

# Deduction of Mechanisms

## 4.2 Transition State Theory

**Observations:** Reaction rates increase almost ever with increasing T

this relation **k vs  $E_a$**  is consistent with the Arrhenius equation

$$k = A \cdot e^{-E_a/RT}$$

k describes the overall reaction rate "constant"

A and  $E_a$  are considered T independent, mostly correct over a small range of  $\Delta T$

$$\text{Transition state theory (TST): } k = \chi \frac{k_B \cdot T}{h} \cdot e^{\Delta S^\ddagger/R} \cdot e^{-\Delta H^\ddagger/RT}$$

$\chi$  = Übergangsfaktor, generally = 1

$k_B$ : Boltzmann

h: Planck

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**Arrhenius:**  $\ln k = \ln A - \frac{E_a}{RT}$  plot  $\ln k$  vs.  $1/T$  liefert  $A$  und  $E_a$

translates into **TST:**  $\ln \frac{k}{T} = \ln \frac{k_B}{h} + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{R \cdot T}$

➔  $\ln(k/T)$  vs.  $T^{-1}$  yields  $\Delta H^\ddagger$  (slope) and  $\Delta S^\ddagger$  with  $\ln(k_B/h) = 23.76$

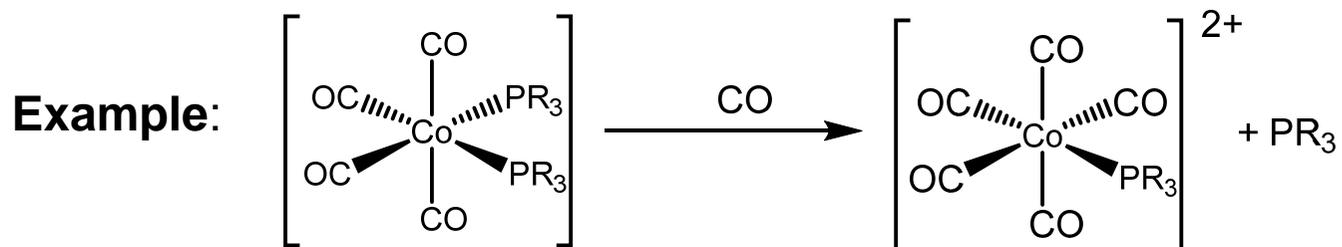
relation between Arrhenius and TST

$$\Delta H^\ddagger = E_a - \underbrace{RT}_{2.6 \text{ kJ/mol bei RT}} \quad \text{and} \quad \Delta S^\ddagger = 4.58(\log A - 13.2)$$

the **activation parameters**  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are very indicative for the mechanism

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$$\Delta H^\ddagger = 37 \text{ kcal/mol} \quad \Delta S^\ddagger = + 25 \text{ e.u.}$$

→ relates to **volume of activation**  $\Delta V^\ddagger$

**thermodynamics:**  $dG = -S \cdot dT + V \cdot dp$       **kinetics:**  $\ln k = \ln k^0 - \frac{\Delta V^\ddagger}{RT} P$

$\ln k$  depends linearly on the pressure

$\ln k$  (or  $\log k$ ) vs  $p$  gives a straight line with  $\Delta V^\ddagger$  as slope

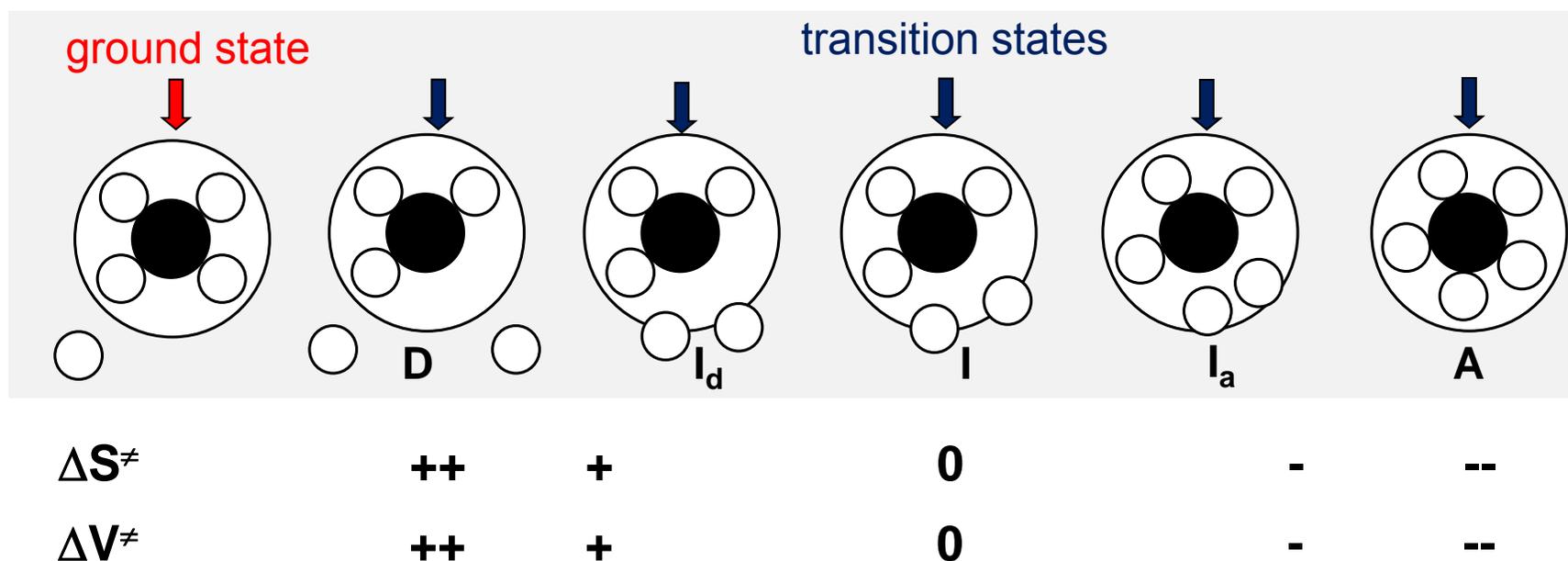
assuming that  $\Delta V^\ddagger$  is pressure independent

what does this tell us with respect to mechanism ?

# Deduction of Mechanisms

## 4.2 Transition State Theory

it gives an insight into the **intimate mechanism** of the rds



D and  $I_d$  and A and  $I_a$  are often difficult to differentiate

$\Delta S^\ddagger$  and  $\Delta V^\ddagger$  give us a clear insight into the mechanism, e.g. ligand exchange

# Deduction of Mechanisms

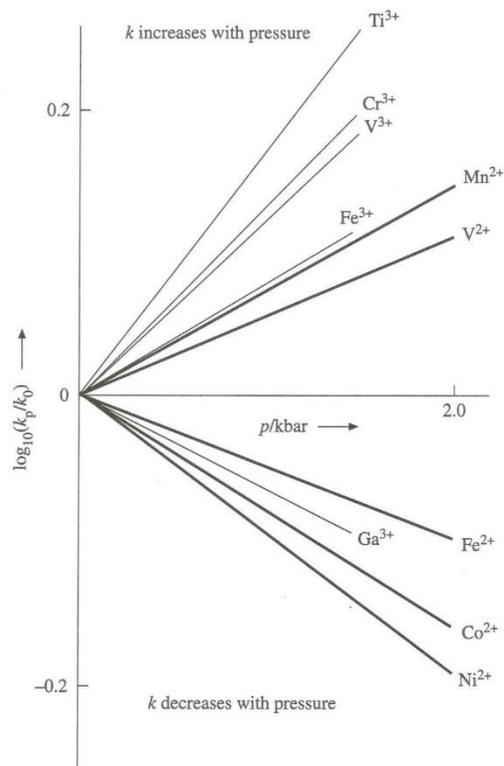
## 4.2 Transition State Theory

ligand self exchange

→ interpretation of  $\Delta S^\ddagger$

→ interpretation of  $\Delta V^\ddagger$

$\Delta V^\ddagger$  represents the sum of the partial mol volumina in the transitions state



← associative

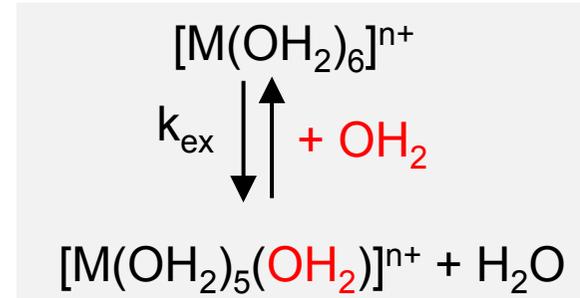
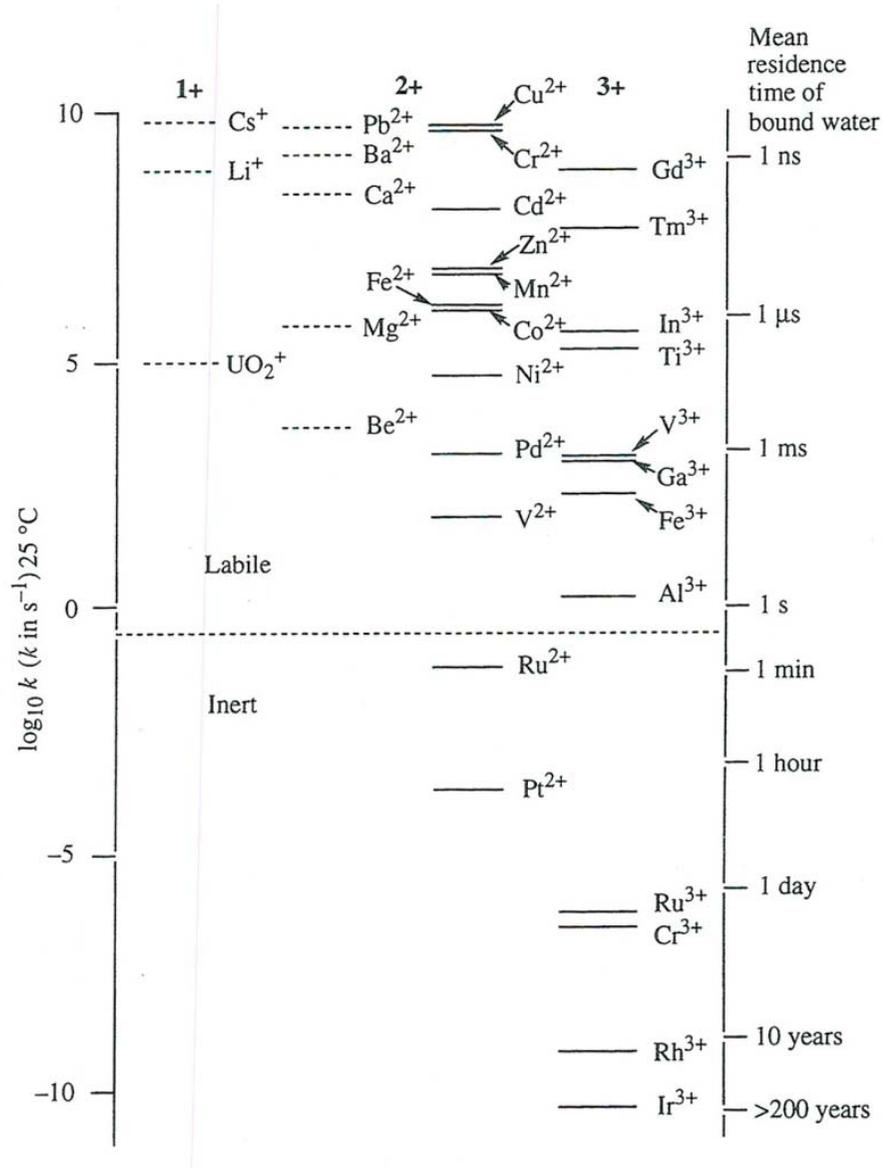
$$\Delta V^\circ (\text{H}_2\text{O}) = 18 \text{ cm}^3 / \text{mol}$$

$$\begin{aligned} \Delta V^\ddagger = -15 \text{ cm}^3 / \text{mol} &\Rightarrow \text{A-process} \\ \Delta V^\ddagger = +15 \text{ cm}^3 / \text{mol} &\Rightarrow \text{D-process} \end{aligned}$$

← dissociative

# Deduction of Mechanisms

## 4.2 Transition State Theory



$k_{\text{ex}}$  covers an extremely broad range

for D processes  $k = k_{\text{ex}}$

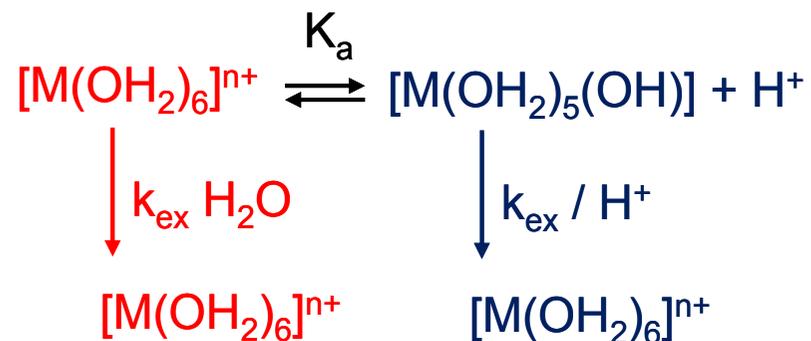
„no reaction" reaction  $\Delta G_0 = 0$

# Deduction of Mechanisms

## 4.2 Transition State Theory

**water self exchange rates:** indicative for substitution mechanisms in general

	$\Delta H^\ddagger$ (kJ·mol <sup>-1</sup> )	$\Delta S^\ddagger$ (eu)	$\Delta V^\ddagger$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	Assigned mechanism
Ga <sup>3+</sup>	67	+30	+5	I <sub>d</sub>
Ga(OH) <sup>2+</sup>			+6	I <sub>d</sub>
Ti <sup>3+</sup>	43	-12	+1	I <sub>a</sub>
Cr <sup>3+</sup>	109	+12	-10	I <sub>a</sub>
Cr(OH) <sup>2+</sup>			+3	I
Fe <sup>3+</sup>	65	+12	-5	I <sub>a</sub>
Fe(OH) <sup>2+</sup>			+7	I <sub>d</sub>
Ru <sup>3+</sup>	90	-48	-8	I <sub>a</sub>
Ru(OH) <sup>2+</sup>			+1	I
Rh <sup>3+</sup>	131	+29	-4	I <sub>a</sub>
Rh(OH) <sup>2+</sup>			+2	I
Ir <sup>3+</sup>	131	+2	-6	I <sub>a</sub>
Ir(OH) <sup>2+</sup>			+1	I



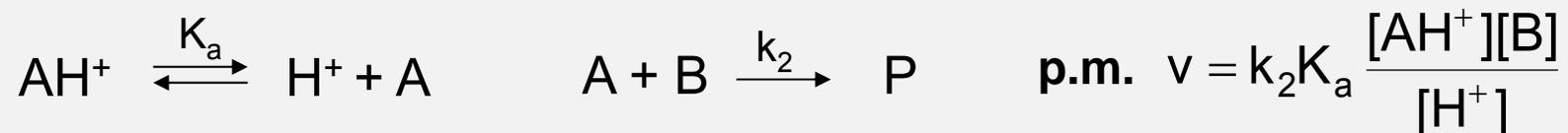
$$v = k_{ex} [M-OH] = \frac{k_{ex} \cdot K_a [M-OH_2]}{[H]^+}$$

# Deduction of Mechanisms

## 4.2 Transition State Theory

**back to data interpretation:** most reactions are not one step...

let's look at a pH dependent scheme



the composed rate constant is:  $k_2 \cdot K_A$

➔ applying TST and van't Hoff

$$k = \frac{k_B T}{h} \exp\left(\frac{\Delta S_2^\ddagger}{R}\right) \exp\left(-\frac{\Delta H_2^\ddagger}{RT}\right) \cdot \exp\left(\frac{\Delta S_a^\theta}{R}\right) \exp\left(-\frac{\Delta H_a^\theta}{RT}\right)$$

$$k = \frac{k_B T}{h} \exp\left(\frac{\Delta S_2^\ddagger + \Delta S_a^\theta}{R}\right) \exp\left(\frac{-\Delta H_2^\ddagger - \Delta H_a^\theta}{RT}\right)$$

# Deduction of Mechanisms

## 4.2 Transition State Theory

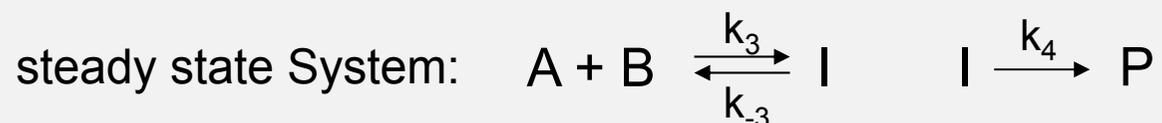
**back to data interpretation:** most reactions are not one step...

**linearization:** we do not get  $\Delta H^\ddagger$  but  $-\Delta H^\ddagger - \Delta H^\ominus$

we must know pre-equilibrium ( $K_a$  in this case) to get the "true"  $\Delta H^\ddagger$

**Question:** find a situation for which  $\Delta G^\ddagger$  is negative

→ e.g. the **reaction becomes slower** with increasing temperature



$$k_{-3} \gg k_4 \quad \text{then:} \quad v = \frac{k_3 k_4}{k_{-3}} [A][B]$$

# Deduction of Mechanisms

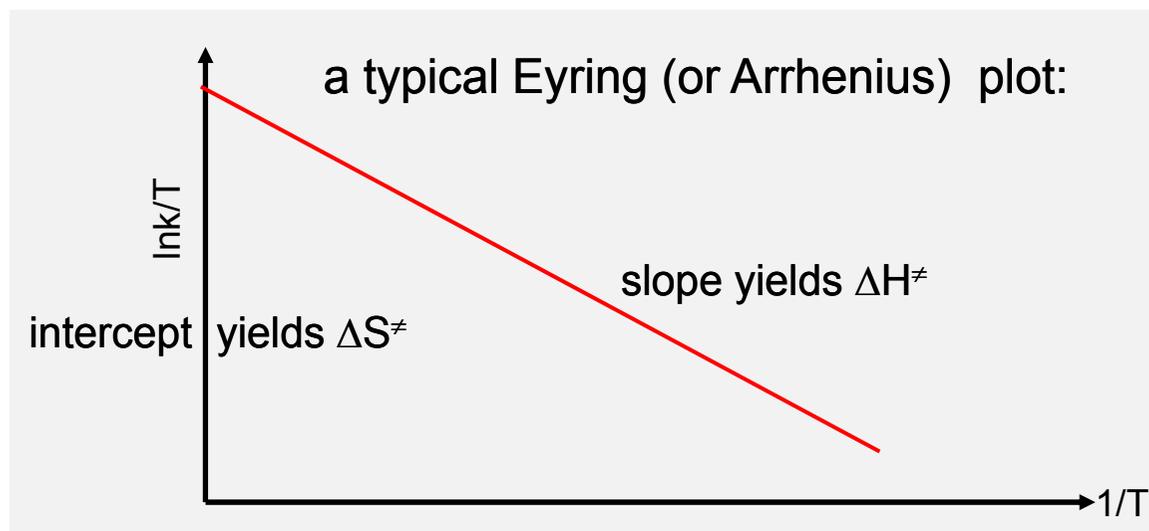
## 4.2 Transition State Theory

**back to data interpretation:** most reactions are not one step...

$$k = \frac{k_B T}{h} \exp\left(\frac{\Delta S_3^\ddagger - \Delta S_{-3}^\ddagger + \Delta S_4^\ddagger}{R}\right) \exp\left(-\frac{\Delta H_3^\ddagger - \Delta H_{-3}^\ddagger + \Delta H_4^\ddagger}{RT}\right)$$

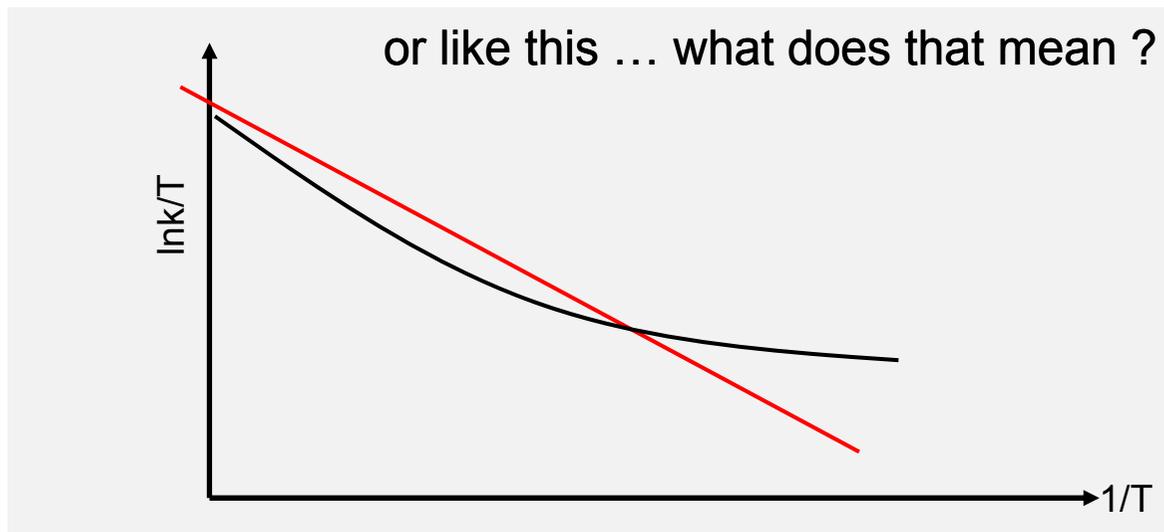
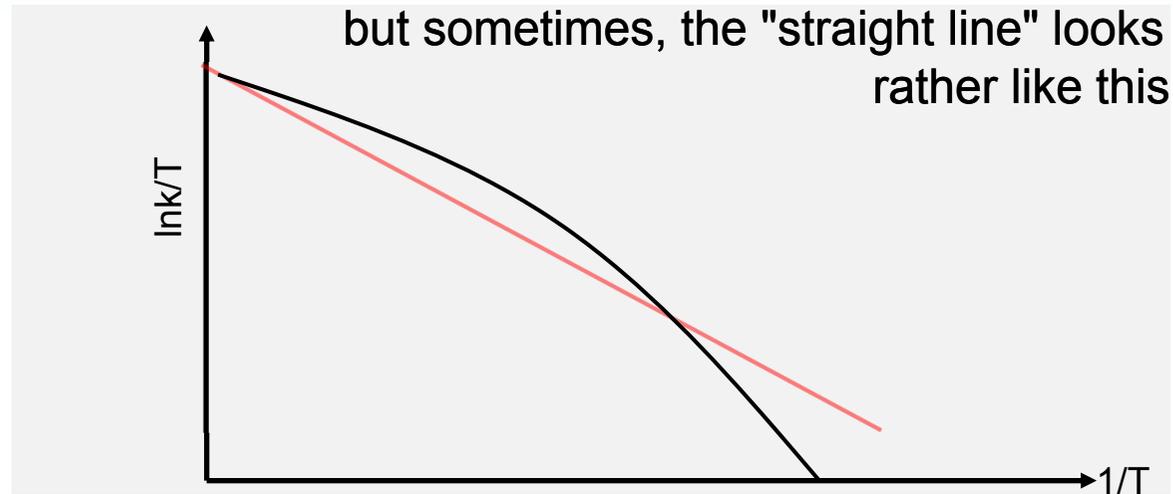
we also get a **"linear" profile**, the parameters are composed of the individual values

➔ **deviations from linearity** in practice



# Deduction of Mechanisms

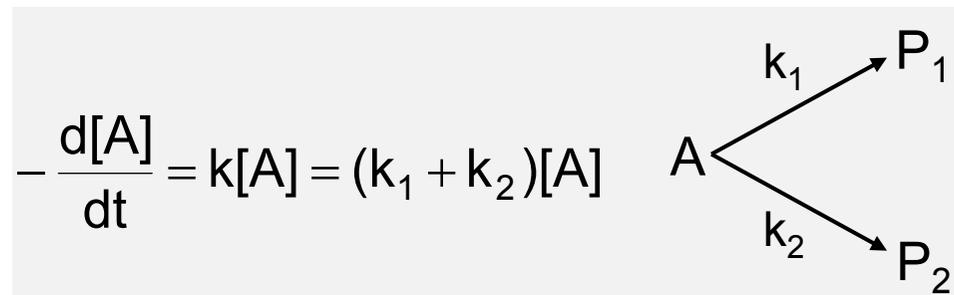
## 4.2 Transition State Theory



**non-linearity** ! often, even in professional presentations still considered as linear...

# Deduction of Mechanisms

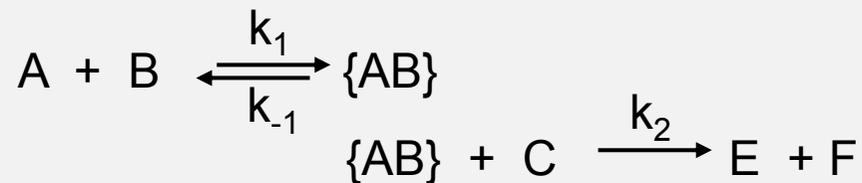
## 4.2 Transition State Theory



concurrent reaction schemes will result in non-linearity

$$k = \frac{k_B T}{h} \left\{ \exp\left(\frac{\Delta S_1^\ddagger}{R}\right) \exp\left(-\frac{\Delta H_1^\ddagger}{RT}\right) + \exp\left(\frac{\Delta S_2^\ddagger}{R}\right) \exp\left(-\frac{\Delta H_2^\ddagger}{RT}\right) \right\}$$

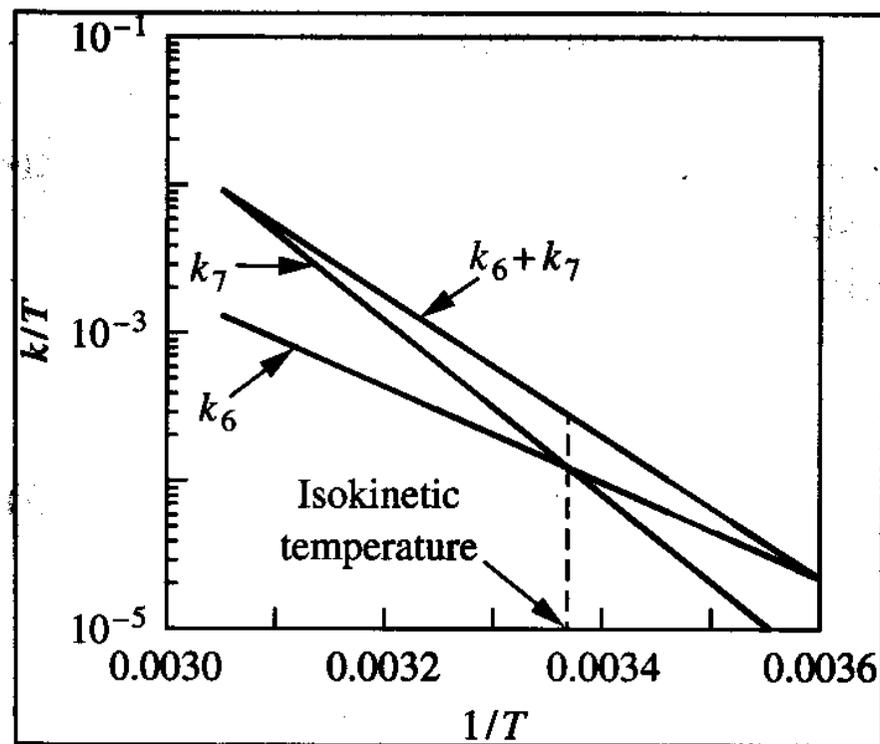
what about a simple **consecutive scheme** like this one



# Deduction of Mechanisms

## 4.2 Transition State Theory

the T profile of such a scheme is **non-linear**

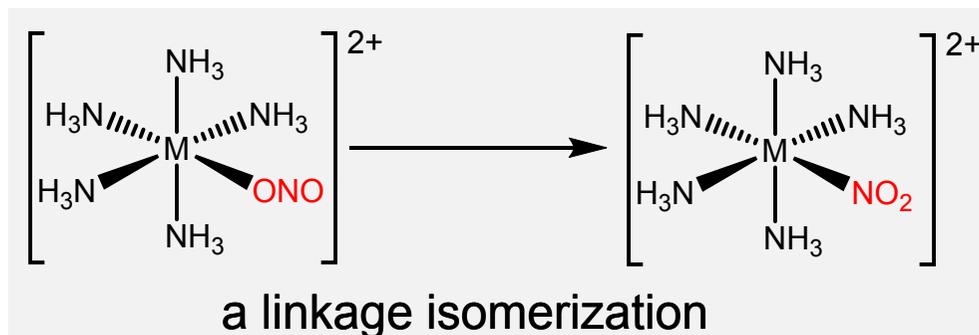


→ it can however be "dissected" in two linear profiles

# Deduction of Mechanisms

## 4.2 Transition State Theory

an simple example from practice:



**activation parameters**

	Co	Rh	Ir	
$\Delta S^\ddagger$	-17 $\pm$ 3	-33 $\pm$ 7	-11 $\pm$ 4	e.u
$\Delta H^\ddagger$	92	80	95	kJ/mol
$\Delta V^\ddagger$	-6.7	-7.4	-5.9	cm <sup>3</sup> /mol

is there an isokinetic relationship ?

what mechanism of isomerization do you suggest ?

