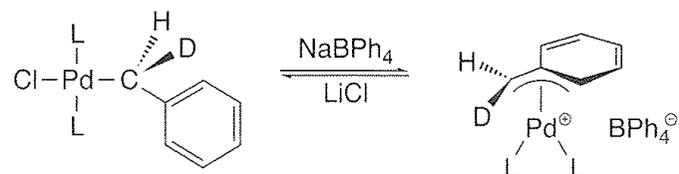
# Allylkomplexe: Synthese



# Allylkomplexe: Synthese

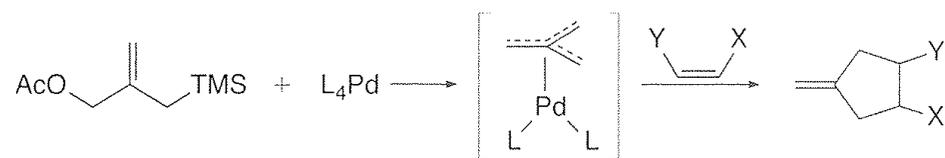
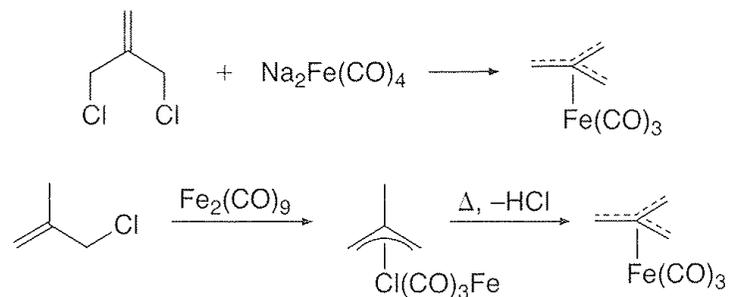


# Benzykomplexe: Synthese



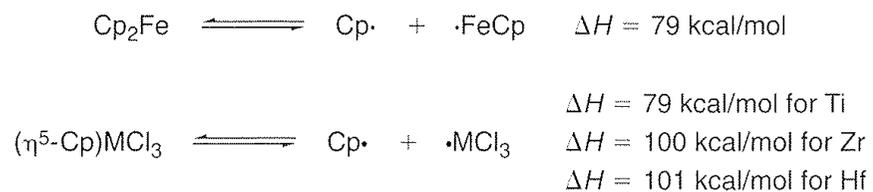
L<sub>2</sub> = Tetramethylethylenediamine (TMEDA)

# Trimetlylenmethan (TMM) Komplexe

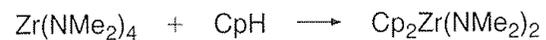


# Cyclopentadienyl (Cp) Komplexe

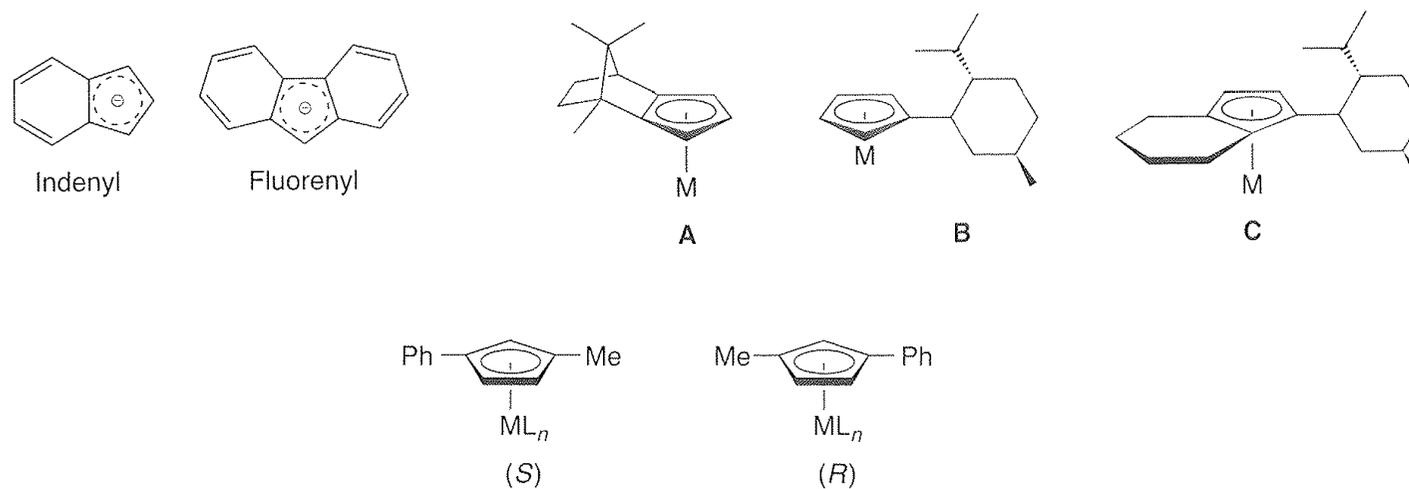
## Thermodynamik



## Synthese

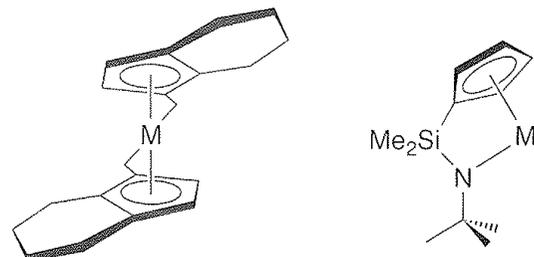


## Cp-Typen

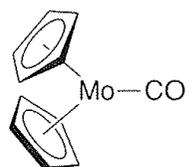
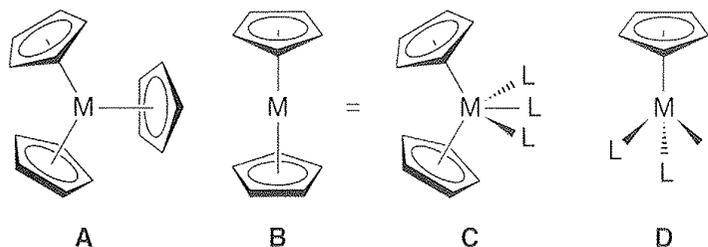


