Reactions: Classical and Organometallic Mechanisms

Reactions at M-bound Ligands:

    Electrophilic attack

    Nucleophilic attack

Ligand Exchange Reactions

    Associative

    Dissociative

    Trans effect (Pt(2+), square planar complexes)

    Cis effect (metal carbonyls)

Migration or Migratory Insertion

Deinsertion (esp β-Hydride elimination)

Oxidative Addition
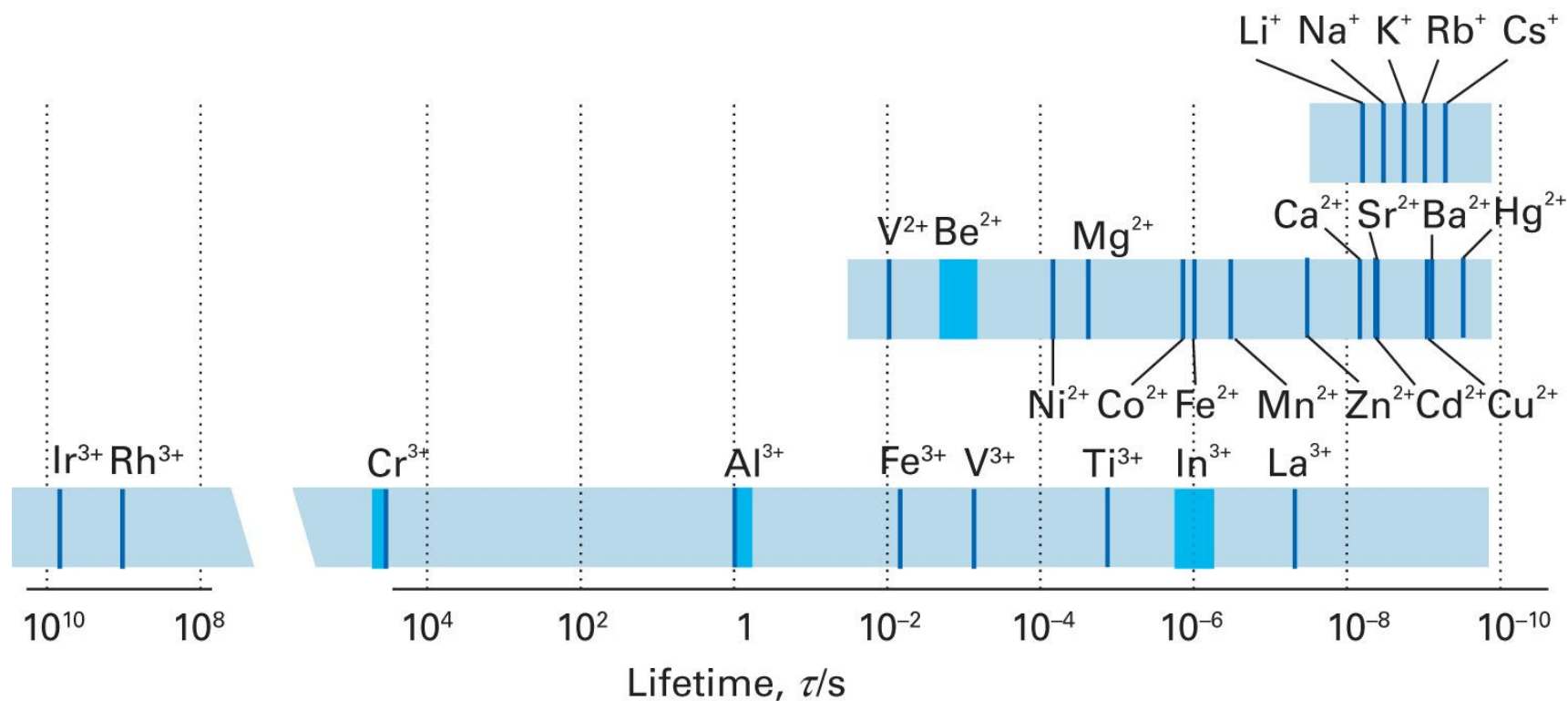
Reductive Elimination

