

Anorganische Strukturen und Reaktionsmechanismen

CHE.367

Christoph Marschner

Institut für Anorganische Chemie
Technische Universität Graz

Übersicht

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

Übersicht

- Kovalente Heteroatom-Liganden
 - Amide
 - Nitrosyl
 - Polydentate N-Donors
 - β -Diketimidinate
 - Alkoxide
 - Boryl
 - Phosphide
 - Silyl
 - Halogenid

Hydrocarbyle

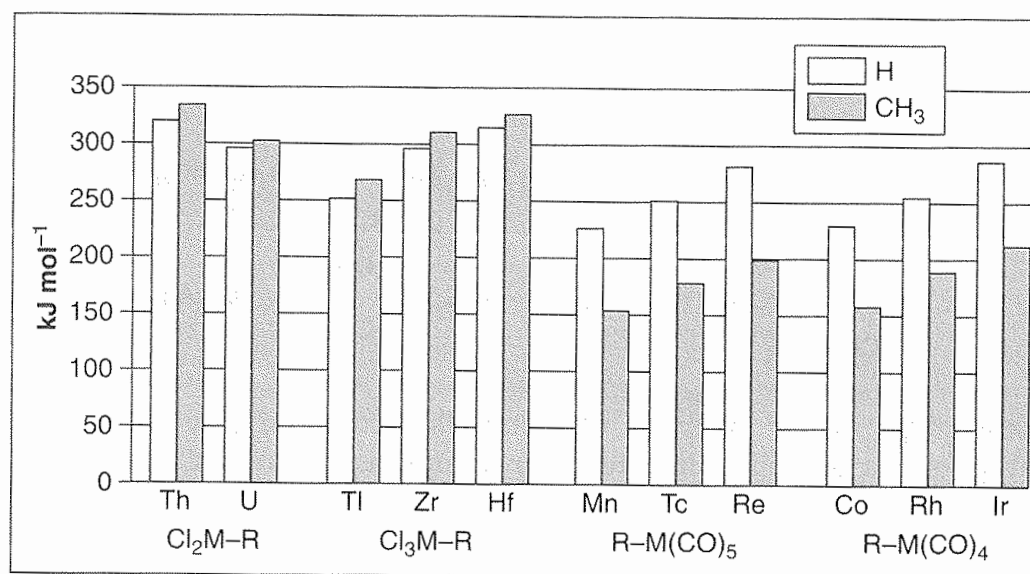
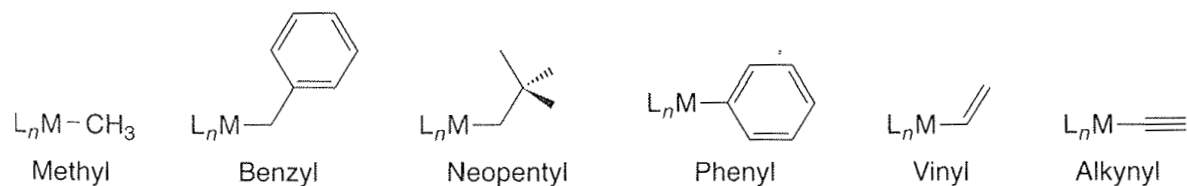


Figure 3.2. Relative strengths of representative M-C bonds. Data from reference 30.

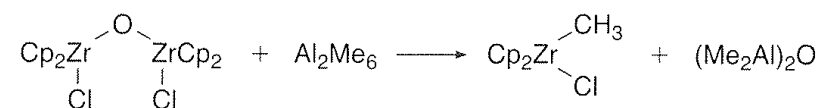
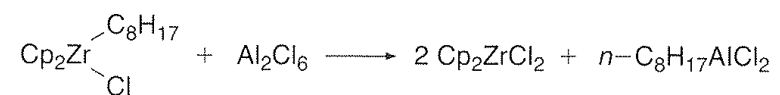
Alkylkomplexe

Transmetallierung

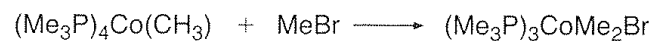
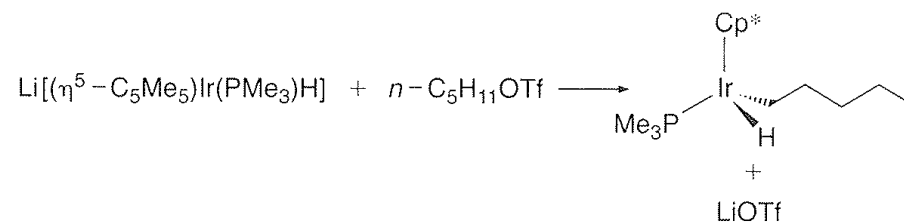
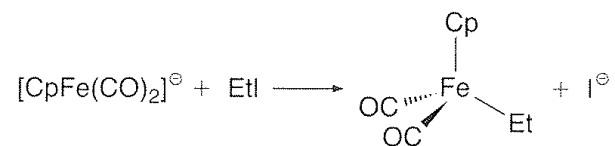


M = Li, Mg, Zn, Al

M' = transition metal

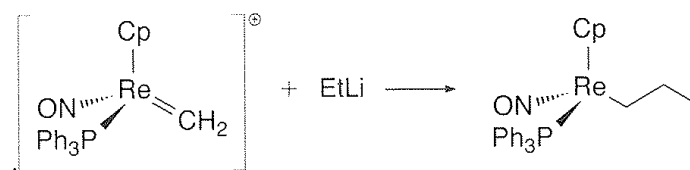
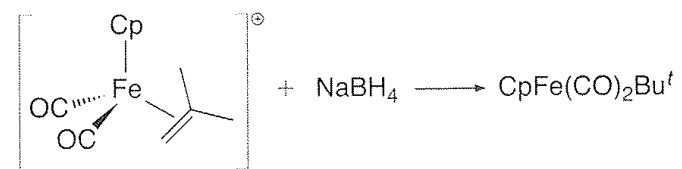
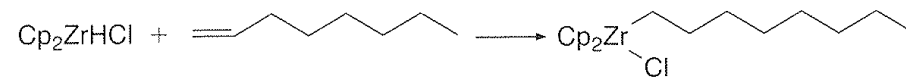


Alkylierung/Oxidative Addition

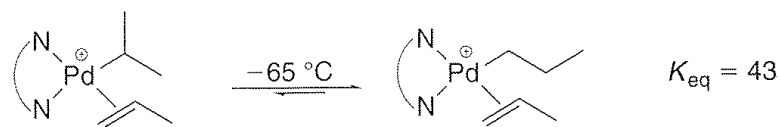
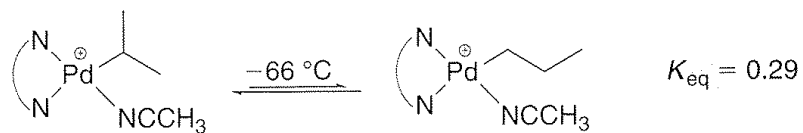
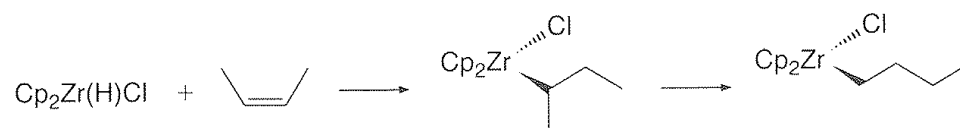
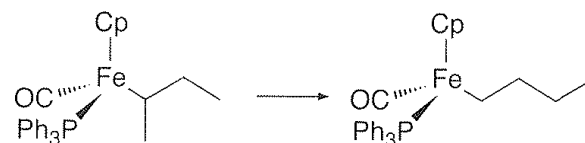
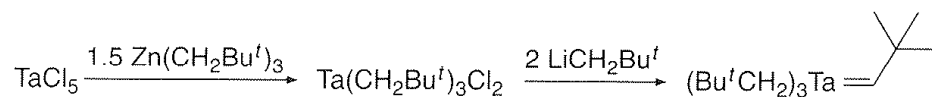


Alkylkomplexe

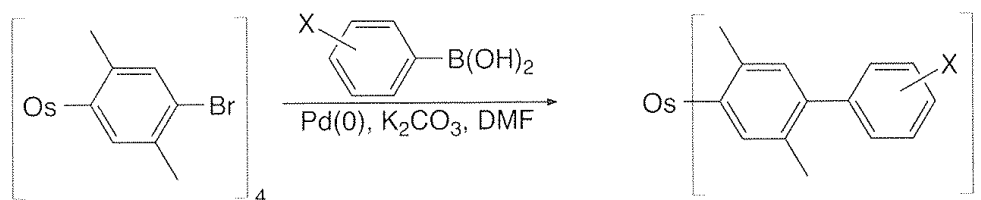
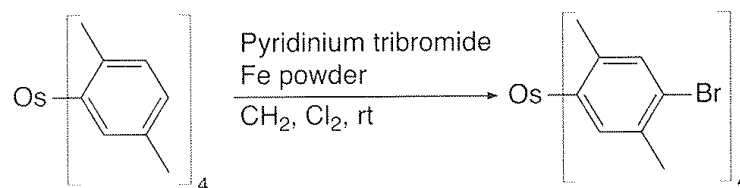
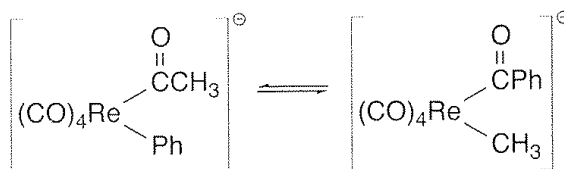
Weiter Methoden