# Deduction of Mechanisms

## 4.3 Microscopic Reversibility

The reaction mechanisms for the forward and the backward reaction are identical, they **are mirror images** of each other

➔ This principle is **always valid**,  
even when multiple steps, equilibria or branched reactions are involved  
if it were not valid, we would run into problems with thermodynamics

let's look at the **simple reaction**



is pH dependent and can be described with:



# Deduction of Mechanisms

## 4.3 Microscopic Reversibility

the rate law:

$$\frac{d[\text{FeNCS}^{2+}]}{dt} = \left( k_1 + \frac{k_2}{[\text{H}^+]} \right) [\text{Fe}^{3+}] [\text{NCS}^-] - \left( k_{-1} + \frac{k_{-2}}{[\text{H}^+]} \right) [\text{FeNCS}^{2+}]$$

forward reaction                      backward reaction

after equilibrium is achieved:  $\frac{d[\text{FeNCS}^{2+}]}{dt} = 0$

and K becomes

$$K = \frac{[(\text{H}_2\text{O})_5\text{FeNCS}^{2+}]_e}{[\text{Fe}(\text{H}_2\text{O})_6^{3+}]_e [\text{NCS}^-]_e} = \frac{k_1 + \frac{k_2}{[\text{H}^+]}}{k_{-1} + \frac{k_{-2}}{[\text{H}^+]}}$$

**pH dependent**

which it is obviously not according to reaction equation ??

# Deduction of Mechanisms

## 4.3 Microscopic Reversibility

Without consideration of the individual steps, pH dependence

→ conflict with thermodynamics

the problem is solved by considering the microscopic reversibility of all individual equilibria involved separately

**pH independent path:**  $k_1[\text{Fe}^{3+}]_e[\text{NCS}^-]_e = k_{-1}[\text{FeNCS}^{2+}]_e$

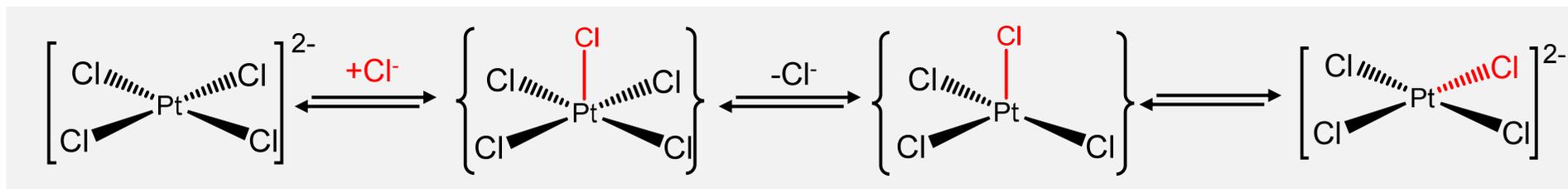
**pH dependent path:**  $k_2 \frac{[\text{Fe}^{3+}]_e[\text{NCS}^-]_e}{[\text{H}^+]_e} = k_{-2} \frac{[\text{FeNCS}^{2+}]_e}{[\text{H}^+]_e}$

**hence:**  $K = \frac{k_1}{k_{-1}} = \frac{k_2}{k_{-2}}$  as it should be

# Deduction of Mechanisms

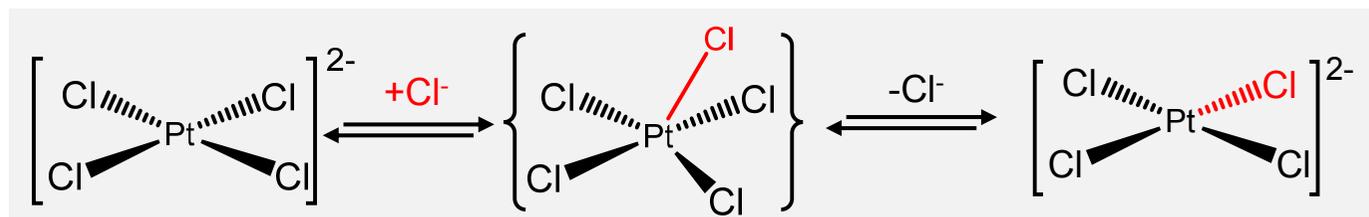
## 4.3 Microscopic Reversibility

a mechanism proposed once upon a time in square planar complexes  
ligand substitution, illustrative for microscopic reversibility



no mirror plane in the mechanism, **impedes the m.r. principle**

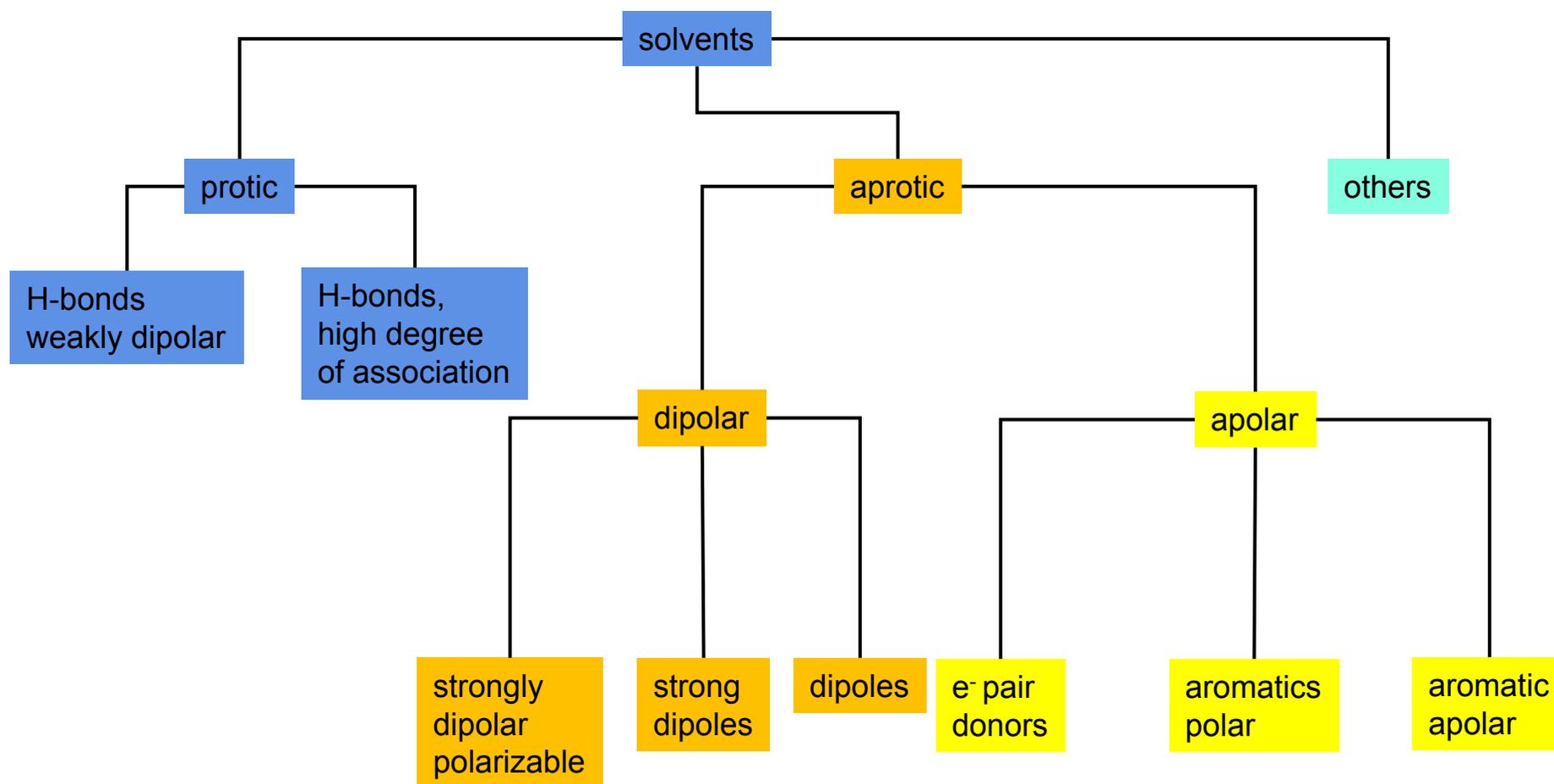
instead



tbp transition state

# Deduction of Mechanisms

## 4.4 Solvent effects

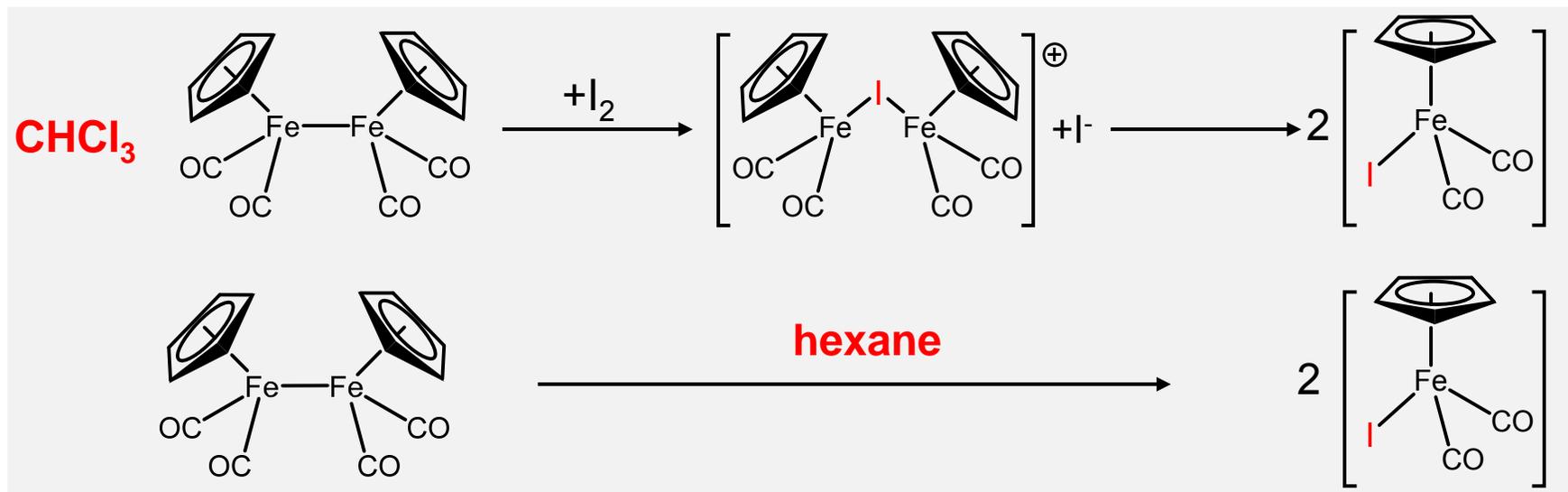


try to find **examples** for this classification!

# Deduction of Mechanisms

## 4.4 Solvent effects

- ➔ The solvent of a reaction may not only **influence the rate** but also the overall **mechanism path**
- ➔ in inorganic or organometallic reactions, solvents often act as "true" ligands
- ➔ solvents may stabilize / destabilize ground – transition states or intermediates ...
- ➔ or they may be completely innocent



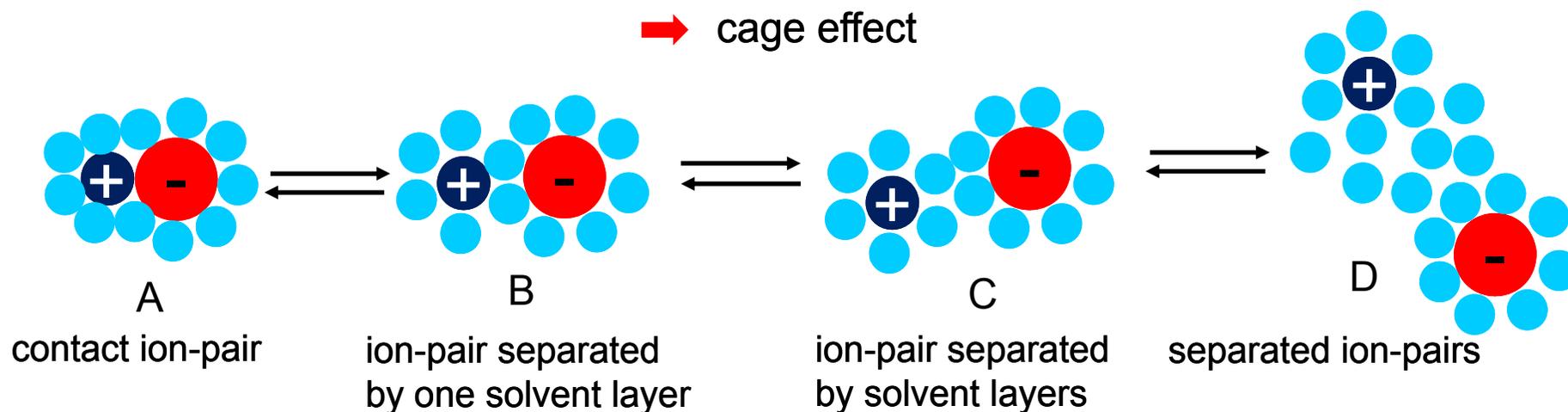
# Deduction of Mechanisms

## 4.4 Solvent effects

solvents may provide a "solvent cage" as the "reaction vessel"

the longer the reactants reside, the faster the reaction

→ cage effect



$$z_1 = z_2 = 1 \equiv 357 \text{ pm}$$

$$z_1 = z_2 = 2 \equiv 1428 \text{ pm}$$

$$z_1 = z_2 = 3 \equiv 3213 \text{ pm}$$

**critical distances** for ion-pair formation

strongly dependent on **dielectric constant  $\epsilon$**

# Deduction of Mechanisms

## 4.4 Solvent effects

**residence time** in the cage given by the rate of diffusion

in water, typically  **$10^{-12}$  bis  $10^{-11}$**  sec time to collide 10 – 100 times

**consequence:** short lived intermediates can not be detected

since the immediately react further

➔ the entity of compounds in a cage is called "**encounter complex**"

the **solvation** of the encounter complex strongly contributes to  $\Delta S^\ddagger$

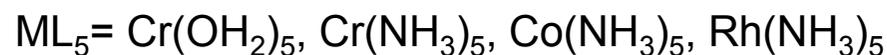
Reaction	Reactands	activated compound	increased polarity
$S_{N1}$	R—X	$R^{\delta+} \cdots X^{\delta-}$	++
$S_{N1}$	R—X <sup>+</sup>	$R^{\delta+} \cdots X^{\delta+}$	-
$S_{N2}$	Y + R—X	$Y^{\delta+} \cdots R \cdots X^{\delta-}$	++
$S_{N2}$	Y <sup>-</sup> + R—X	$Y^{\delta-} \cdots R \cdots X^{\delta-}$	-
$S_{N2}$	Y + R—X <sup>+</sup>	$Y^{\delta-} \cdots R \cdots X^{\delta+}$	-
$S_{N2}$	Y <sup>-</sup> + R—X <sup>+</sup>	$Y^{\delta-} \cdots R \cdots X^{\delta+}$	--

# Deduction of Mechanisms

## 4.4 Solvent effects

the **solvation** of the encounter complex strongly contributes to  $\Delta S^\ddagger$

Reaction	Charge product $Z_A Z_B$	$\Delta S^\ddagger$ (J K <sup>-1</sup> mol <sup>-1</sup> )	
		measured	calculated
$S_2O_3^{2-} + SO_3^{2-}$	4+	-126	-170
$[ML_5X]^{2+} + Hg^{2+}$	4+	-60 to -104	-170
$BrCH_2CO_2^- + S_2O_3^{2-}$	2+	-71	-85
$ClCH_2CO_2^- + OH^-$	1+	-50	-40
$BrCH_2CO_2ME + S_2O_3^{2-}$	0	+25	0
$[Co(NH_3)_5Br]^{2+} + OH^-$	2-	+92	+85
$[Co(NH_3)_5(H_2O)]^{3+} + Cl^-$	3-	+142	+125
$ReCl_6^{2-} + Hg^{2+}$	4-	+142	+170



How to interpret these data with respects to the solvent water?

# Deduction of Mechanisms

## 4.4 Solvent effects

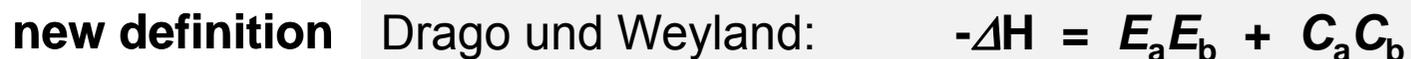
**donor/acceptor numbers** are an indication for the behaviour of solvents



useful to compare relative characters of solvents

no obvious relationship to  $\epsilon$

**Drago:** concept doesn't consider **hard/soft** (electrostatic – covalent)



E = electrostatic, C = covalent a=acid, b=base

# Deduction of Mechanisms

## 4.4 Solvent effects

**new definition** Drago und Weyland:  $-\Delta H = E_a E_b + C_a C_b$



$$-\Delta H_{\text{ber}} = (0.5 \cdot 1.78) + (2.0 \cdot 3.54) = 7.97 \text{ kcal/mol} \quad (-\Delta H_{\text{exp}} = 7.8 \text{ kcal/mol})$$

"acidic" solvents which tend to **interact electrostatically** (large  $E_s$ )

interact preferentially with bases with large  $E_b$

and

acids which prefer **covalent interaction** (large  $C_a$ ) interact

with bases of large  $C_b$

# Deduction of Mechanisms

## 4.4 Solvent effects: Drago-Weyland, Donor and Acceptor numbers

Säure	$E_s$	$C_s$	$R_s$	Säure	$E_s$	$C_s$	$R_s$
I <sub>2</sub>	0.50	2.00	---	H <sup>+</sup>	45.00	13.03	130.21
H <sub>2</sub> O	1.54	0.13	0.20	CH <sub>3</sub> <sup>+</sup>	19.70	12.61	55.09
SO <sub>2</sub>	0.56	1.52	0.85	Li <sup>+</sup>	11.72	1.45	24.21
HF <sup>b</sup>	2.03	0.30	0.47	K <sup>+b</sup>	3.78	0.10 <sup>b</sup>	20.79
HCN <sup>b</sup>	1.77	0.50	0.54	NO <sup>+b</sup>	0.1 <sup>b</sup>	6.86	45.99
CH <sub>3</sub> OH	1.25	0.75	0.39	NH <sub>4</sub> <sup>+b</sup>	4.31	4.31	18.52
H <sub>2</sub> S <sup>b</sup>	0.77	1.46	0.56	(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> <sup>+</sup>	3.21	0.70	20.72
HCl <sup>b</sup>	3.69	0.74	0.55	(CH <sub>3</sub> ) <sub>4</sub> N <sup>+b</sup>	1.96	2.36	8.33
C <sub>6</sub> H <sub>5</sub> OH	2.27	1.07	0.39	C <sub>5</sub> H <sub>5</sub> NH <sup>+</sup>	1.81	1.33	21.72
(CH <sub>3</sub> ) <sub>3</sub> COH	1.36	0.51	0.48	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH <sup>+</sup>	2.43	2.05	11.81
HCCl <sub>3</sub>	1.49	0.46	0.45	(CH <sub>3</sub> ) <sub>3</sub> NH <sup>+b</sup>	2.60	1.33	15.95
CH <sub>3</sub> CO <sub>2</sub> H <sup>b</sup>	1.72	0.86	0.63	H <sub>3</sub> O <sup>+</sup>	13.27	7.89	20.01
CF <sub>3</sub> CH <sub>2</sub> OH	2.07	1.06	0.38	(H <sub>2</sub> O) <sub>2</sub> H <sup>+</sup>	11.39	6.03	7.36
C <sub>2</sub> H <sub>5</sub> OH	1.34	0.69	0.41	(H <sub>2</sub> O) <sub>3</sub> H <sup>+</sup>	11.21	4.66	2.34
<i>i</i> -C <sub>3</sub> H <sub>7</sub> OH	1.14	0.90	0.46	(H <sub>2</sub> O) <sub>4</sub> H <sup>+b</sup>	10.68	4.11	3.25
PF <sub>3</sub> <sup>b</sup>	0.61	0.36	0.87	(CH <sub>3</sub> ) <sub>3</sub> Sn <sup>+</sup>	7.05	3.15	26.93
B(OCH <sub>3</sub> ) <sub>3</sub> <sup>b</sup>	0.54	1.22	0.84	(C <sub>5</sub> H <sub>5</sub> )Ni <sup>+</sup>	11.88	3.49	32.64
AsF <sub>3</sub> <sup>b</sup>	1.48	1.14	0.78	(CH <sub>3</sub> )NH <sub>3</sub> <sup>+b</sup>	2.18	2.38	20.68
Fe(CO) <sub>3</sub> <sup>b</sup>	0.10	0.27	1.00				
CHF <sub>3</sub> <sup>b</sup>	1.32	0.91	0.27				
B(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> <sup>b</sup>	1.70	2.71	0.61				

# Deduction of Mechanisms

## 4.4 Solvent effects: Drago-Weyland, Donor and Acceptor numbers

Base <sup>c</sup>	$E_B$	$C_B$	$T_B$	Base <sup>c</sup>	$E_B$	$C_B$	$T_B$
NH <sub>3</sub>	2.31	2.04	0.56	C <sub>5</sub> H <sub>5</sub> NO	2.29	2.33	0.67
CH <sub>3</sub> NH <sub>2</sub>	2.16	3.12	0.59	(CH <sub>3</sub> ) <sub>3</sub> P	1.46	3.44	0.90
(CH <sub>3</sub> ) <sub>2</sub> NH	1.80	4.21	0.64	(CH <sub>3</sub> ) <sub>2</sub> O	1.68	1.50	0.73
(CH <sub>3</sub> ) <sub>3</sub> N	1.21	5.61	0.75	(CH <sub>3</sub> ) <sub>2</sub> S	0.25	3.75	1.07
C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub>	2.35	3.30	0.54	CH <sub>3</sub> OH	1.80	0.65	0.70
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	1.32	5.73	0.76	C <sub>2</sub> H <sub>5</sub> OH	1.85	1.09	0.70
HC(C <sub>2</sub> H <sub>4</sub> ) <sub>3</sub> N	0.80	6.72	0.83 <sup>d</sup>	C <sub>6</sub> H <sub>6</sub>	0.70	0.45	0.81
C <sub>5</sub> H <sub>5</sub> N	1.78	3.54	0.73	H <sub>2</sub> S <sup>b</sup>	0.04	1.56	1.13
4-CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> N	1.74	3.93	0.73 <sup>d</sup>	HCN <sup>b</sup>	1.19	0.10	0.90
3-CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> N	1.76	3.72	0.74 <sup>d</sup>	H <sub>2</sub> CO <sup>b</sup>	1.56	0.10	0.76
3-ClC <sub>5</sub> H <sub>4</sub> N	1.78	2.81	0.75 <sup>d</sup>	CH <sub>3</sub> Cl <sup>b</sup>	2.54	0.10	0.23
CH <sub>3</sub> CN	1.64	0.71	0.83	CH <sub>3</sub> CHO <sup>b</sup>	1.76	0.81	0.74
CH <sub>3</sub> C(O)CH <sub>3</sub>	1.74	1.26	0.80	H <sub>2</sub> O <sup>b</sup>	2.28	0.10	0.43
CH <sub>3</sub> C(O)OCH <sub>3</sub>	1.63	0.95	0.86	(CH <sub>3</sub> ) <sub>3</sub> COH <sup>b</sup>	1.92	1.22	0.71
CH <sub>3</sub> C(O)OC <sub>2</sub> H <sub>5</sub>	1.62	0.98	0.89	C <sub>6</sub> H <sub>5</sub> CN <sup>b</sup>	1.75	0.62	0.85
HC(O)N(CH <sub>3</sub> ) <sub>2</sub>	2.19	1.31	0.74 <sup>d</sup>	F <sup>-</sup>	9.73	4.28	37.40
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	1.80	1.63	0.76	Cl <sup>-b</sup>	7.50	3.76	12.30
O(CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> O	1.86	1.29	0.71	Br <sup>-b</sup>	6.74	3.21	5.86
(CH <sub>2</sub> ) <sub>4</sub> O	1.64	2.18	0.75	I <sup>-</sup>	5.48	2.97	6.26
(CH <sub>2</sub> ) <sub>5</sub> O	1.70	2.02	0.74 <sup>d</sup>	CN <sup>-</sup>	7.23	6.52	9.20
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> S	0.24	3.92	1.10 <sup>d</sup>	OH <sup>-b</sup>	10.43	4.60	50.73
(CH <sub>3</sub> ) <sub>2</sub> SO	2.40	1.47	0.65	CH <sub>3</sub> O <sup>-b</sup>	10.03	4.42	33.77

# Deduction of Mechanisms

## 4.4 Acids as solvents and super acids

most Brønsted acids show **auto dissociation**, like water

**pH-scale** and value defined by the **degree of auto dissociation**

➔ therefore, each acid has its individual pH-scale

all acid/base pairs which are **inside** these limits act as **electrolyte**

➔ all acid/base pairs **outside** these limits will be **levelled** by the acid solvent

$\text{CH}_3\text{COOH}$  is an acid in water and an electrolyte

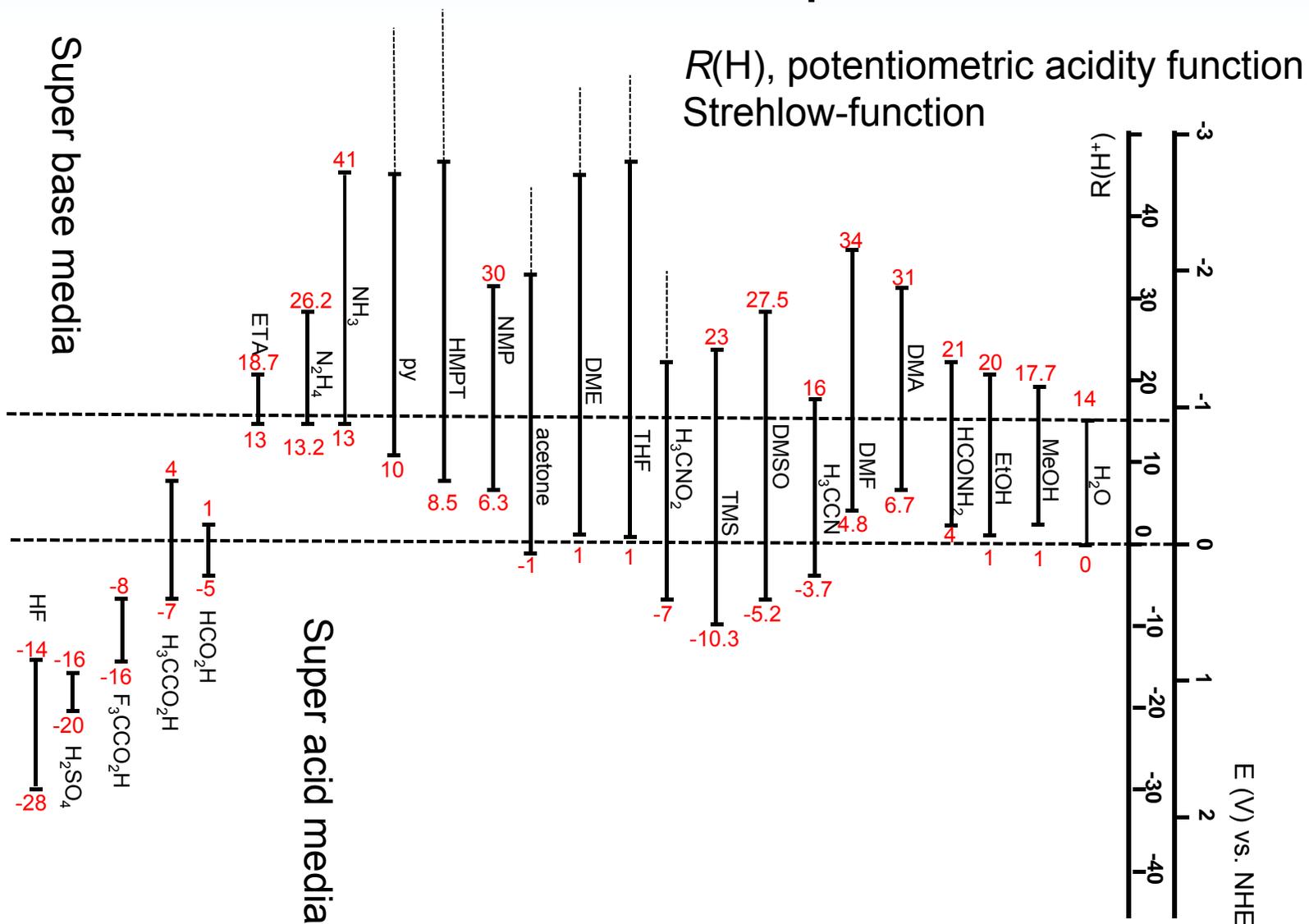
$\text{CH}_3\text{COOH}$  in  $\text{H}_2\text{SO}_4$  is a base, base strength levelled by  $[\text{HSO}_4]^-$

