Anorganische Strukturen und Reaktionsmechanismen

CHE.367

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  - Mechanismen
  - 16 und 17 e^- Komplexe
  - Assoziative Substitution
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  - Dissoziative Substitution
  - Polyhaptoliganden

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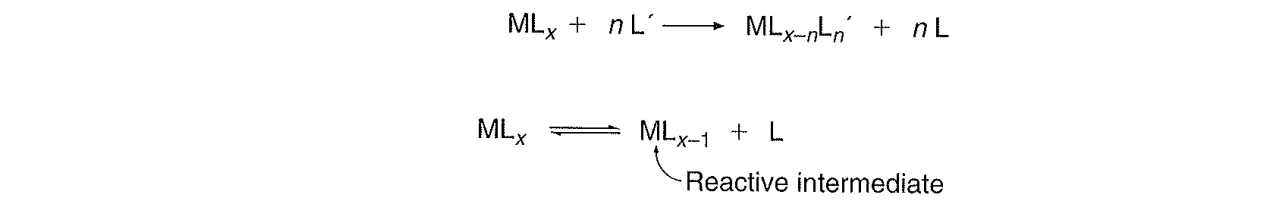
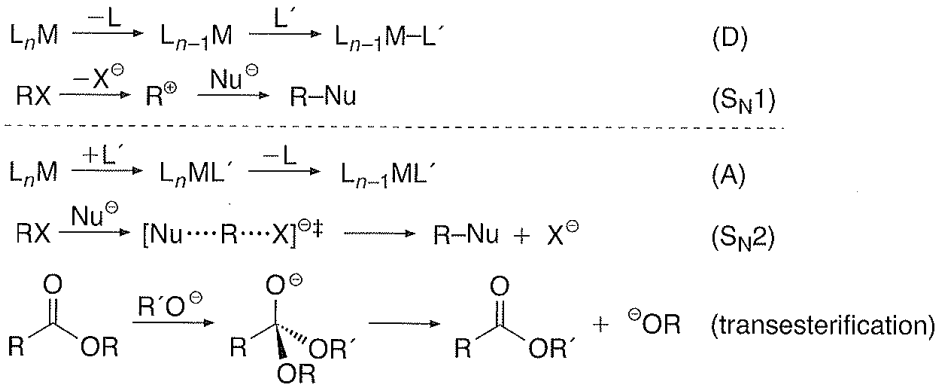
  - Wasserstoff
  - H-Silane
  - C-H Bindungen
  - Addition von H_2 und C-H ohne Ox. Add.
    - σ-Bindungsmetathese
    - [2+2 Additionen]
- Ox Add Polarer Reagentien
  - S_N2
  - Radikalisch
  - Konzertiert
  - Dinuklear

Ligandenaustausch





Ligandenaustausch

Trends for associative and dissociative substitution reactions.

	Associative mechanisms	Dissociative mechanisms
Type of complex	Occurs with 16-e⁻ and 17-e⁻ complexes	Occurs with 18-e⁻ complexes
Rate law	First order in entering ligand	Typically zero order in entering ligand
Activation parameters	Large negative $\Delta S^{\ddagger}$ Large negative $\Delta V^{\ddagger}$	Small positive $\Delta S^{\ddagger}$ Small positive $\Delta V^{\ddagger}$
Electronic effects	Ligand: Favored for more basic entering ligands Metal: Favored for more electrophilic metal centers	Can be favored for more electron-rich or more electron-poor metal centers
Effect of departing ligand	Affected only slightly by the departing ligand	Affected strongly by the strength of the bond to the departing ligand
Steric effects	Favored for sterically accessible metal centers	Favored for sterically hindered metal centers
Additional factors		Cationic complexes can react through "encounter" complexes Reduction weakens M–L and accelerates dissociation of a ligand

Ligandenaustausch: Thermodynamik

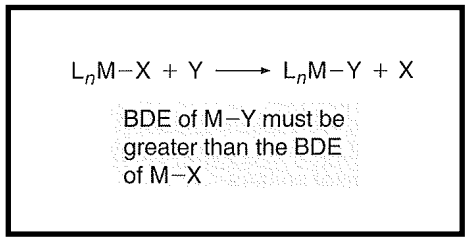
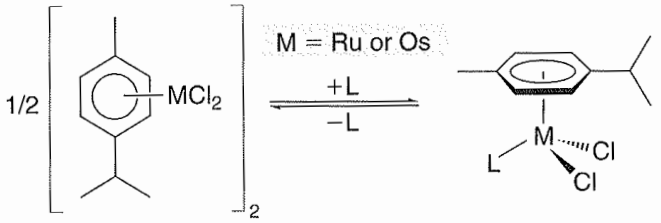


Table 5.3. Relative enthalpies for coordination of various phosphorus ligands to ruthenium and osmium dimers.

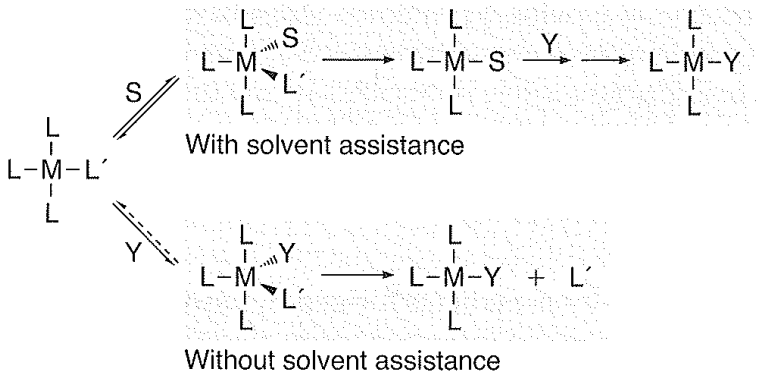


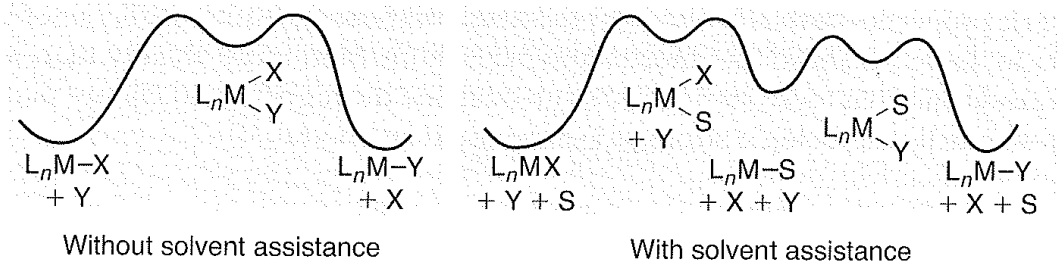
	Reaction enthalpy (kcal/mol)	
L	**Os**	**Ru**
PPh_3	43.1	36.3
$P(OMe)_3$	49.8	39.0
PMe_3	61.6	55.3
PEt_3	54.9	51.3
PCy_3	47.9	34.4

Table 5.2. Selected M–L bond dissociation energy estimates (gas-phase values unless indicated; otherwise, *D* = BDE in kcal/mol).

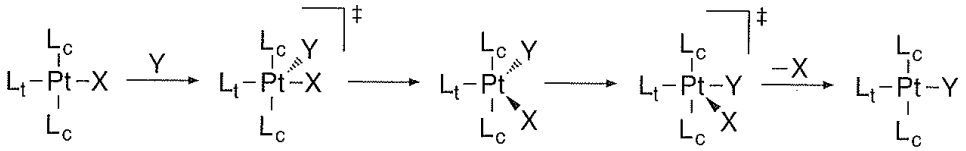
Compound process	References
$Ni(CO)_4 \longrightarrow Ni(CO)_3 + CO$ $D = 25 \pm 2$	a, b
$Fe(CO)_5 \longrightarrow Fe(CO)_4 + CO$ $D = 41 \pm 2$ (singlet) $D = 41$ (triplet)	b, c
$M(CO)_6 \longrightarrow M(CO)_5 + CO$ $D(Cr) = 37 \pm 2$ $D(Mo) = 40 \pm 2$ $D(W) = 46 \pm 2$	b
$IrCl(PPr^i_3)_2CO \xrightarrow[D > 72]{} IrCl(PPr^i_3)_2 + CO$	d
$Mn_2(CO)_{10} \xrightarrow[D = 36 \pm 2]{} Mn_2(CO)_9 + CO$	e, f
$Mn_2(CO)_{10} \xrightarrow[D = 38 \pm 5]{\text{hexane}} 2\,\bullet Mn(CO)_5$	g, h
$CpNi^{\oplus}(\text{ethylene}) \xrightarrow[D = 38 \pm 5]{} CpNi^{\oplus} + \text{ethylene}$	i
$Cp_2Co(III)^{\oplus} \xrightarrow[D_1 = 118 \pm 10]{-Cp\bullet} CpCo(II)^{\oplus} \xrightarrow[D_2 = 85 \pm 10]{-Cp\bullet} Co(I)^{\oplus}$	j
$[W(PCy_3)_2(CO)_3L] \longrightarrow [W(PCy_3)_2(CO)_3] + L$ $L = H_2$, 9.9; N_2, 13.5; $NCCH_3$, 15.1; py, 18.9; $P(OMe)_3$, 26.5; CO, 30.4	k