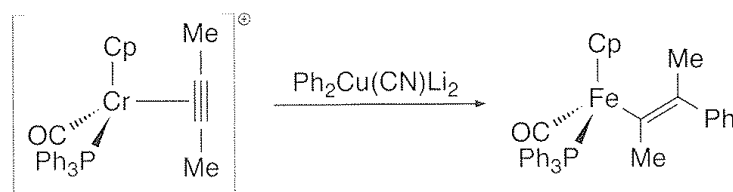
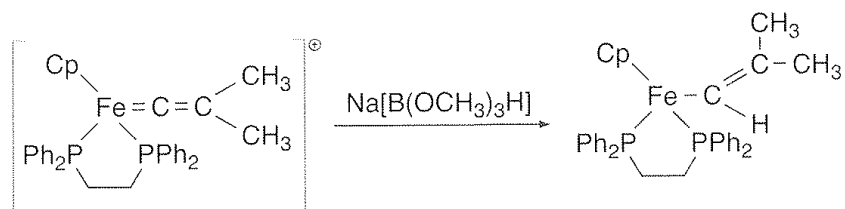
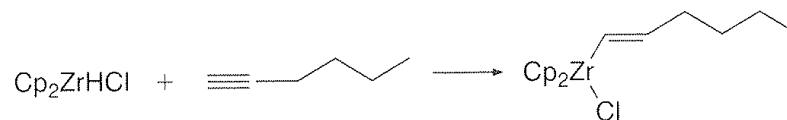
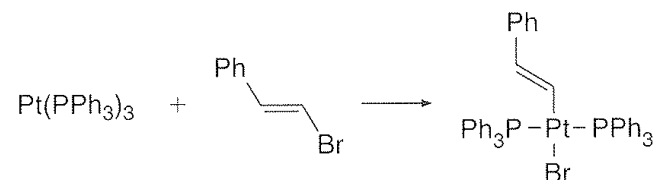
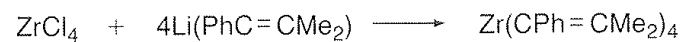
Alkylkomplexe Reaktivität



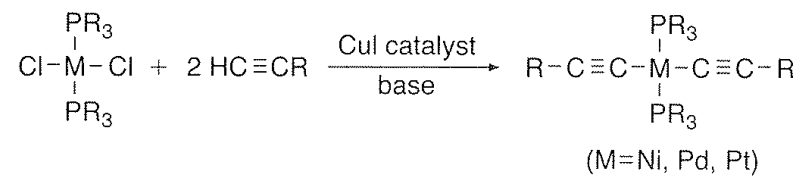
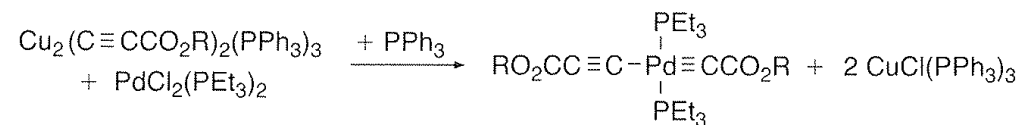
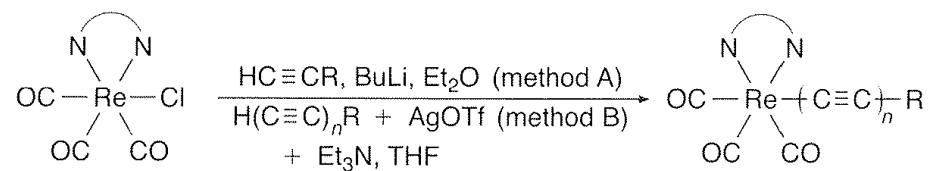
Arylkomplexe: Reaktivität



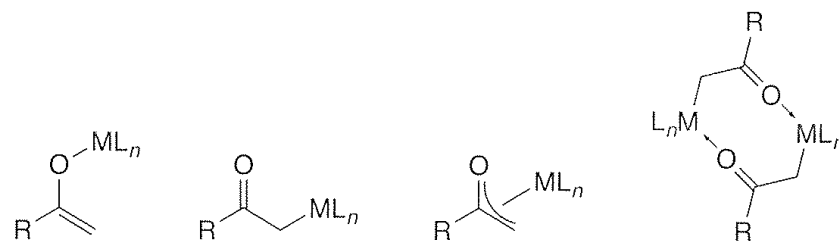
Vinylkomplexe



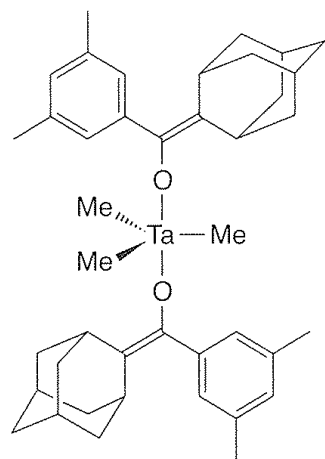
Alkynylkomplexe



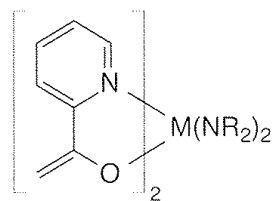
Enolatkomplexe



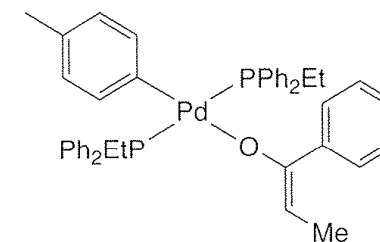
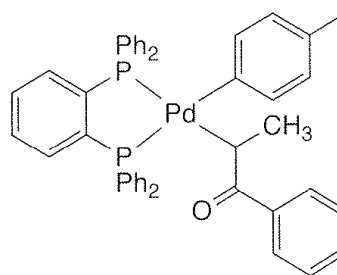
Binding modes of transition metal enolate complexes.



Early metals

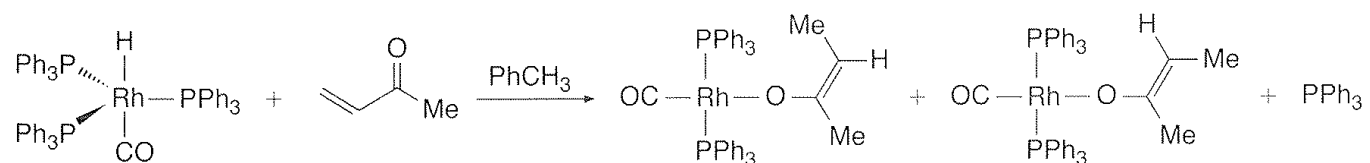
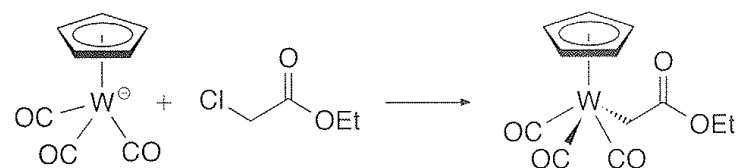
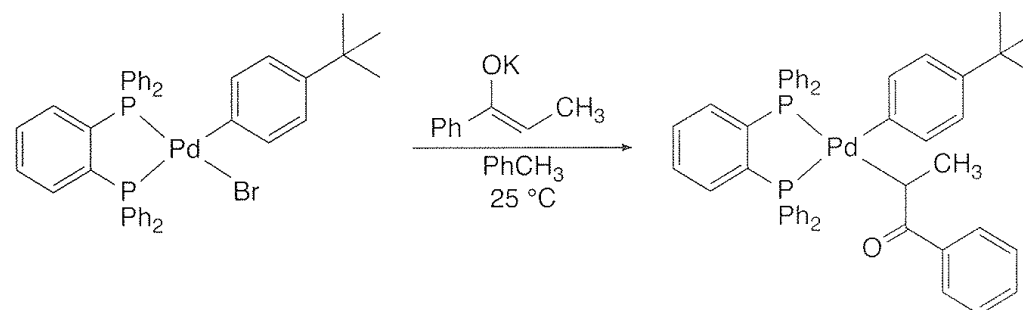
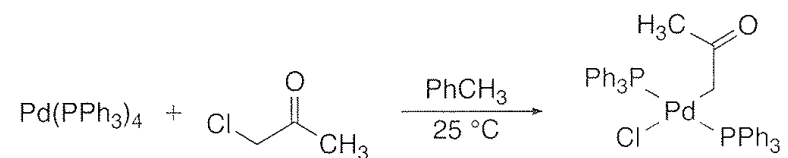