# Cyclopentadienyl (Cp) Komplexe

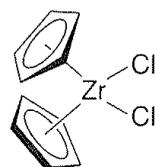
## Ansa-Komplexe



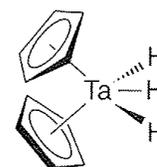
## Cp-Komplexarten



**A**  
 $\text{Cp}_2\text{Mo}(\text{CO})$   
 $\text{Mo}(\text{II}), d^4, 18 e^-$

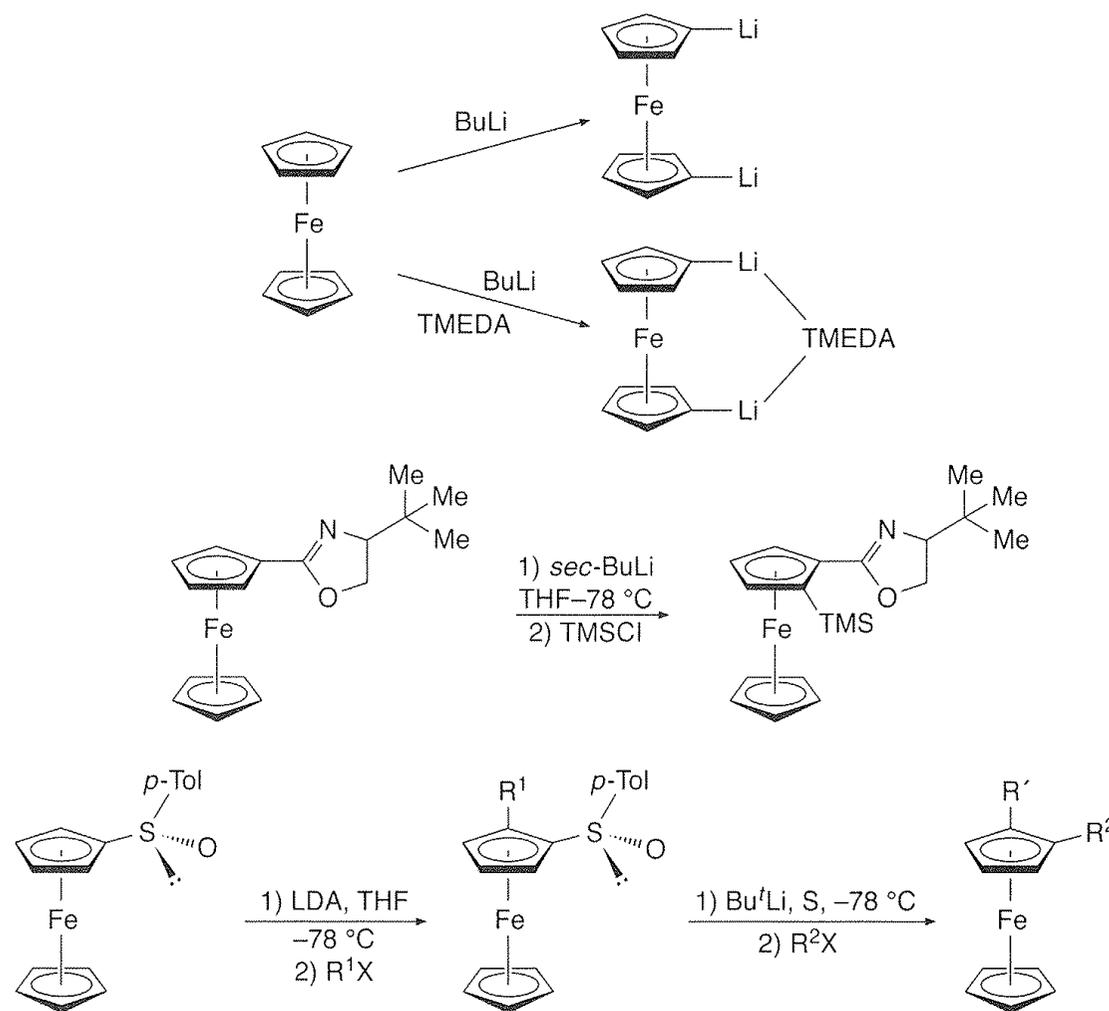


**B**  
 $\text{Cp}_2\text{ZrCl}_2$   
 $\text{Zr}(\text{IV}), d^0, 16 e^-$



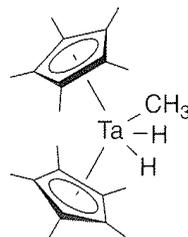
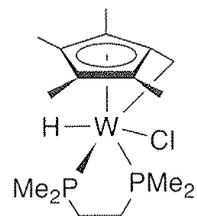
**C**  
 $\text{Cp}_2\text{TaH}_3$   
 $\text{Ta}(\text{V}), d^0, 18 e^-$

# Cyclopentadienyl (Cp) Komplexe

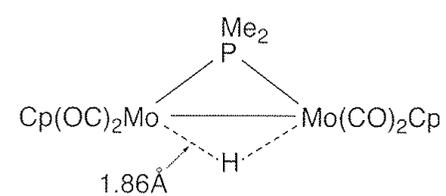
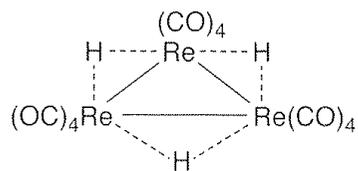
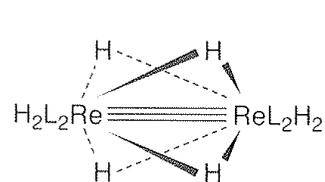