Assoziative Substitution: d^8-Komplexe



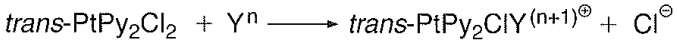


Retention der Stereochemie



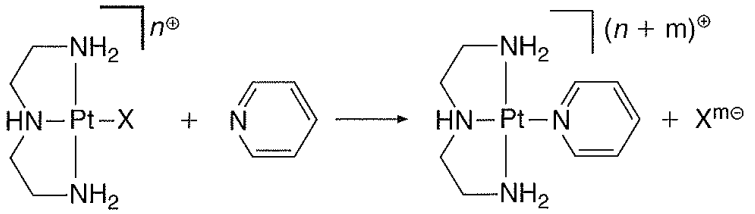
Einfluss von Eintritts- und Abgangsgruppe

Eintrittsgruppe



Y	$k(M^{-1}\ s^{-1}) \times 10^3$
Cl^-	0.45
NH_3	0.47
NO_2^-	0.68
N_3^-	1.55
Br^-	3.7
I^-	10.7
SCN^-	180
PPh_3	249,000

Austrittsgruppe



X	Rate constant $k_{ds} \times 10^6\ s^{-1}$
NO_3^-	Fast
H_2O	1900
Cl^-	35
Br^-	23
I^-	10
N_3^-	0.83
SCN^-	0.3
NO_2^-	0.05
CN^-	0.017

cis und *trans* Effekte: d^8-Komplexe

trans-$Pt(PEt_3)_2(X)Cl$ + py $\overset{EtOH}{\rightleftharpoons}$ *trans*-$Pt(PEt_3)_2(X)(py)^{\oplus}$ + $Cl^{\ominus}$

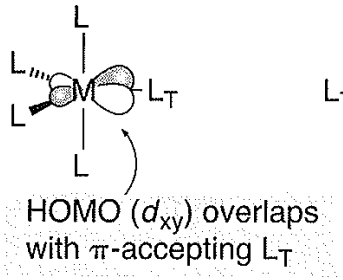
X	$k_{obs}(s^{-1})^b$	*t* (°C)
H^-	4.7×10^{-2}	0
Me^-	6.0×10^{-4}	25
$C_6H_5^-$	1.2×10^{-4}	25
Cl^-	3.5×10^{-6}	25

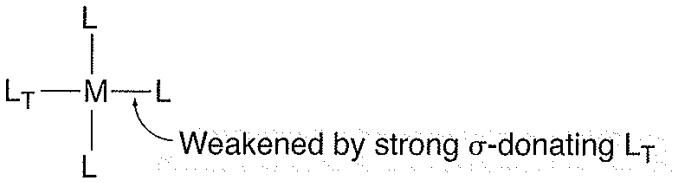
cis-$Pt(PEt_3)_2(X)Cl$ + py $\overset{MeOH}{\rightleftharpoons}$ *cis*-$Pt(PEt_3)_2(X)(py)^{\oplus}$ + $Cl^{\ominus}$

X	$k_{obs}(s^{-1})^b$	*t* (°C)
Me^-	11.4	25
$C_6H_5^-$	7.92	25
Cl^-	4.17	25

***trans* Effekt:**

$R_3Si^- > H^- \sim CH_3^- \approx CN^- \approx$ olefins, $CO > PR_3 \approx NO_2^- \approx I^- \approx SCN^- > Br^- > Cl^- > RNH_2 \approx NH_3 > OH^- > NO_3^- \approx H_2O$

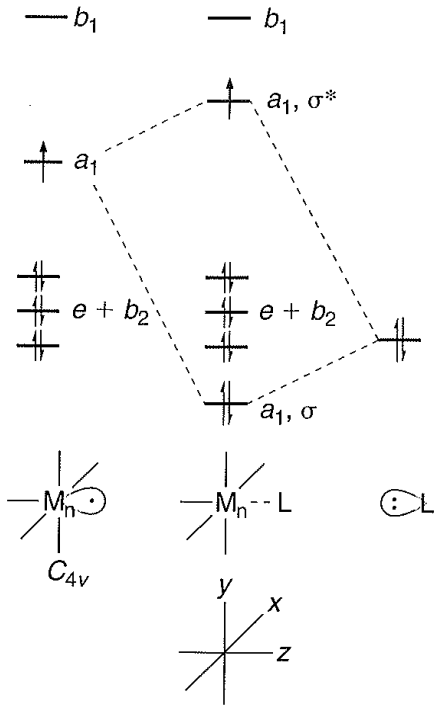


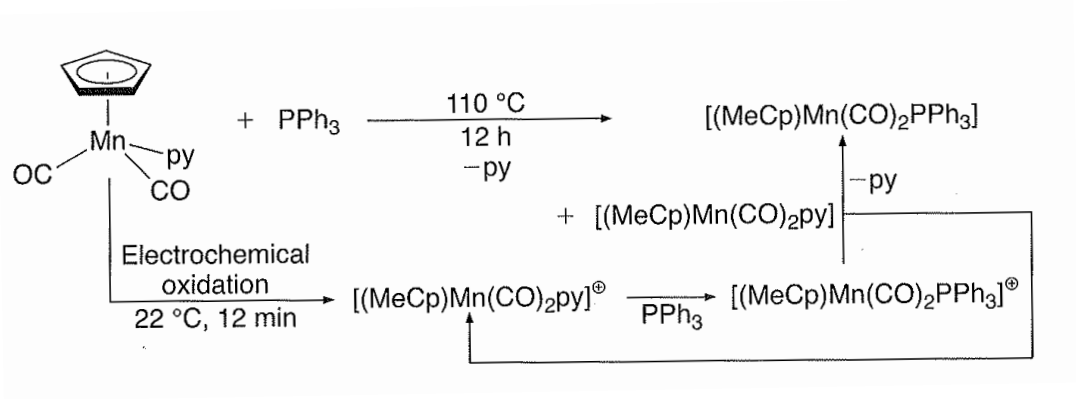


Starke σ-Donoren (destabilisieren Grundzustand) und starke π-Akzeptoren (stabilisieren Übergangszustand) erzeugen starken *trans* Effekt

Assoziative Substitution: 17 e⁻ Komplexe

Molecular orbital scheme for the interaction of the •$Mn(CO)_5$ fragment with a Lewis base.





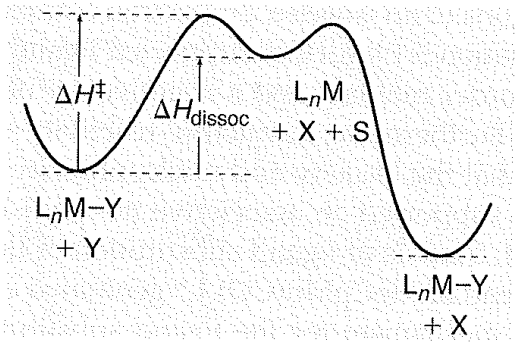
$(CO)_5Mn{-}Mn(CO)_5 \xrightarrow{h\nu} (CO)_5Mn\cdot \xrightarrow{CCl_4} (CO)_5MnCl$

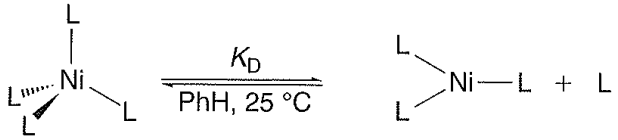
$(CO)_5Mn\cdot \xrightarrow{PPh_3} (PPh_3)(CO)_5Mn\cdot \xrightarrow{-CO} (PPh_3)(CO)_4Mn\cdot \xrightarrow{CCl_4} (PPh_3)(CO)_4MnCl$

$(CO)_5MnCl/(PPh_3)(CO)_4MnCl$ was independent of [CO]

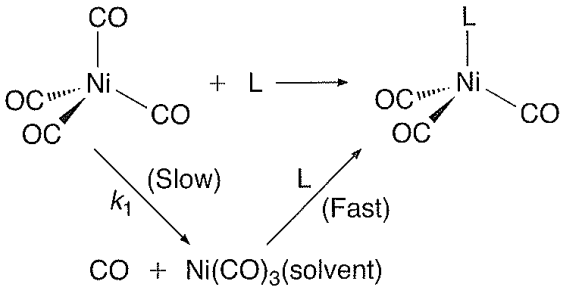
Dissoziative Substitution: 18 e- Komplexe

Reaction coordinate diagram for a dissociative substitution reaction.