Water Exchange Rates

Lifetime, τ/s

Table 21.1 Representative timescales of chemical and physical processes

Timescale*	Process	Example
10^8 s	Ligand exchange (inert complex)	$[Cr(OH_2)_6]^{3+} - H_2O$ (c. 6 days)
60 s	Ligand exchange (nonlabile complex)	$[V(OH_2)_6]^{3+} - H_2O$ (50 s)
1 ms	Ligand exchange (labile complex)	$[Pt(OH_2)_4]^{2+} - H_2O$ (0.4 ms)
1 μs	Intervalence charge transfer	$(H_3N)_5Ru^{II}-N$⟨ ⟩$N- Ru^{III}(NH_3)$ (0.5 μs)
1 ns	Ligand exchange (labile complex)	$[Ni(OH_2)_5(py)]^{2+} - H_2O$ (1 ns)
10 ps	Ligand association	$Cr(CO)_5 + THF$ (10 ps)
1 ps	Rotation time in liquid	CH_3CN (1 ps)
1 fs	Molecular vibration	$Sn-Cl$ stretch (300 fs)

* Approximate time at room temperature.

Table 21.8 Activation parameters for the H_2O exchange reactions
$[M(OH_2)_6]^{2+} + H_2^{17}O \rightarrow [M(OH_2)_5(^{17}OH_2)]^{2+} + H_2O$

|	$\Delta^{\ddagger}H/(\text{kJ mol}^{-1})$	LFSE*/Δ_o	(LFSE)‡/$\Delta_o^{\dagger}$	LFAE/Δ_o	$\Delta^{\ddagger}V/(\text{cm}^3 \text{ mol}^{-1})$
$Ti^{2+}(d^2)$		0.8	0.91	−0.11	
$V^{2+}(d^3)$	68.6	1.2	1	0.2	−4.1
$Cr^{2+}(d^4, hs)$		0.6	0.91	−0.31	
$Mn^{2+}(d^5, hs)$	33.9	0	0	0	−5.4
$Fe^{2+}(d^6, hs)$	31.2	0.4	0.46	−0.06	+3.8
$Co^{2+}(d^7, hs)$	43.5	0.8	0.91	−0.11	+6.1
$Ni^{2+}(d^8)$	58.1	1.2	1	0.2	+7.2

* Octahedral. † Square pyramidal. hs, high spin.

**Table 21.6** Complex formation by the $[Ni(OH_2)_6]^{2+}$ ion

| Ligand	$k_{r,obs}/(dm^3\ mol^{-1}\ s^{-1})$	$K_E/(dm^3\ mol^{-1})$	$(k_{r,obs}/K_E)/s^{-1}$
$CH_3CO_2^-$	1×10^5	3	3×10^4
F^-	8×10^5	1	8×10^3
HF	3×10^3	0.15	2×10^4
H_2O^*			3×10^3
NH_3	5×10^3	0.15	3×10^4
$[NH_2(CH_2)_2NH_3]^+$	4×10^2	0.02	2×10^4
SCN^-	6×10^3	1	6×10^3

* The solvent is always in encounter with the ion so that K_E is undefined and all rates are inherently first order.