**more practical:** dissolution of amide  $\text{H}_2\text{N}^-$  is levelled by base strength of  $[\text{OH}]^-$

since **outside the pH scale of water**

# Deduction of Mechanisms

## 4.4 Acids as solvents and super acids



B. Trémillon, D. Inman, *Reactions in Solution, An Applied Analytical Approach*, Wiley, 1997, pp. 227-300

# Deduction of Mechanisms

## 4.4 Acids as solvents and super acids

acids which are more acidic than sulfuric acid are called **super acids**

Hammett acidity function  $H_0 = \text{p}K_{\text{BH}^+} - \log \frac{[\text{BH}^+]}{[\text{B}]}$  B = nitroanilin indicator



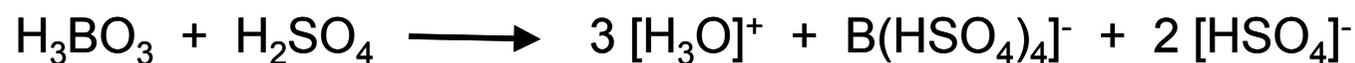
Pyroschwefelsäure

super acids $H_0$ :	$\text{H}_2\text{SO}_4$	-11.9
	HF	-11.0
	$\text{HClO}_4$	-13
	$\text{HSO}_3\text{F}$	-15.6
	$\text{HSO}_3\text{F}/\text{SbF}_5$	-21.0 bis -25.0

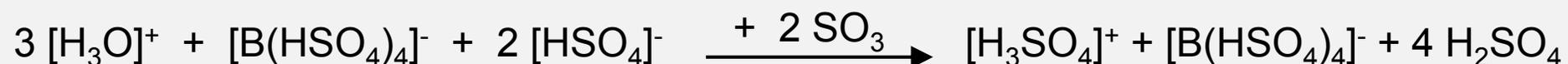
# Deduction of Mechanisms

## 4.4 Acids as solvents and super acids

very strong acids in  $\text{H}_2\text{SO}_4$



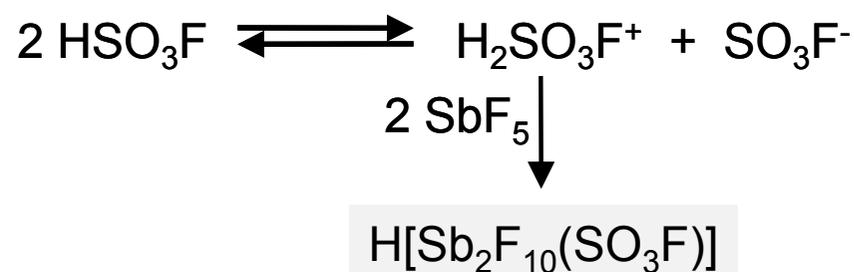
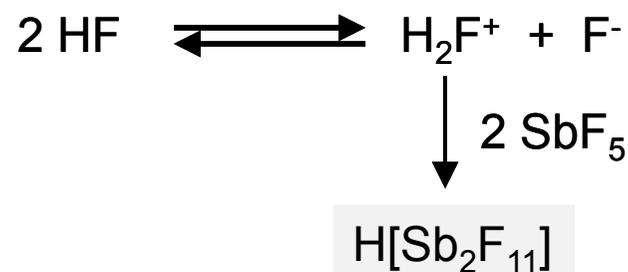
with  $\text{SO}_3$   $[\text{H}_3\text{O}]^+$  and  $[\text{HSO}_4]^-$  is removed



## „Magic acids“

$\text{HF}/\text{SbF}_5$

-21.0 bis -28.0



# Deduction of Mechanisms

## 4.4 Acids as solvents and super acids

- the strongest known acids are based on **Carborane anions**  
the conjugate base of the super acid may not coordinate or oxidize

→ need for **delocalization** over many atoms

principle behind synthesis: Brønsted acidity induced by Lewis acidity



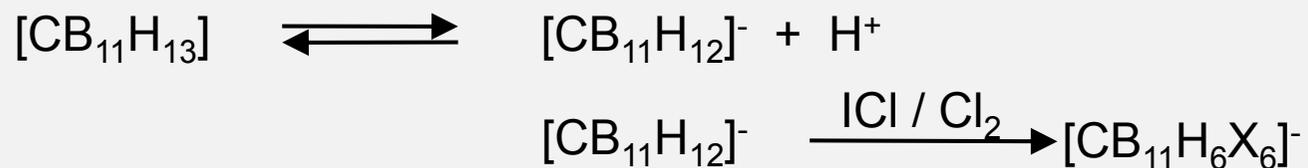
a classical **hard-soft** problem

extrem starke LS:	→	Silylkationen $\{\text{R}_3\text{Si}\}^+$
starke LB:	→	$\text{Cl}^-$
A:	→	extrem schwaches Nucleophil

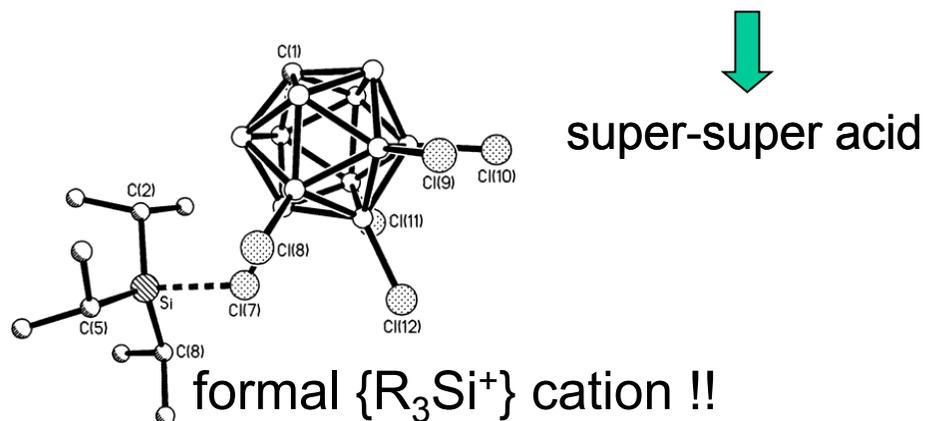
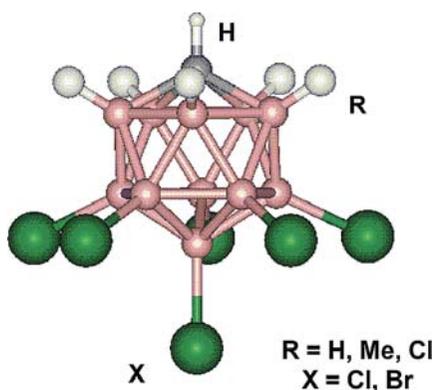
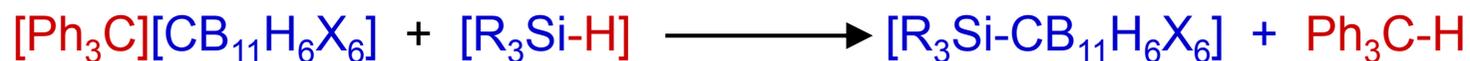
# Deduction of Mechanisms

## 4.4 Acids as solvents and super acids

**Carborane anions** are extremely acidic and not oxidizing!



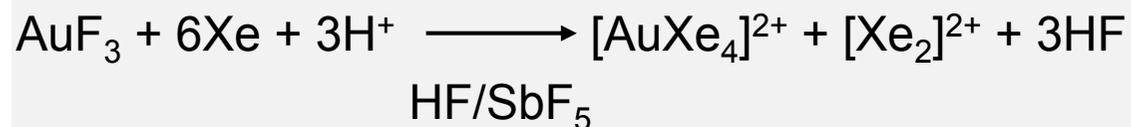
the  $\text{H}^+$  can only be introduced via LA-LB interactions



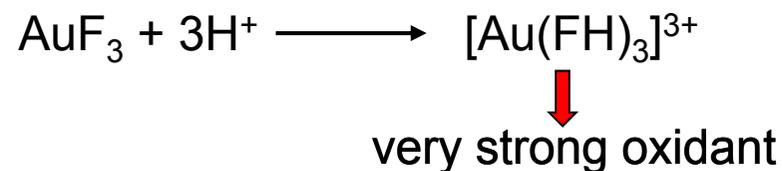
# Deduction of Mechanisms

## 4.4 Acids as solvents and super acids

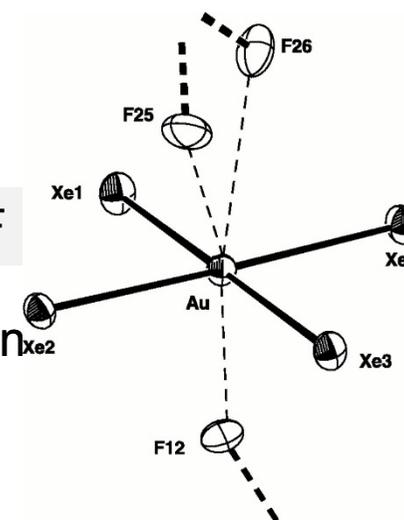
what can we do with super-super acids?



mechanistic principle: super-super acid protonates  $\text{AuF}_3$



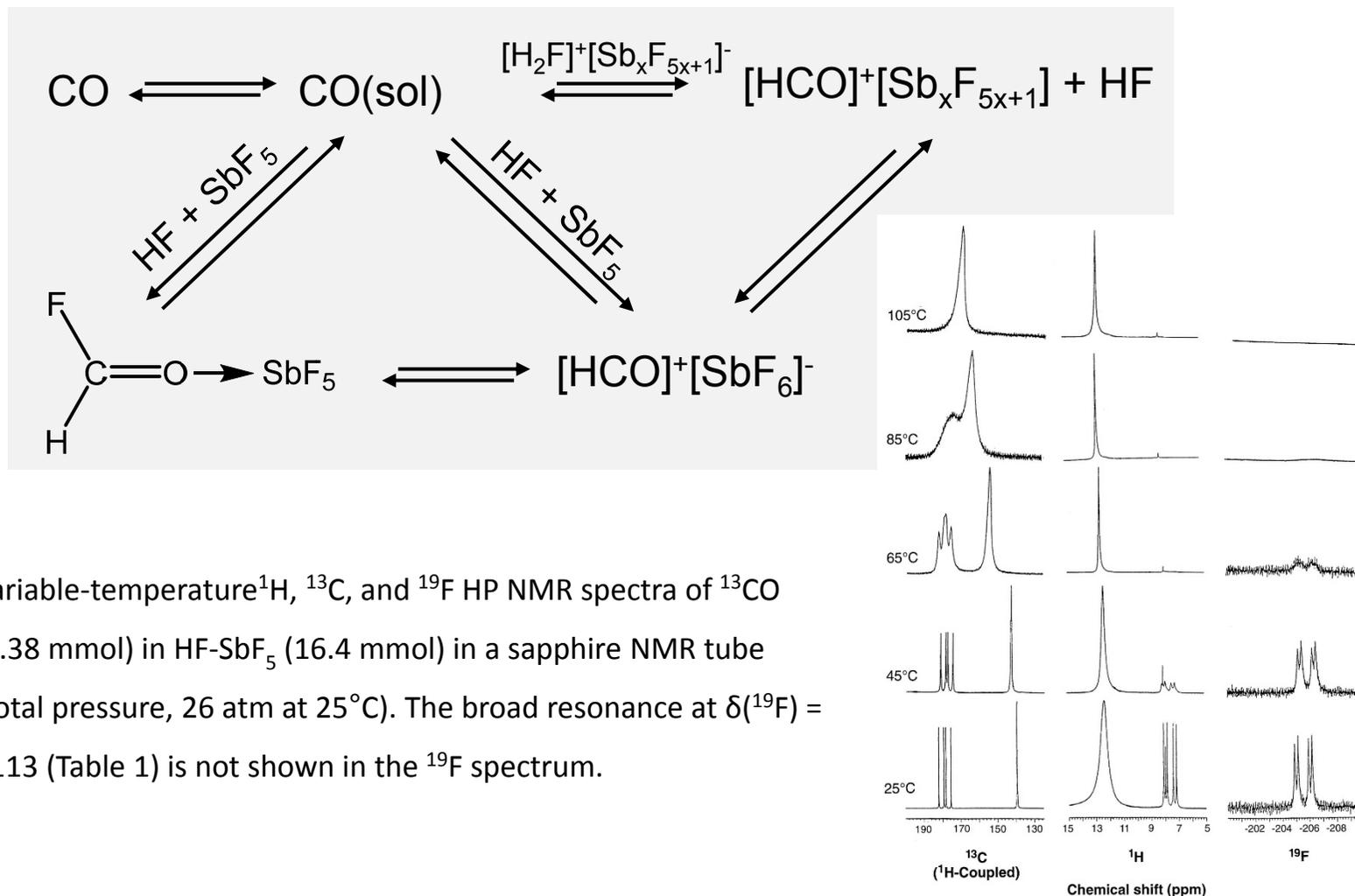
$[\text{Sb}_2\text{F}_{11}]^-$  is the counter-ion



# Deduction of Mechanisms

## 4.4 Acids as solvents and super acids

Protonation of CO and generation of the formyl cation  $\text{HCO}^+$



# Deduction of Mechanisms

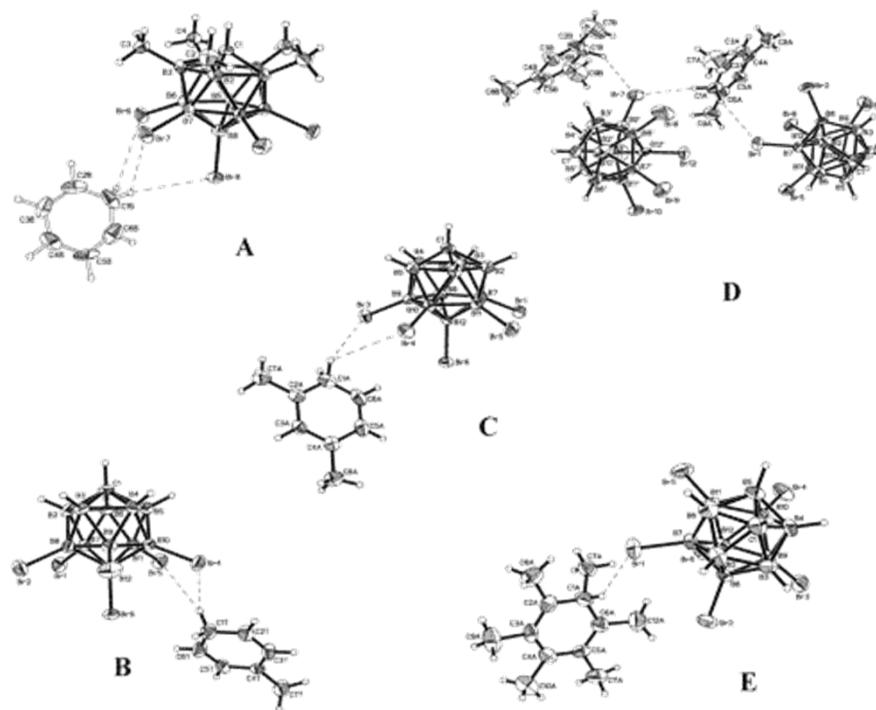
## 4.4 Acids as solvents and super acids

Beside CO, super acids also protonate alkanes, but also small molecules like N<sub>2</sub>, Ar a.o.

fullerene



*benzene derivatives*

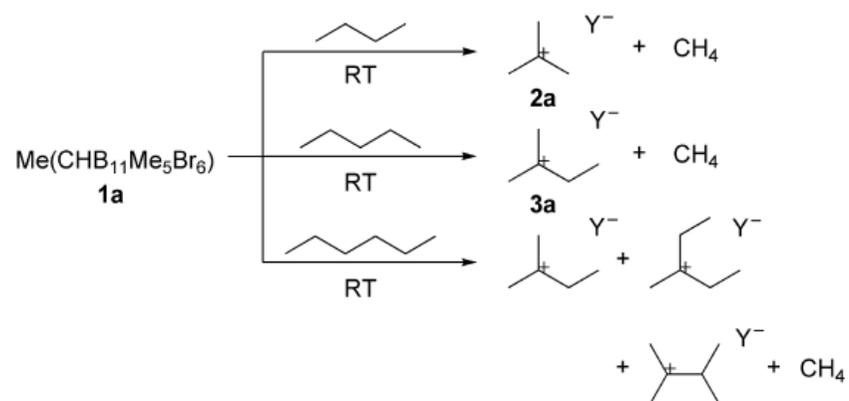
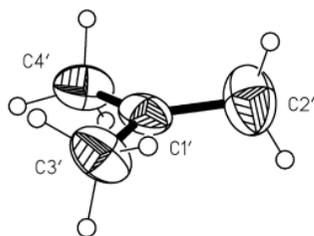
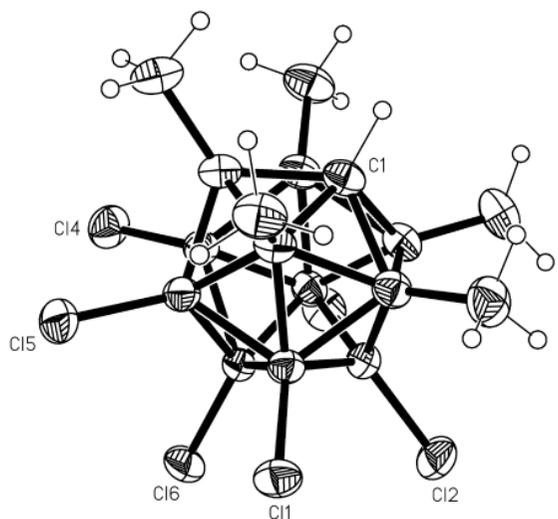


# Deduction of Mechanisms

## 4.4 Acids as solvents and super acids

Beside CO, super acids also protonate alkanes, but also small molecules like N<sub>2</sub>, Ar a.o.

→ protonation frequently under alkane elimination, makes s.a. synthetically useful



a <sup>t</sup>butyl cation which can be stored in bottles

# Deduction of Mechanisms

## 4.5 Diffusion controlled reactions

if the rate of a reaction is given by **the collision probability**, it runs at maximum speed.

such a reaction runs at a **diffusion controlled rate**

the frequency is defined by the Fick law of diffusion

the relevant relationship is  $k_{dc} = 4000 \cdot \pi \cdot N \cdot r_{AB} \cdot D_{AB}$  (Smoluchowski)

$r_{AB}$  is the **reaction cross section**,  $D_{AB} = D_A + D_B$  the diffusion constant,

a typical range for  $D_{AB}$  is  $2 \cdot 10^{-9} \text{ m}^2 \cdot \text{sec}^{-1}$ , for  $r_A$  **0.2 nm** or  $2 \cdot 10^{-10} \text{ m}$

depends on the viscosity of the solvent

 the resulting rate constant is  $k_{dc} \sim 6 \cdot 10^9 \text{ M}^{-1} \cdot \text{sec}^{-1}$

# Deduction of Mechanisms

## 4.5 Diffusion controlled reactions

$k_{dc}$  **does not depend** significantly on the reaction partners

**a big molecule diffuses slower** but may have a larger reaction cross section

for other solvents, the diffusion constant can be calculated according to **Einstein-Stokes**

Solvent	$\eta/10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$	$k_{dc}/\text{L mol}^{-1} \text{ s}^{-1}$
n-Pentane	2.15	$3.1 \cdot 10^{10}$
Diethyl ether	2.22	$3.0 \cdot 10^{10}$
Acetone	3.16	$2.1 \cdot 10^{10}$
Benzene	6.03	$1.1 \cdot 10^{10}$
Water	8.98	$7.4 \cdot 10^9$
Acetic acid	11.6	$5.7 \cdot 10^9$
Benzonitrile	14.5	$4.6 \cdot 10^9$
Ethylene glycol	136	$4.9 \cdot 10^8$
Cyclohexanol	410	$1.6 \cdot 10^8$
Glycerol	9450	$7.0 \cdot 10^6$

$$D_A = \frac{k_B \cdot T}{6 \cdot \pi \cdot r_A \cdot \eta}$$

if  $v_A \sim v_B$   $k_{dc} \geq \frac{8000 \cdot R \cdot T}{3\eta}$

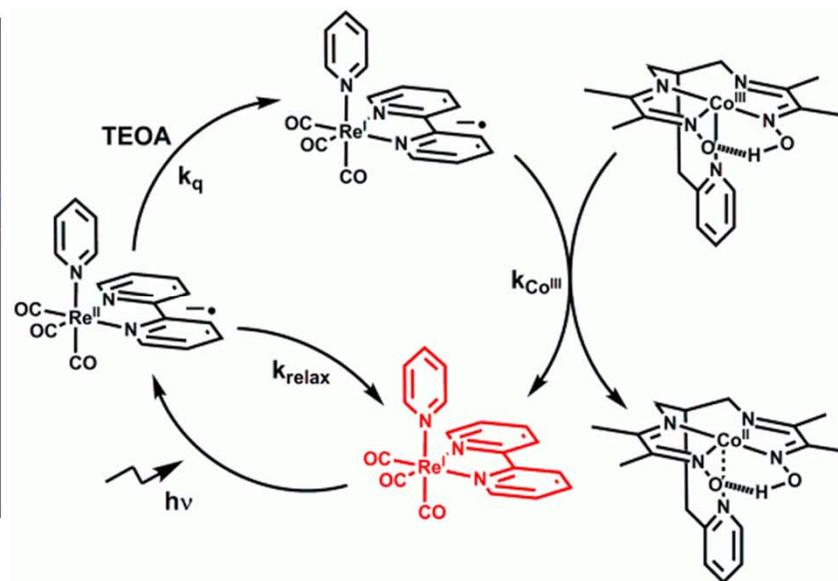
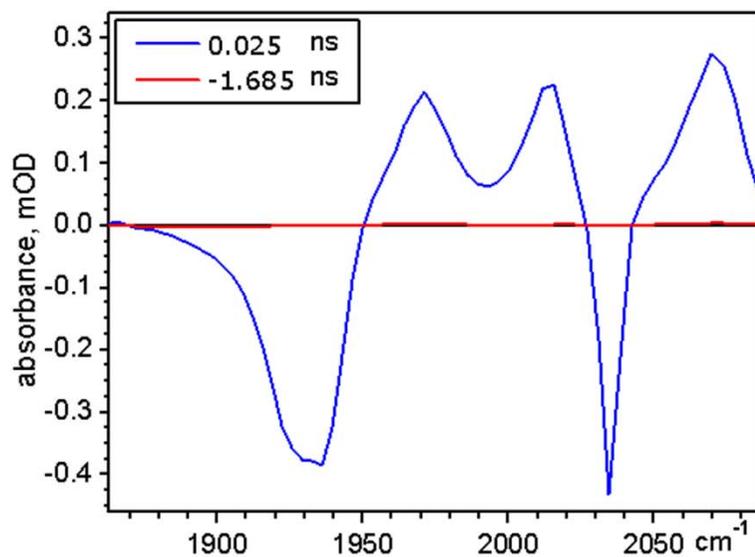
mit  $\eta$  = Viskosität

resulting activation energy from  $k_{dc}$   $\rightarrow E_a \sim 4 - 20 \text{ kJ/mol}$

# Deduction of Mechanisms

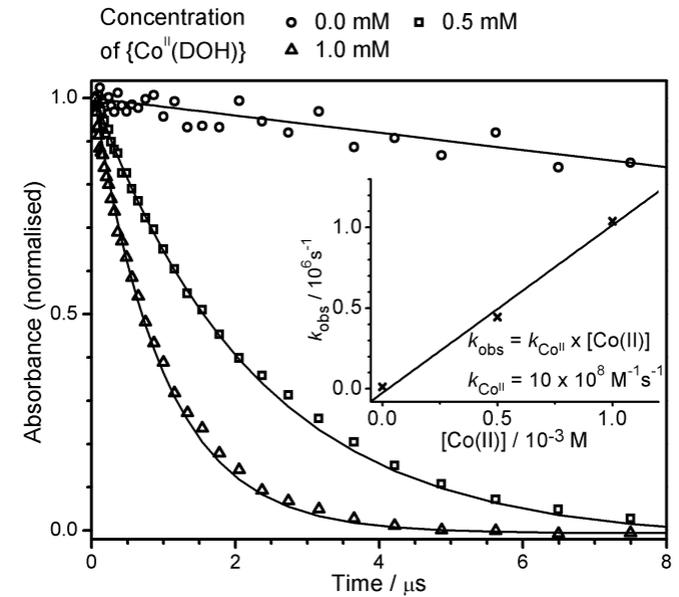
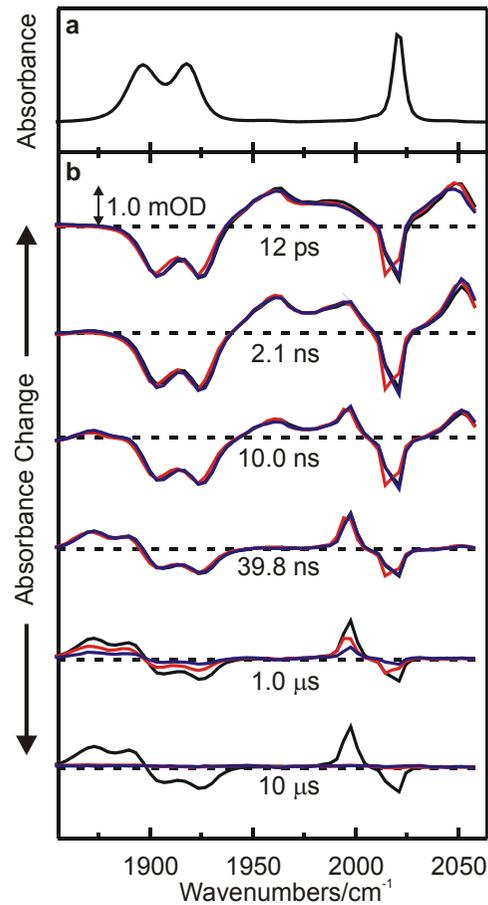
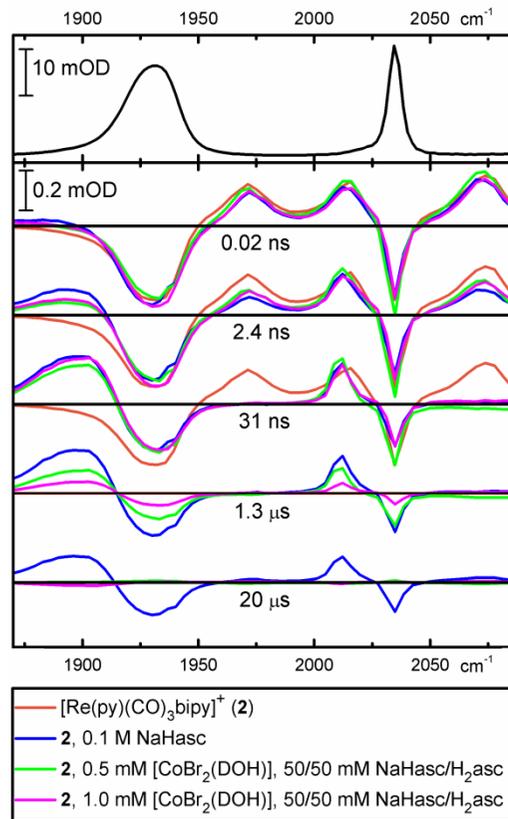
## 4.5 Diffusion controlled reactions

example for a rapid reaction



# Deduction of Mechanisms

## 4.5 Diffusion controlled reactions



# Deduction of Mechanisms

## 4.6 Kinetic Isotope Effect

Exchanging isotopes is often a good hint to a reaction mechanism and the relevance of individual elementary steps