M = Zr or Ti
R = Et or Me

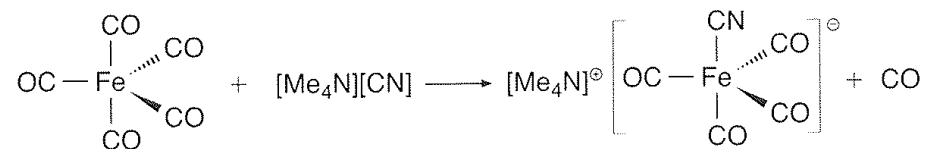
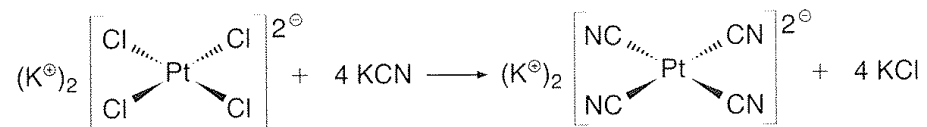
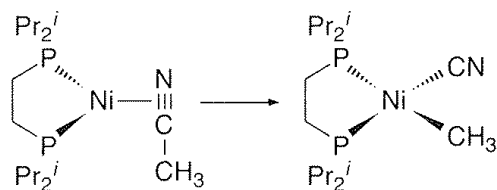
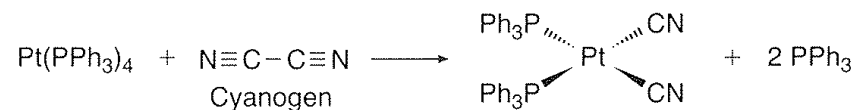
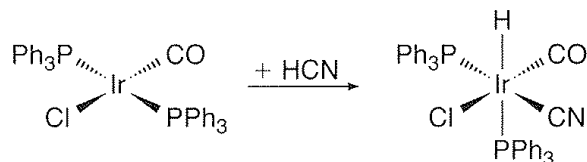


The effect of the trans ligand on C- vs. O-binding modes of palladium enolates.

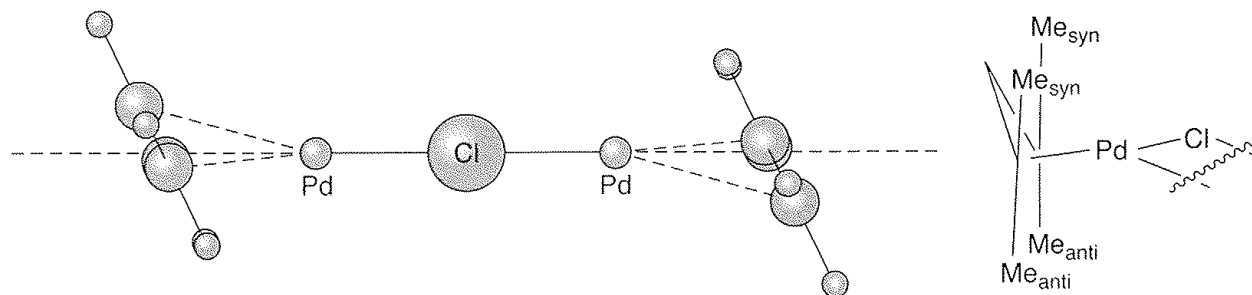
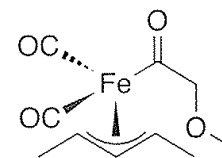
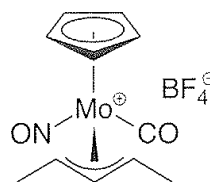
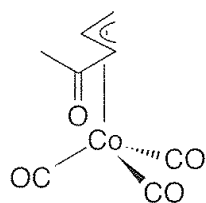
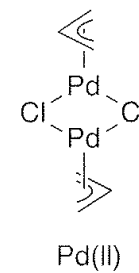
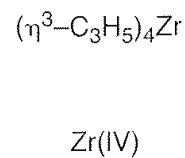
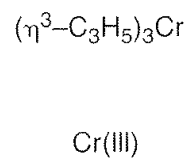
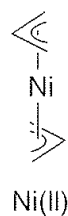
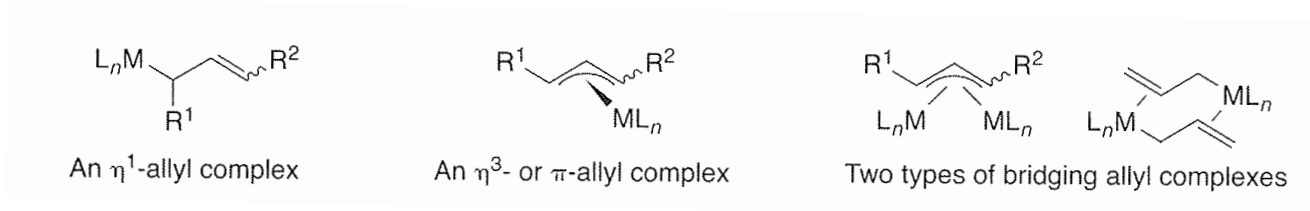
Enolatkomplexe: Synthese



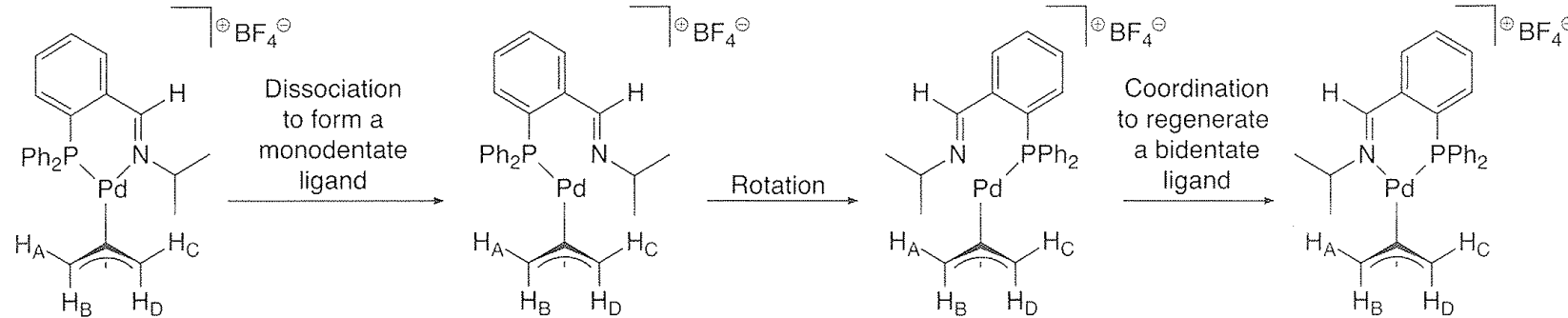
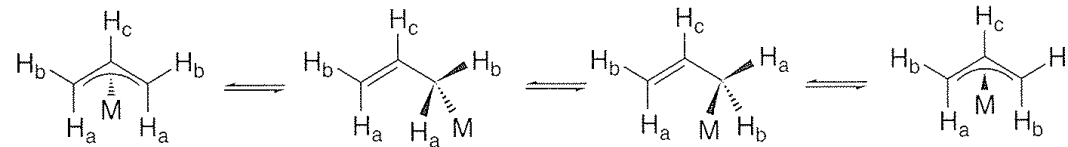
Cyanidkomplexe: Synthese



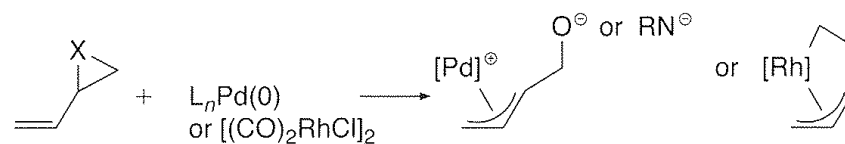
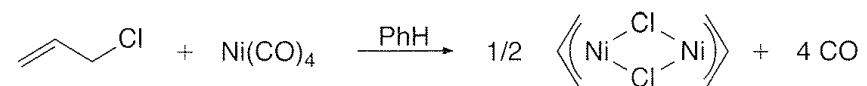
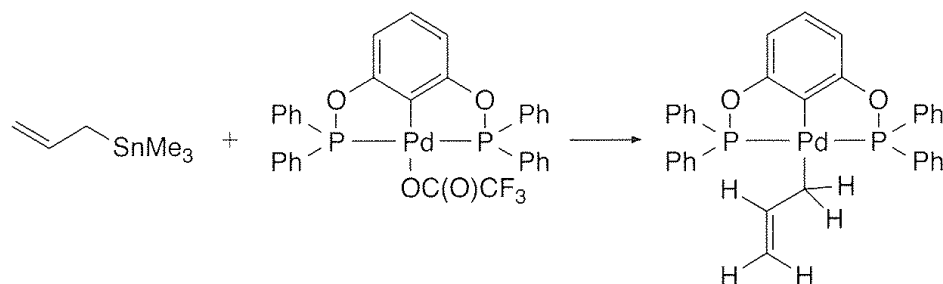
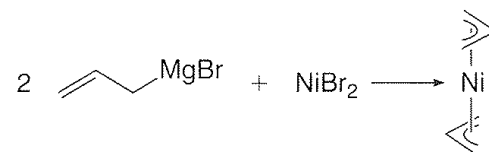
Allylkomplexe