# Hydride

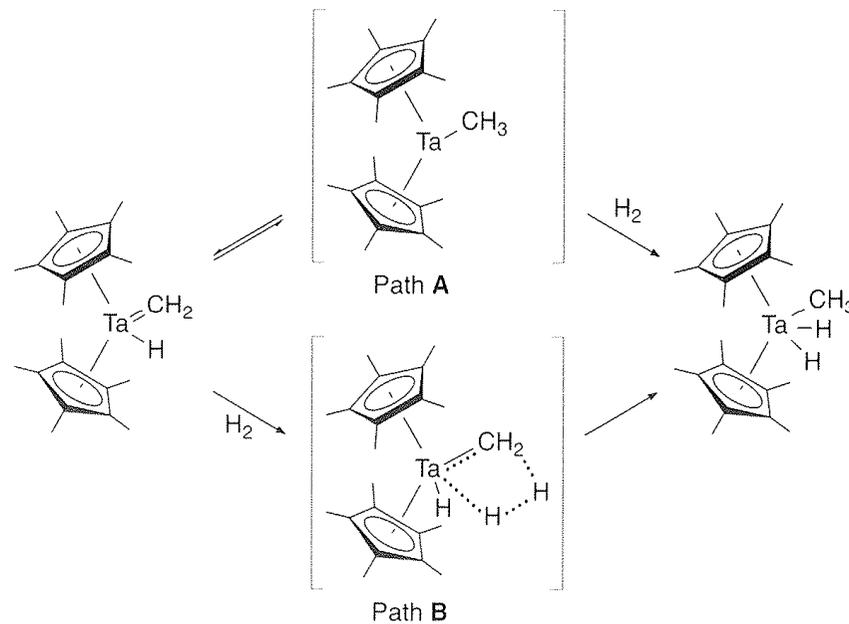
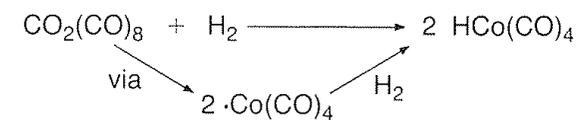
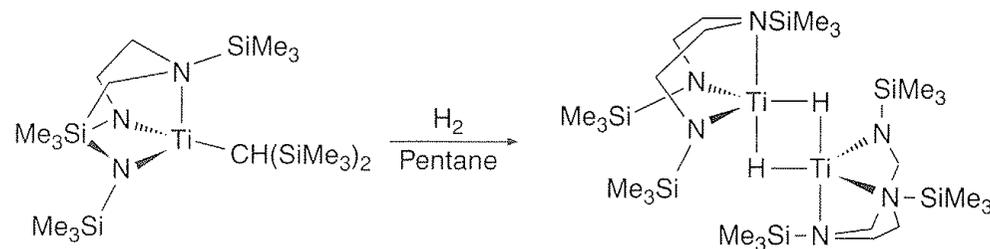
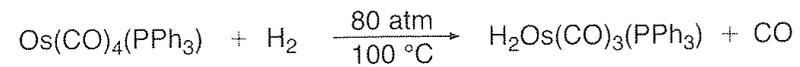
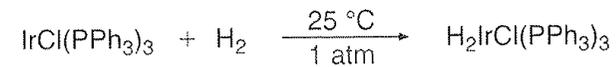
## Terminale



## Verbrückende

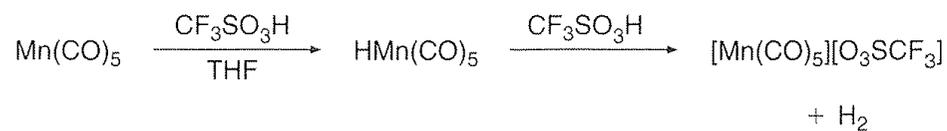
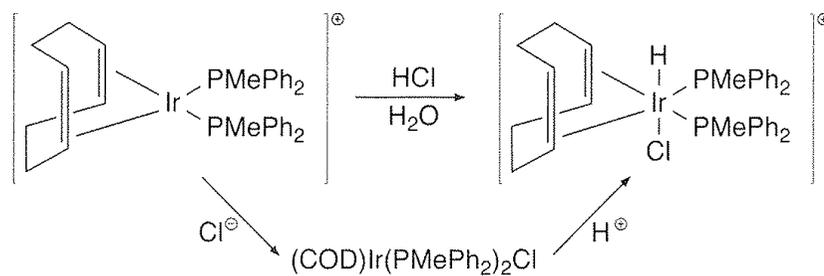
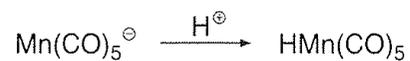


# Hydride: Synthese mit H<sub>2</sub>

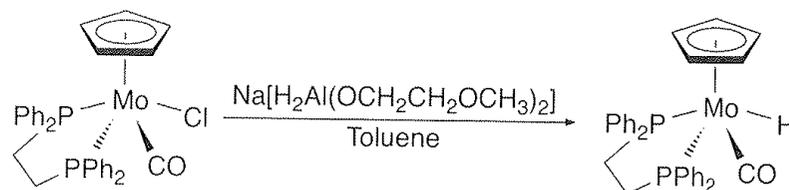
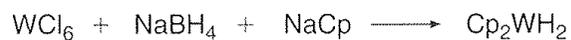