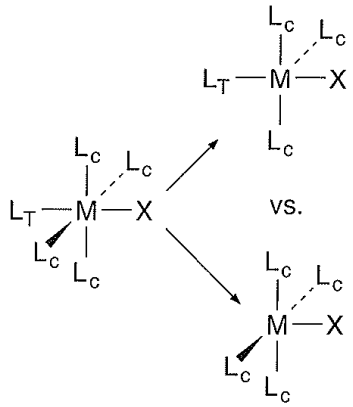




L	P(OEt)$_3$	P(O-*p*-tolyl)$_3$	P(O-i-Pr)$_3$	P(O-*o*-tolyl)$_3$	PPh$_3$
Tolman cone angle	109°	128°	130°	141°	145°
K_D (M)	Too small to measure	6×10^{-10}	2.7×10^{-5}	4.0×10^{-2}	No NiL_4 detected



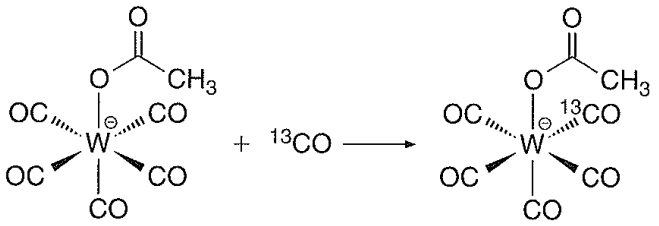
Dissoziative Substitution: Elektronische Effekte

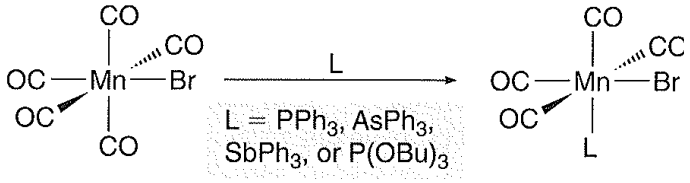


Stabilized by bidentate binding of X
Destabilized by strong σ-donation by X
Destabilized by strong π-acceptance by X

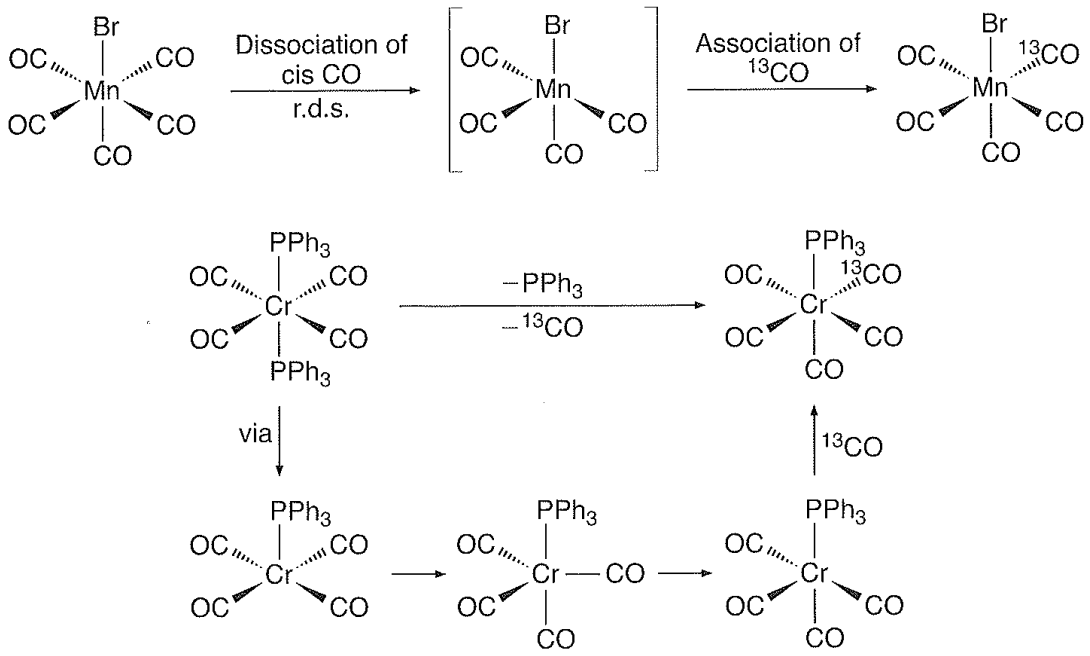
Stärke des *cis*-Effekt:

$NO_3^- > OAc^-, HCO_2^-, RC(O)^- > NHR > SH^{-126} > OR > Cl^- > Br^- > I^- > carbene > PPh_3 > H^-, CO.$



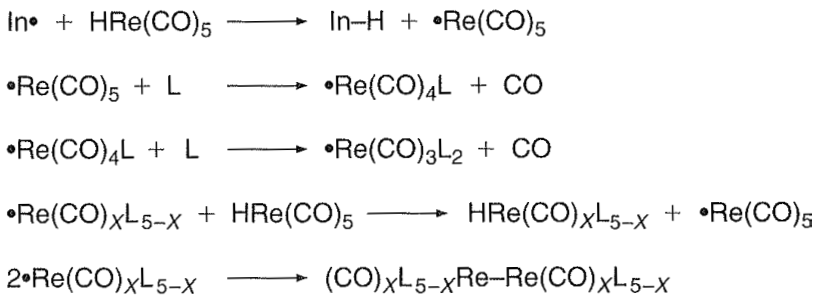


Dissoziative Substitution: Stereochemie

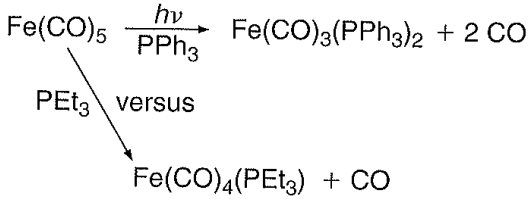


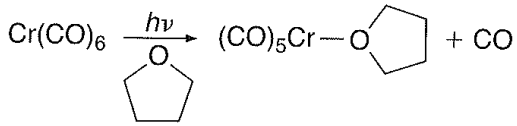
Induzierte Substitution

Radikalisch

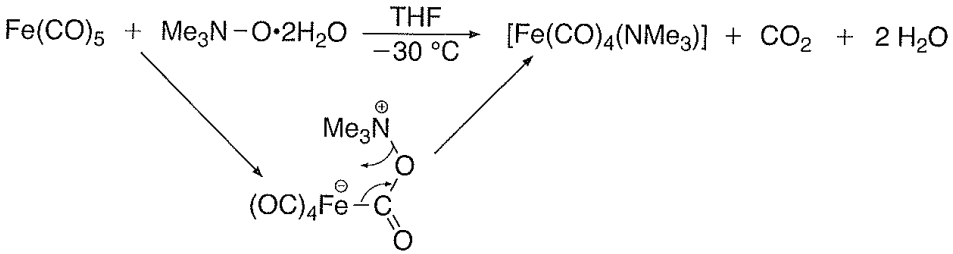


Photochemisch

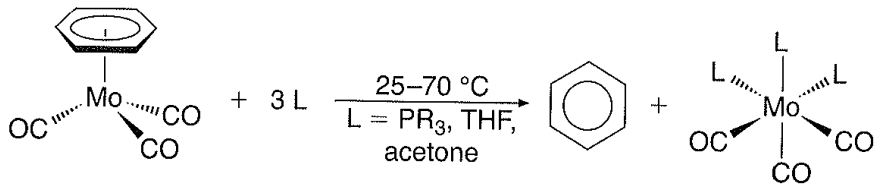


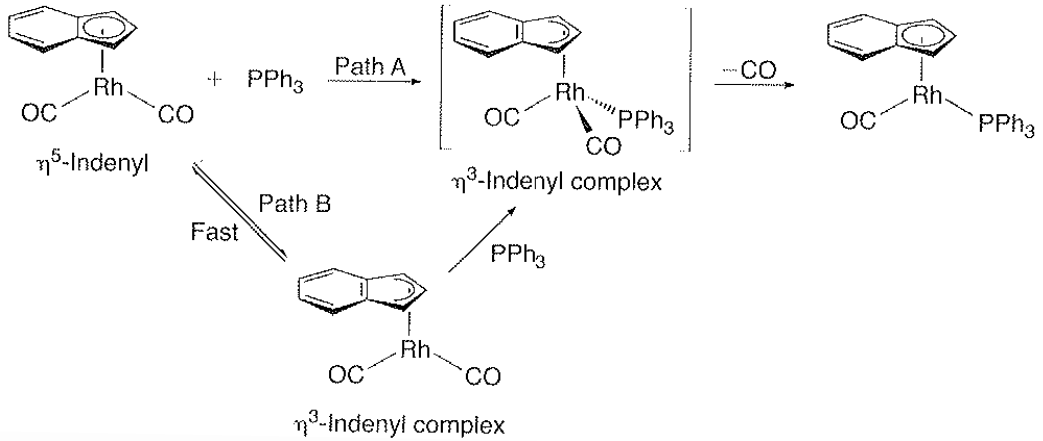


Oxidation von CO

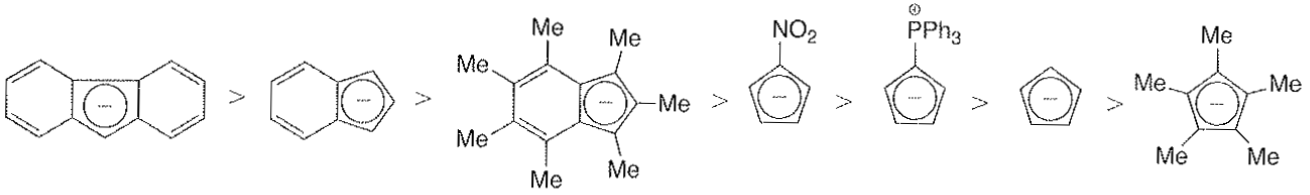


Polyhaptoliganden



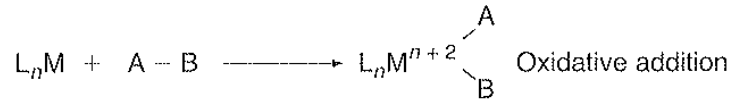


Effect of η^5 ligands on the rate of ligand substitution in $(\eta^5\text{-Cp}')\text{Co(CO)}_2$.