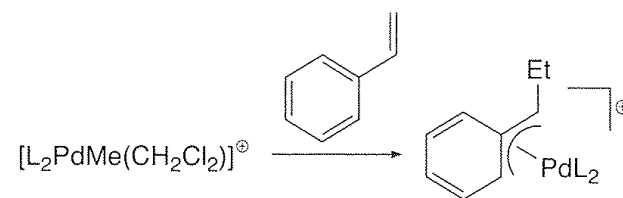
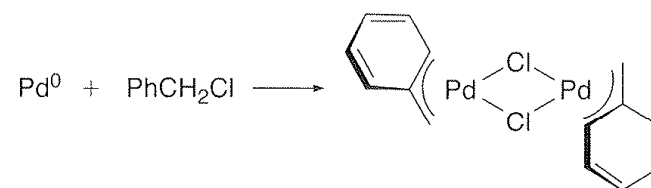
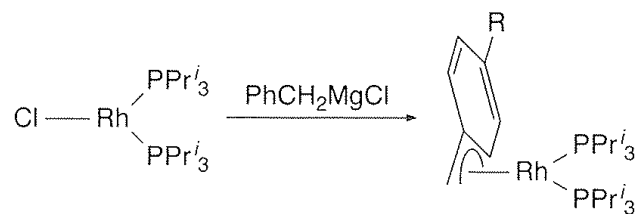
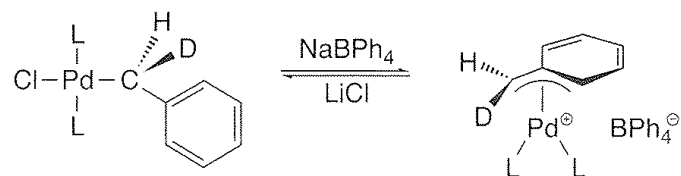
Allylkomplexe: Dynamik



Allylkomplexe: Synthese

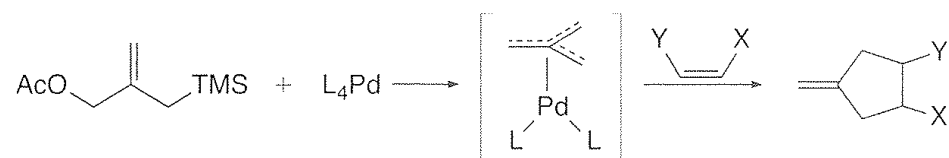
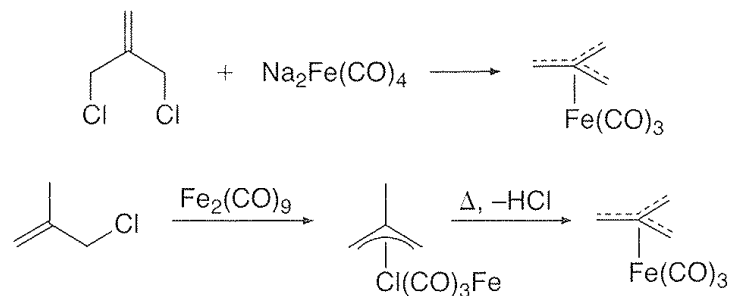


Benzykomplexe: Synthese



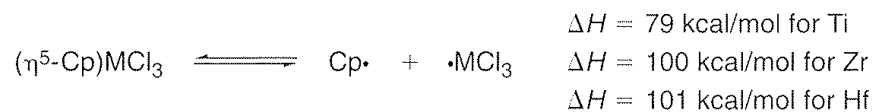
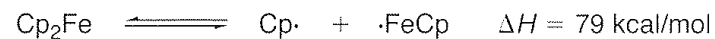
L_2 = Tetramethylethylenediamine (TMEDA)

Trimetylenmethan (TMM) Komplexe

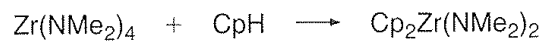


Cyclopentadienyl (Cp) Komplexe

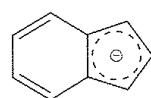
Thermodynamik



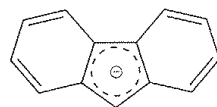
Synthese



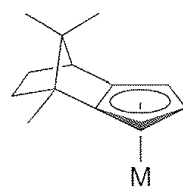
Cp-Typen



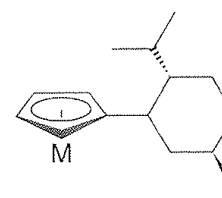
Indenyl



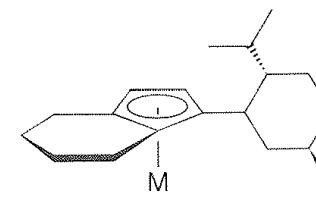
Fluorenyl



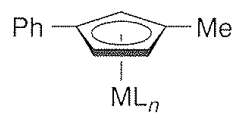
A



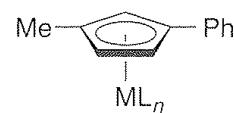
B



C



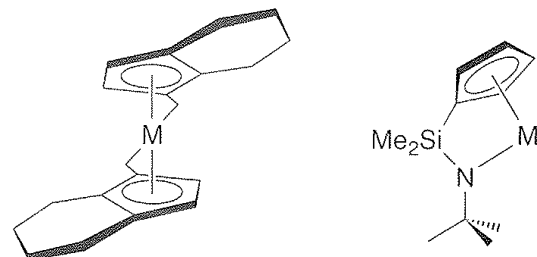
(S)



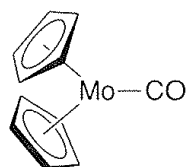
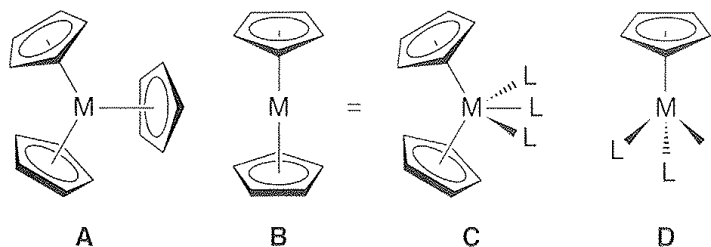
(R)

Cyclopentadienyl (Cp) Komplexe

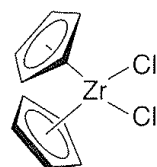
Ansa-Komplexe



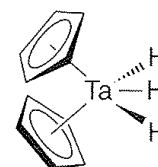
Cp-Komplexarten



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

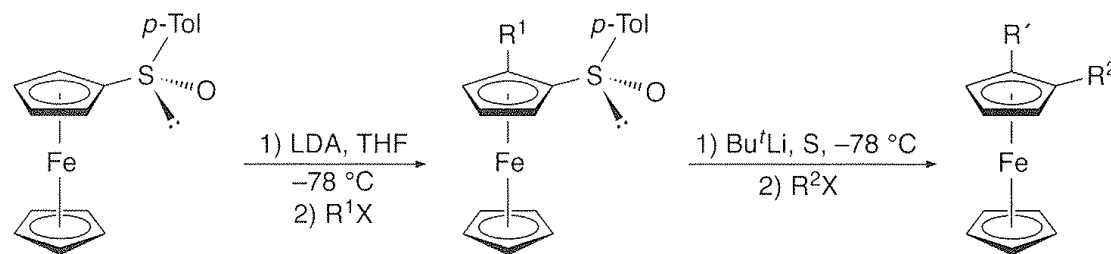
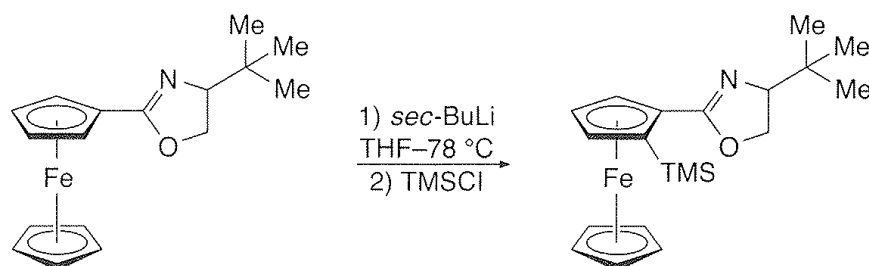
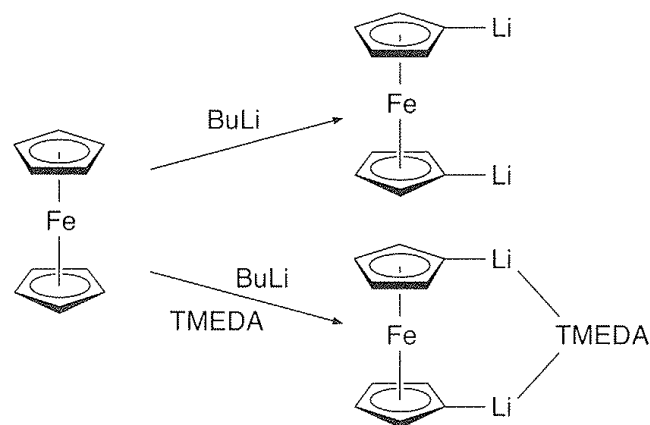


B
 Cp_2ZrCl_2
 $\text{Zr}(\text{IV}), d^0, 16 e^-$



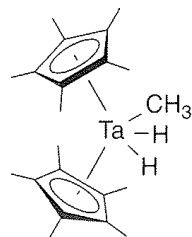
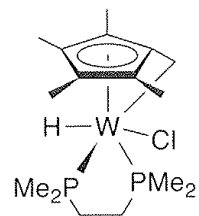
C
 Cp_2TaH_3
 $\text{Ta}(\text{V}), d^0, 18 e^-$