# Hydride: Synthese

## Protonierung



## Hydride



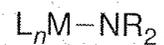
# Hydride: Acidität

Metal hydride M–H	$pK_a$ (M–H)	$E^\circ$ (M <sup>+/0</sup> /M) <sup>a</sup> (V) vs. FcH <sup>+/0</sup> /FcH	BDE (M–H) (kcal mol <sup>-1</sup> )	References <sup>b</sup>
HV(CO) <sub>4</sub> (dppe) <sup>c</sup>	17.4	-1.12	57.5	434
CpCr(CO) <sub>3</sub> H	13.3	-0.69	61	435,436
CpCr(CO) <sub>2</sub> (PPh <sub>3</sub> )H	21.8	-1.29	60	437,438
Cp <sup>+</sup> Cr(CO) <sub>3</sub> H	17.0	-0.83	63.6 62.3 <sup>d</sup>	434,438,439
CpMo(CO) <sub>3</sub> H	13.9	-0.50 <sup>e</sup>	69	435,436
Cp <sup>+</sup> Mo(CO) <sub>3</sub> H	17.1	-0.71 <sup>e</sup>	69	435,436
TpMo(CO) <sub>3</sub> H	10.7	-0.52	62	440
CpW(CO) <sub>3</sub> H	16.1	-0.49 <sup>e</sup>	72	435,436
CpW(CO) <sub>2</sub> (PMe <sub>3</sub> )H	26.6	-1.23 <sup>e</sup>	70	435,436
[CpW(CO) <sub>2</sub> (PMe <sub>3</sub> )H <sub>2</sub> ] <sup>+</sup>	5.6			441
TpW(CO) <sub>3</sub> H	14.4	-0.58	66	440
Mn(CO) <sub>5</sub> H	14.1	-0.56 <sup>e</sup>	68	435,436
Mn(CO) <sub>4</sub> (PPh <sub>3</sub> )H	20.4	-0.87 <sup>e</sup>	68	435,436
Re(CO) <sub>5</sub> H	21.1	-0.69 <sup>e</sup>	75	435,436
CpFe(CO) <sub>2</sub> H	19.4	-1.35 <sup>e</sup>	57	435,436
Fe(CO) <sub>4</sub> H <sub>2</sub>	11.4	-0.40 <sup>e</sup>	68	435,436
CpRu(CO) <sub>2</sub> H	20.2	-1.06 <sup>e</sup>	65	435,436
Cp <sup>+</sup> <sub>2</sub> OsH <sup>+</sup>	9.9	-0.06	71	442
H <sub>2</sub> Os <sub>2</sub> (CO) <sub>8</sub>	20.4			427
[Rh <sub>13</sub> (CO) <sub>24</sub> H <sub>3</sub> ] <sup>2-</sup>	11.0			443
[Rh <sub>13</sub> (CO) <sub>24</sub> H <sub>2</sub> ] <sup>3-</sup>	16.5			443
HNi(depp) <sub>2</sub> <sup>+c</sup>	23.3	-1.34	55 <sup>f</sup>	444
HNi(depe) <sub>2</sub> <sup>+c</sup>	23.8	-1.29	62	445

Vgl:  $pK_a$  von HCl in MeCN: 8-9

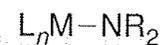
# Amide

Early-metal-  
amido complexes



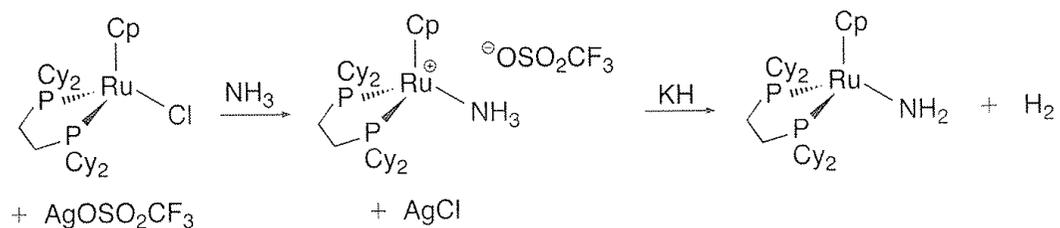
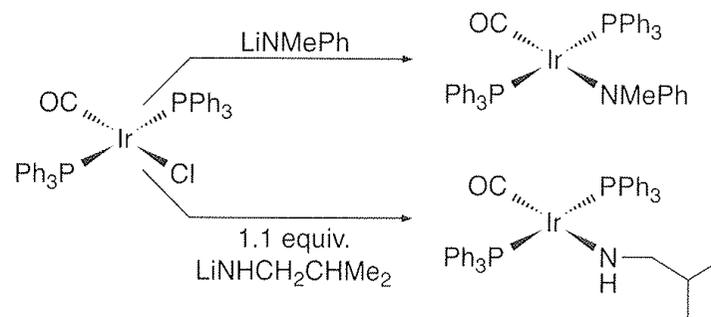
- Stronger  $\pi$ -bonding
- More ionic bonding
- Hard-hard match
- Stronger bonds

Late-metal-  
amido complexes

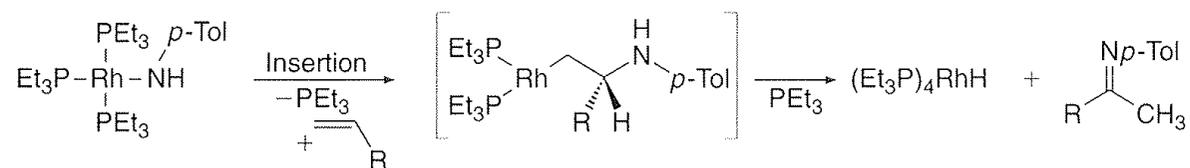
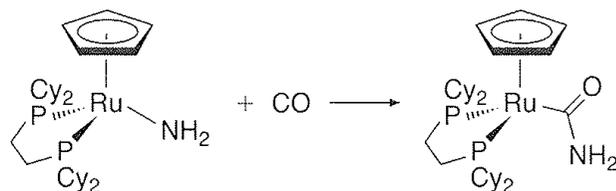
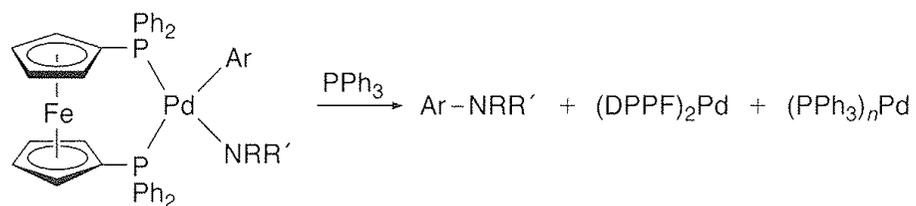
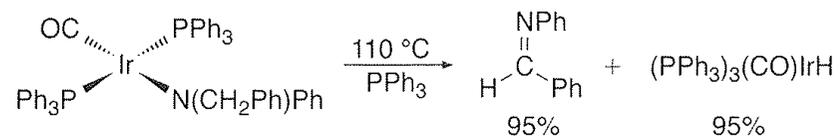


- $\pi$ -Repulsion more common
- Less ionic bonding
- Hard-soft mismatch
- Weaker bonds