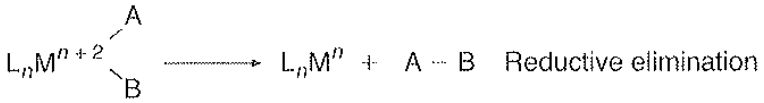
——	3.8×10^8	6.1×10^5	1.2×10^4	1.1×10^2	1	2.2×10^{-2}

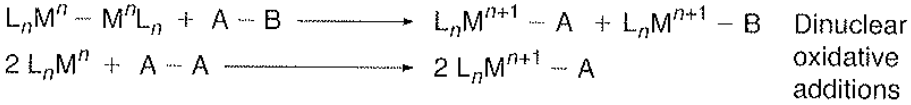
Oxidative Addition



X valence electrons at M
m d-electrons
n oxidation state of M

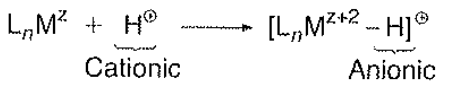
X + 2 valence electrons at M
m − *d*-electrons
n + 2 oxidation state of M

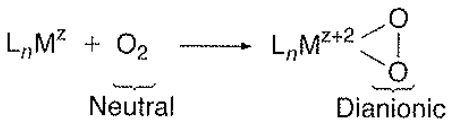




X valence electrons at M
m d-electrons
n oxidation state of M

X + 1 valence electrons at M
m − 1 *d*-electrons
n + 1 oxidation state of M





Oxidative Addition

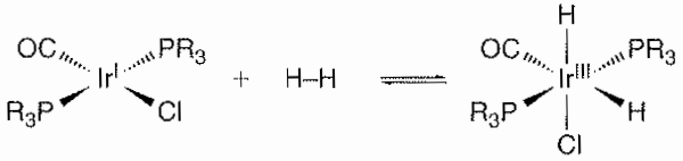
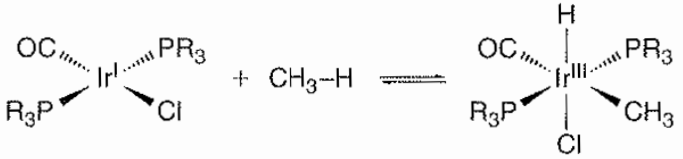
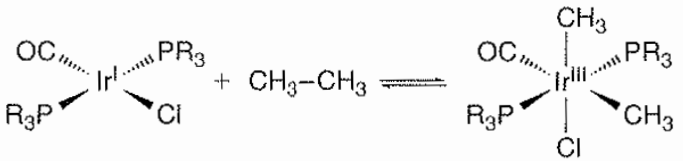
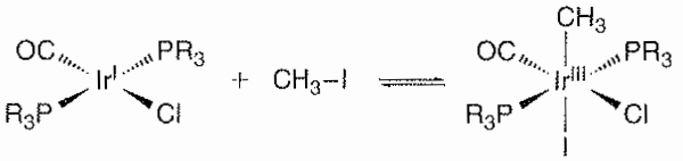
Table 6.1. Examples of reagents with low polarity, high polarity, and intermediate polarity that undergo oxidative addition to transition metal complexes.

Reagents that are nonpolar or have low polarity:
H_2, RH, ArH, R_3SiH, R_3SnH, $R_3Sn–SnR_3$, R_2B-H, R_2BBR_2, RSSR, NC–CN, and Ph-PPh_2
Reagents that are highly polar:
HX, X_2, RCO_2H, RX, ROTs, RC(O)X, RSO_2X, $ROSO_2X$, RC(O)–OPh, HgX_2, and $SnCl_4$, $GeCl_4$, R_3SnCl, R_3PbCl
Reagents with medium polarity:
RSH, ROH, RNH_2, ArX, ArCN, CCl_4, and $CHCl_3$

General trends for oxidative addition and reductive elimination:

1. Oxidative addition tends to be more favorable to electron-rich metal centers, and reductive elimination more favorable from electron-poor metal centers.
2. Oxidative addition tends to be favored by less-hindered metal centers, and reductive elimination favored by more-hindered metal centers.
3. Oxidative addition of nonpolar reagents requires a site of unsaturation and a *d*-electron count of 16 or less.
4. Rates and equilibrium constants for ligand dissociation or association that occur prior to oxidative addition affect the rates of the addition processes.

Oxidative Addition: Thermodynamik

Reaction	ΔH (estimated)[a] (kcal/mol)	ΔG (estimated)[a] (kcal/mol)
	−15[b]	−6[b]
	−2	+3
	−4	+6
	−35[c]	−25

Oxidative Addition: Thermodynamik

Table 6.3. Metal–ligand bond energies for two different Ir(III) systems.

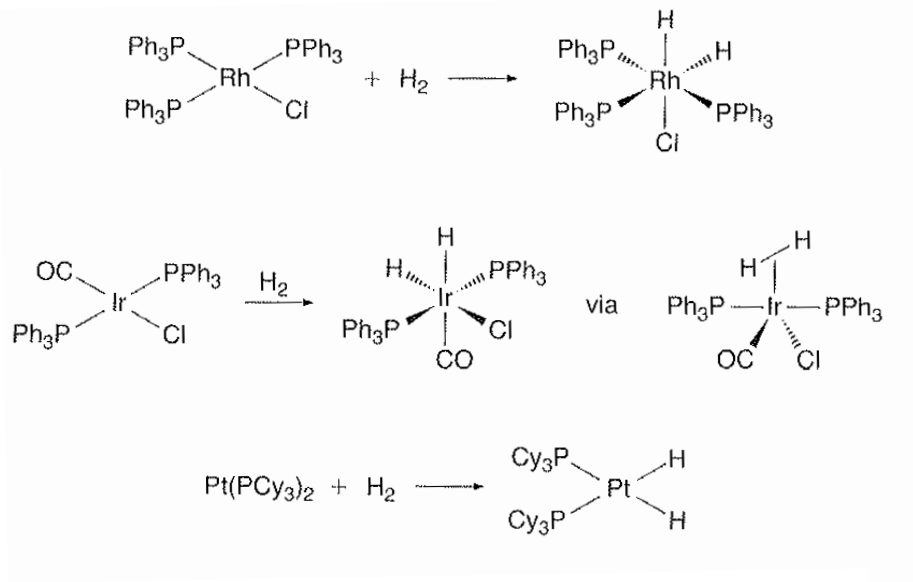
X	$Cp^*Ir(PMe_3)X_2$[a]	$L_2Cl(CO)IrX_2$[b]
H	74.2	60
Cl	90.3	71
Br	76.0	53
I	63.8	35
CH_3		35.4
C_6H_{11}	50.8[c]	
C_6H_5	80.6[c]	

Table 6.4. Enthapy for oxidative addition of various reagents to $Cp^*Ir(PMe_3)$.

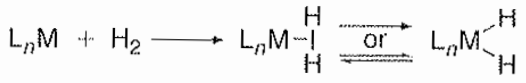
$Cp^*(PMe_3)Ir + A–B \rightarrow Cp^*(PMe_3)Ir(A)(B)$

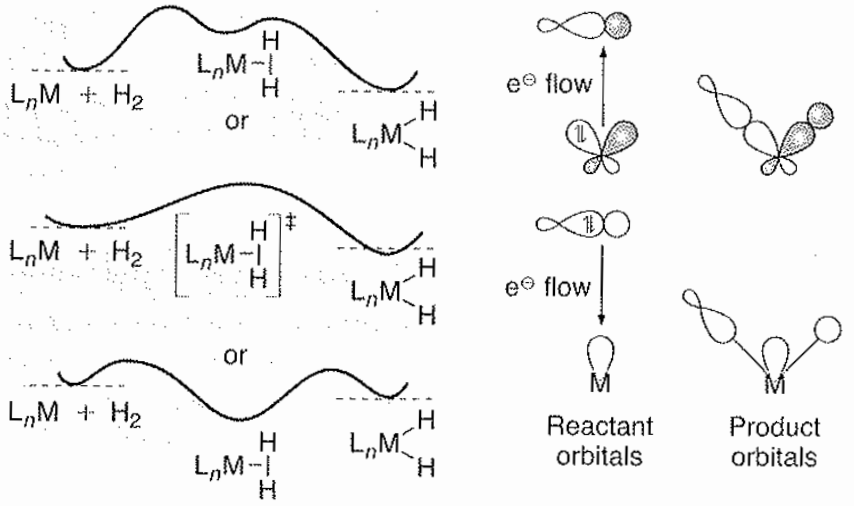
A–B	$-\Delta H^a$	A–B	$-\Delta H^b$	A–B	$-\Delta H^a$
$C_6H_{11}–C_6H_{11}$	22	Cl_2	123	HCl	61
$C_6H_{11}–H$	30	Br_2	106	HBr	63
H–H	44[b]	I_2	91	HI	57
$C_6H_3–H$	45				
$C_6H_5–C_6H_5$	49				