Cyclopentadienyl (Cp) Komplexe

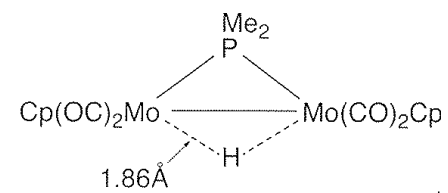
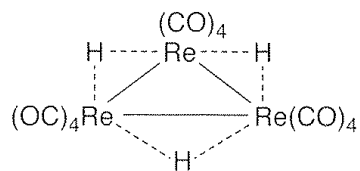
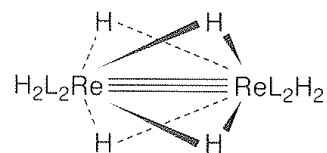


Hydride

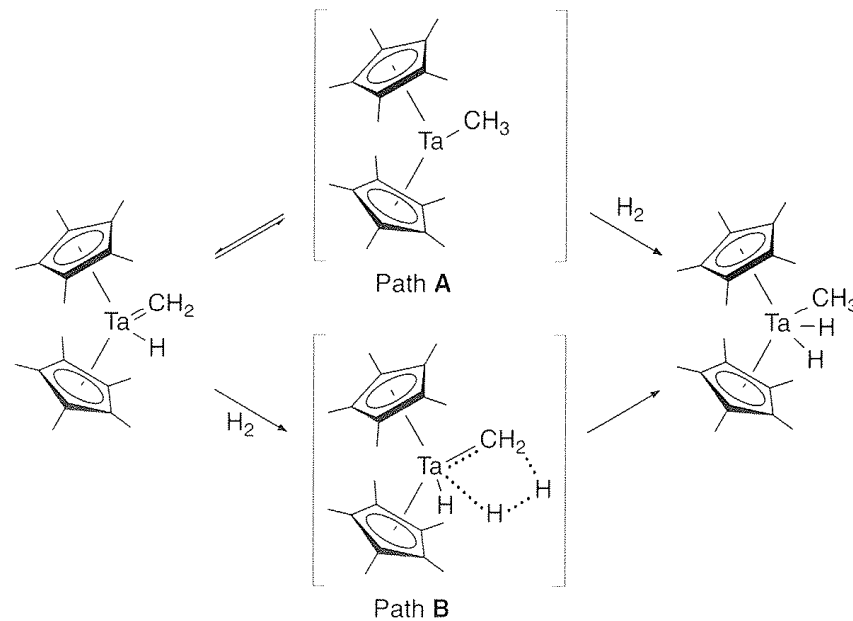
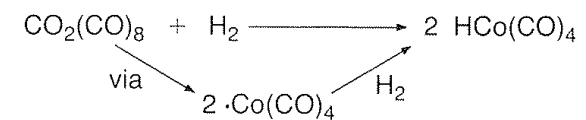
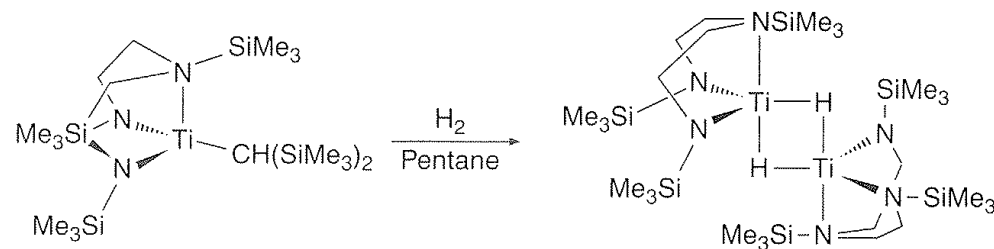
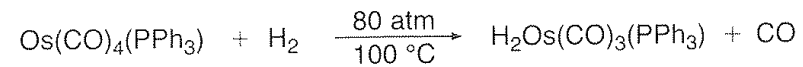
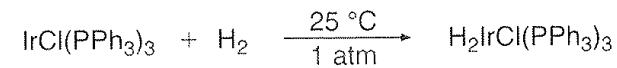
Terminale



Verbrückende

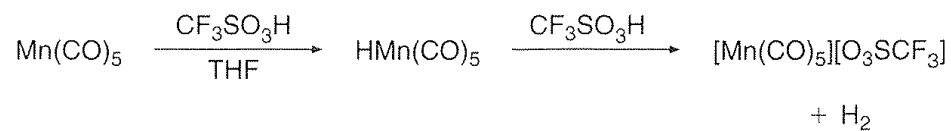
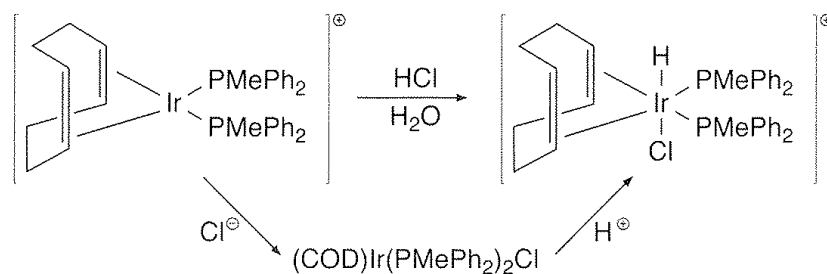
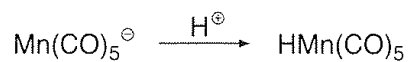


Hydride: Synthese mit H₂

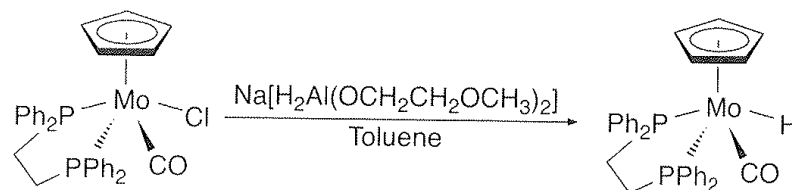
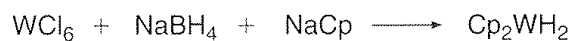


Hydride: Synthese

Protonierung



Hydride



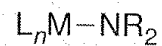
Hydride: Acidität

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

Vgl: pK_a von HCl in MeCN: 8-9

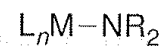
Amide

Early-metal-
amido complexes



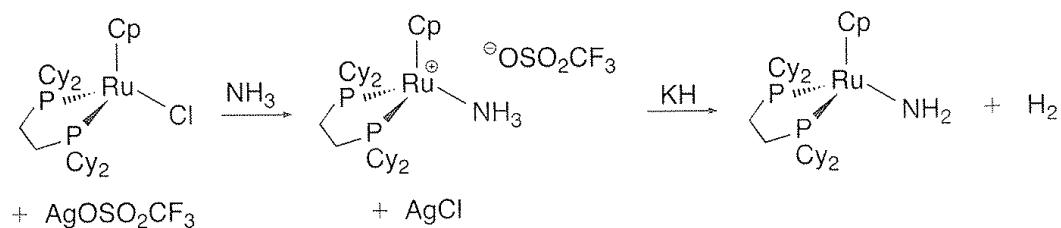
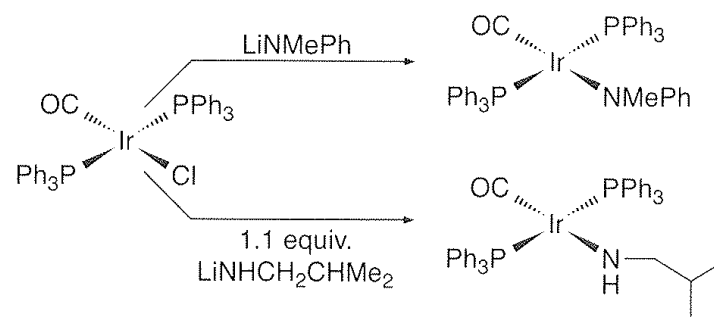
- Stronger π -bonding
- More ionic bonding
- Hard-hard match
- Stronger bonds

Late-metal-
amido complexes

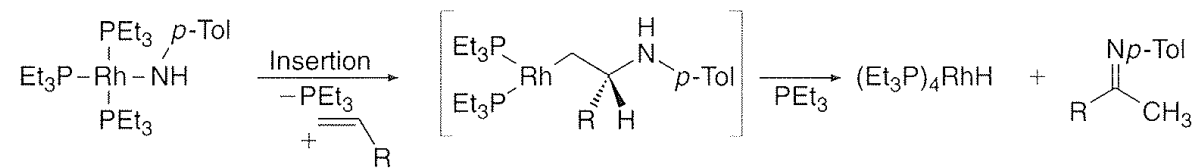
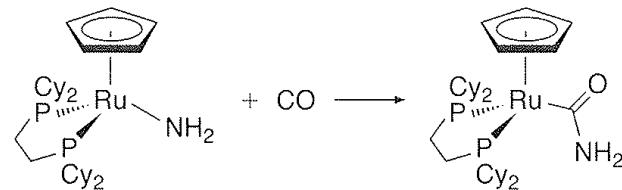
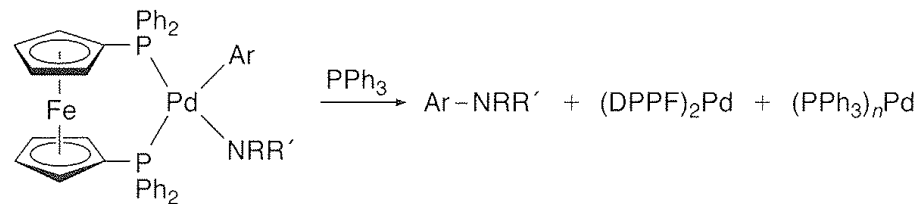
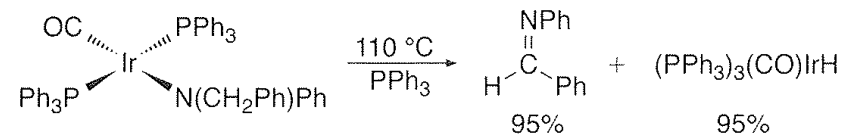