If a reaction rate depends on the isotope (H/D),  
then this step is rate determining

An isotopic effect is generally observable with H/D  
but is very difficult to detect with other isotopes e.g.  $^{12}\text{C}/^{13}\text{C}$

**vibrational energy** of a molecule:  $E_n = (n + 1/2) \cdot h \cdot \nu$

**harmonic oscillator**  $\nu = \frac{1}{2\pi} \sqrt{\frac{k'}{\mu}}$

if **force constants** for R-H and R-D are equal:  $\rightarrow \frac{\nu_{\text{R-H}}}{\nu_{\text{R-D}}} = \sqrt{\frac{m_{\text{D}}}{m_{\text{H}}}} = \sqrt{2}$

# Deduction of Mechanisms

## 4.6 Kinetic Isotope Effect

**Principle of kie:** Difference of activation energy is equal to the difference of ground state energies since R-H(D) bonds must be broken

$$E_a^H - E_a^D = E_0^D - E_0^H$$

from Arrhenius:  $\frac{k_H}{k_D} = \exp\left[\frac{h(\nu_{R-H} - \nu_{R-D})N}{2RT}\right]$  or  $\ln \frac{k_H}{k_D} = \ln\left(\frac{A_H}{A_D}\right) - \frac{\Delta E}{R \cdot T}$

and for R = C follows that  $k_H/k_D = 7.8$

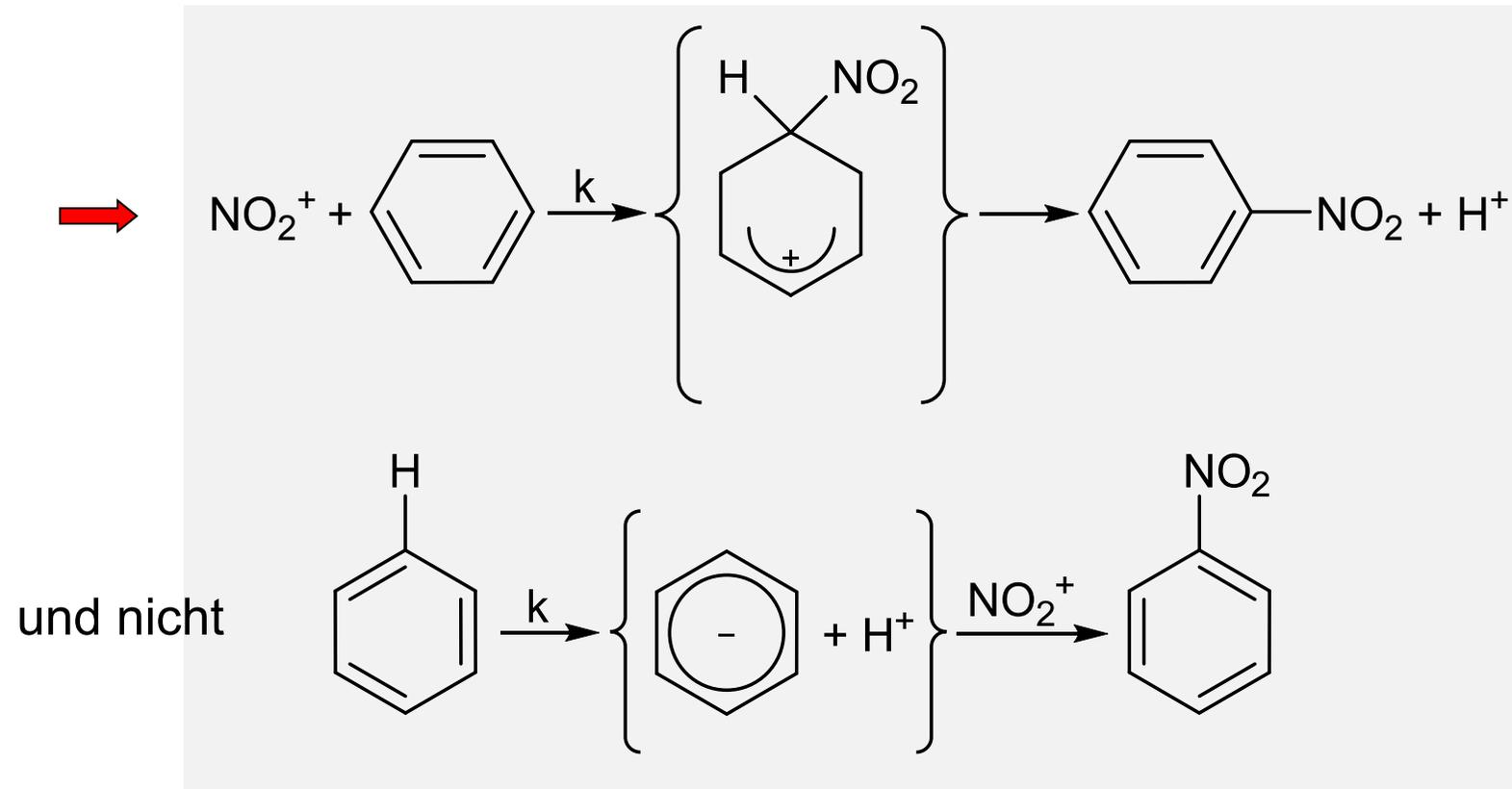
accordingly:

Bond	$\nu_H/\text{cm}^{-1}$	$k_H/k_D$
C-H	2900	7.8
O-H	3300	10.3
N-H	3100	8.9
S-H	2600	6.3

# Deduction of Mechanisms

## 4.6 Kinetic Isotope Effect

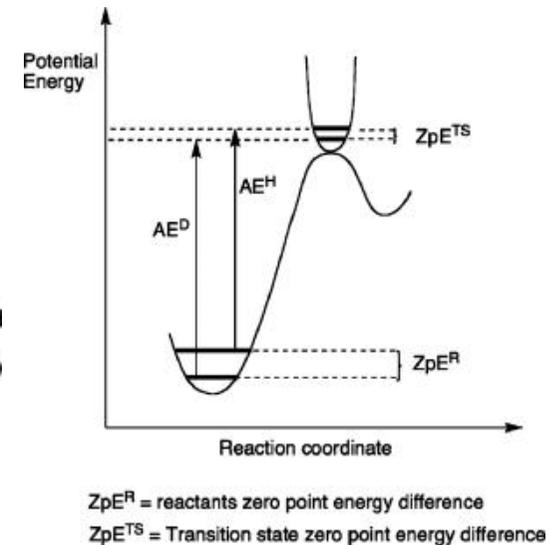
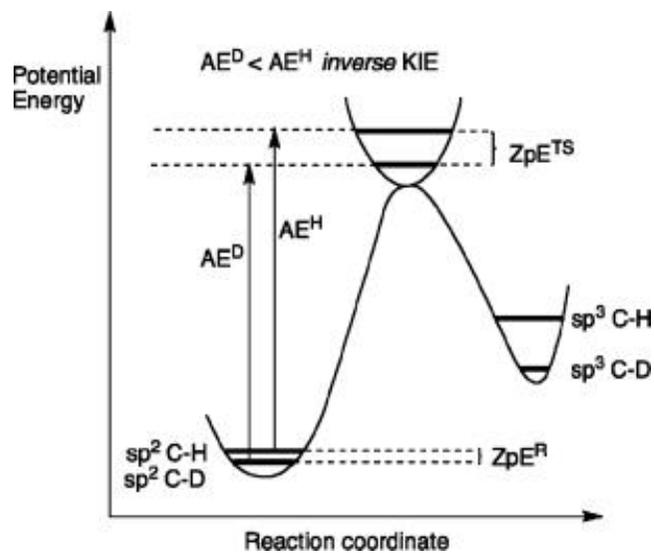
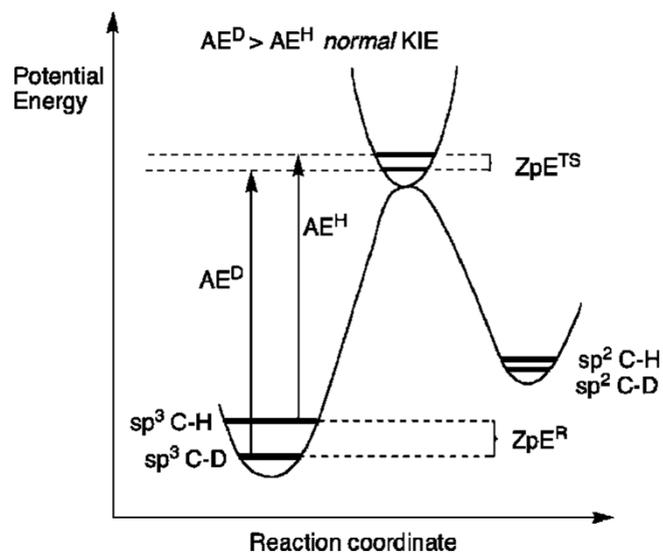
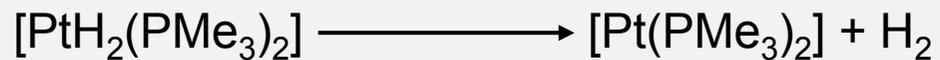
Beispiel: Nitrierung von  $C_6H_6$  zeigt keinen Isotopeneffekt



# Deduction of Mechanisms

## 4.6 Kinetic Isotope Effect

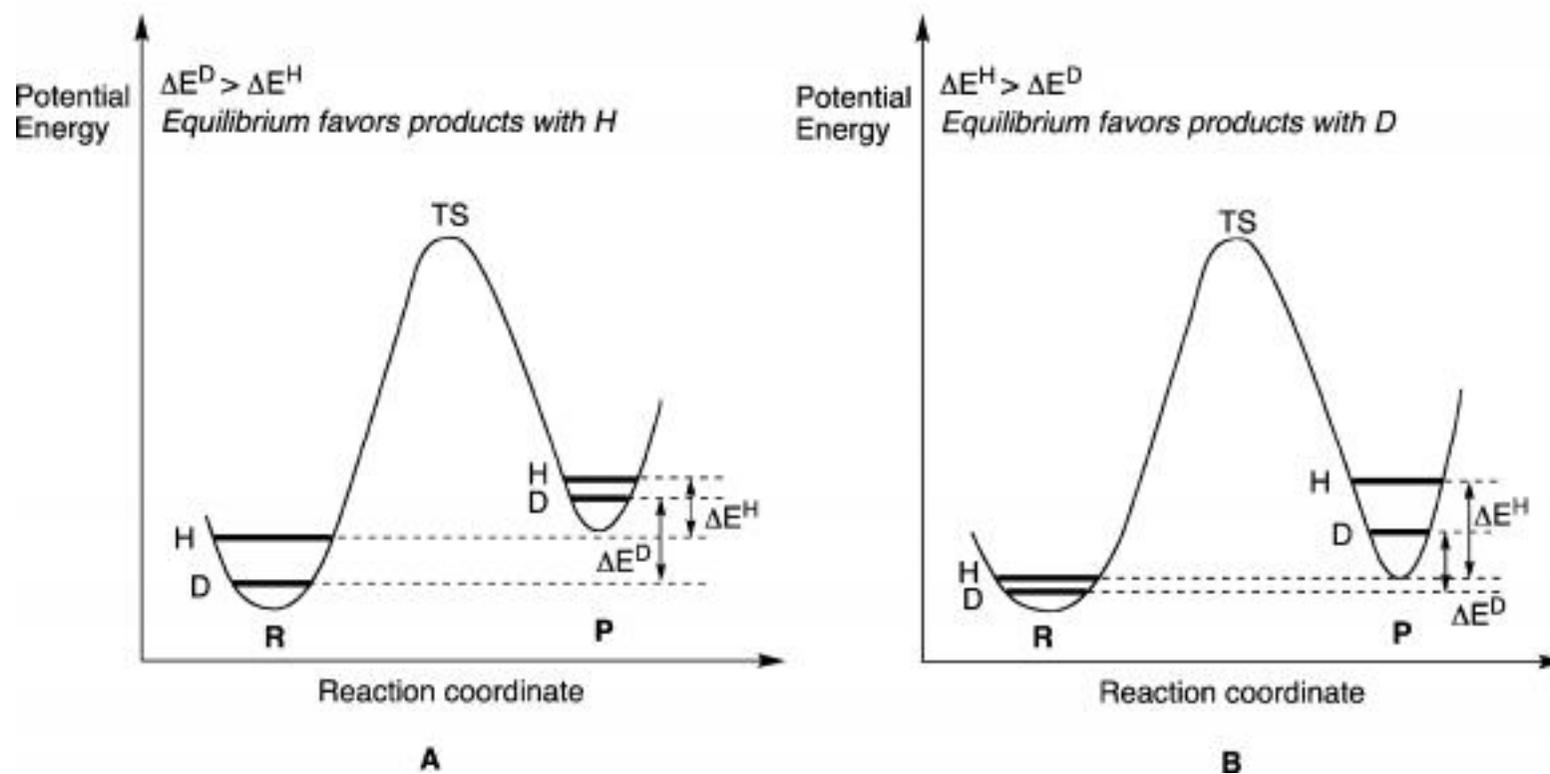
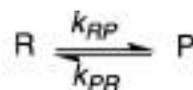
the following reaction has a kie of 0.45, why?



# Deduction of Mechanisms

## 4.6 Kinetic Isotope Effect

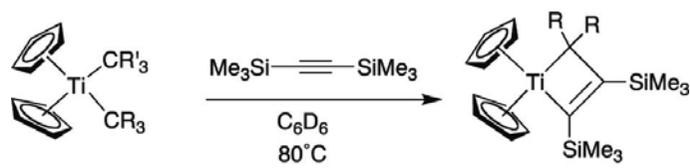
How thermodynamics influences the magnitude of the kie



# Deduction of Mechanisms

## 4.6 Kinetic Isotope Effect

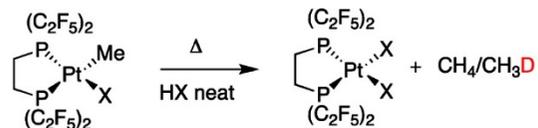
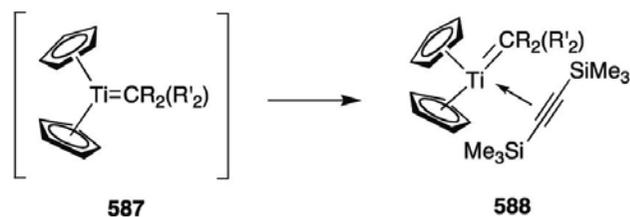
a few examples for normal and inverted kie's



**586-d<sub>0</sub>** R = R' = H  
**586-d<sub>3</sub>** R = H, R' = D  
**586-d<sub>6</sub>** R = R' = D

**589-d<sub>0</sub>** R = H  
**589-d<sub>2</sub>** R = D

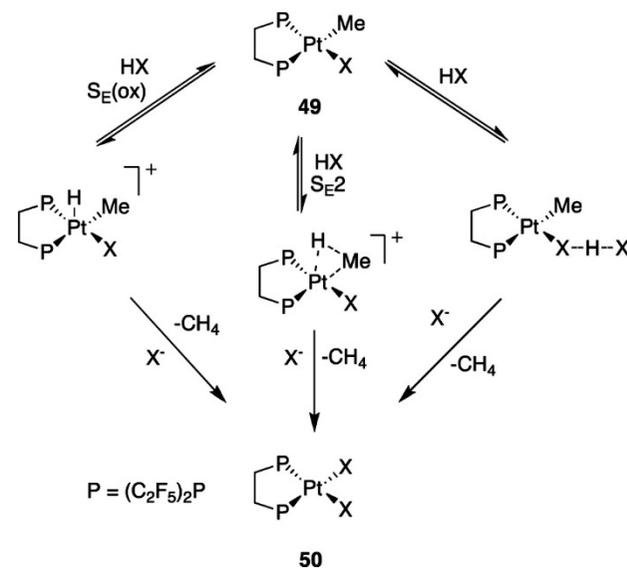
rds ↓     **586-d<sub>0</sub>/586-d<sub>3</sub>**;  $k_H/k_D = 2.0$   
                  **586-d<sub>0</sub>/586-d<sub>6</sub>**;  $k_H/k_D = 6.4$   
                  **586-d<sub>3</sub>/586-d<sub>6</sub>**;  $k_H/k_D = 3.2$



**49**

**50**

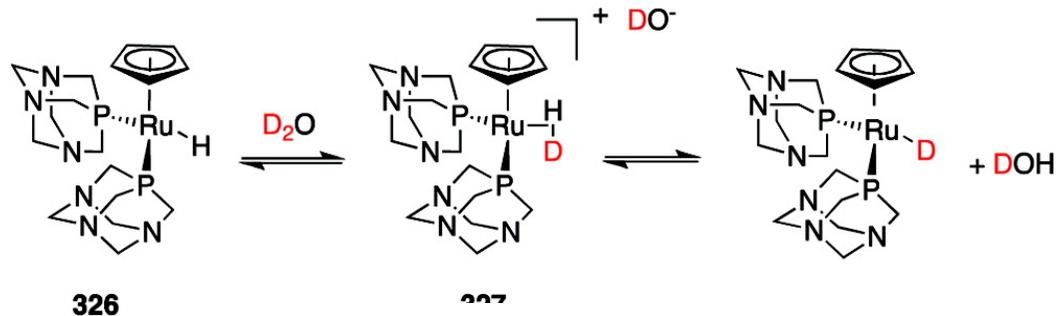
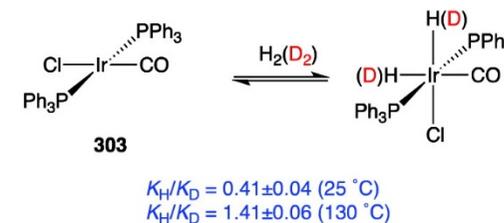
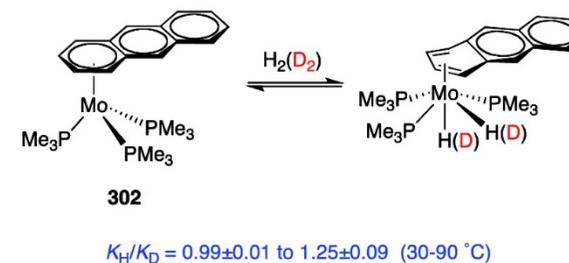
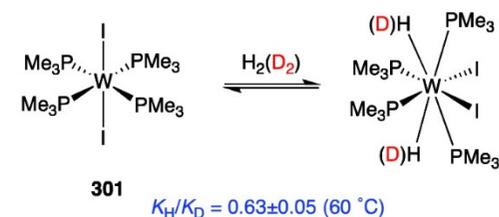
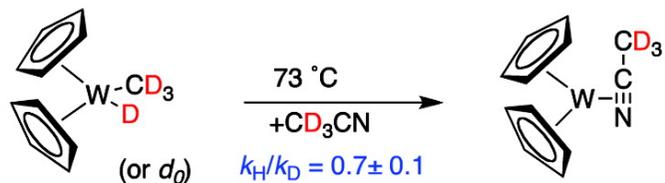
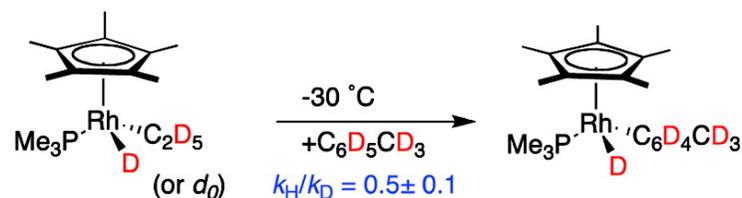
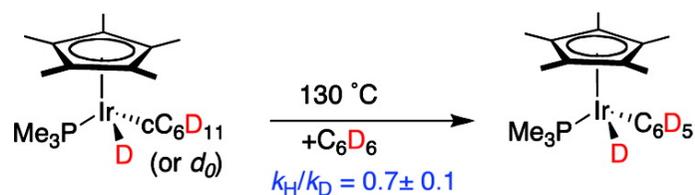
XH = CF<sub>3</sub>CO<sub>2</sub>H(D),  $k_H/k_D = 9 \pm 2$   
 XH = (D<sub>2</sub>)H<sub>2</sub>SO<sub>4</sub>,  $k_H/k_D = 7 \pm 2$   
 XH = CF<sub>3</sub>SO<sub>3</sub>H(D),  $k_H/k_D = 2.7 \pm 0.7$



# Deduction of Mechanisms

## 4.6 Kinetic Isotope Effect

a few examples for normal and inverted kie's

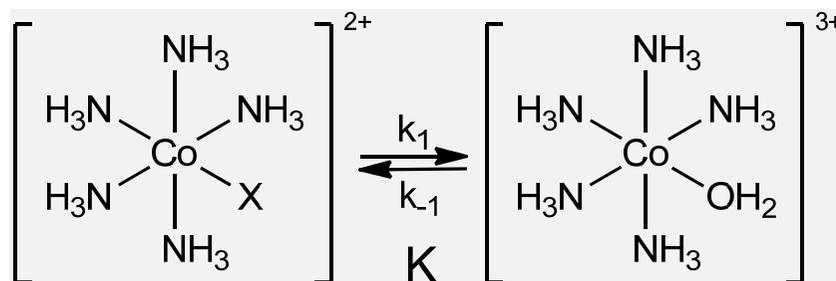


what would you expect?

# 5. Linear Free Energy Relationships LFER

**Kinetic rate laws** describe the time course of a reaction as a function of the **elementary steps**

- ➔ a relationship between **kinetics and thermodynamics** of a reaction
- ➔ is called a **Linear Free Energy Relationship LFER**
- ➔ LFER are a **semi quantitative** way of “systematizing” our ideas about the **similarity of reactions**.
- ➔  $\Delta G^\ddagger$  and  $\Delta G$  are correlated, although they have sometimes nothing to do with each other
- ➔ only sets of closely related reactions should be compared in that way



# Linear Free Energy Relationships LFER

➔ only sets of closely related reactions should be compared in that way

the most useful examples have well-defined domains of applicability, such as

the **Hammett equation**,

the **Brønsted catalysis law**

and the **Marcus equation** (see later).

an LFER is of the general form  $\ln k = m \cdot \ln K_c + b$  since

$$\ln k = \ln \frac{k \cdot T}{h} - \frac{\Delta G^*}{R \cdot T}$$

$$\ln K_c = - \frac{\Delta G^0}{R \cdot T}$$

$$\Delta G^* = m \Delta G^0 + b'$$

whereas the parameters  $m$  and  $b'$  may tell us something about the mechanism

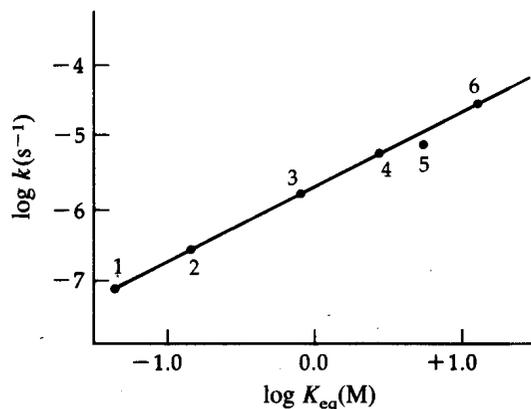
# Linear Free Energy Relationships LFER

**example:**  $K = \frac{k_1}{k_{-1}}$  oder  $\log k_1 = \log K + \log k_{-1}$

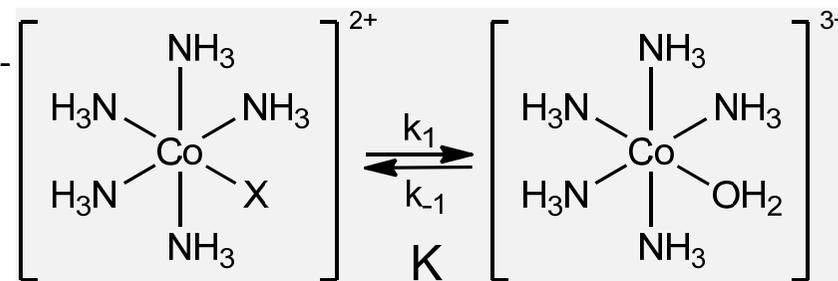
If the process is **dissociative** and goes through a CN=5 then,

**$k_{-1}$  must be constant** due to the microscopic reversibility

thus, we must have an **LFER** between  **$\log k$  and  $\log K$**  as a function of X



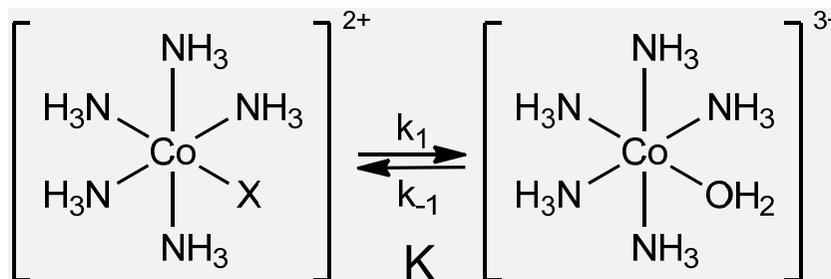
- (1)  $X^- = F^-$
- (2)  $X^- = H_2PO_4^-$
- (3)  $X^- = Cl^-$
- (4)  $X^- = Br^-$
- (5)  $X^- = I^-$
- (6)  $X^- = NO_3^-$



# Linear Free Energy Relationships LFER

**example:**  $K = \frac{k_1}{k_{-1}}$  oder  $\log k_1 = \log K + \log k_{-1}$

... and vice versa, if the mechanism is associative, CN=7 in transitions state, we must find a LFER between  $\log k_{-1}$  vs.  $\log K$

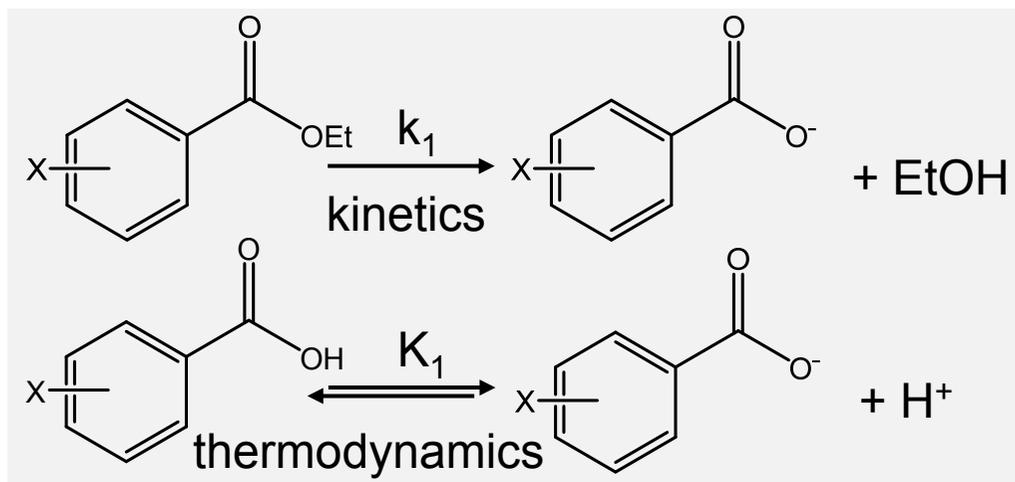


frequently, "**logK**" is not known, then a correlation can also be made with a similar physico-chemical parameter  
e.g. in this case with the  $\text{p}K_a$  values or with NMR shifts

# Linear Free Energy Relationships LFER

## 5.1 Hammett Correlation

This relationship correlates the influence of *m,p*-substituents in aromatic systems (originally) to the hydrolysis of benzoic-acid esters



$$\text{LFER: } \log k_1 - \log k_1^0 = \rho \cdot (\log K_a - \log K_a^0)$$

$$\text{or: } \log \frac{k_1}{k_1^0} = \rho \cdot \log \frac{K_a}{K_a^0} \quad \text{and} \quad \rho \cdot \log \frac{K_a}{K_a^0} = \sigma$$

$\sigma$  = Hammett Parameter

# Linear Free Energy Relationships LFER

## 5.1 Hammett Correlation

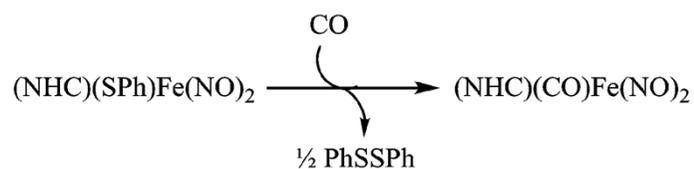
**negative  $\sigma$ -values** stand for donating, **positive  $\sigma$ -values** for accepting groups

inspection of curvature e.g.  $k_1$  vs  $s$  gives an insight into the type of mechanism