Oxidative Addition: H_2

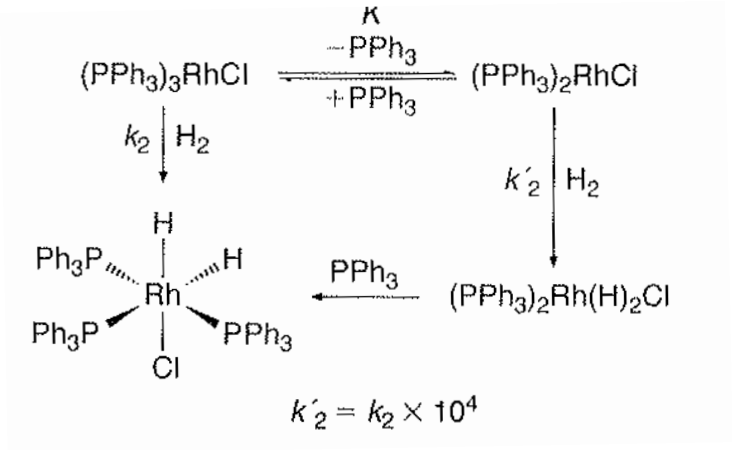


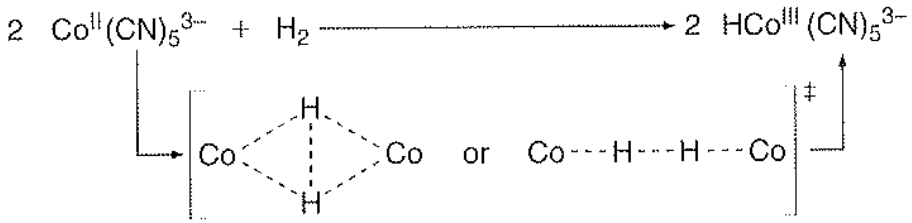
Reaction coordinate diagrams and orbital interactions that occur during the oxidative addition of H_2 to transition metal complexes. (Orbital interactions from Hall, M. B. et al. *Chem. Rev.* **2000**, *100*, 353.)



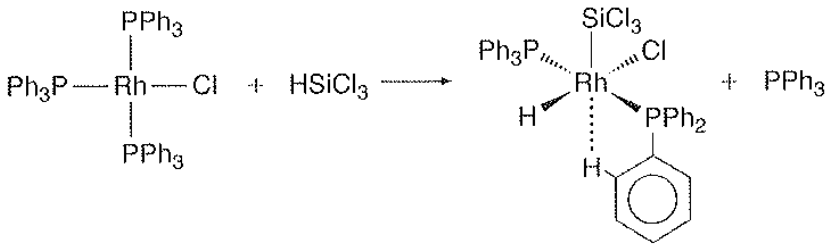


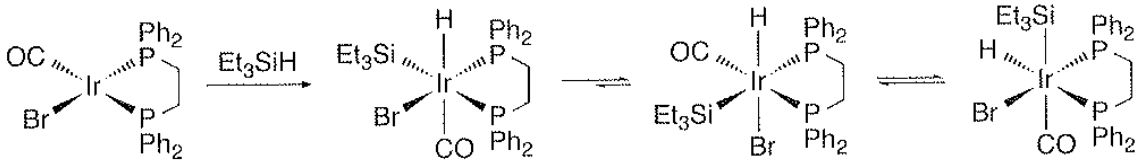
H_2 Addition: Mechanismen

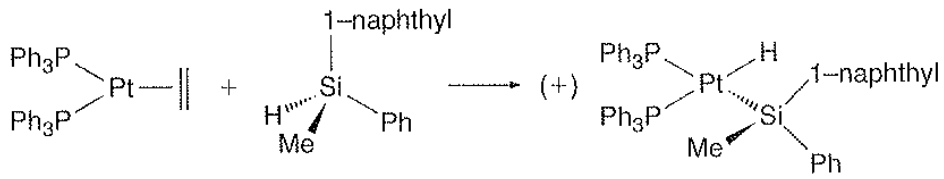


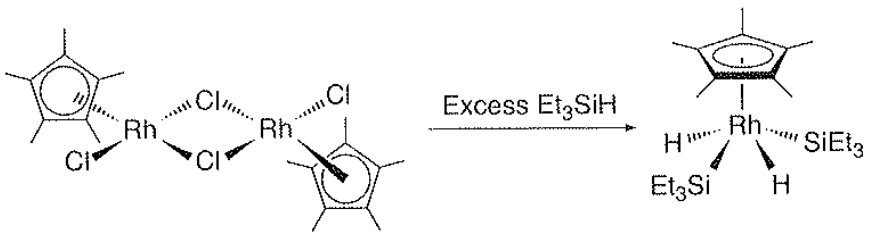


Oxidative Addition: Silane



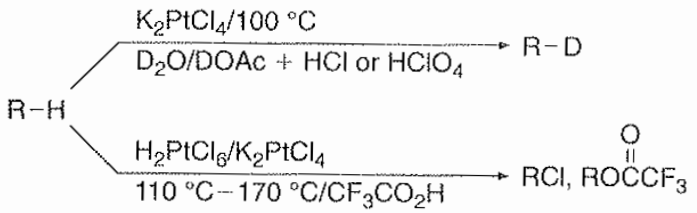


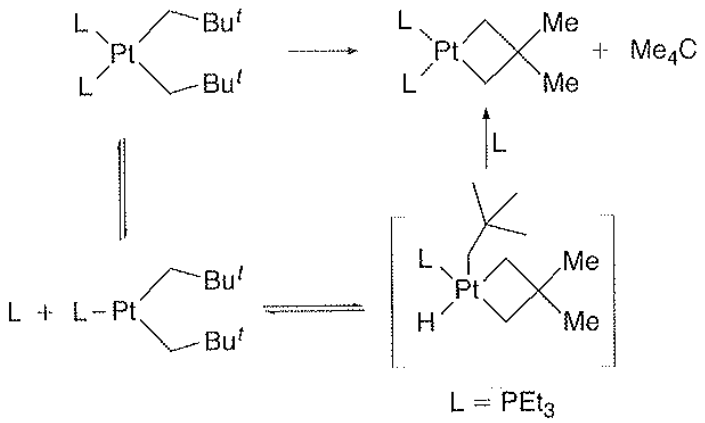




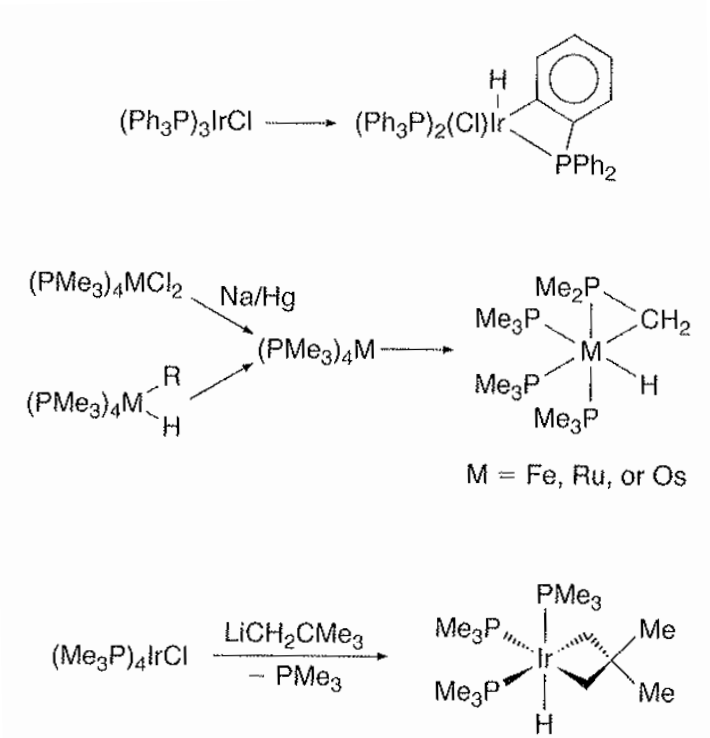
Oxidative Addition: Alkane

Shilov:

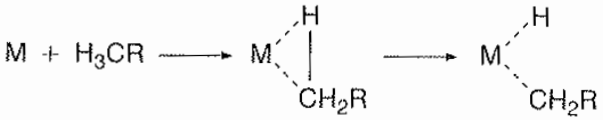




Intramolekulare Addition:

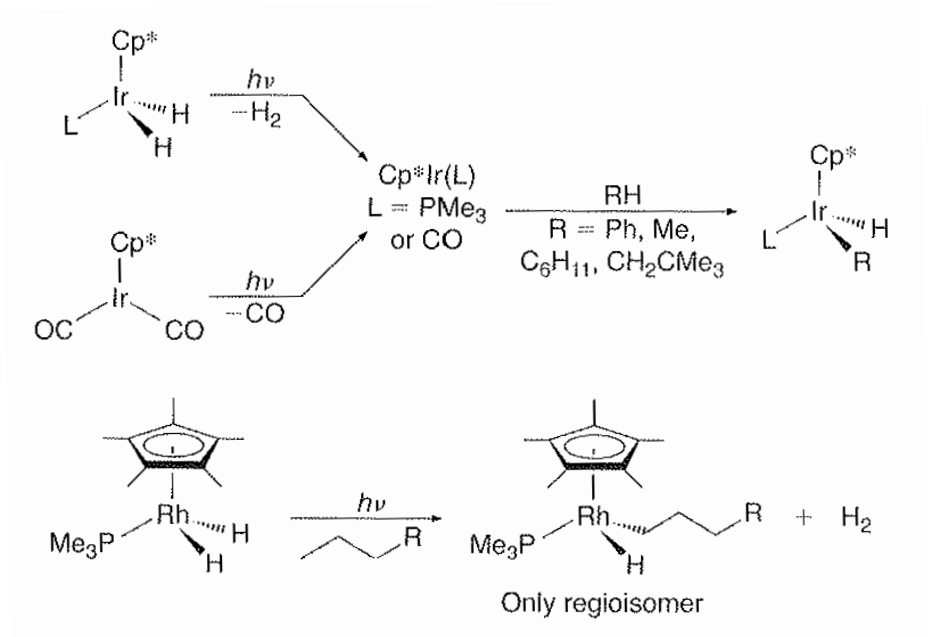


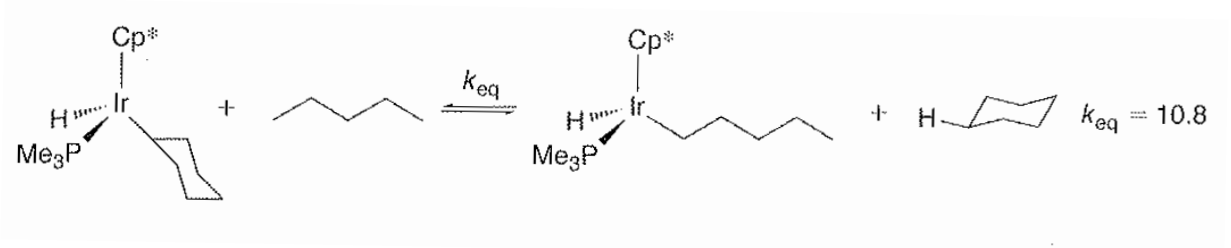
Mechanismus



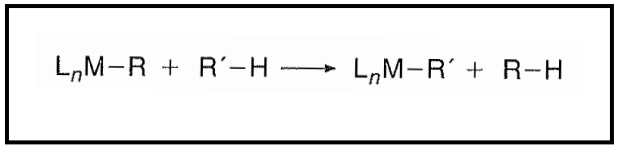
Oxidative Addition: Alkane

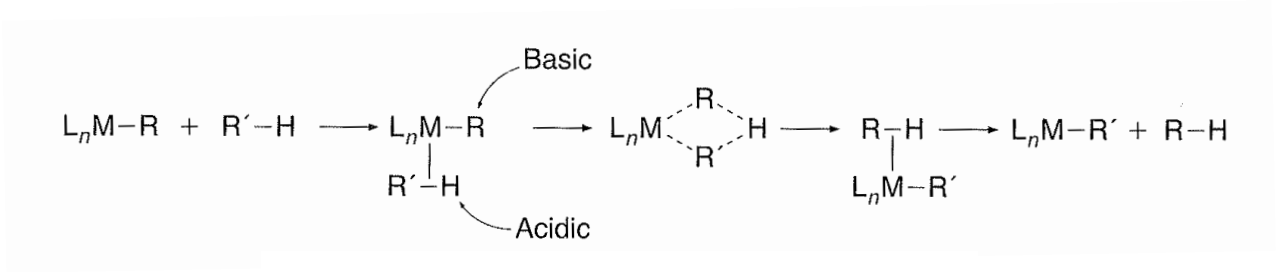
Intermolekulare Addition:

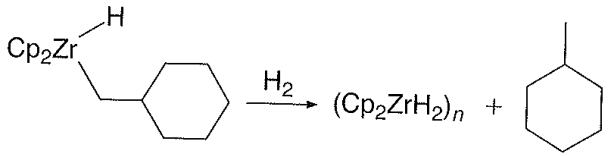




σ-Bindungsmetathese





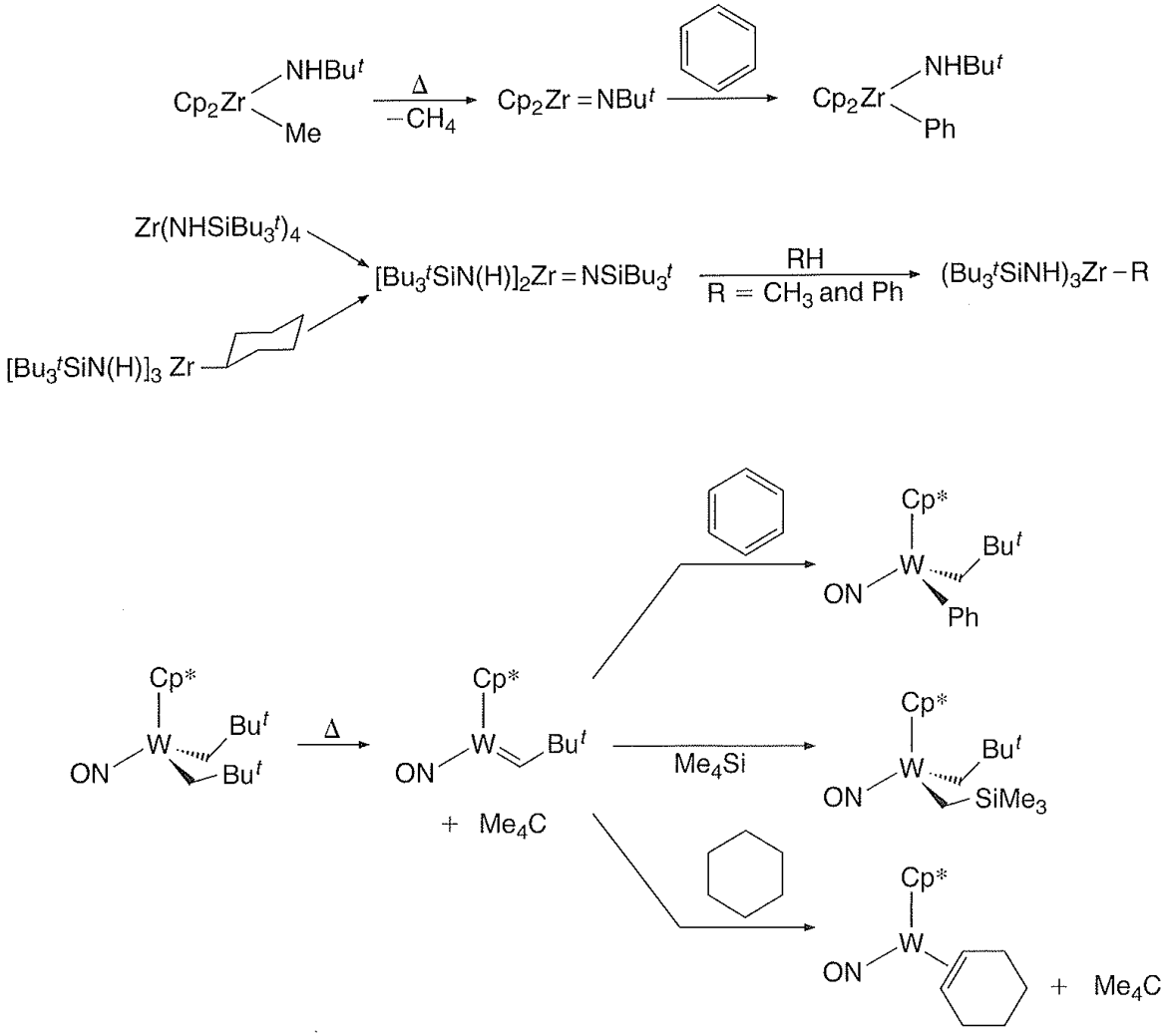


$Cp^*_2ScMe + R-H \longrightarrow Cp^*_2ScR + CH_4$

Rate: $R = Ph > {}^{13}CH_3$

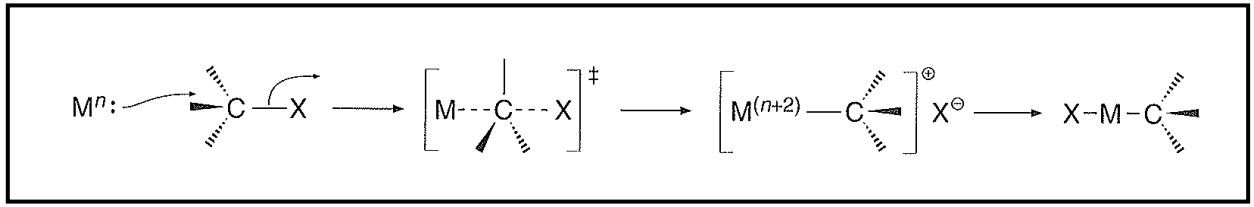
$Cp^*_2Lu-Me + {}^{13}CH_3 \longrightarrow Cp^*_2Lu-{}^{13}CH_3 + CH_4$