- π -Repulsion more common
- Less ionic bonding
- Hard-soft mismatch
- Weaker bonds

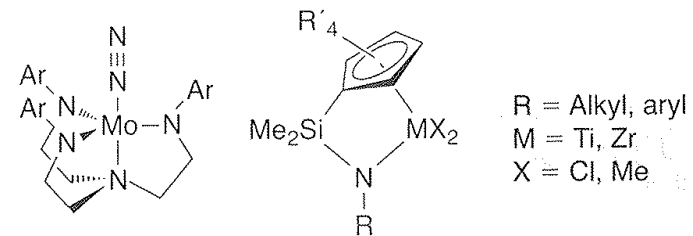
Late Metal-Amides



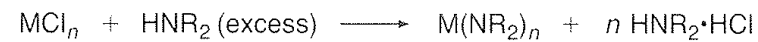
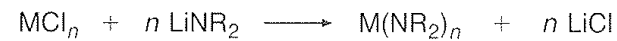
Amide der späten Metalle: Reaktivität



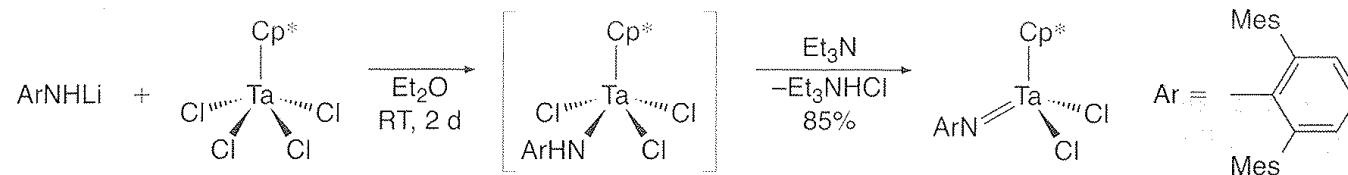
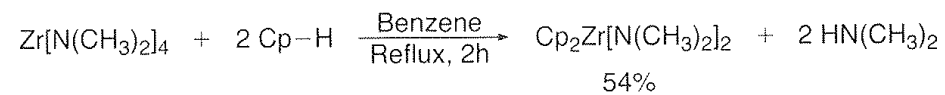
Amide der frühen Metalle



Synthese

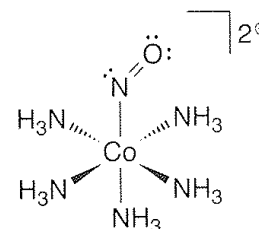
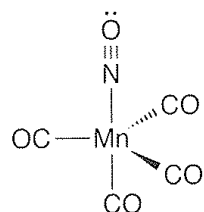
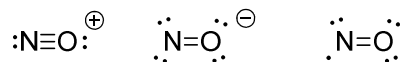


Reaktivität



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 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 NH_3 ligands = $10 e^-$
- 2+ total charge = $-2 e^-$
- Total = $18 e^-$

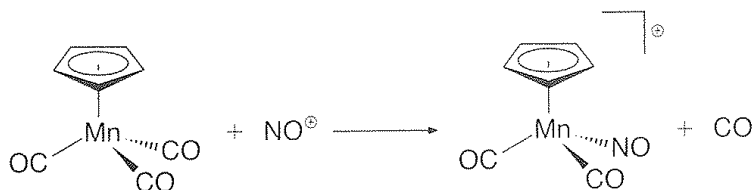
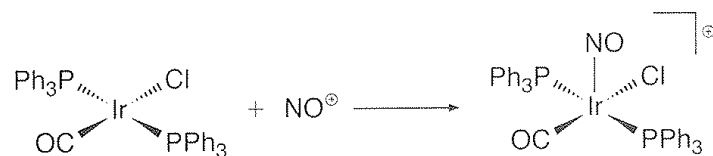
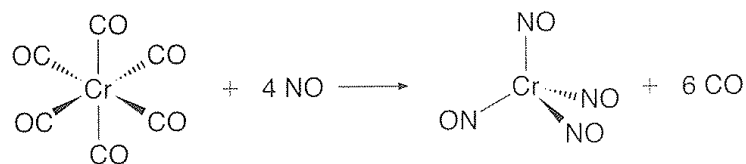
Ionic electron counting-method:

- $\text{Co}^{3+} = 6 e^-$
- Bent NO \Rightarrow NO^- ligand = $2 e^-$
- Five NH_3 ligands = $10 e^-$
- Total = $18 e^-$

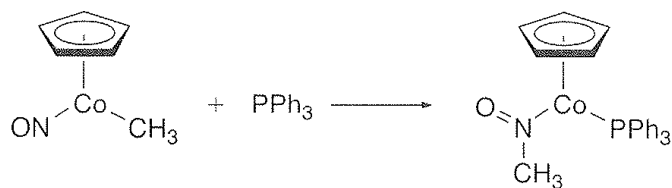
Die Änderung des Koordinationsmodus von gewinkelt auf linear geht mit einer Oxidation des Metalls einher!