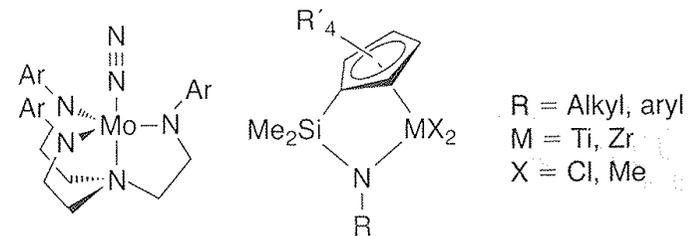
Late Metal-Amides



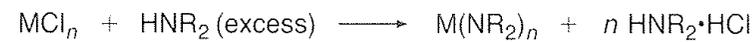
# Amide der späten Metalle: Reaktivität



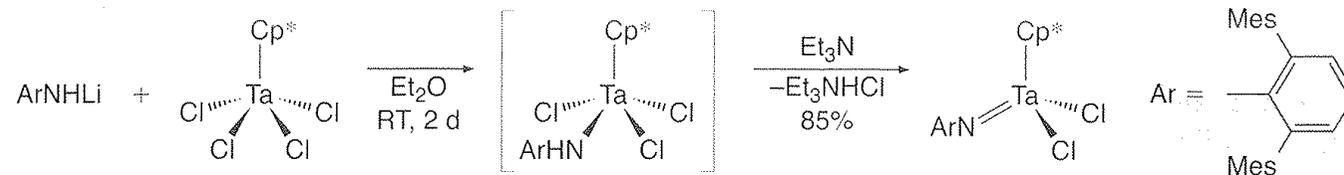
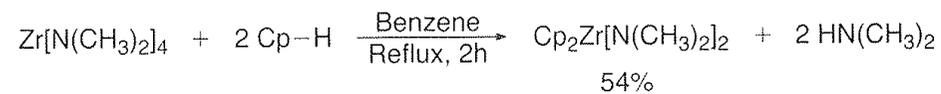
# Amide der frühen Metalle



## Synthese

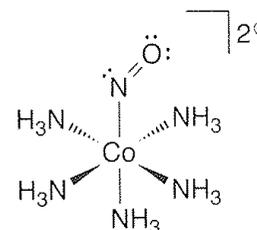
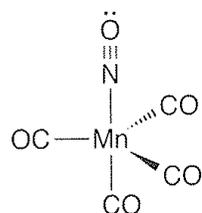
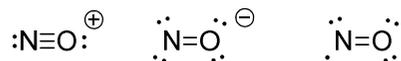


## Reaktivität



# Nitrosylkomplexe

Linear vs. gewinkelt



$\text{Mn}(\text{NO})(\text{CO})_4$  containing a linear metal–nitrosyl group

Covalent electron-counting method:

- Mn =  $7 e^-$
- One linear NO ligand =  $3 e^-$
- Four CO ligands =  $8 e^-$
- Total =  $18 e^-$

Ionic electron-counting method:

- $\text{Mn}^- = 8 d e^-$
- Linear NO  $\Rightarrow$   $\text{NO}^+$  ligand =  $2 e^-$
- Four CO ligands =  $8 e^-$
- Total =  $18 e^-$

$[\text{Co}(\text{NO})(\text{NH}_3)_5]^{2+}$  containing a bent metal–nitrosyl group

Covalent electron-counting method:

- Co =  $9 e^-$
- One bent NO ligand =  $1 e^-$
- Five  $\text{NH}_3$  ligands =  $10 e^-$
- 2+ total charge =  $-2 e^-$
- Total =  $18 e^-$

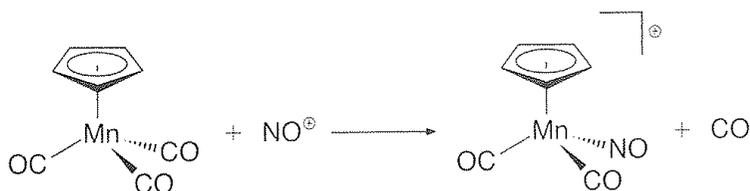
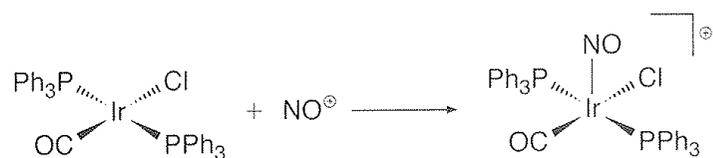
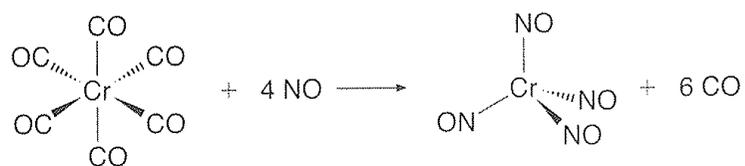
Ionic electron counting-method:

- $\text{Co}^{3+} = 6 e^-$
- Bent NO  $\Rightarrow$   $\text{NO}^-$  ligand =  $2 e^-$
- Five  $\text{NH}_3$  ligands =  $10 e^-$
- Total =  $18 e^-$

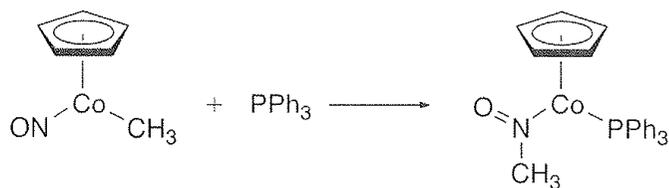
**Die Änderung des Koordinationsmodus von gewinkelt auf linear geht mit einer Oxidation des Metalls einher!**