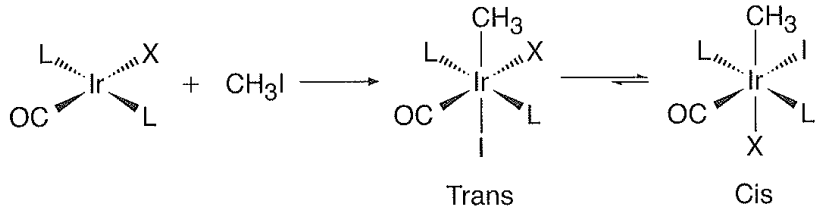
[2+2]-Additionen

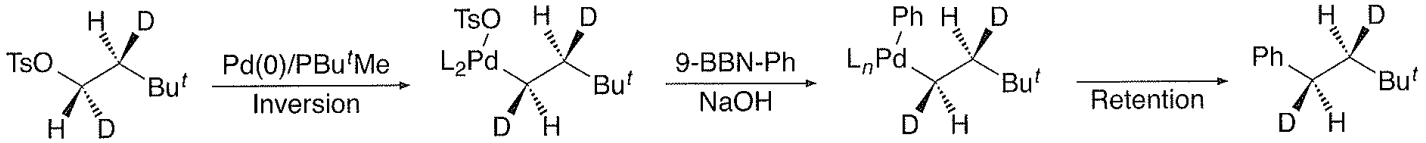


Oxidative Addition polarer Reagentien

S_N2 Mechanismus:

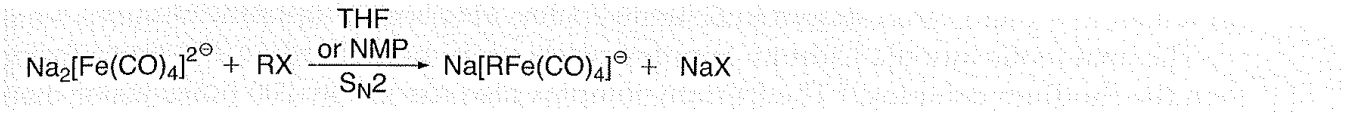




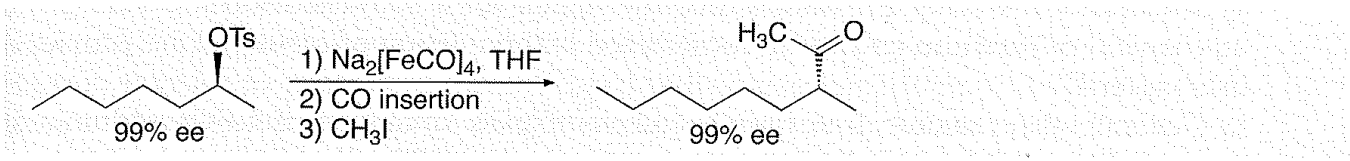


Oxidative Addition polarer Reagentien

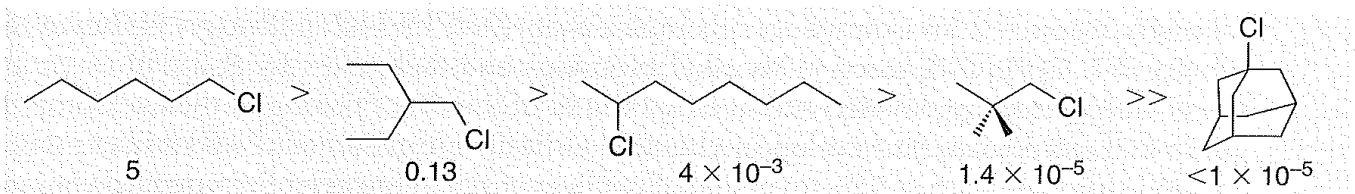
Stoichiometry:



Stereochemistry:



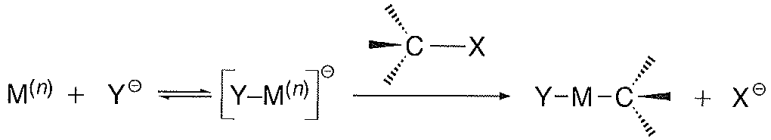
Structural–reactivity relationship:



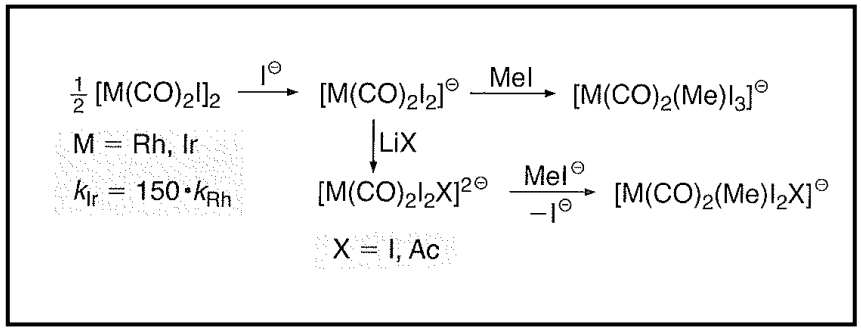
Leaving group effect (R = n–$C_{10}H_{21}$)