Hammett equation has been modified, to include

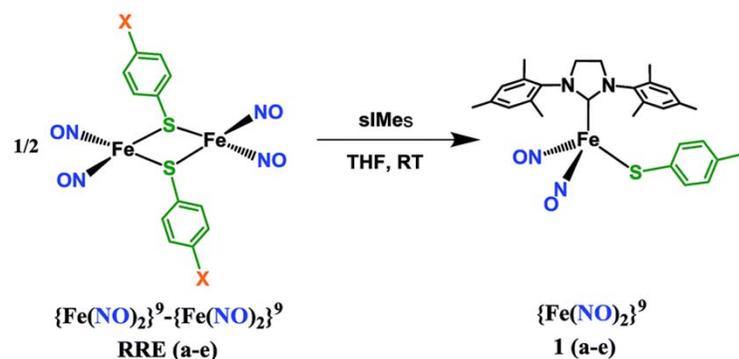
**steric, inductive or resonance effects (Taft)**

**Example** from organometallic chemistry: disulfide elimination



$$\text{rate} = k \cdot [\text{CO}] \cdot [(\text{NHC})(\text{SPh})\text{Fe}(\text{NO})_2]$$

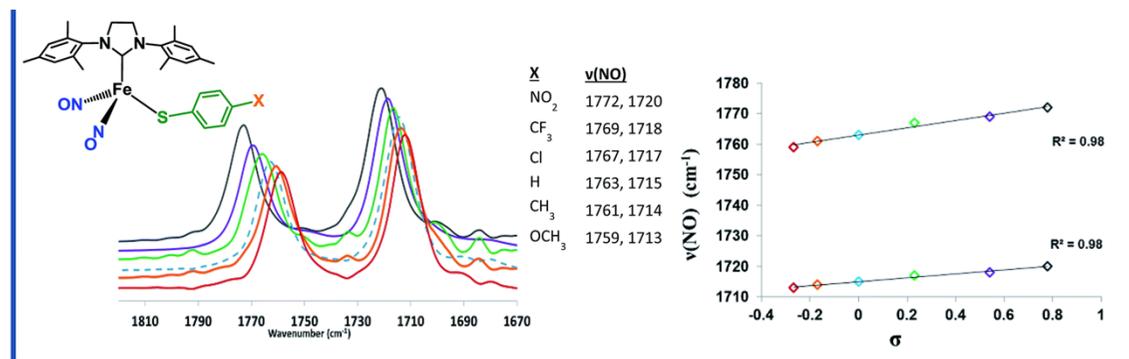
$$\Delta H^* = 7.8 \text{ kcal/mol} \quad \Delta S^* = -45 \text{ e.u.}$$



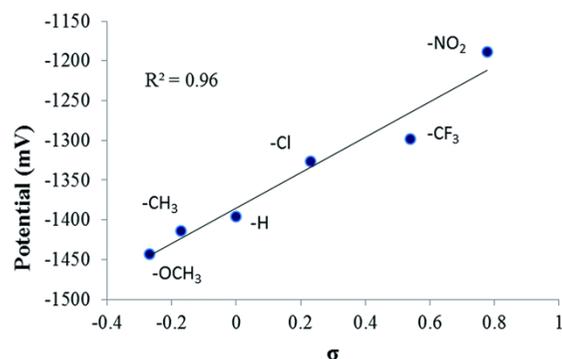
	a	b	RRE/1	c	d	e
X	OCH <sub>3</sub>	CH <sub>3</sub>	H	Cl	CF <sub>3</sub>	NO <sub>2</sub>
$\sigma_p^{41}$	-0.268	-0.170	0.000	0.230	0.540	0.778

# Linear Free Energy Relationships LFER

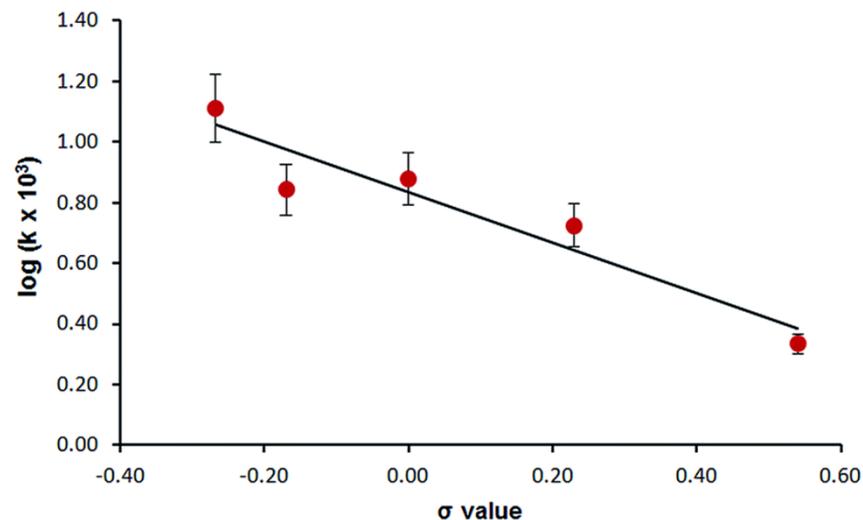
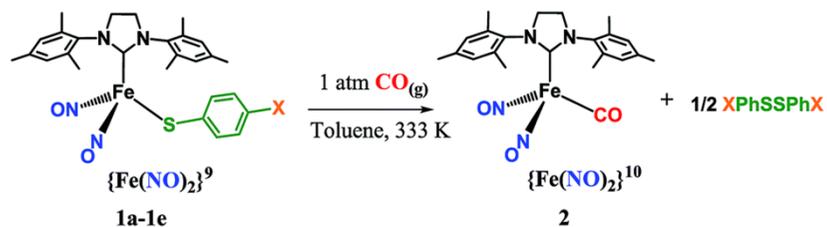
## 5.1 Hammett Correlation



correlation of  $\nu_{\text{NO}}$  vs. Hammett Parameter  $\sigma$



$E_{1/2}$  vs  $\sigma$



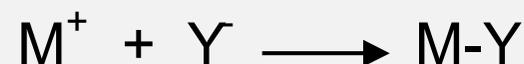
rate retardation by e<sup>-</sup> withdrawing substituents

in agreement with mechanism

# Linear Free Energy Relationships LFER

## 5.2 Ligand Field Stabilization Energies

**Pro memoria:** Classification of substitution mechanisms



Hughes-Ingold:  $S_{N1}$  - **Langford-Gray:** D



Hughes-Ingold:  $S_{N1}$  - **Langford-Gray:**  $I_d / I_a$



Hughes-Ingold:  $S_{N2}$  - **Langford-Gray:** A

# Linear Free Energy Relationships LFER

## 5.2 Ligand Field Stabilization Energies

**A or D mechanisms** may show different LFER, the LFSE plays a role

**intimate mechanisms** if in between

must be elucidated from a **series of experiments**, e.g. with LFER relations

nomenclature:

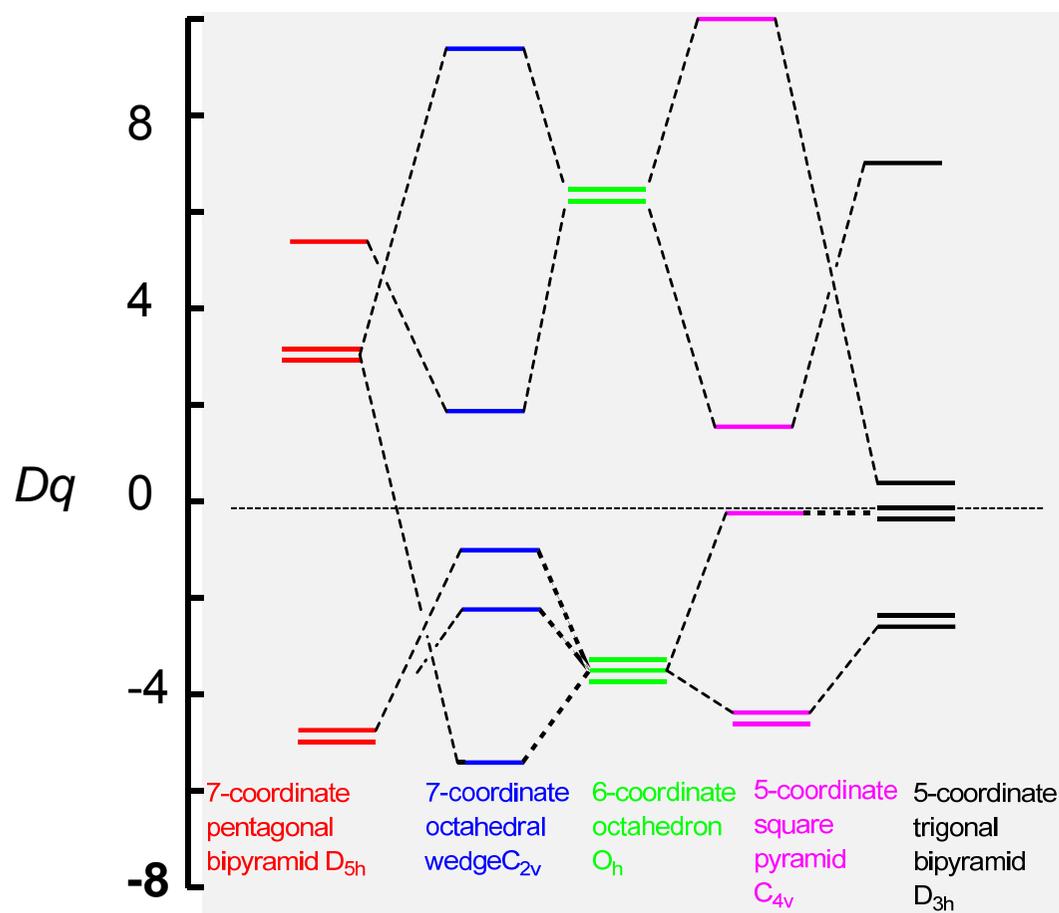
- dissociative activation  $I_d$   influence of leaving group
- associative activation  $I_a$   influence of entering group

# Linear Free Energy Relationships LFER

## 5.2 Ligand Field Stabilization Energies

Mechanisms: **Crystal Field Activation Approach (CFSE)**

**Assumption:** changes in transition GS  $\rightarrow$  TS determines mechanism



# Linear Free Energy Relationships LFER

## 5.2 Ligand Field Stabilization Energies

Mechanisms: **Crystal Field Activation Approach (CFSE)**

Symmetry transition state	$D_{3h}$	$C_{4v}$	$C_{2v}$	$D_{5h}$
$d^0$	0	0	0	0
$d^1$	1.28	-0.57	-2.08	1.28
$d^2$	2.56	-1.14	-0.68	-2.56
$d^3$	5.75	2.00	1.80	4.26
$d^4$ low spin	7.02	1.43	-0.26	2.98
$d^4$ high spin	-1.08	-3.14	-2.79	1.07
$d^5$ low spin	8.30	0.86	1.14	1.70
$d^5$ high spin	0	0	0	0
$d^6$ low spin	11.48	4.00	3.63	8.52
$d^6$ high spin	0.27	-0.57	-2.08	-1.28
$d^7$ low spin	4.66	-1.14	-0.98	5.34
$d^7$ high spin	2.55	-1.14	-0.68	-2.56
$d^8$	5.73	2.00	1.80	4.26
$d^9$	-1.08	3.14	-2.79	1.07
$d^{10}$	0	0	0	0

Mode of activation

 dissociative

 associative

# Linear Free Energy Relationships LFER

## 5.2 Ligand Field Stabilization Energies

- ➔ Crystal field activation energy (CFAE) is (almost) always positive.  
**CFAE is zero for  $d^0$ ,  $d^5$  hs.  $d^{10}$**  (if we don't have a spin crossover)

$d^3$ ,  $d^6$  (ls),  $d^8$  → inert centres

$d^4$ ,  $d^7$ ,  $d^9$  gain energy in other states

  
Jahn-Teller states

➔ square pyramide favoured (KZ = 5)

➔ capped octahedral favored (KZ = 7)

Analyse von CFAE is not quantitative, but enables a certain prediction

# Linear Free Energy Relationships LFER

## 5.3 Substitution in square planar complexes

square planar, specially stabilized are  $d^8$  systems

Mn(-I)	Fe(0)	Co(I)	Ni(II)	Cu(III)
		Rh(I)	Pd(II)	Ag(III)
		Ir(I)	Pt(II)	Au(III)

$\text{Pd}^{2+}$  about  $10^5$  time more reactive than  $\text{Pt}^{2+}$

### Classical reaction:



$$v = k_1 \cdot [\text{PdCl}_2(\text{Me}_2\text{S})_2] \cdot [\text{Me}_2\text{S}]$$

and

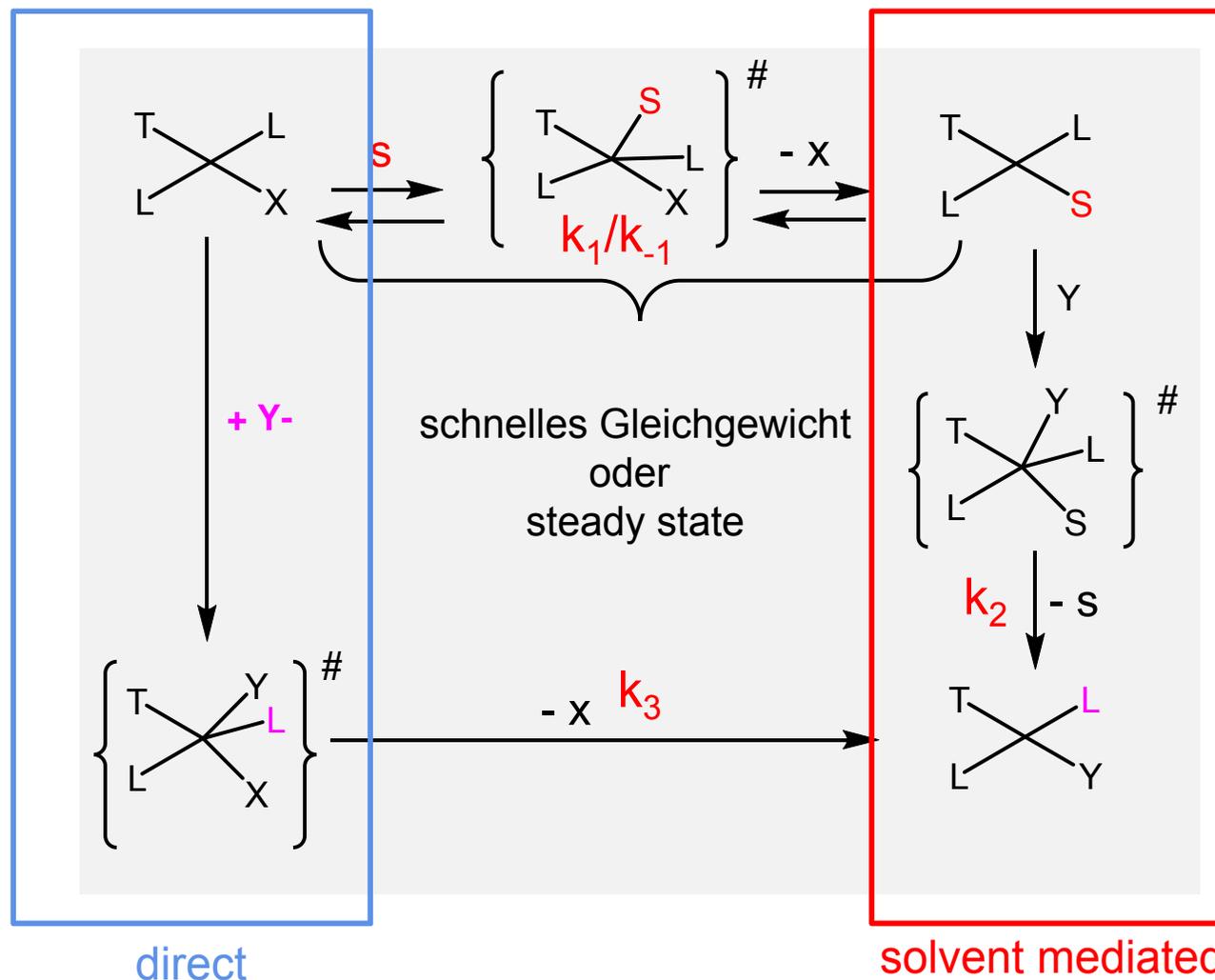


$$v = k_1 \cdot [\text{PtCl}_2(\text{Me}_2\text{S})_2] \cdot [\text{Me}_2\text{S}]$$

# Linear Free Energy Relationships LFER

## 5.3 Substitution in square planar complexes

**Associatively driven** reaction, often in combination with the solvent

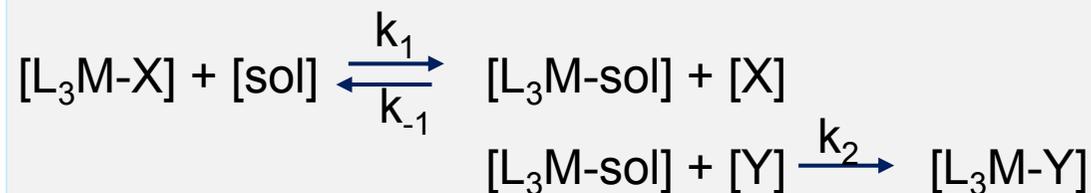


# Linear Free Energy Relationships LFER

## 5.3 Substitution in square planar complexes



**steady state** assumption for solvent mediated path



$$\frac{dP}{dt} = \frac{k_1 \cdot k_2 \cdot [L_3M-X] \cdot [Y]}{k_{-1} \cdot [X] + k_2 \cdot [Y]} \quad \begin{array}{l} \rightarrow \text{if } k_2 \text{ very fast: } v = k_1 \cdot [L_3M-X] \\ \rightarrow \text{if } [X] \text{ very large: suppression of this path} \end{array}$$

**direct path:**  $\frac{dP}{dt} = k_3 \cdot [L_3M-X] \cdot [Y]$

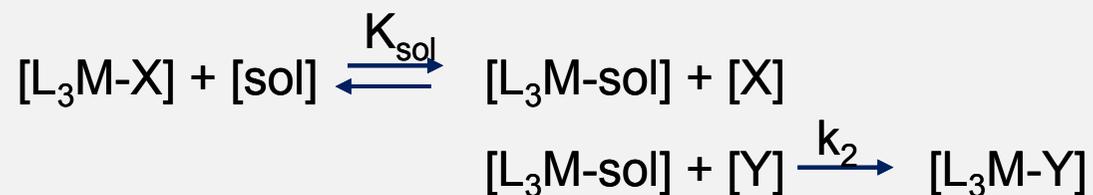
$$\rightarrow \frac{dP}{dt} = k_3 \cdot [L_3M-X] \cdot [Y] + k_1 \cdot [L_3M-X] \quad \text{mit } k_{obs} = (k_1 + k_3 \cdot [Y])$$

# Linear Free Energy Relationships LFER

## 5.3 Substitution in square planar complexes



**prior equilibrium** assumption for solvent mediated path



$$K = \frac{[L_3M-sol] \cdot [X]}{[L_3M-X] \cdot [sol]} \quad f_B = \frac{[B]}{[A] + [B]} = \frac{K \cdot [sol]}{K \cdot [sol] + [X]} \quad [B] = f_B \cdot [A]$$

$$v = \frac{k_2 \cdot K \cdot [A] \cdot [Y] \cdot [sol]}{K \cdot [sol] + [X]} \quad \begin{array}{l} \rightarrow \text{if } K \text{ very large: } v = k_2 \cdot [A][Y] \\ \rightarrow \text{if } K \text{ small: suppression of this path} \end{array}$$

# Linear Free Energy Relationships LFER

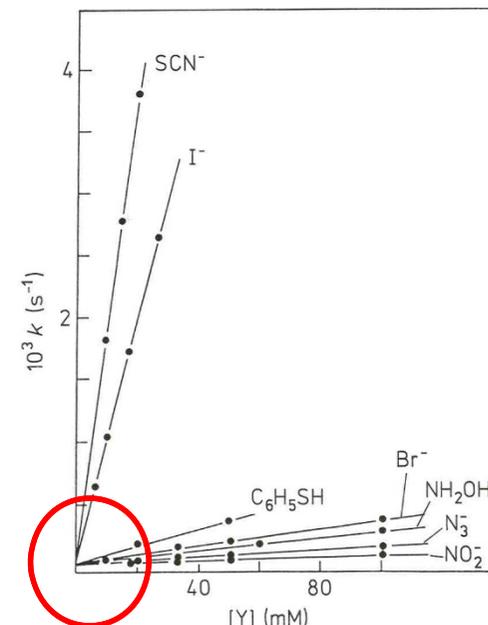
## 5.3 Substitution in square planar complexes

### Activation parameters for substitution in s.p. complexes

$$v = k_{\text{obs}} \cdot [\text{PtCl}(\text{PEt}_3)_2\text{L}]$$

$$k_{\text{obs}} = k_1 + k_2 \cdot [\text{I}^-]$$

L	$k_1$ [s <sup>-1</sup> ]	$k_2$ [l mol <sup>-1</sup> s <sup>-1</sup> ]
CH <sub>3</sub> <sup>-</sup>	$1.7 \cdot 10^{-4}$	$6.7 \cdot 10^{-2}$
C <sub>6</sub> H <sub>5</sub> <sup>-</sup>	$3.3 \cdot 10^{-5}$	$1.6 \cdot 10^{-2}$
Cl <sup>-</sup>	$1.0 \cdot 10^{-6}$	$4.0 \cdot 10^{-4}$
H <sup>-</sup>	$1.8 \cdot 10^{-2}$	
PEt <sub>3</sub>	$1.7 \cdot 10^{-2}$	



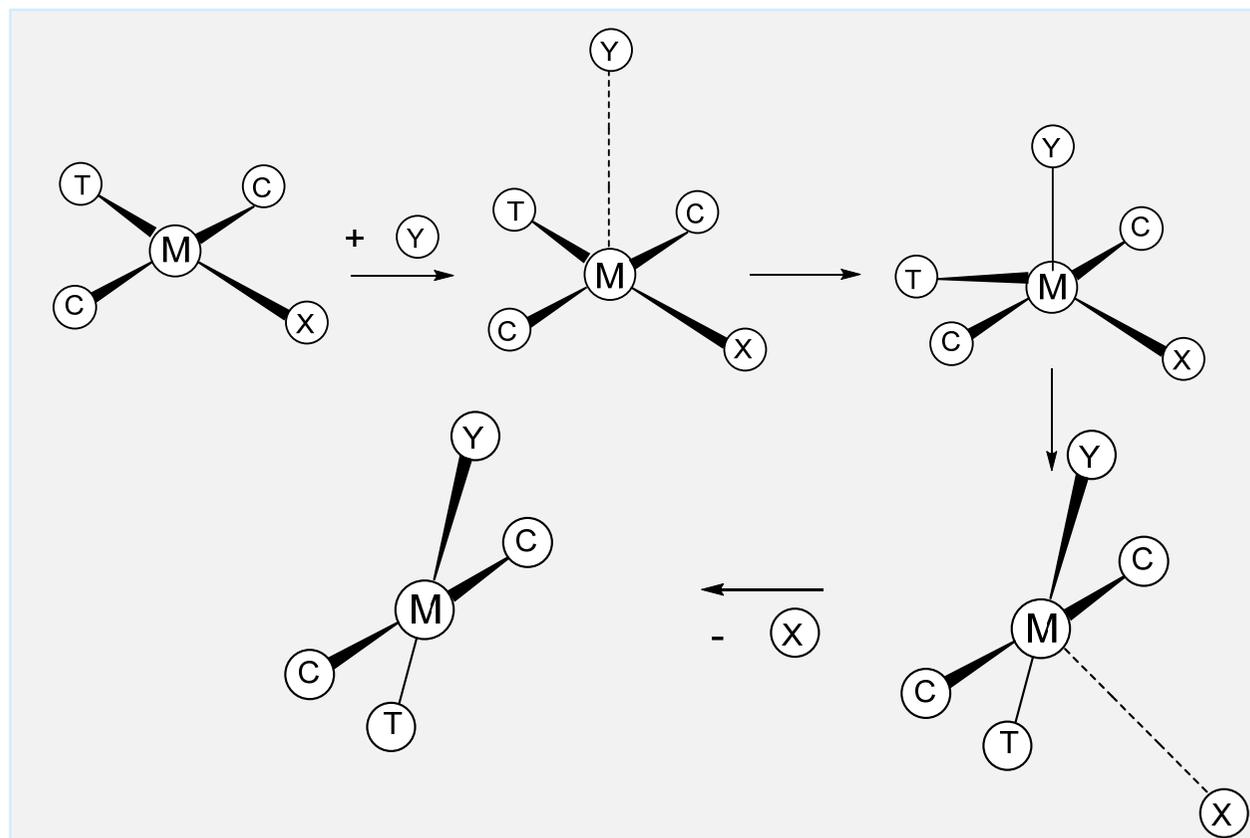
Reaktion		$k_1$			$k_2$		
		$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta V^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta V^\ddagger$
<i>trans</i> -[PtCl(NO <sub>2</sub> )(py) <sub>2</sub> ]	+ py	50	-100	-38			
<i>trans</i> -[PtBr(Mes)(PEt <sub>3</sub> ) <sub>2</sub> ] <sup>*</sup>	+ SC(NH <sub>2</sub> ) <sub>2</sub>	71	-84	-46	46	-138	-54
<i>cis</i> -[PtBr(Mes)(PEt <sub>3</sub> ) <sub>2</sub> ] <sup>*</sup>	+ I <sup>-</sup>	84	-59	-67	63	-121	-63
<i>cis</i> -[PtBr(Mes)(PEt <sub>3</sub> ) <sub>2</sub> ] <sup>*</sup>	+ SC(NH <sub>2</sub> ) <sub>2</sub>	79	-71	-71	59	-121	-54
[AuCl(dien)] <sup>2+</sup>	+ Br <sup>-</sup>	54	-17				

\* Mes = 2,4,6-Trimethylphenyl Enthalpieterme in kJ mol<sup>-1</sup>, Entropie in J K<sup>-1</sup> mol<sup>-1</sup>, Volumina in cm<sup>3</sup> mol<sup>-1</sup>.