# Nitrosylkomplexe

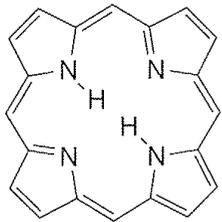
## Synthese



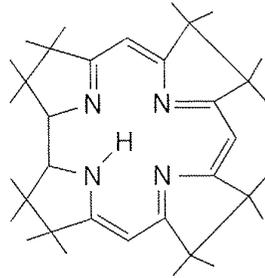
## Reaktivität



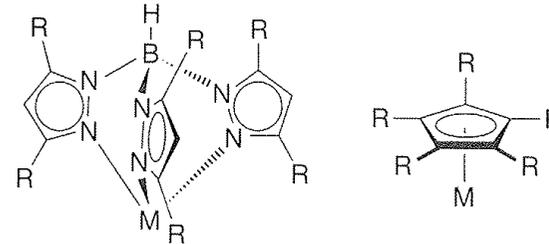
# Mehrzählige N-Liganden



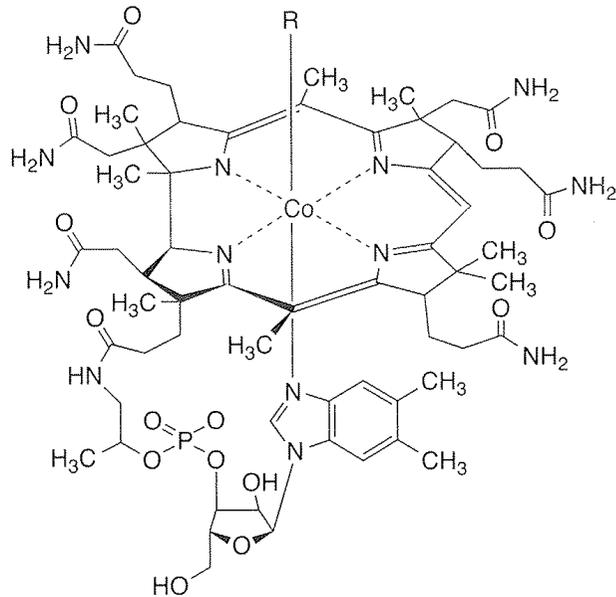
The core ring system of a porphyrin



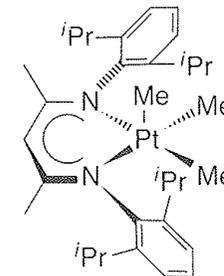
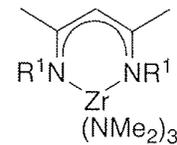
The core ring system of a corrin



Polypyrozolyliganden sind isoelektrisch zu Cp

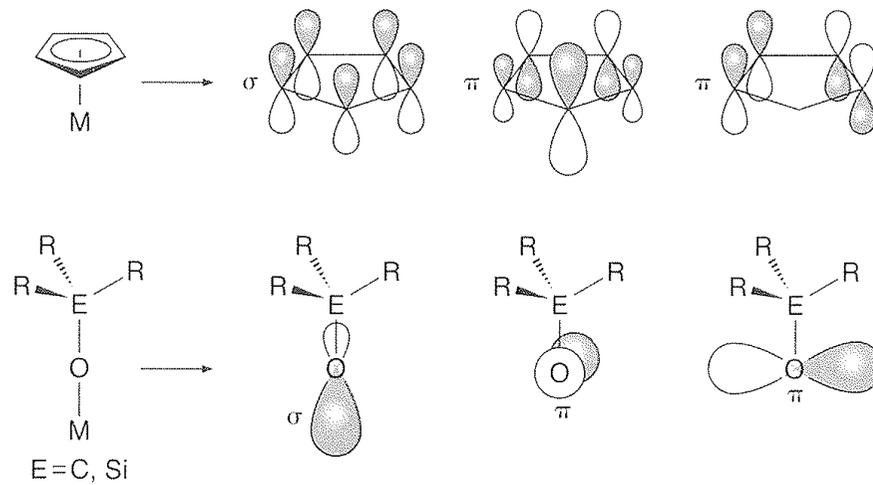


Vitamin B<sub>12</sub>

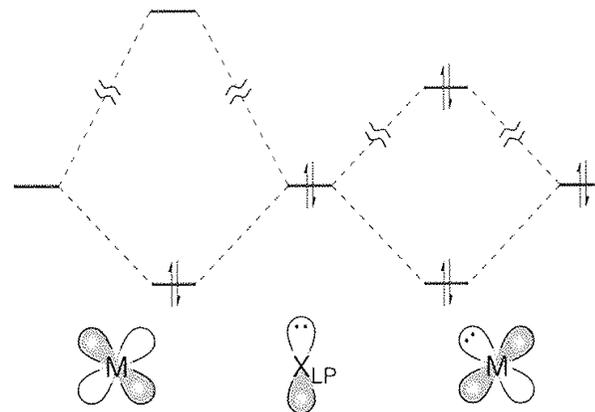


$\beta$ -Ketimidate donieren 2, 4 oder 6 e<sup>-</sup>

# Alkoxidkomplexe

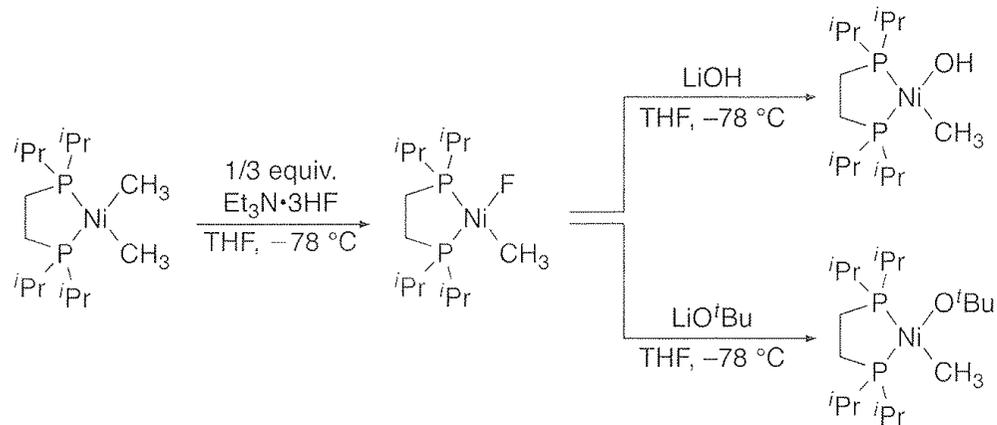
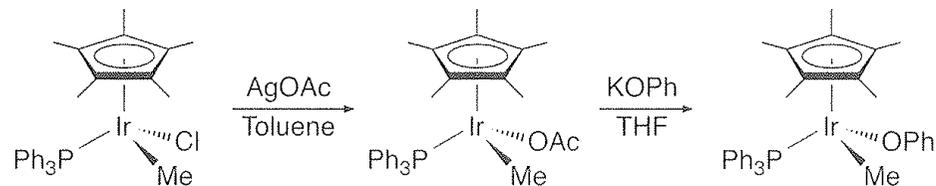
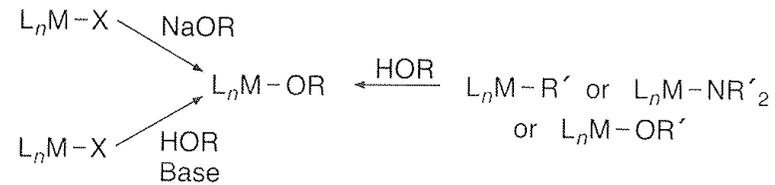