Nitrosylkomplexe

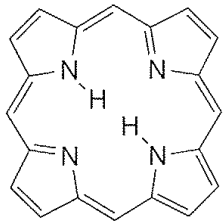
Synthese



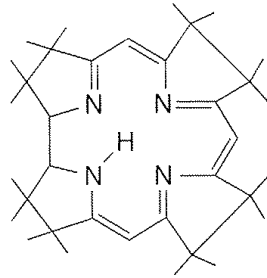
Reaktivität



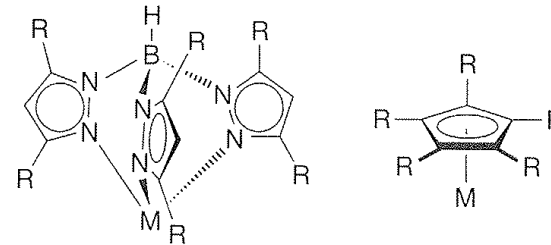
Mehrzählige N-Liganden



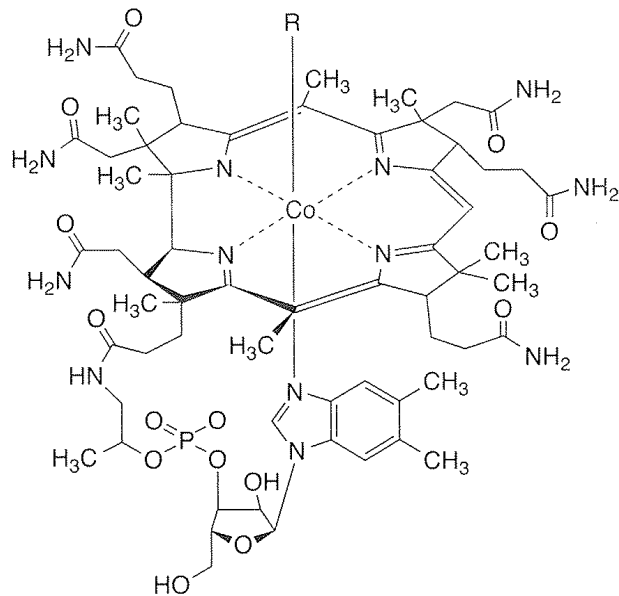
The core ring system of a porphyrin



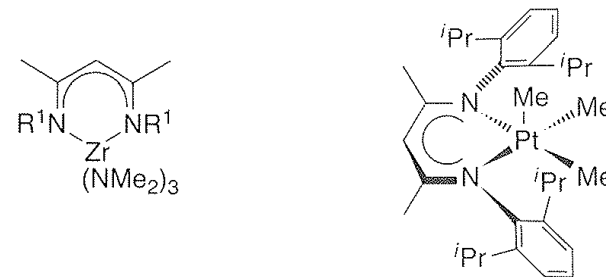
The core ring system of a corrin



Polypyrozolyliganden sind isoelektrisch zu Cp

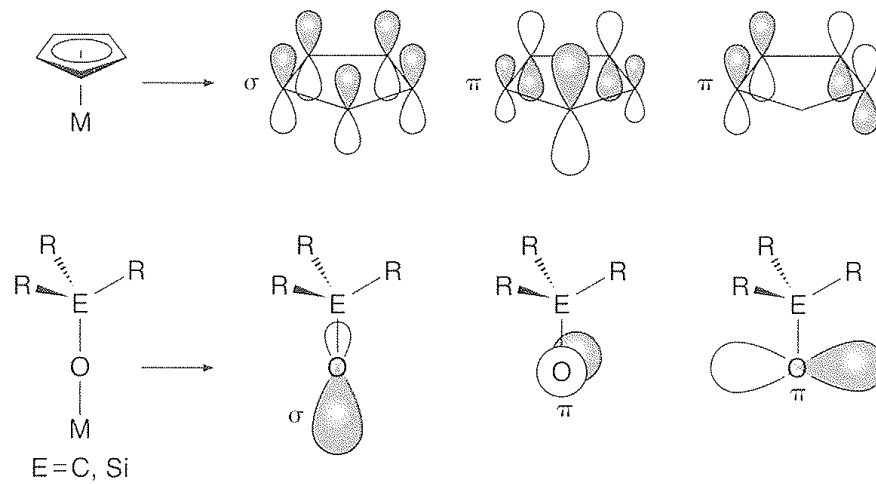


Vitamin B₁₂

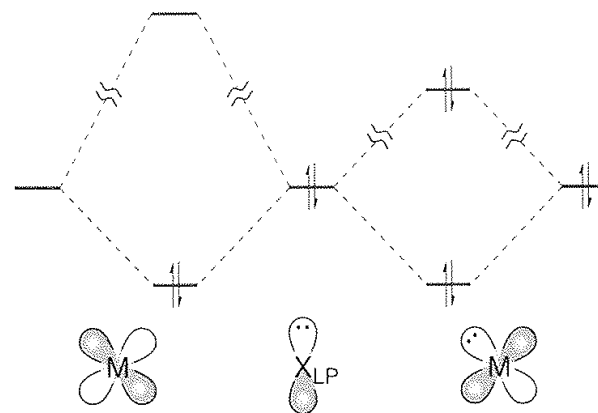


β -Ketimidate donieren 2, 4 oder 6 e⁻

Alkoxidkomplexe

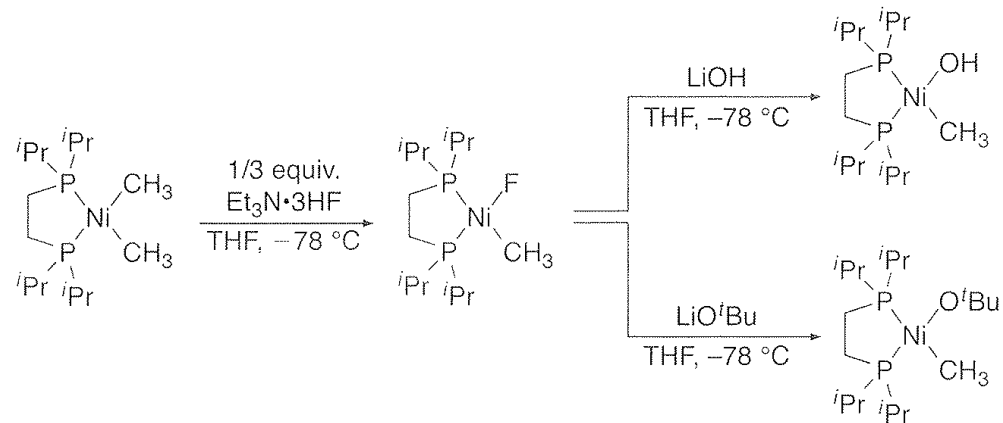
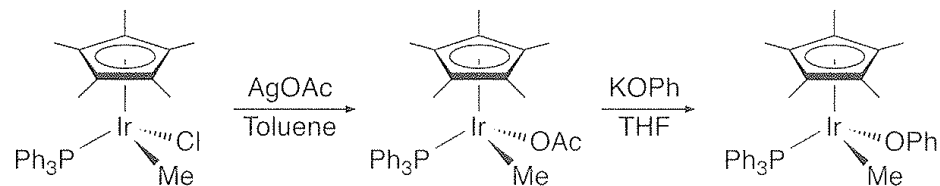
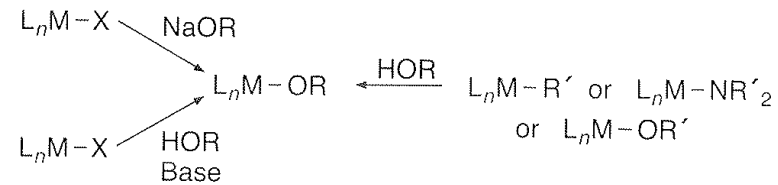


Orbitalanalogie zwischen Cp und RO Liganden

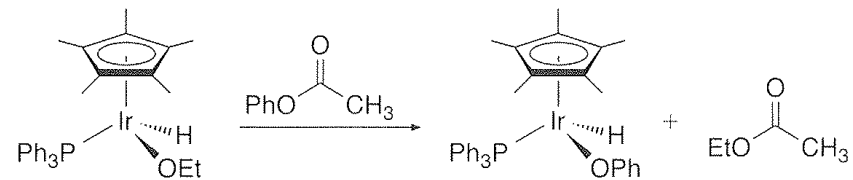
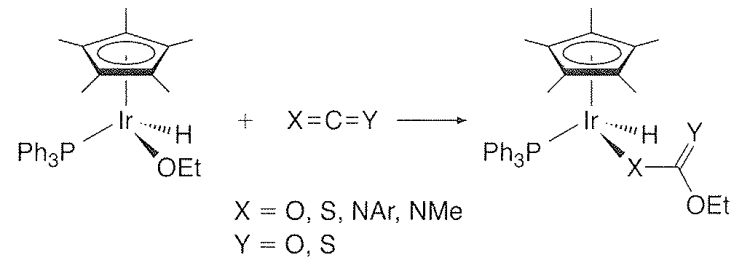
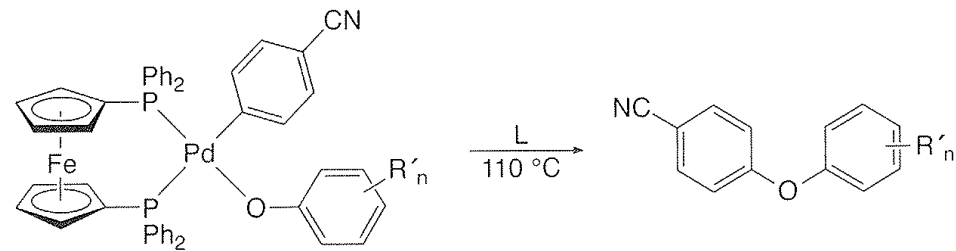
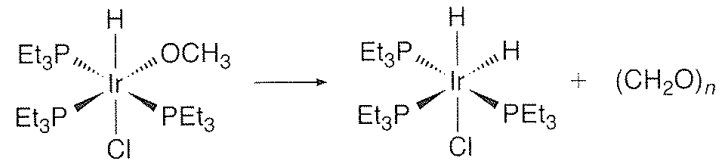


Wechselwirkung zwischen den Lone-Pairs des Alkoxids und den d-Orbitalen des Metalls

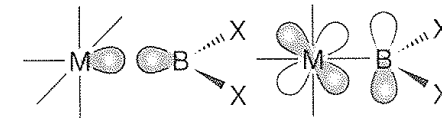
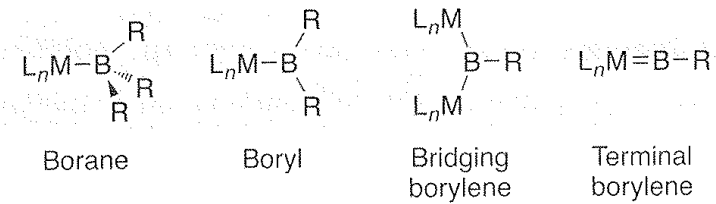
Alkoxidkomplexe: Synthese



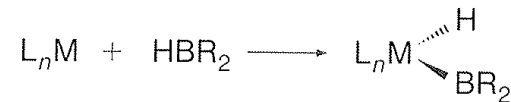
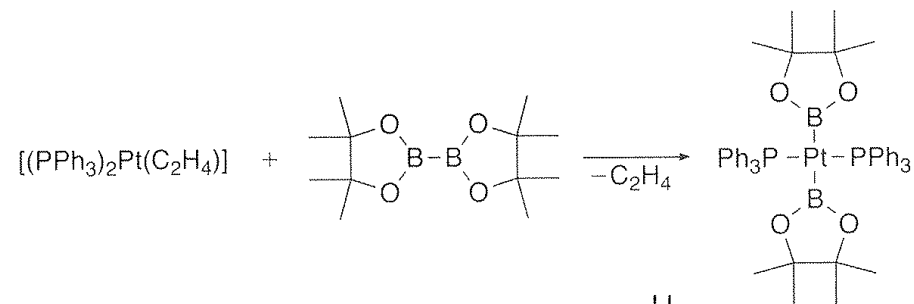
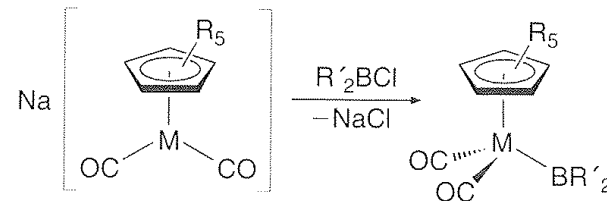
Alkoxidkomplexe: Reaktivität