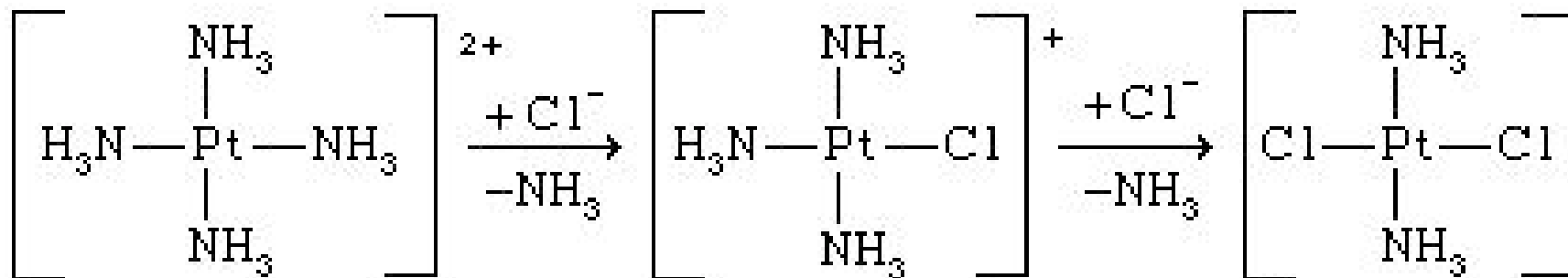**Typical form of reaction profile for dissociative mechanism**
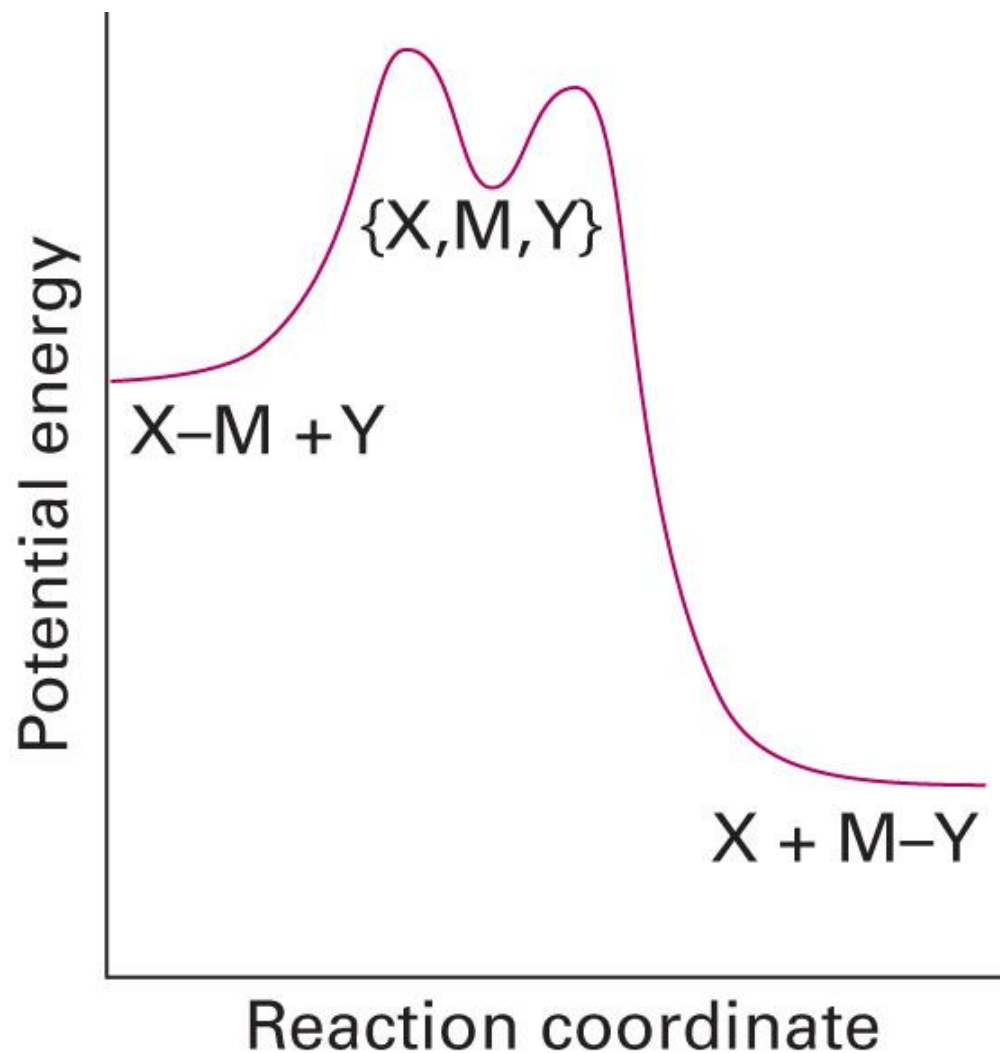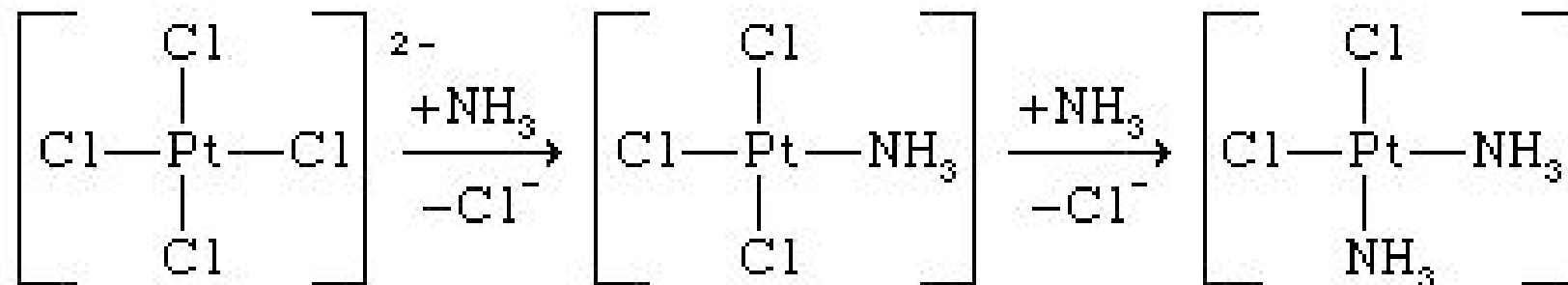
Typical form of reaction profile for associative mechanism