Orbitalanalogie zwischen Cp und RO Liganden

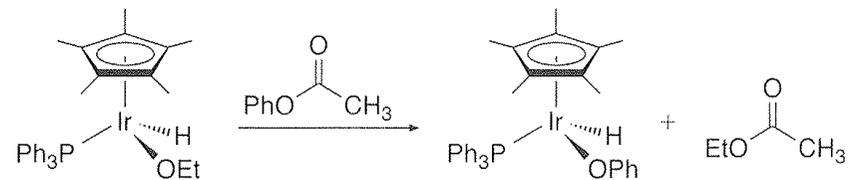
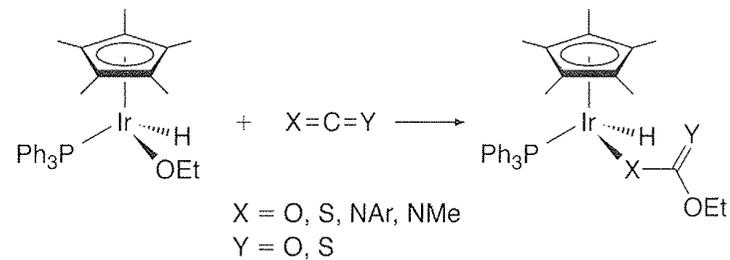
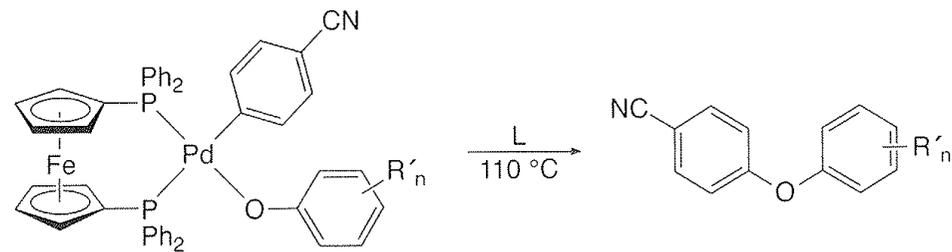
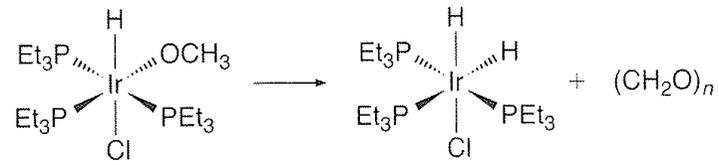


Wechselwirkung zwischen den Lone-Pairs des Alkoxids und den d-Orbitalen des Metalls

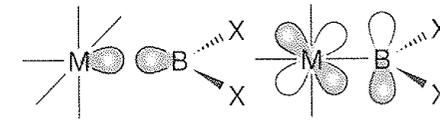
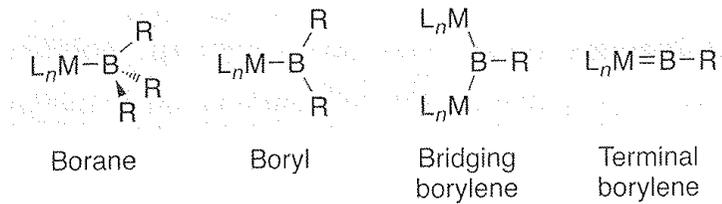
# Alkoxidkomplexe: Synthese



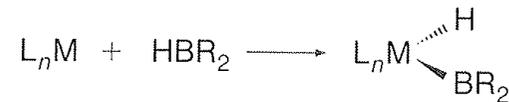
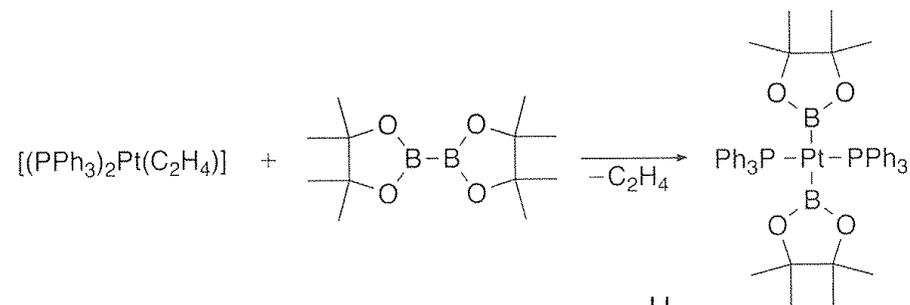
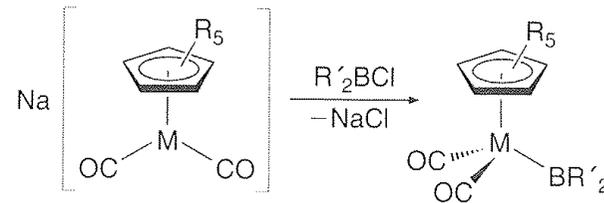
# Alkoxidkomplexe: Reaktivität