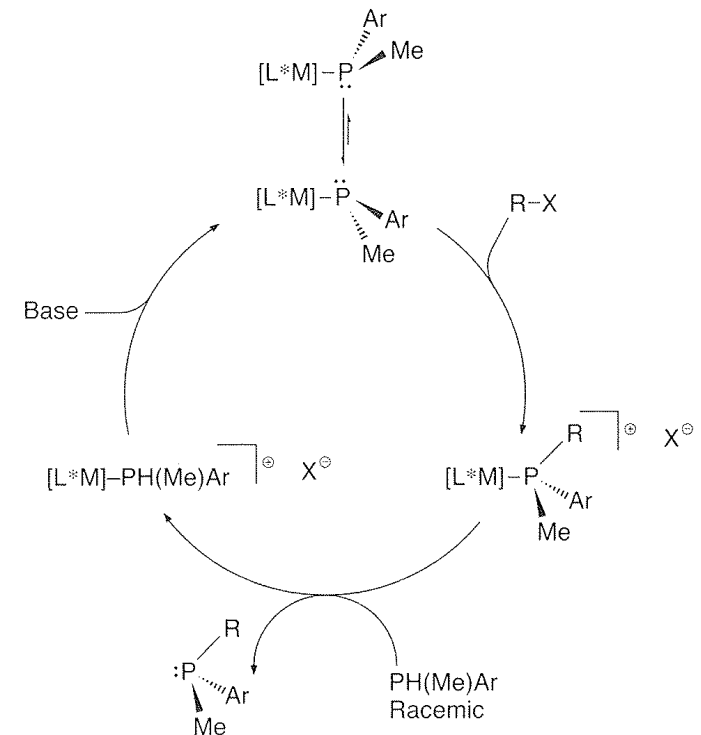
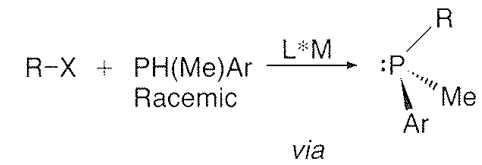
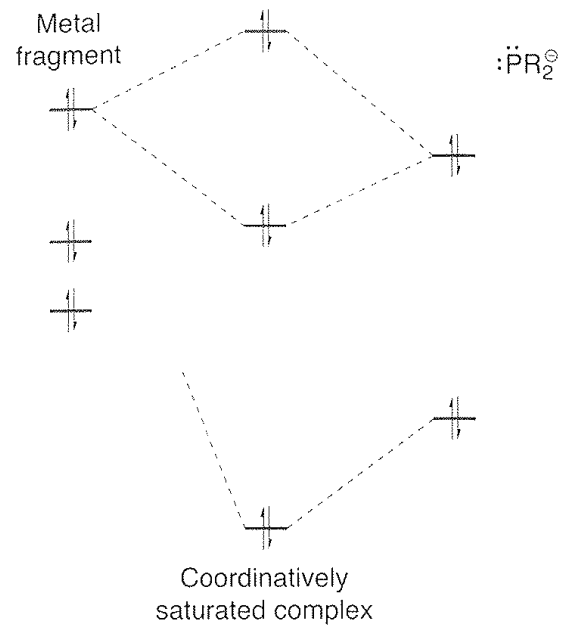
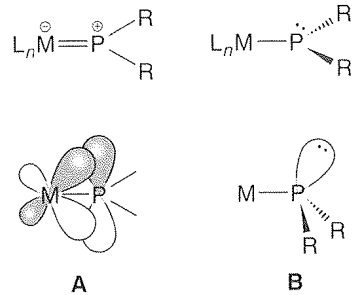
Borylkomplexe



Synthese

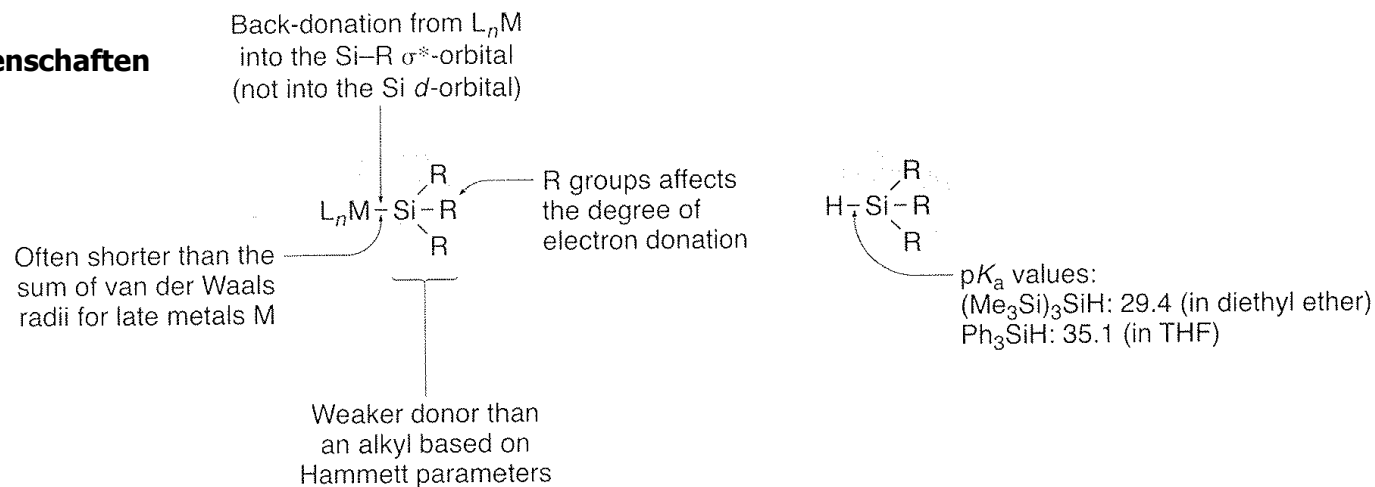


Phosphidkomplexe

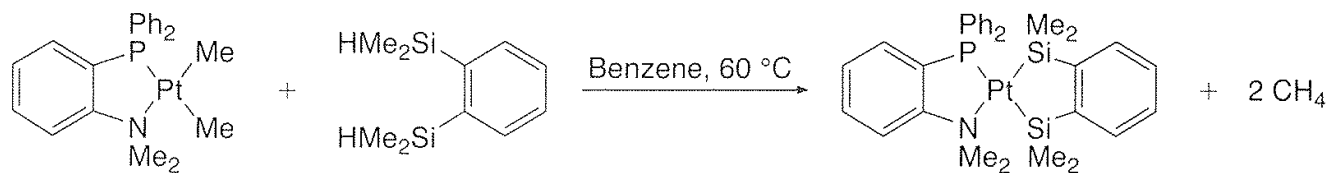
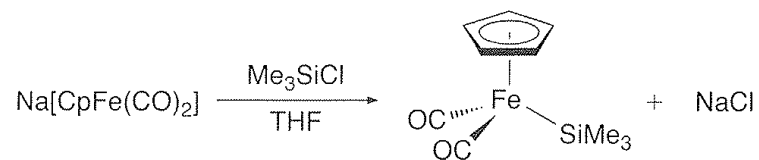


Silylkomplexe

Elektronische Eigenschaften

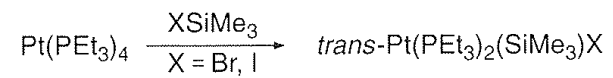
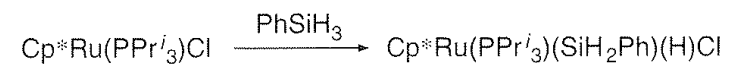
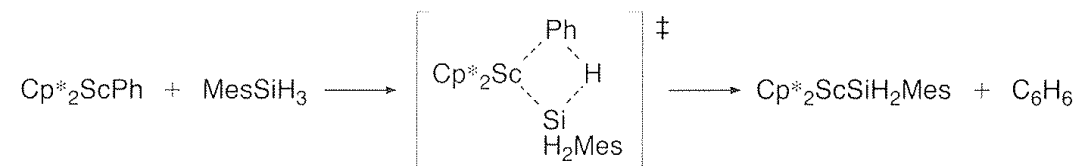


Synthese



Silylkomplexe

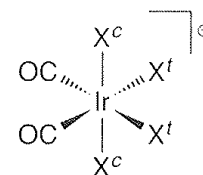
Synthese



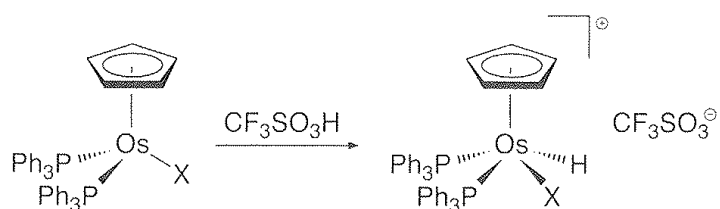
Halogenide

Steric properties of halides and halide ligands.

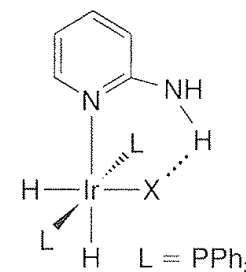
	F	Cl	Br	I
Ionic radius (Å) ⁵¹⁰	1.36	1.81	1.95	2.16
Cone angle (°) ⁵⁰⁹	92	102	105	107



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 ⁻¹)
I	14.1
Br	16.3
Cl	19.7
F	37.3



X	Ir X–HN (kcal mol ⁻¹)
I	< 1.3
Br	1.8
Cl	2.1
F	5.2

Cp* ₂ ZrCl ₂	Zr–Cl _{ave} 115 kcal/mol
Cp* ₂ ZrI ₂	Zr–I _{ave} = 80.4 kcal/mol

H-Brückenbindung