	RI	> RBr	> ROTs	> RCl
k (relative)	51	1.0	0.58	2.3×10^{-3}

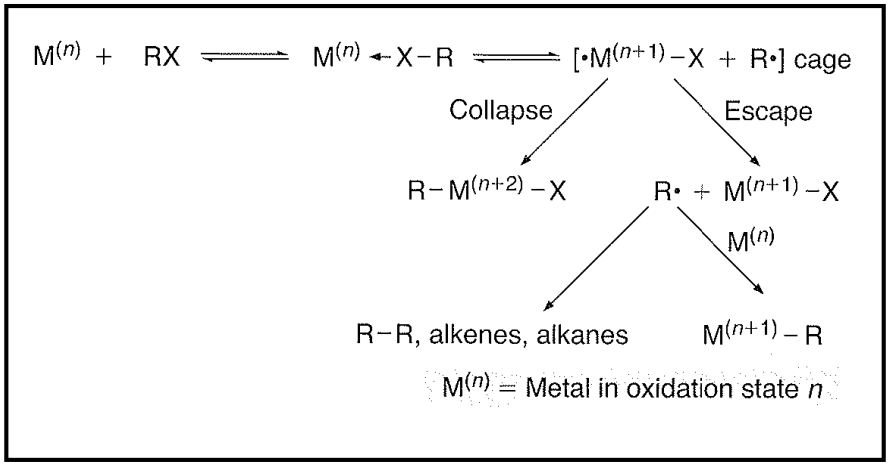
Aktivierung durch Anionen

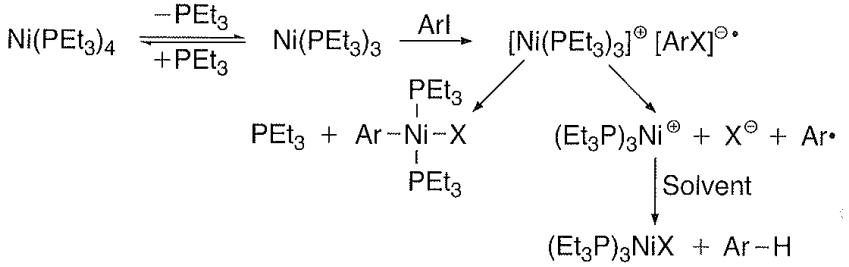


Monsanto Essigsäure

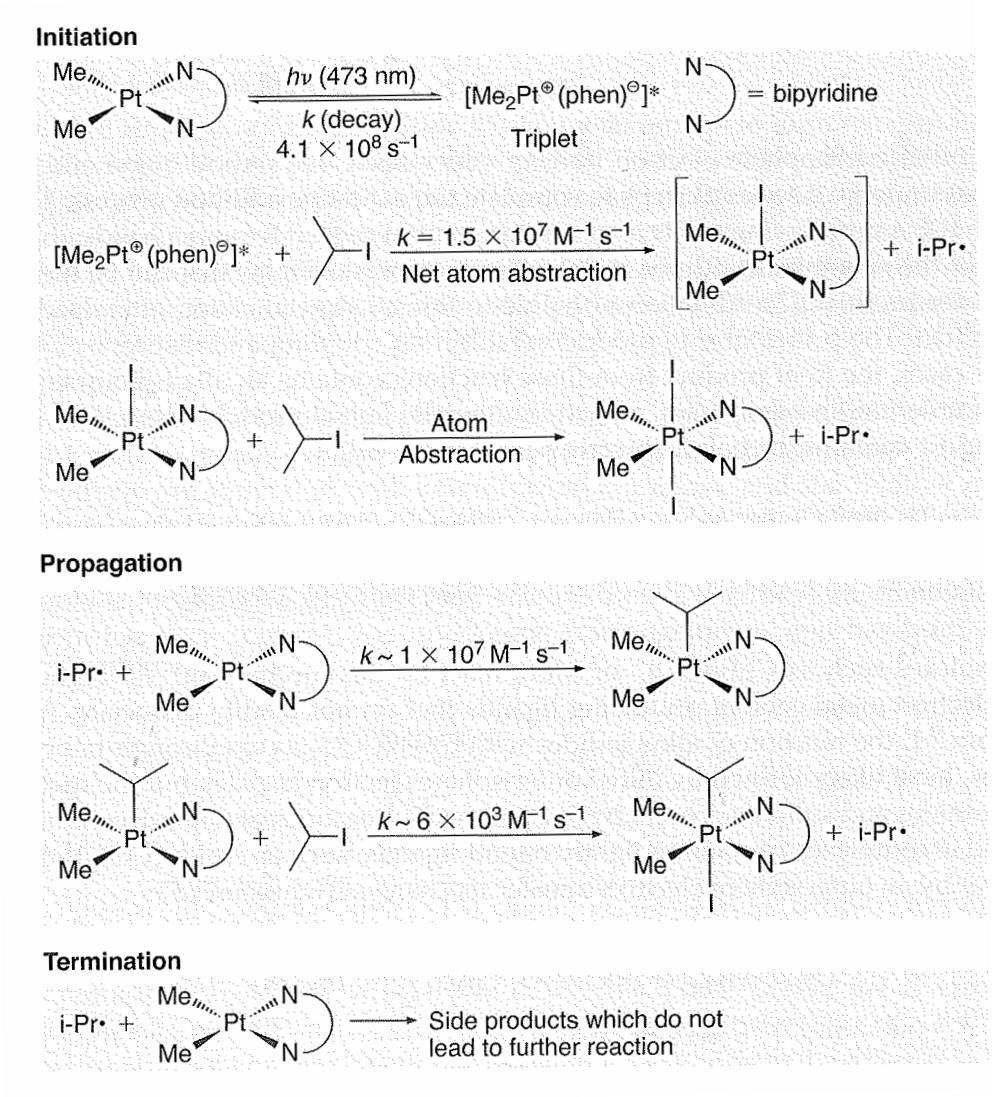


Inner-Sphere Elektronentransfer

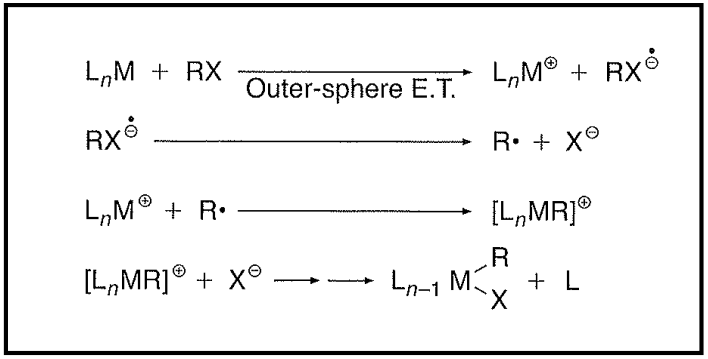


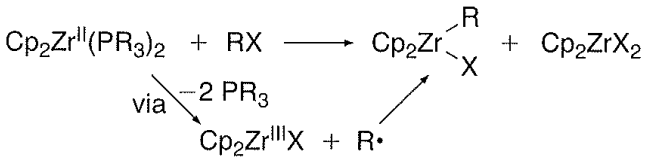


Radikalkettenreaktion

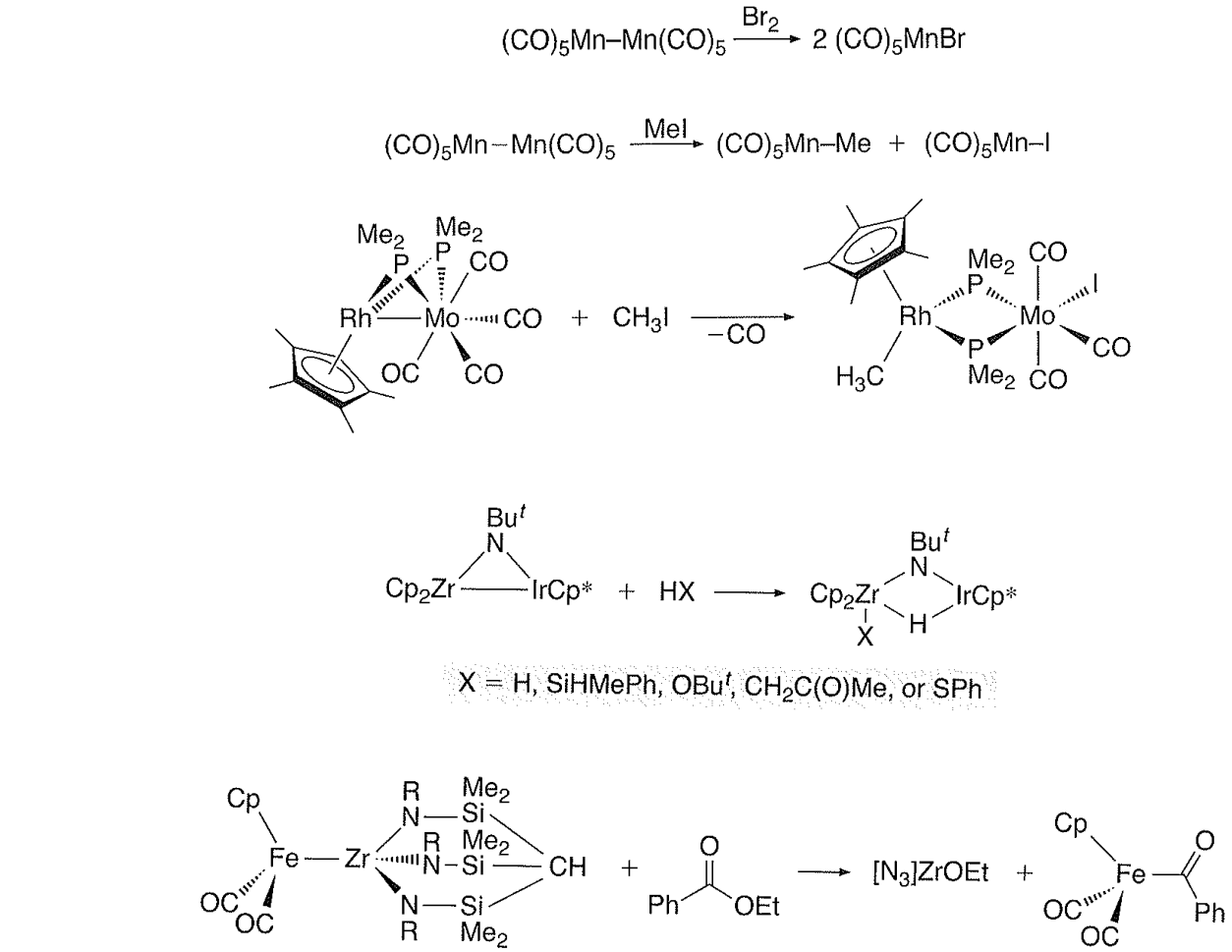


Outer-Sphere Elektronentransfer

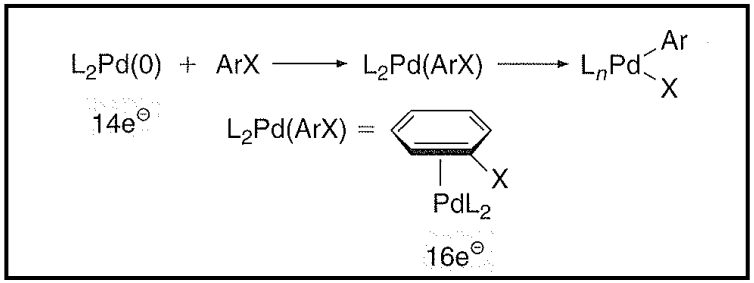




Dinukleare Addition



Konzertiert polar



Dissoziation

$$(PPh_3)_4Pd \longrightarrow (PPh_3)_3Pd \rightleftharpoons (PPh_3)_2Pd \xrightarrow{ArI} (PPh_3)_2Pd(Ar)(X)$$

$(PPh_3)_3Pd$: + PPh_3; $(PPh_3)_2Pd$: + PPh_3

Ligand

$$R_3P-Pd-PR_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_3P-Pd \xrightarrow[k_2]{ArBr} R_3P-Pd(Ar)(Br) \xrightarrow{\text{For R = } o\text{-tol}} \text{L}(\text{Ar})\text{Pd}(\text{Br})_2\text{Pd}(\text{Ar})\text{L}$$

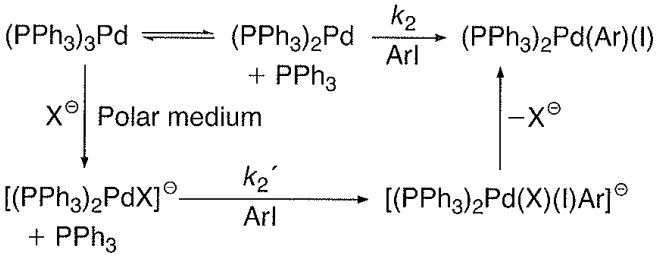
R_3P-Pd: + L

R = *o*-tol or Bu^t

$k_{-1}[L] \geq k_2$ for R = *o*-tol

$k_{-1}[L] \leq k_2$ for R = Bu^t

Anion



$k_2 > k_2'$, but $[(PPh_3)_2PdX]^{\ominus} > [(PPh_3)_2Pd]$ in polar media