# Linear Free Energy Relationships LFER

## 5.3 Substitution in square planar complexes

Stereochemistry: generally, the relative configuration is maintained → **Retention**

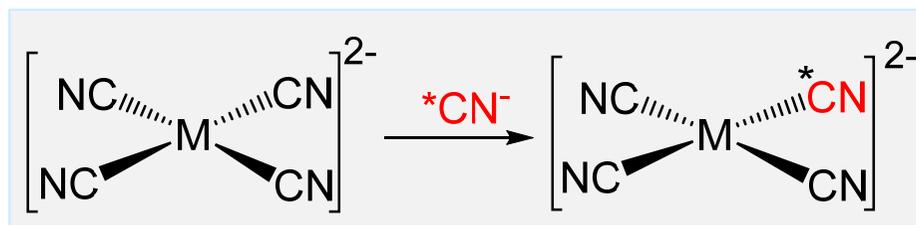


5-coordinate transition state with entering/leaving groups in the eq. plane

# Linear Free Energy Relationships LFER

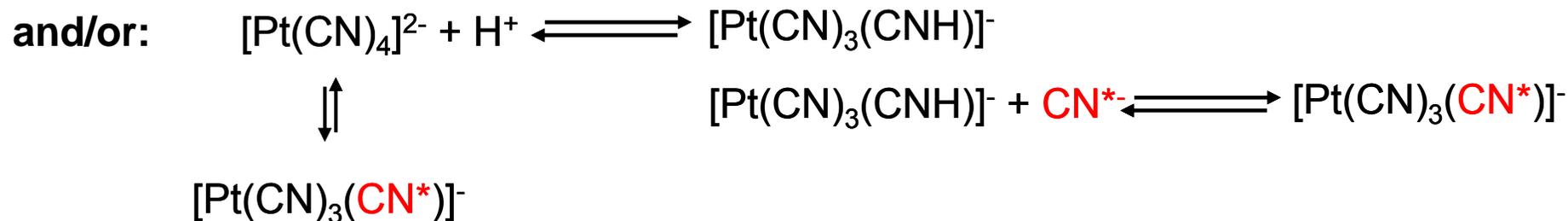
## 5.3 Substitution in square planar complexes

**example:** is the cyanide exchange at  $[\text{Pt}(\text{CN})_4]^{2-}$  proton mediated?



substitution on  $d^8$  systems purely A

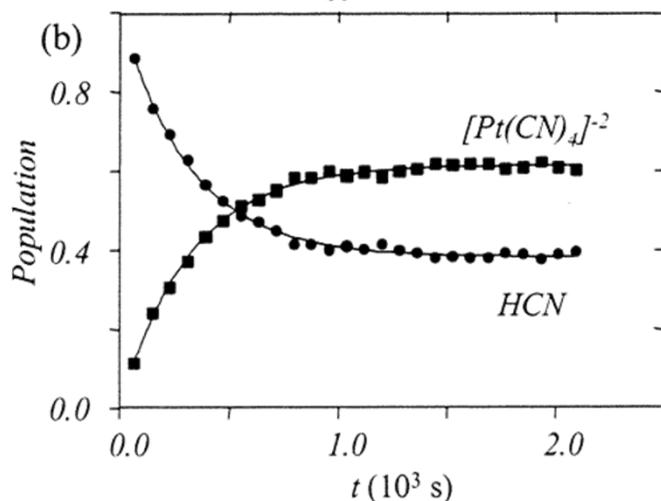
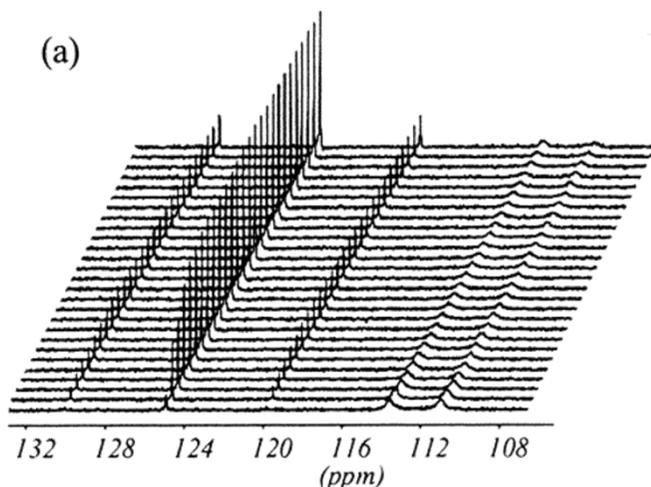
**rate law:**  $\frac{dP}{dt} = k[\text{Pt}(\text{CN})_4][* \text{CN}]$



# Linear Free Energy Relationships LFER

## 5.3 Substitution in square planar complexes

**Cyanide exchange:**  $[\text{Pt}(\text{CN})_4]^{2-}$  is very stable:  $\log \beta_4 \approx 40$



Exchange followed by NMR

pH = 6.0 /  $[\text{Pt}] = 0.1 \text{ M}$  /  $[\text{CN}] = 0.26 \text{ M}$

Kinetics is purely 2<sup>nd</sup> order ...

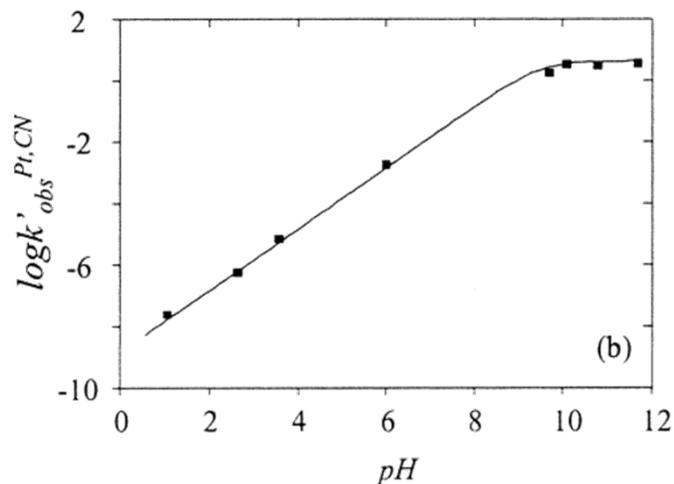
$$\frac{d[\text{Pt}]}{dt} = k_2[\text{CN}][\text{Pt}]$$

$$\frac{d[\text{Pt}]}{dt} = k_2[\text{CN}]_0 \frac{K_a}{K_a + [\text{H}^+]}$$

⇒ ... and pH dependent ?

# Linear Free Energy Relationships LFER

## 5.3 Substitution in square planar complexes



$$\Delta H^\ddagger = 25 \text{ kJ/mol}$$

$$\Delta S^\ddagger = -142 \text{ e.u.}$$

$$\Delta V^\ddagger = -27 \text{ cm}^3 \text{ mol}^{-1}$$

$$k_2 = 11 \text{ sec}^{-1}\text{M}^{-1}$$

pure 2<sup>nd</sup> order means only direct exchange is important

→ protonation of  $[\text{Pt}(\text{CN})_4]^{2-}$  does not play any role

→ why do we still see a linear increase?

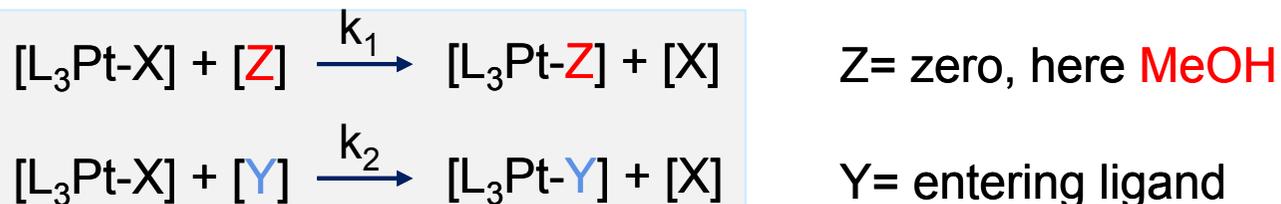
# Linear Free Energy Relationships LFER

## 5.4 trans-effect trans-influence

since substitution reactions on s.p. complexes are **associative A**  
there might be a relationship between the **free energy of activation**  
and the **nucleophilic** character of the entering group, i.e. **an LFER**

These scales are **metal dependent** and require a "**zero**" point (as in Hammett)

we compare two reactions



**nucleophilicity for Pt<sup>II</sup>:**

reaction in MeOH is pseudo 1<sup>st</sup> order  $k_1^0 = k_1[\text{MeOH}]$

$$\eta_{\text{Pt}} = \log \frac{k_2}{k_1} \quad \text{scaled to } \eta_{\text{Pt}}^0 = \eta_{\text{Pt}} + \log 24.3 = \eta_{\text{Pt}} + 1.39$$

# Linear Free Energy Relationships LFER

## 5.4 trans-effect trans-influence

$$\eta_{\text{Pt}} = \log \frac{k_2}{k_1} \quad \text{scaled to } \eta_{\text{Pt}}^0 = \eta_{\text{Pt}} + \log 24.3 = \eta_{\text{Pt}} + 1.39$$

represents an LFER scale for the nucleophilicity of Pt<sup>II</sup>

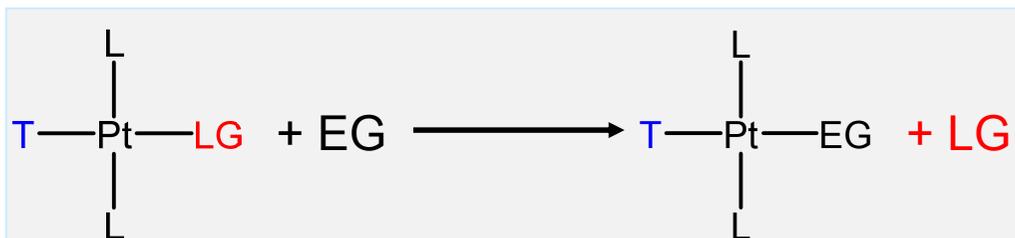
examples:

Carbon	$\eta_{\text{Pt}}^0$	Nitrogen		Sulfur	
C <sub>6</sub> H <sub>11</sub> NC	6.34	NH <sub>3</sub>	3.07	PhSH	4.15
CN <sup>-</sup>	7.14	C <sub>5</sub> H <sub>5</sub> N	3.19	Et <sub>2</sub> S	4.52
halogens	$\eta_{\text{Pt}}^0$	NO <sub>2</sub> <sup>-</sup>	3.22	Me <sub>2</sub> S	4.87
F <sup>-</sup>	<2.2	N <sub>3</sub> <sup>-</sup>	3.48	SCN <sup>-</sup>	5.75
Cl <sup>-</sup>	3.04	NH <sub>2</sub> OH	3.85	(NH <sub>2</sub> ) <sub>2</sub> CS	7.17
Br <sup>-</sup>	4.18	Phosphor	$\eta_{\text{Pt}}^0$	Selenium	
I <sup>-</sup>	5.46	PPh <sub>3</sub>	8.93	Me <sub>2</sub> Se	5.70
		Et <sub>3</sub> P	8.99	SeCN <sup>-</sup>	7.11

# Linear Free Energy Relationships LFER

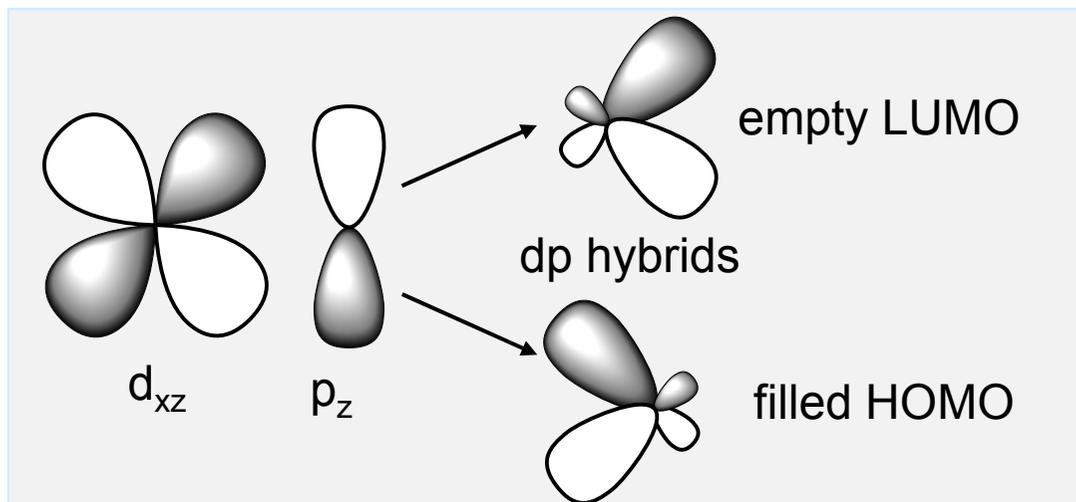
## 5.4 trans-effect trans-influence

the influence of the non-participating ligands is called **trans-effect** or **trans-influence**



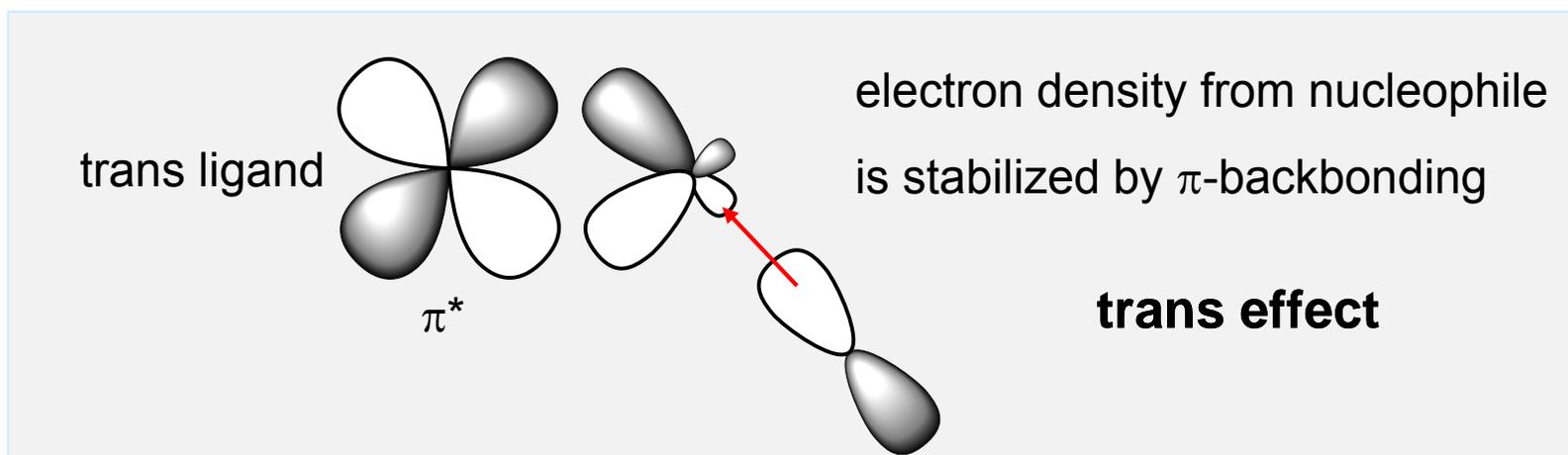
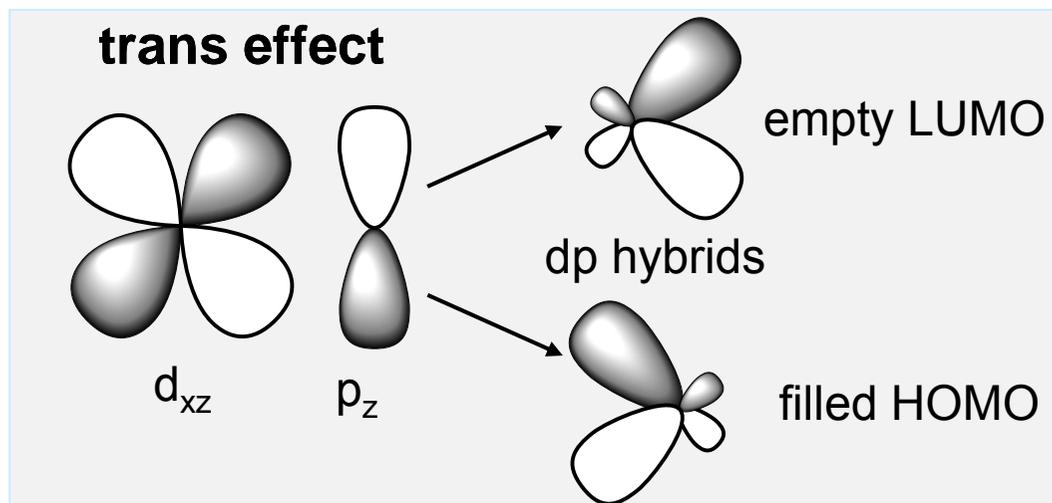
trans-directing influence of a ligand T

**question:** is there a cis-directing mechanism?



# Linear Free Energy Relationships LFER

## 5.4 trans-effect trans-influence

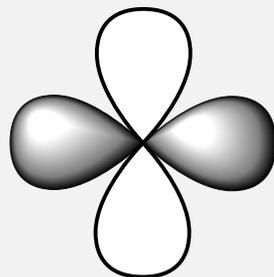


the better the  $\pi$ -accepting properties of "T", the more stable the transition state

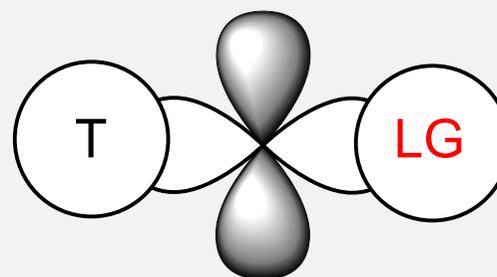
# Linear Free Energy Relationships LFER

## 5.4 trans-effect trans-influence

### trans influence

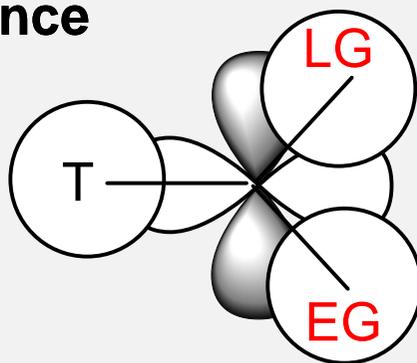


d or 2·p



### trans influence

trans ligand



**strong M-T bond weakens**

**bond trans to it**

**ground state destabilization**

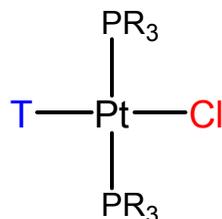
trans-effect and -influence are two different molecular phenomena **with the same effect**

# Linear Free Energy Relationships LFER

## 5.4 trans-effect trans-influence

**trans-influence** weakens ground state binding energy of M-LG

mirrored by bond-lengths



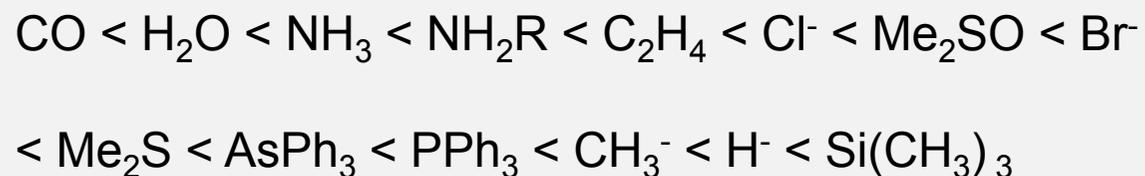
trans-ligand	PR <sub>3</sub>	Pt-Cl (Å)
Cl <sup>-</sup>	PEt <sub>3</sub>	2.294
C <sub>2</sub> F <sub>5</sub> <sup>-</sup>	PMePh <sub>2</sub>	2.361
C <sub>6</sub> H <sub>5</sub> <sup>-</sup>	PPh <sub>3</sub>	2.408
CH <sub>3</sub> <sup>-</sup>	PMePh <sub>2</sub>	2.412
(H <sub>3</sub> C) <sub>3</sub> SiCH <sub>2</sub> <sup>-</sup>	PMe <sub>2</sub> Ph	2.415
H <sup>-</sup>	PEtPh <sub>2</sub>	2.422
Ph <sub>2</sub> MeSi <sup>-</sup>	PMePh <sub>2</sub>	2.45

# Linear Free Energy Relationships LFER

## 5.4 trans-effect trans-influence

**the trans influence mirrors an LFER** since destabilization of ground state directly translate into acceleration of substitution

trans influence goes about along with  $\sigma$ -**donating** properties, i.e. nucleophilicity

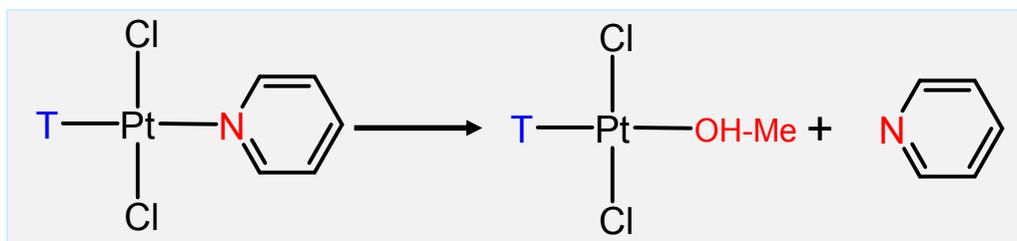


➔ to disentangle from the **kinetic trans effect**, rate measurements are required since the effect comes from the **transition state stabilization**

# Linear Free Energy Relationships LFER

## 5.4 trans-effect trans-influence

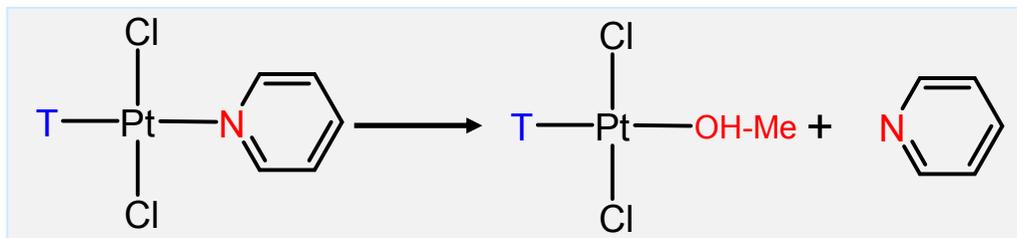
➔ to disentangle from the **kinetic trans effect**, rate measurements are required since the effect comes from the **transition state stabilization**



Trans-ligand	$k_1 \times 10^3 \text{ (s}^{-1}\text{)}$	$k_1 \times 10^3 \text{ (s}^{-1}\text{)}$
C <sub>2</sub> H <sub>4</sub>	6800	too fast
CO	1210	too fast
P(OMe) <sub>3</sub>	365	5240
PPh <sub>3</sub>	27	635
PEt <sub>3</sub>	26	495
PBu <sub>3</sub>	23	380
PMe <sub>3</sub>	15	275
AsEt <sub>3</sub>	1.7	39
Me <sub>2</sub> SO	0.1	2.8

# Linear Free Energy Relationships LFER

## 5.4 trans-effect trans-influence



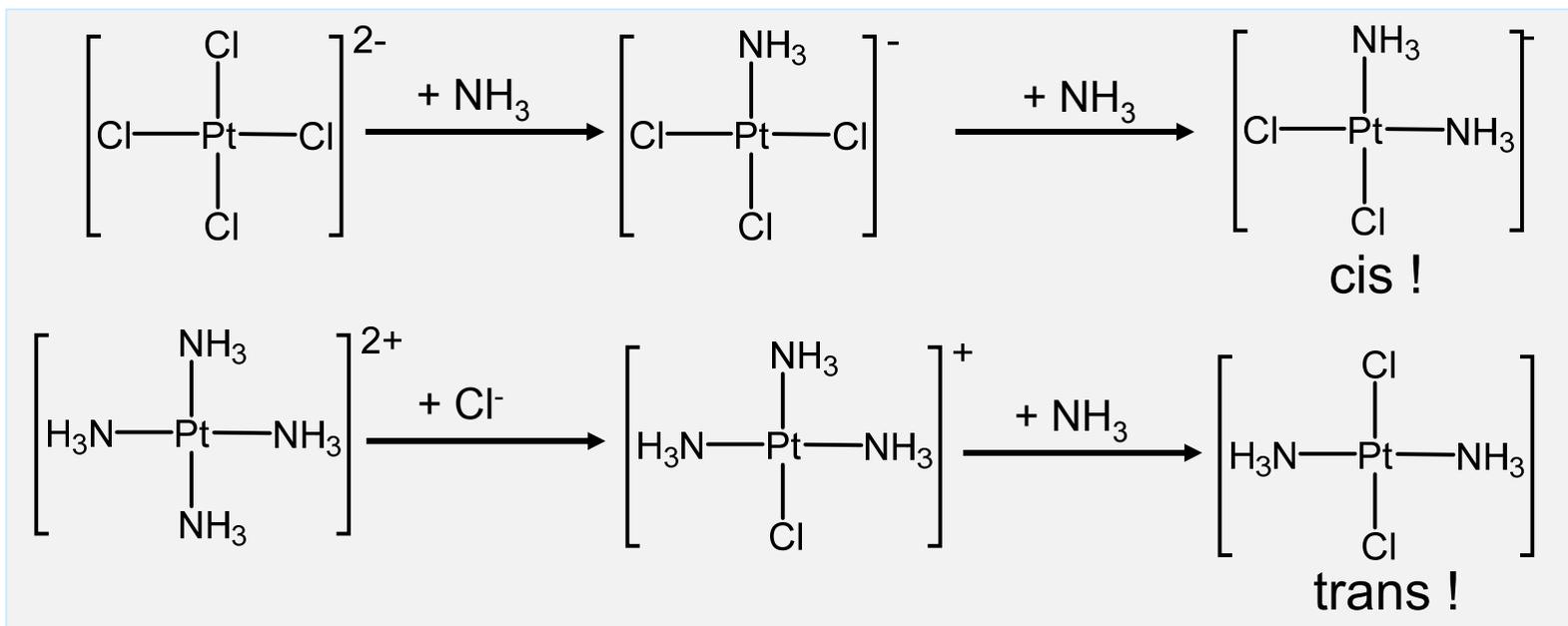
**trans effect series:**  $\text{H}_2\text{O} < \text{NH}_3 < \text{Cl}^- < \text{Br}^- < \text{I}^- \approx [\text{NO}_2]^- < \text{Me}_2\text{S} < \text{Et}_2\text{S} < \text{Me}_2\text{SO} < \text{AsEt}_3$   
 $< \text{Ph}^- < \text{Me}^- < \text{PPh}_3 < \text{PMe}_3 < \text{P(OMe)}_3 \approx \text{H}^- \ll \text{CO} \approx \text{CN}^- < \text{C}_2\text{H}_4$

Trans-ligand	$k_1 \times 10^3 \text{ (s}^{-1}\text{)}$	$k_1 \times 10^3 \text{ (s}^{-1}\text{)}$
$\text{C}_2\text{H}_4$	6800	too fast
CO	1210	too fast
$\text{P(OMe)}_3$	365	5240
$\text{PPh}_3$	27	635
$\text{PEt}_3$	26	495
$\text{PBu}_3$	23	380
$\text{PMe}_3$	15	275
$\text{AsEt}_3$	1.7	39
$\text{Me}_2\text{SO}$	0.1	2.8

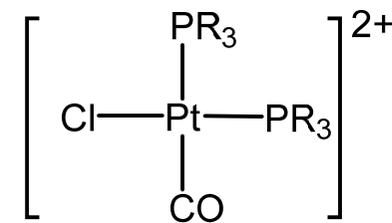
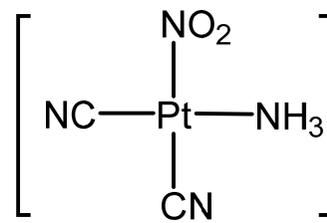
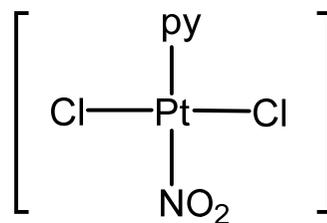
# Linear Free Energy Relationships LFER

## 5.4 trans-effect trans-influence

trans-effect useful for syntheses



how to prepare?

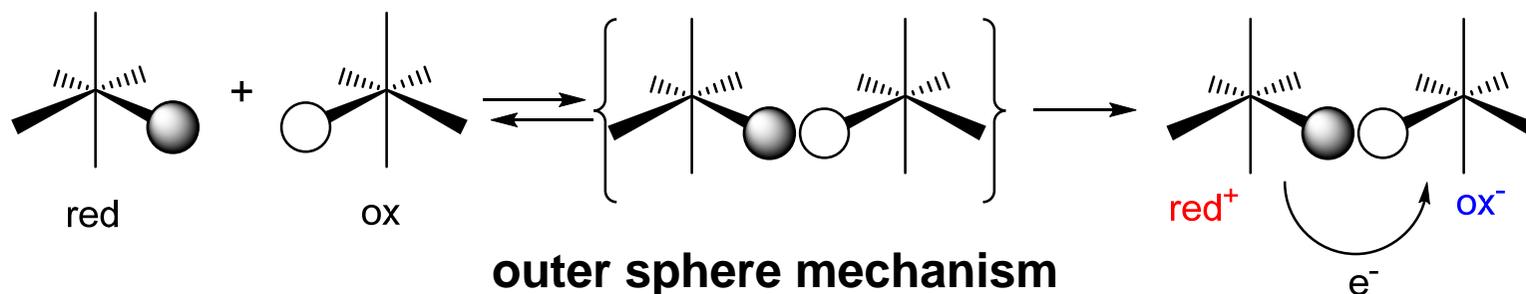
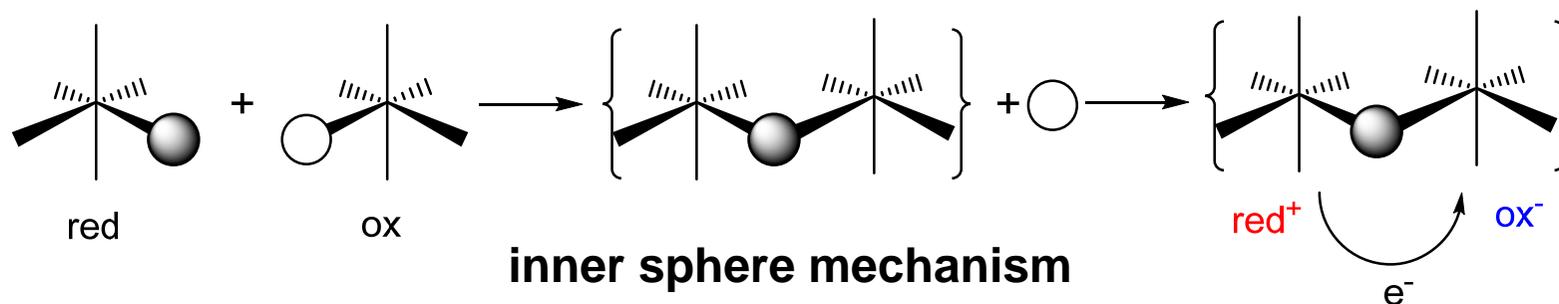


# Electron Transfer Reactions

Redox reactions are ubiquitous in chemistry

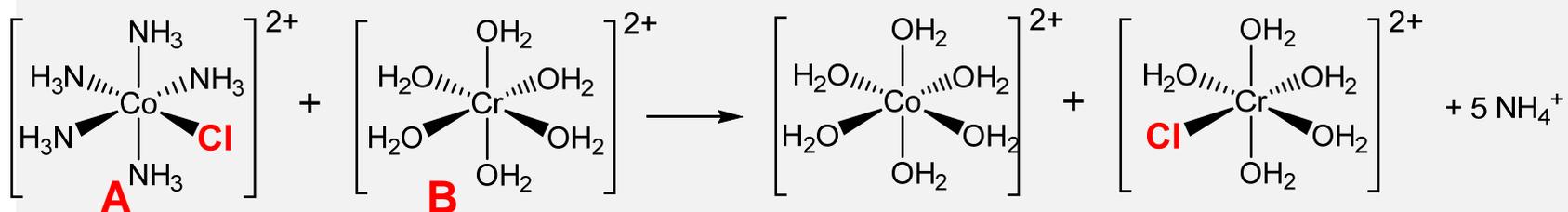
How are electrons transferred from the oxidant to the reductant?