# Borylkomplexe



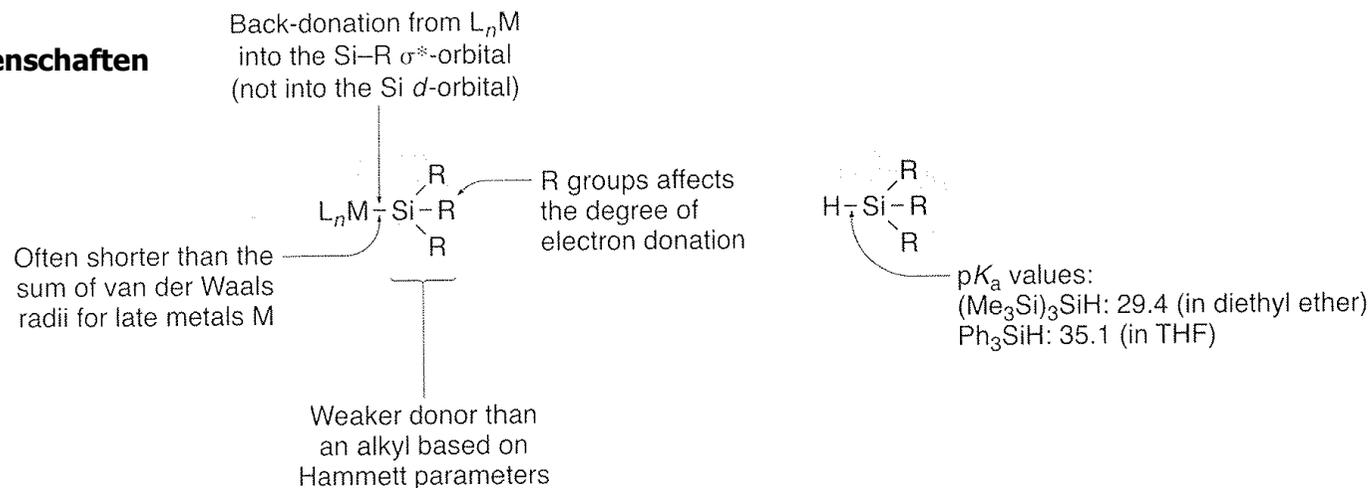
## Synthese



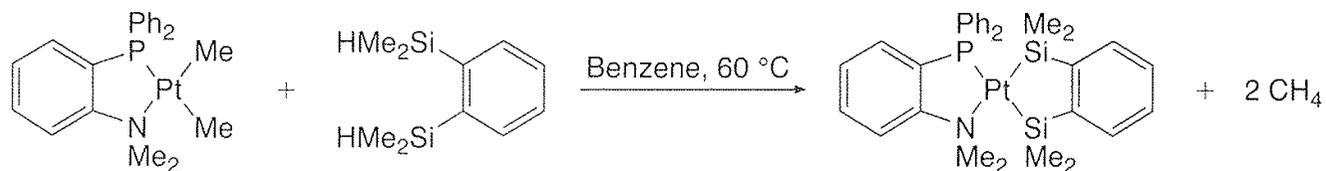
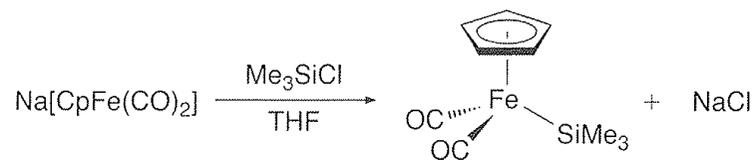


# Silylkomplexe

## Elektronische Eigenschaften

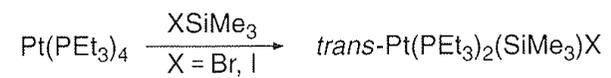
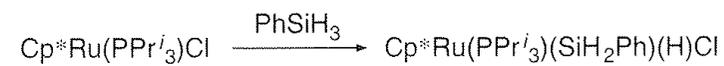
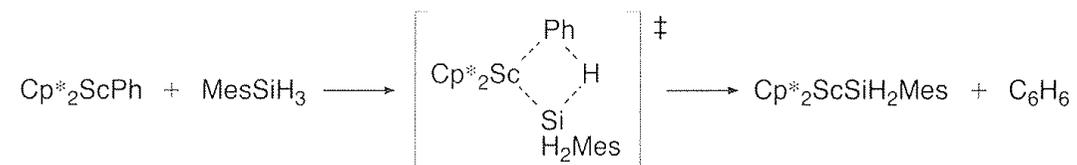


## Synthese



# Silylkomplexe

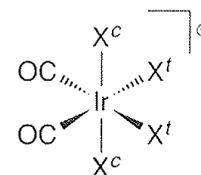
## Synthese



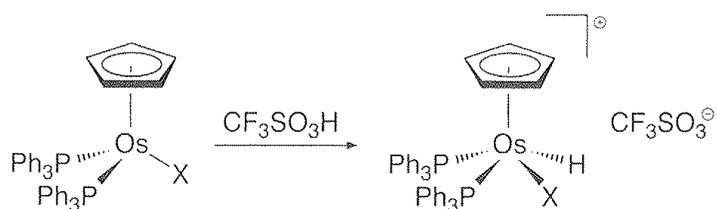
# Halogenide

Steric properties of halides and halide ligands.

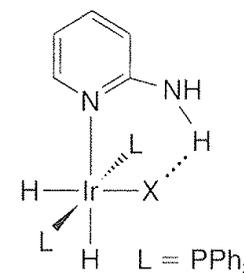
	F	Cl	Br	I
Ionic radius (Å) <sup>510</sup>	1.36	1.81	1.95	2.16
Cone angle (°) <sup>509</sup>	92	102	105	107



Relative binding affinities:  
 $X^t = \text{Cl} > \text{Br} > \text{I}$   
 $X^c = \text{I} > \text{Br} > \text{Cl}$



	$-\Delta H_{\text{HM}}$ (kcal mol <sup>-1</sup> )
I	14.1
Br	16.3
Cl	19.7
F	37.3



X	Ir X-HN (kcal mol <sup>-1</sup> )
I	< 1.3
Br	1.8
Cl	2.1
F	5.2

$\text{Cp}^*_2\text{ZrCl}_2$	$\text{Zr-Cl}_{\text{ave}} = 115 \text{ kcal/mol}$
$\text{Cp}^*_2\text{ZrI}_2$	$\text{Zr-I}_{\text{ave}} = 80.4 \text{ kcal/mol}$

H-Brückenbindung