We discern two different type of electron transfer reactions:



# Electron Transfer Reactions

## Taube's famous Experiment



rate constant of overall reaction:  $6 \cdot 10^5 \text{ mol}^{-1} \cdot \text{s}^{-1}$  ( $t_{1/2} \approx 1 \text{ ms}$ )

**puzzling:** substitution rate  $\text{Cl}^-$  for  $\text{H}_2\text{O}$  in **A** is  $2 \cdot 10^{-6} \text{ s}^{-1}$

**equally puzzling:** substitution rate of  $\text{H}_2\text{O}$  for  $\text{Cl}^-$  in **B** is  $3 \cdot 10^{-8} \text{ s}^{-1}$

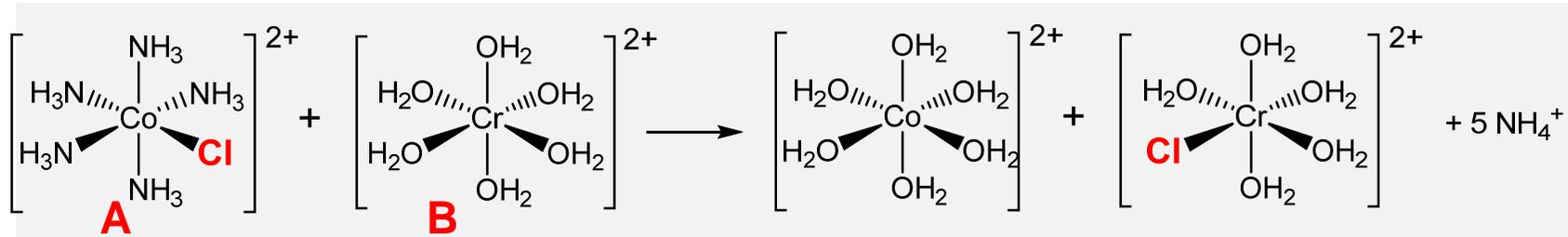
➔  $\text{Cl}^-$  can not bind to  $\text{Cr}^{\text{III}}$  **after** the redox process

**only explanation:**  $\text{Cl}^-$  must bridge the two centres before and during e-transfer

➔ inner sphere electron transfer

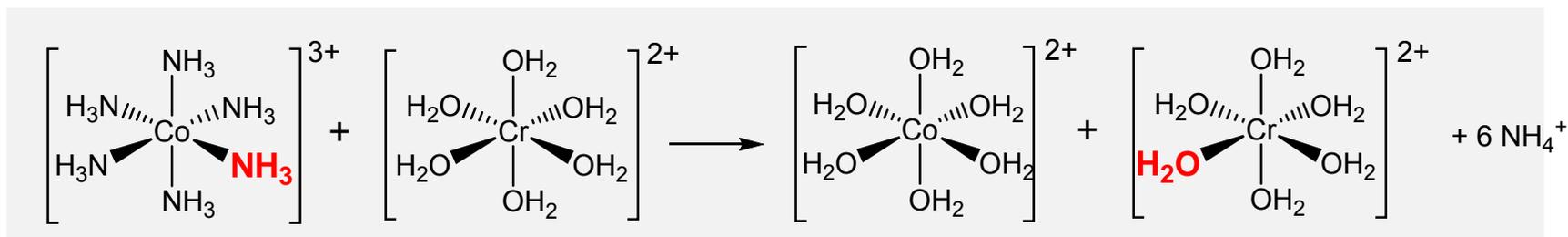
# Electron Transfer Reactions

## Inner sphere electron transfer reactions



rate constant of overall reaction:  $6 \cdot 10^5 \text{ mol}^{-1} \cdot \text{s}^{-1}$  ( $t_{1/2} \approx 1 \text{ ms}$ )

compare to



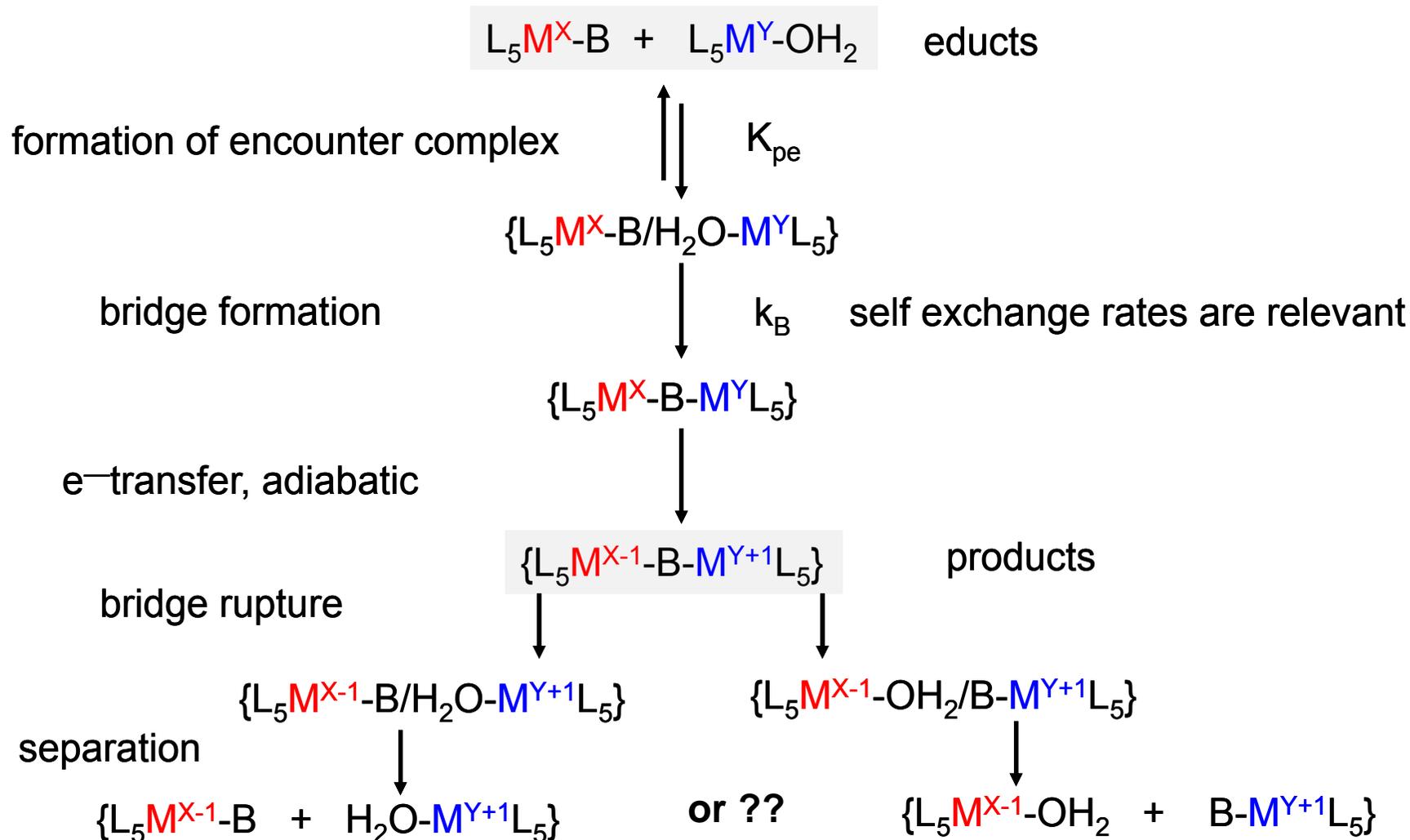
rate constant of overall reaction:  $10^{-3} \text{ mol}^{-1} \cdot \text{s}^{-1}$  ( $t_{1/2} \approx ?$ )

➔ does not mean that outer sphere reactions are à priori slower

# Electron Transfer Reactions

## Inner sphere electron transfer reactions

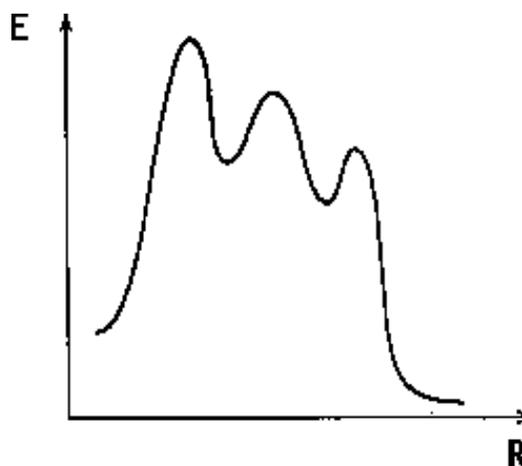
individual steps in is mechanisms



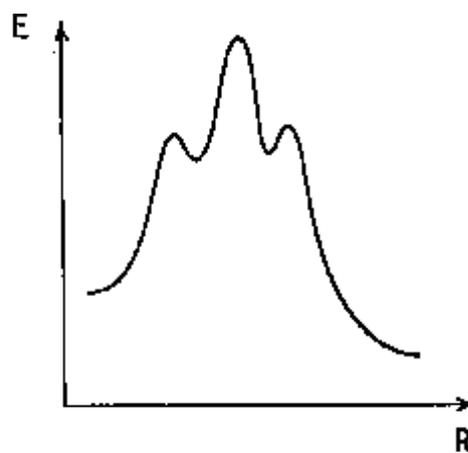
# Electron Transfer Reactions

## Inner sphere electron transfer reactions

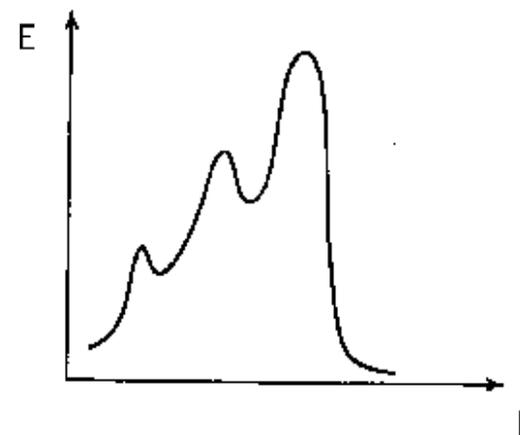
reaction profiles with different rate determining steps



encounter complex



bridge formation



rupture of bridge  
(after e<sup>-</sup>-transfer)

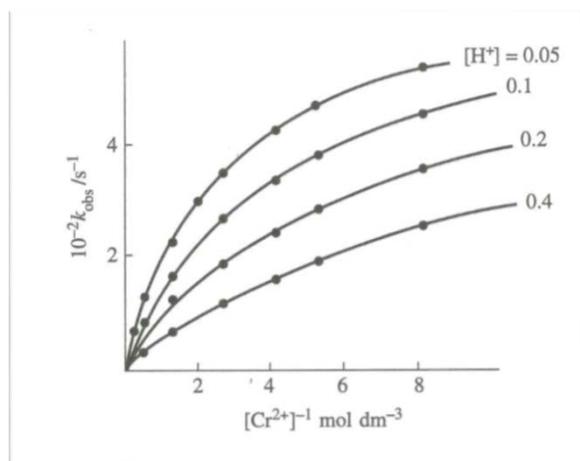
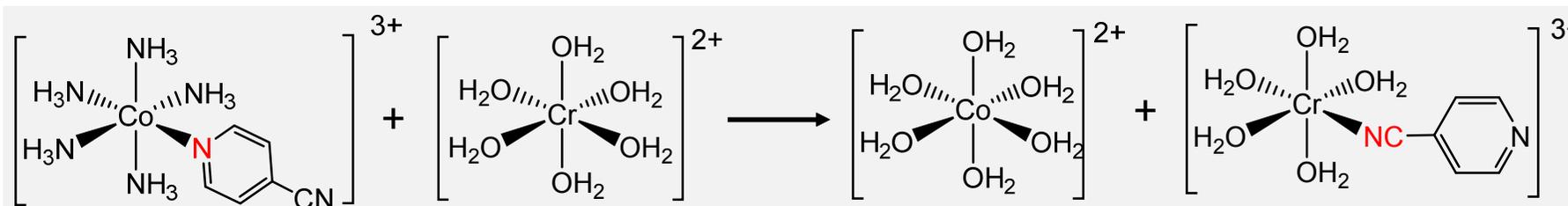
# Electron Transfer Reactions

## Inner sphere electron transfer reactions

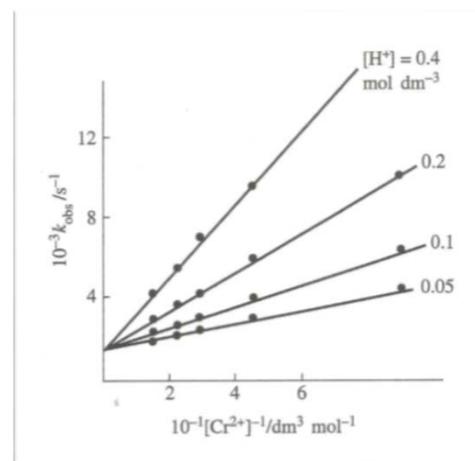
rate law for an inner sphere mechanism

$$v = \frac{k_b \cdot K_{pe} \cdot [M^X] \cdot [M^Y]}{1 + K_{pe} \cdot [M^Y]}$$

$k_{et}$  is included in  $k_b$  since adiabatic (extremely fast)



kinetics



# Electron Transfer Reactions

## Inner sphere electron transfer reactions

very strong bridging ligand dependence

oxidant	k (M <sup>-1</sup> s <sup>-1</sup> )	ΔS*
[Co(NH <sub>3</sub> ) <sub>5</sub> F] <sup>2+</sup>	2.5 · 10 <sup>5</sup>	
[Co(NH <sub>3</sub> ) <sub>5</sub> Cl] <sup>2+</sup>	6.0 · 10 <sup>5</sup>	
[Co(NH <sub>3</sub> ) <sub>5</sub> Br] <sup>2+</sup>	1.4 · 10 <sup>6</sup>	
[Co(NH <sub>3</sub> ) <sub>5</sub> I] <sup>2+</sup>	3.0 · 10 <sup>6</sup>	
[Co(NH <sub>3</sub> ) <sub>5</sub> OH] <sup>2+</sup>	1.5 · 10 <sup>6</sup>	
[Co(NH <sub>3</sub> ) <sub>5</sub> (OH <sub>2</sub> )] <sup>3+</sup>	0.1	
[Co(NH <sub>3</sub> ) <sub>5</sub> (NCS)] <sup>2+</sup>	19 (remote)	-121
[Co(NH <sub>3</sub> ) <sub>5</sub> (SCN)] <sup>2+</sup>	1.9 · 10 <sup>5</sup>	
[Co(NH <sub>3</sub> ) <sub>5</sub> (O <sub>2</sub> CH)] <sup>2+</sup>	7.2	-113
[Co(NH <sub>3</sub> ) <sub>5</sub> (O <sub>2</sub> CCH <sub>3</sub> )] <sup>2+</sup>	0.35	-138
[Co(NH <sub>3</sub> ) <sub>5</sub> (O <sub>2</sub> CC(CH <sub>3</sub> ) <sub>3</sub> )] <sup>2+</sup>	0.007	-130
[Co(NH <sub>3</sub> ) <sub>5</sub> (O <sub>2</sub> CCH <sub>2</sub> NH <sub>3</sub> )] <sup>3+</sup>	0.064	
[Co(NH <sub>3</sub> ) <sub>5</sub> (O <sub>2</sub> CNH <sub>2</sub> )] <sup>2+</sup>	2.42	-78
[Co(NH <sub>3</sub> ) <sub>5</sub> (OC(S)NHCH <sub>3</sub> )] <sup>2+</sup>	68	
[Co(NH <sub>3</sub> ) <sub>5</sub> (SC(O)NHCH <sub>3</sub> )] <sup>2+</sup>	6.5 · 10 <sup>4</sup>	

(red = [Cr(OH<sub>2</sub>)<sub>6</sub>]<sup>2+</sup>)

# Electron Transfer Reactions

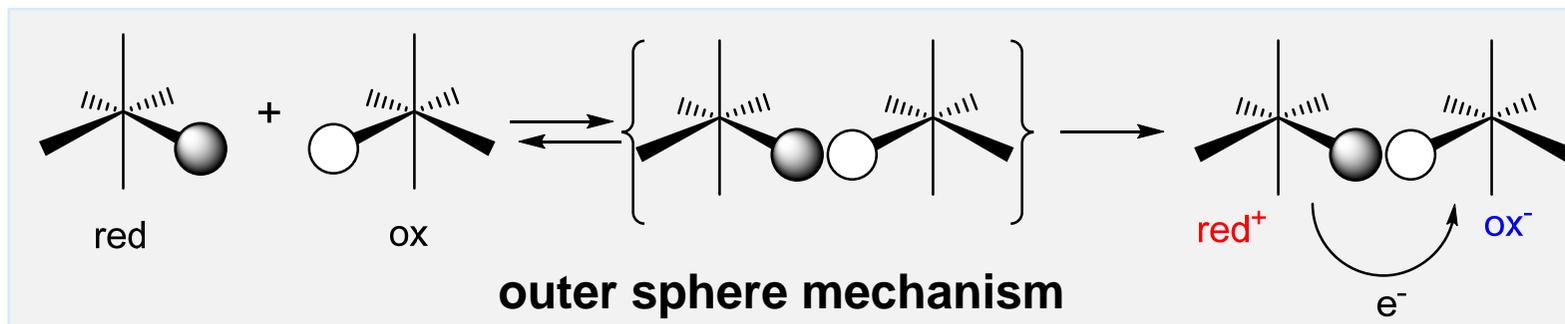
## Inner sphere electron transfer reactions

**criteria** for inner sphere reactions:

- reasonable **bridging ligands** (typically with a lone pair)
- conductive ligands
- if the e<sup>-</sup>-transfer is equal or slower than **rates of substitution**
- (if rates of e<sup>-</sup>-transfer are faster than e.g. ligand self exchange then it must be os)  
if reactions are faster than predicted by Marcus-Hush correlation (see later)
- HSAB aspects

# Electron Transfer Reactions

## Outer sphere electron transfer reactions



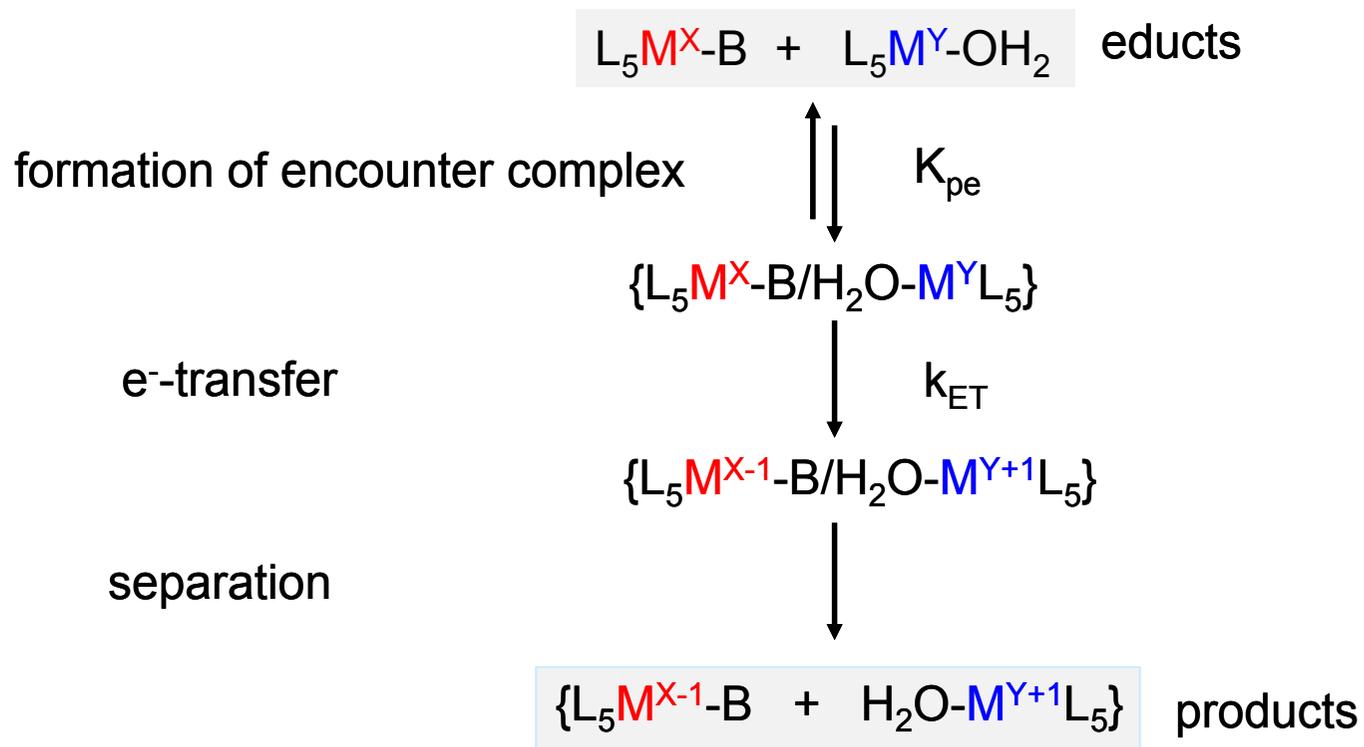
**classical** experiment:  $\Delta$ -[Os(bpy)<sub>3</sub>]<sup>3+</sup> does not racemize at all

addition of  $\Lambda$ - [Os(bpy)<sub>3</sub>]<sup>2+</sup> leads to **very rapid racemization**

how does this work?

# Electron Transfer Reactions

## Outer sphere electron transfer reactions



rate laws follow a typical **Langford-Gray mechanism**

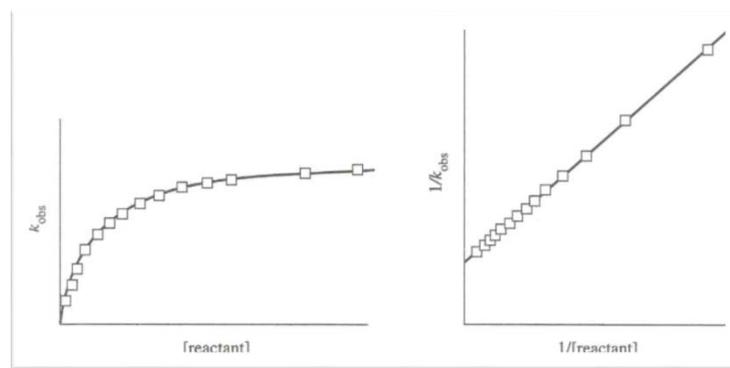
$$v = \frac{k_{ET} \cdot K_{pe} \cdot [M^X] \cdot [M^Y]}{1 + K_{pe} \cdot [M^Y]} \quad k_{obs} = \frac{k_{ET} \cdot K_{pe} \cdot [M^Y]}{1 + K_{pe} \cdot [M^Y]}$$

➔ much simpler than inner sphere !!

# Electron Transfer Reactions

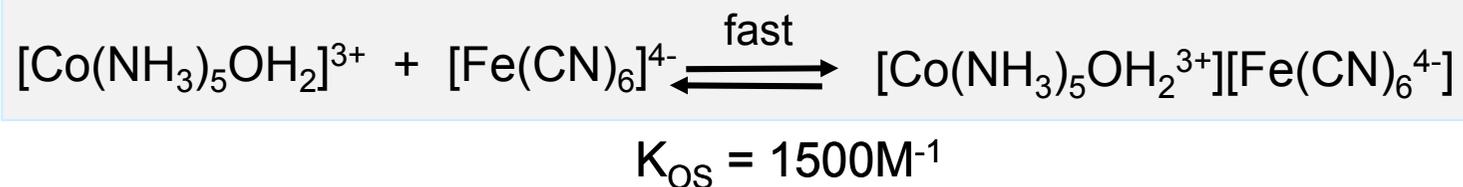
## Outer sphere electron transfer reactions

this relationship leads to typical saturation kinetic behaviour

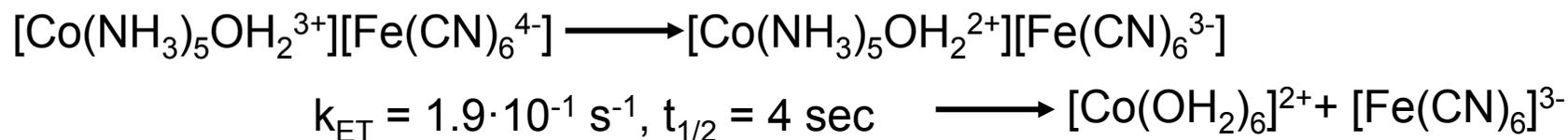


**encounter complex formation**

**example:**



**activation – electron transfer - separation**



# Electron Transfer Reactions

## Outer sphere electron transfer reactions

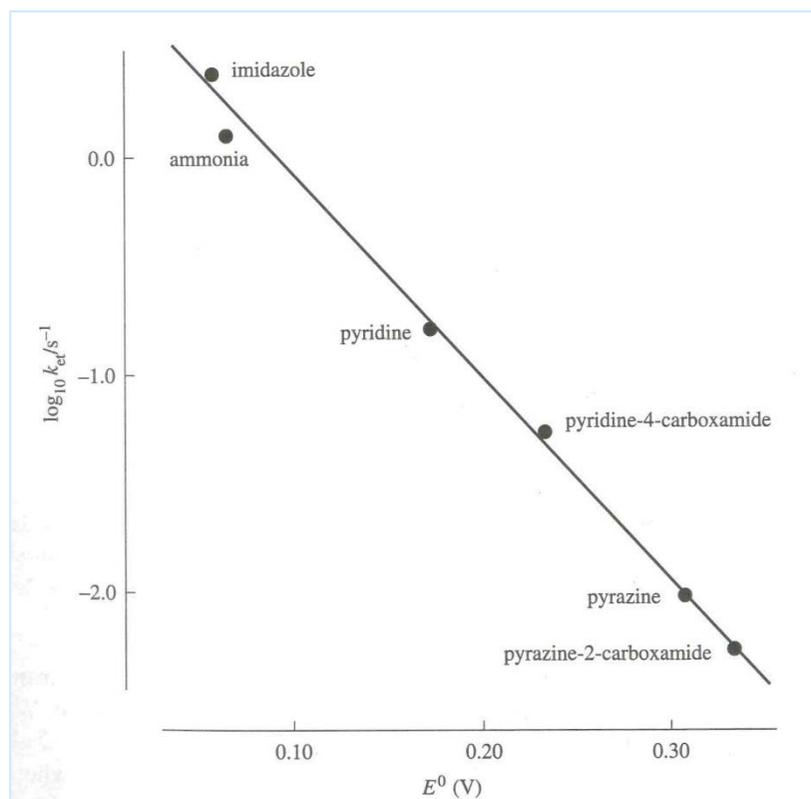
The charges of the encounter complex is essential for the overall rate

	Ox	Red	$K_{OS}$	$K_{et} (s^{-1})$
12-	$[Co(NH_3)_5(OH_2)]^{3+}$	$[Fe(CN)_6]^{4-}$	1500	0.19
	$[Co(NH_3)_5(py)]^{3+}$		2400	0.015
	$[Co(NH_3)_5(bpy)]^{3+}$		2300	0.024
9-	$[Co(NH_3)_5(dmsO)]^{3+}$	$[Fe(CN)_5L]^{3-}$		
		L=Imidazol	450	2.6
		L=NH3	420	1.3
		L=Pyridine	490	0.15
		L=Isonicotinamid	600	0.05
8-		L=pyrazine	360	0.0089
	$[Co(NH_3)_5(ac)]^{2+}$	$[Fe(CN)_6]^{4-}$	300	0.00037
	$[Co(NH_3)_5(benzoat)]^{2+}$		240	0.00062
	$[Co(NH_3)_5(Cl)]^{2+}$		38	0.027
	$[Co(NH_3)_5(N_3)]^{2+}$		49	0.00062

# Electron Transfer Reactions

## Outer sphere electron transfer reactions

is  $k_{\text{et}}$  dependent of the driving force, i.e.  $\Delta E^\circ$  ?



# Electron Transfer Reactions

## Outer sphere electron transfer reactions

some more activation parameters for outer sphere reactions

		ket (s-1)	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta V^\ddagger$
$[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$	$[\text{Fe}(\text{CN})_6]^{4-}$	$1.2 \cdot 10^{-1}$	102	79	26.5
$[\text{Co}(\text{NH}_3)_5\text{py}]^{3+}$		$9.3 \cdot 10^{-2}$	118	113	29.8
$[\text{Co}(\text{NH}_3)_5(\text{OSMe}_2)]^{3+}$		$2.0 \cdot 10^{-1}$	84	25	34.4
$[\text{Co}(\text{NH}_3)_5\text{N}_3]^{2+}$		$6.2 \cdot 10^{-4}$	104	44	18.8
$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$		$2.7 \cdot 10^{-2}$	85	11	25.9
$[\text{Co}(\text{phen})_3]^{2+}$		$2.4 \cdot 10^{-1}$	32	-148	

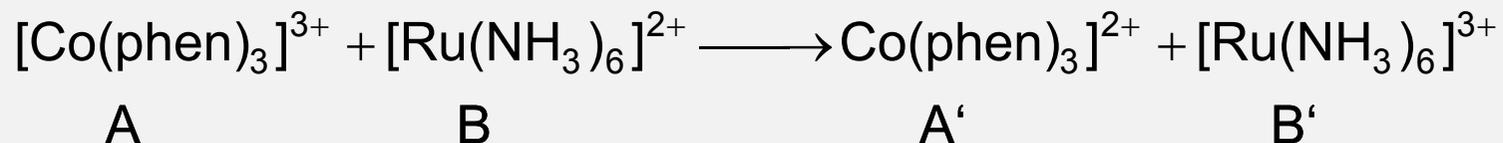
# Electron Transfer Reactions

some more activation parameters for outer sphere reactions

Oxidant	Reductant	k (M <sup>-1</sup> s <sup>-1</sup> )	$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )	$\Delta S^\ddagger$ (J K <sup>-1</sup> mol <sup>-1</sup> )
[Co(bpy) <sub>3</sub> ] <sup>3+</sup>	[Cr(phen) <sub>3</sub> ] <sup>2+</sup>	2.0 · 10 <sup>8</sup>		
[Ru(bpy) <sub>3</sub> ] <sup>3+</sup>	[Ru(NH <sub>3</sub> ) <sub>6</sub> ] <sup>2+</sup>	3.7 · 10 <sup>9</sup>		
[Co(phen) <sub>3</sub> ] <sup>3+</sup>	[Co(terpy) <sub>2</sub> ] <sup>2+</sup>	4.2 · 10 <sup>2</sup>	27.6	-100
[Co(phen) <sub>3</sub> ] <sup>3+</sup>	[Ru(NH <sub>3</sub> ) <sub>6</sub> ] <sup>2+</sup>	1.5 · 10 <sup>4</sup>	18	-105
[Co(bpy) <sub>3</sub> ] <sup>3+</sup>	[Co(terpy) <sub>2</sub> ] <sup>2+</sup>	3.0 · 10 <sup>1</sup>	21	-155
[Co(phen) <sub>3</sub> ] <sup>3+</sup>	[Ru(NH <sub>3</sub> ) <sub>5</sub> py] <sup>2+</sup>	1.9 · 10 <sup>3</sup>	21	-100
[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup>	[Ru(NH <sub>3</sub> ) <sub>6</sub> ] <sup>2+</sup>	1.1 · 10 <sup>-2</sup>	56	-1
[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	[Ru(NH <sub>3</sub> ) <sub>5</sub> py] <sup>2+</sup>	7.8 · 10 <sup>4</sup>	20	-84
[Ru(NH <sub>3</sub> ) <sub>5</sub> py] <sup>3+</sup>	[V(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	3.0 · 10 <sup>5</sup>	0	-138
[Co(phen) <sub>3</sub> ] <sup>3+</sup>	[V(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	4.0 · 10 <sup>3</sup>	16	-121
[Co(terpy) <sub>2</sub> ] <sup>3+</sup>	[V(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	3.8 · 10 <sup>3</sup>	7.9	-150
[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup>	[Cr(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	1.0 · 10 <sup>-3</sup>		
[Ni(bpy) <sub>3</sub> ] <sup>3+</sup>	[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	6.7 · 10 <sup>6</sup>	7	-92
[Co(en) <sub>3</sub> ] <sup>3+</sup>	[V(pic) <sub>3</sub> ] <sup>-</sup>	3.1 · 10 <sup>3</sup>	52	-4
[Fe(bpy) <sub>3</sub> ] <sup>3+</sup>	[Co(edta)] <sup>2-</sup>	3.3 · 10 <sup>4</sup>	29	-63
[Co(edta)] <sup>-</sup>	[Fe(pdta)] <sup>2</sup>	1.3 · 10 <sup>1</sup>	30	-128
[IrCl <sub>3</sub> ] <sup>2-</sup>	[Ru(CN) <sub>6</sub> ] <sup>4-</sup>	6.6 · 10 <sup>4</sup>	19	-88
[Co(ox) <sub>3</sub> ] <sup>3-</sup>	[Ru(NH <sub>3</sub> ) <sub>6</sub> ] <sup>2+</sup>	1.8 · 10 <sup>-1</sup>	45	-108
[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	[Co(phen) <sub>3</sub> ] <sup>2+</sup>	6.0 · 10 <sup>6</sup>		

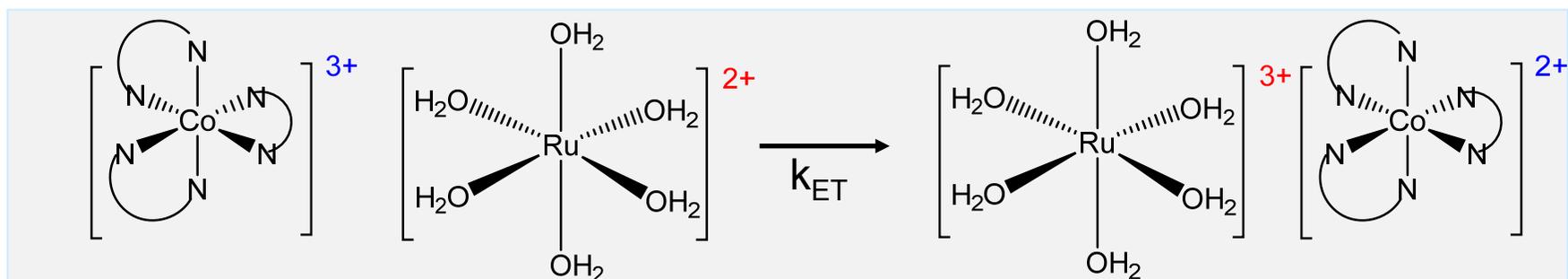
# Electron Transfer Reactions

The electron transfer step



**overall** electron transfer rate constant:  $1.5 \cdot 10^4 \text{ M}^{-1} \text{ s}^{-1}$

$K_{\text{OS}} = 0.25 \text{ M}^{-1}$  **small** due to repulsion



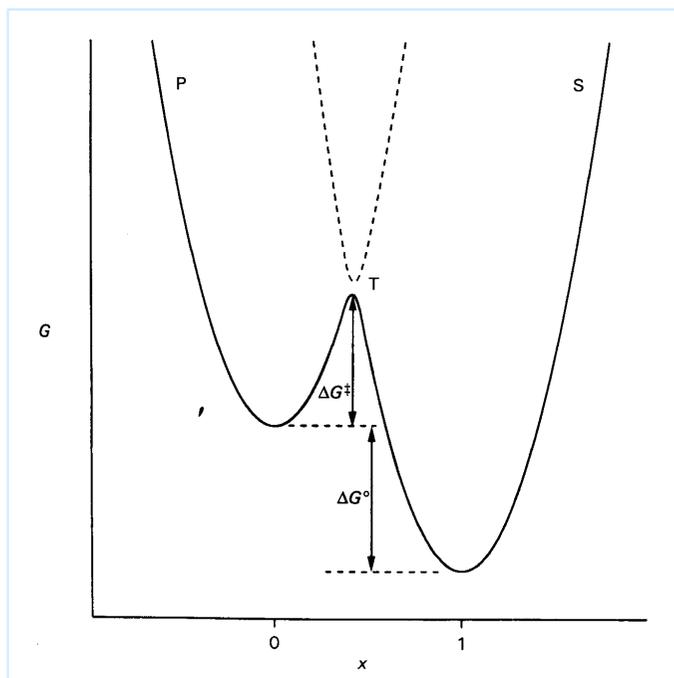
A: Co-N = 1.91 Å    B: Ru-N = 2.14 Å    B': Ru-N = 2.11 Å    A': Co-N = 2.11 Å

→ relaxation leads to energy dissipation: Thermodynamics?

# Electron Transfer Reactions

The electron transfer step

electron transfer must obey the **Franck-Condon** principles



electron transfer occurs after structural changes which can be illustrated with a potential diagram

**reaction profile**

describes precursor p ( $x=0$ ) and product ( $x=1$ ),  
e<sup>-</sup>-transfer probability=1 where they intersect

$$G_p = \lambda_p \cdot x^2 \quad G_s = \lambda_s (1-x)^2 + \Delta G^\circ$$

$$\Delta G^\ddagger = \frac{1}{4} \lambda (1 + \Delta G^\circ / \lambda)^2$$

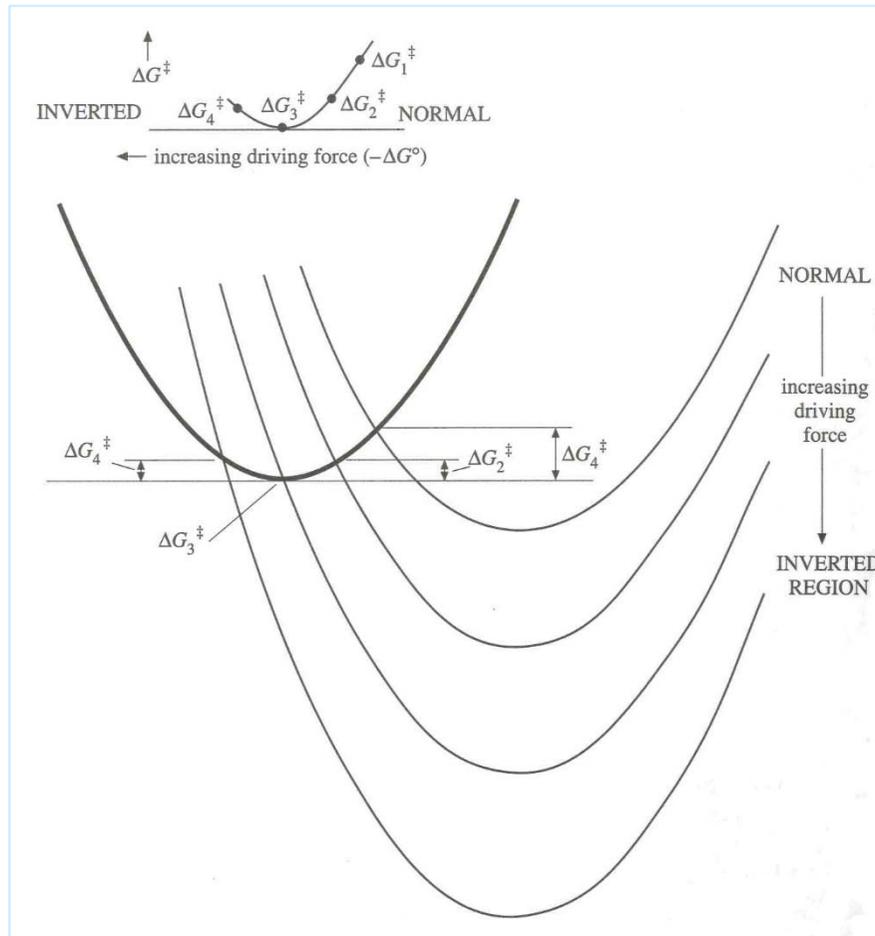
$\Delta G$  dependent on  $\Delta G^\circ$  and  $\lambda_p/\lambda_s$  !!

# Electron Transfer Reactions

The electron transfer step

electron transfer must obey the **Franck-Condon** principles

different possibilities



# Electron Transfer Reactions

The electron transfer step

The Marcus equation for outer sphere e<sup>-</sup>-transfer reactions



e<sup>-</sup>-self exchange rates



The different states can be expressed as follows:

Kinetics:

$$G_{AA}^\ddagger = G^\ddagger(A) + G^\ddagger(A^-) - G^\circ(A) - G^\circ(A^-)$$
$$G_{BB}^\ddagger = G^\ddagger(B) + G^\ddagger(B^-) - G^\circ(B) - G^\circ(B^-)$$
$$G_{AB}^\ddagger = G^\ddagger(A^-) + G^\ddagger(B) - G^\circ(B) - G^\circ(A^-)$$

Thermodynamics:

$$G_{AB}^\circ = G^\circ(B^-) + G^\circ(A) - G^\circ(B) - G^\circ(A^-)$$

# Electron Transfer Reactions

The electron transfer step

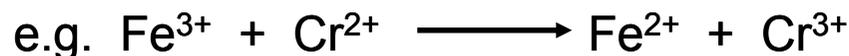
with some algebra (up to you) and the principle of microscopic reversibility

we arrive at:  $\Delta G^\ddagger_{AB} = \Delta G^\ddagger(AA) + \Delta G^\ddagger(BB) + \Delta G^\circ(AB)$

if this is translated into rate constants with  $k_{ij} = Z_{ij} \cdot \exp \frac{-\Delta G^\ddagger_{ij}}{RT}$   $i, j = A, B$

Marcus correlation  $k_{AB} = (k_{AA} \cdot k_{BB} \cdot K_{AB} \cdot F)^{1/2}$   $F = \frac{Z_{AB}^2}{Z_{AA} \cdot Z_{BB}}$

if the charges remain the same left and right,  $F \approx 1$



# Electron Transfer Reactions

## The electron transfer step

	$\Delta d^\circ$	$k_{AA}(\text{M}^{-1}\text{s}^{-1})$		$\Delta d^\circ$	$k_{AA}(\text{M}^{-1}\text{s}^{-1})$
$[\text{Fe}(\text{OH}_2)_6]^{3+/2+}$	0.13	1.1	$[\text{Co}(\text{phen})_3]^{3+/2+}$	0.19	12
$[\text{Co}(\text{OH}_2)_6]^{3+/2+}$	0.21	5	$[\text{Fe}(\text{phen})_3]^{3+/2+}$	0	$1.3 \cdot 10^7$
$[\text{Cr}(\text{OH}_2)_6]^{3+/2+}$	0.20	$1.9 \cdot 10^{-5}$	$[\text{Co}(\text{bipy})_3]^{3+/2+}$	0.19	5.7
$[\text{V}(\text{OH}_2)_6]^{3+/2+}$	0.13	$1 \cdot 10^{-2}$	$[\text{Ru}(\text{bipy})_3]^{3+/2+}$	0	$4 \cdot 10^8$
$[\text{Co}(\text{en})_3]^{3+/2+}$	0.21	$7.7 \cdot 10^{-5}$	$[\text{Fe}(\text{bipy})_3]^{3+/2+}$	0	$3 \cdot 10^8$
$[\text{Co}(\text{NH}_3)_6]^{3+/2+}$	0.22	$2 \cdot 10^{-8}$	$[\text{Cr}(\text{bipy})_3]^{3+/2+}$	0.1	$10^9$
$[\text{Ru}(\text{en})_3]^{3+/2+}$	0.05	$3.1 \cdot 10^4$	$[\text{Fe}(\text{CN})_6]^{3-/4-}$	0.03	$2 \cdot 10^4$

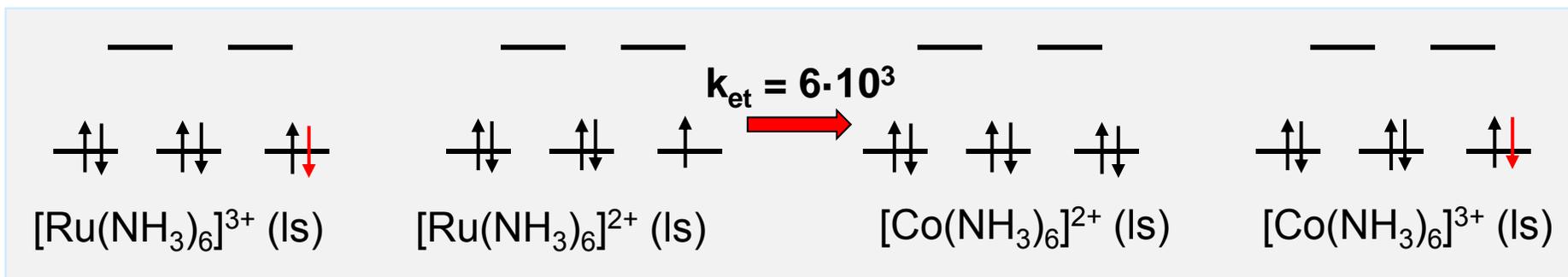
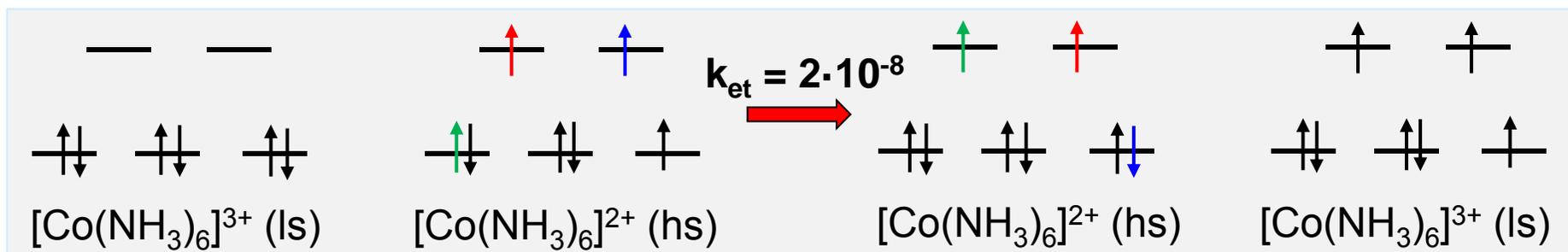
	$k_{\text{exp}}(\text{M}^{-1}\text{s}^{-1})$	$k_{\text{calc}}(\text{M}^{-1}\text{s}^{-1})$
$[\text{Co}(\text{OH}_2)_6]^{3+} + [\text{Fe}(\text{OH}_2)_6]^{2+}$	50	4
$[\text{Co}(\text{OH}_2)_6]^{3+} + [\text{V}(\text{OH}_2)_6]^{2+}$	$9 \cdot 10^5$	$2 \cdot 10^6$
$[\text{Co}(\text{OH}_2)_6]^{3+} + [\text{Cr}(\text{OH}_2)_6]^{2+}$	$1.3 \cdot 10^4$	$7 \cdot 10^3$
$[\text{V}(\text{OH}_2)_6]^{3+} + [\text{Cr}(\text{OH}_2)_6]^{2+}$	0.2	$2 \cdot 10^{-5}$
$[\text{Fe}(\text{OH}_2)_6]^{3+} + [\text{Cr}(\text{OH}_2)_6]^{2+}$	$5.7 \cdot 10^2$	68
$[\text{Fe}(\text{OH}_2)_6]^{3+} + [\text{V}(\text{OH}_2)_6]^{2+}$	$1.8 \cdot 10^4$	$3 \cdot 10^4$
$[\text{Fe}(\text{OH}_2)_6]^{3+} + [\text{Ru}(\text{OH}_2)_6]^{2+}$	$2.3 \cdot 10^3$	$1 \cdot 10^3$

# Electron Transfer Reactions

The electron transfer step

influence of d-electron configuration

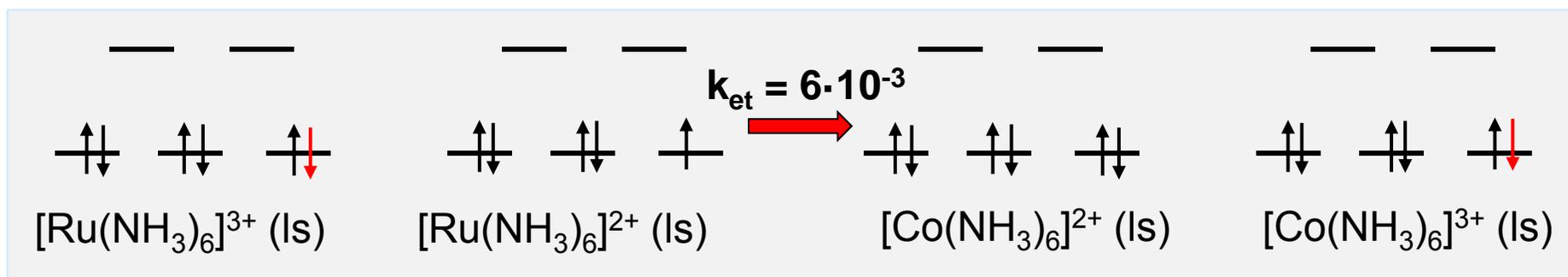
p.m. large structural and electronic changes **decelerates** (e<sup>-</sup>transfer) reactions



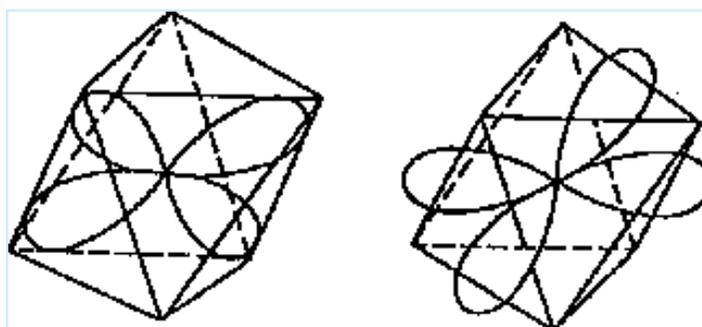
# Electron Transfer Reactions

The electron transfer step

influence of d-electron configuration



$t_{2g} \rightarrow t_{2g}$  much faster than  $e_g \rightarrow e_g$



$t_{2g}$  orbitals are not pointing towards the ligands but in between

# Electron Transfer Reactions

The electron transfer step

influence of d-electron configuration

	$k_{\text{exp}}(\text{M}^{-1}\text{s}^{-1})$	$k_{\text{calc}}(\text{M}^{-1}\text{s}^{-1})$
$[\text{Fe}(\text{H}_2\text{O})_6]^{2+} + [\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	4	$(t_{2g})^4(e_g)^2 \rightarrow (t_{2g})^3(e_g)^2$
$[\text{Fe}(\text{phen})_3]^{2+} + [\text{Fe}(\text{phen})_3]^{3+}$	$3 \cdot 10^7$	$(t_{2g})^6 \rightarrow (t_{2g})^5$
$[\text{Ru}(\text{NH}_3)_6]^{2+} + [\text{Ru}(\text{NH}_3)_6]^{3+}$	$8.2 \cdot 10^2$	$(t_{2g})^6 \rightarrow (t_{2g})^5$
$[\text{Ru}(\text{phen})_3]^{2+} + [\text{Ru}(\text{phen})_3]^{3+}$	$> 10^7$	$(t_{2g})^6 \rightarrow (t_{2g})^5$
$[\text{Co}(\text{H}_2\text{O})_6]^{2+} + [\text{Co}(\text{H}_2\text{O})_6]^{3+}$	5	$(t_{2g})^5(e_g) \rightarrow (t_{2g})^6$
$[\text{Co}(\text{NH}_3)_6]^{2+} + [\text{Co}(\text{NH}_3)_6]^{3+}$	$2 \cdot 10^{-8}$	$(t_{2g})^5(e_g)^2 \rightarrow (t_{2g})^6$
$[\text{Co}(\text{en})_3]^{2+} + [\text{Co}(\text{en})_3]^{3+}$	$1.4 \cdot 10^{-4}$	$(t_{2g})^5(e_g)^2 \rightarrow (t_{2g})^6$
$[\text{Co}(\text{phen})_3]^{2+} + [\text{Co}(\text{phen})_3]^{3+}$	1.1	$(t_{2g})^5(e_g)^2 \rightarrow (t_{2g})^6$

	Reduktionsmittel	Oxidationsmittel	Brücke = X	$k_2$ (25 °C) [ $M^{-1}s^{-1}$ ]
mittel	$Cr^{2+}$	$Co(NH_3)_5X^{n+}$	$CH_3COO$	$1.8 \cdot 10^{-1}$
	$Cr^{2+}$	$Co(NH_3)_5X^{n+}$	-NCS	$1.9 \cdot 10^1$
	$Cr^{2+}$	$Co(NH_3)_5X^{n+}$	-CN	$3.6 \cdot 10^1$
	$Cr^{2+}$	$Co(NH_3)_5X^{n+}$	-F	$2.5 \cdot 10^5$
	$Cr^{2+}$	$Co(NH_3)_5X^{n+}$	-N <sub>3</sub>	$3.0 \cdot 10^5$
	$Cr^{2+}$	$Co(NH_3)_5X^{n+}$	-Cl	$6.0 \cdot 10^5$
	$Cr^{2+}$	$Co(NH_3)_5X^{n+}$	-Br	$1.4 \cdot 10^6$
	$Cr^{2+}$	$Co(NH_3)_5X^{n+}$	-I	$3.4 \cdot 10^6$
	$Cr^{2+}$	$Co(NH_3)_5X^{n+}$	-PO <sub>4</sub>	$4.8 \cdot 10^9$
	$Cr^{2+}$	$Cr(NH_3)_5X^{2+}$	-F	$2.7 \cdot 10^{-4}$
	$Cr^{2+}$	$Cr(NH_3)_5X^{2+}$	-Cl	$5.1 \cdot 10^{-2}$
	$Cr^{2+}$	$Cr(NH_3)_5X^{2+}$	-Br	$3.2 \cdot 10^{-1}$
weich	$Co(CN)_5^{3-}$	$Co(NH_3)_5X^{n+}$	-PO <sub>4</sub>	$5.2 \cdot 10^2$
	$Co(CN)_5^{3-}$	$Co(NH_3)_5X^{n+}$	-NCS	$1.1 \cdot 10^6$
	$Co(CN)_5^{3-}$	$Co(NH_3)_5X^{n+}$	-N <sub>3</sub>	$1.6 \cdot 10^6$
	$Co(CN)_5^{3-}$	$Co(NH_3)_5X^{n+}$	-Cl	$5.0 \cdot 10^7$
	$Co(CN)_5^{3-}$	$Co(NH_3)_5X^{n+}$	-Br	$2.0 \cdot 10^9$
	$Co(CN)_5^{3-}$	$Co(NH_3)_5X^{n+}$	-I	zu schnell
hart	$Fe^{2+}$	$Co(NH_3)_5X^{n+}$	-Br	$7.3 \cdot 10^{-4}$
	$Fe^{2+}$	$Co(NH_3)_5X^{n+}$	-Cl	$1.4 \cdot 10^{-3}$
	$Fe^{2+}$	$Co(NH_3)_5X^{n+}$	-NCS	$3.0 \cdot 10^{-3}$
	$Fe^{2+}$	$Co(NH_3)_5X^{n+}$	-F	$6.6 \cdot 10^{-3}$
	$Fe^{2+}$	$Co(NH_3)_5X^{n+}$	-N <sub>3</sub>	$8.7 \cdot 10^{-3}$
	$Fe^{2+}$	$Co(NH_3)_5X^{n+}$	-SCN	$1.2 \cdot 10^{-1}$