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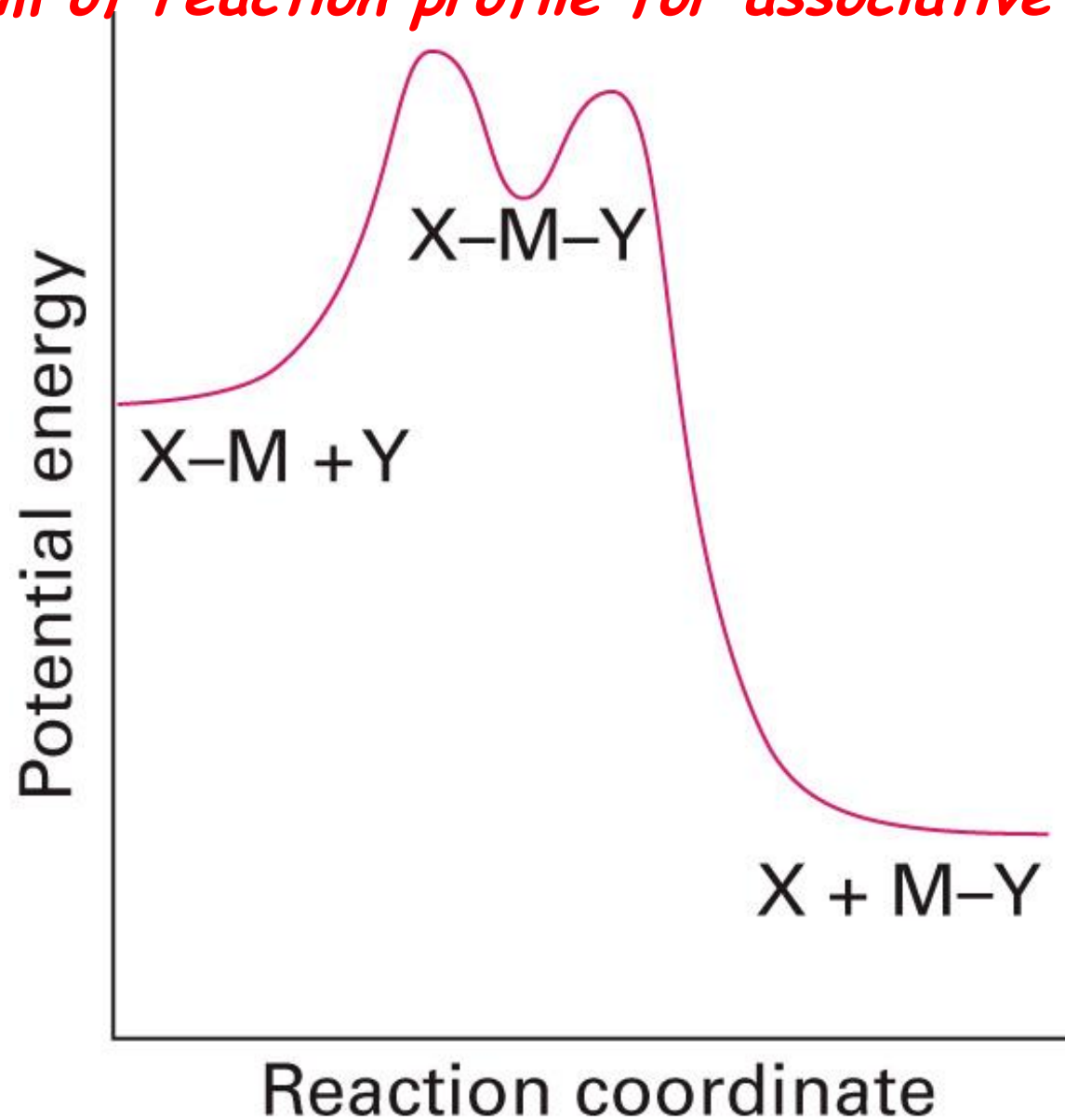
Typical form of reaction profile for interchange mechanism

(d)

(e) *cis*

(a) *trans*

(b)
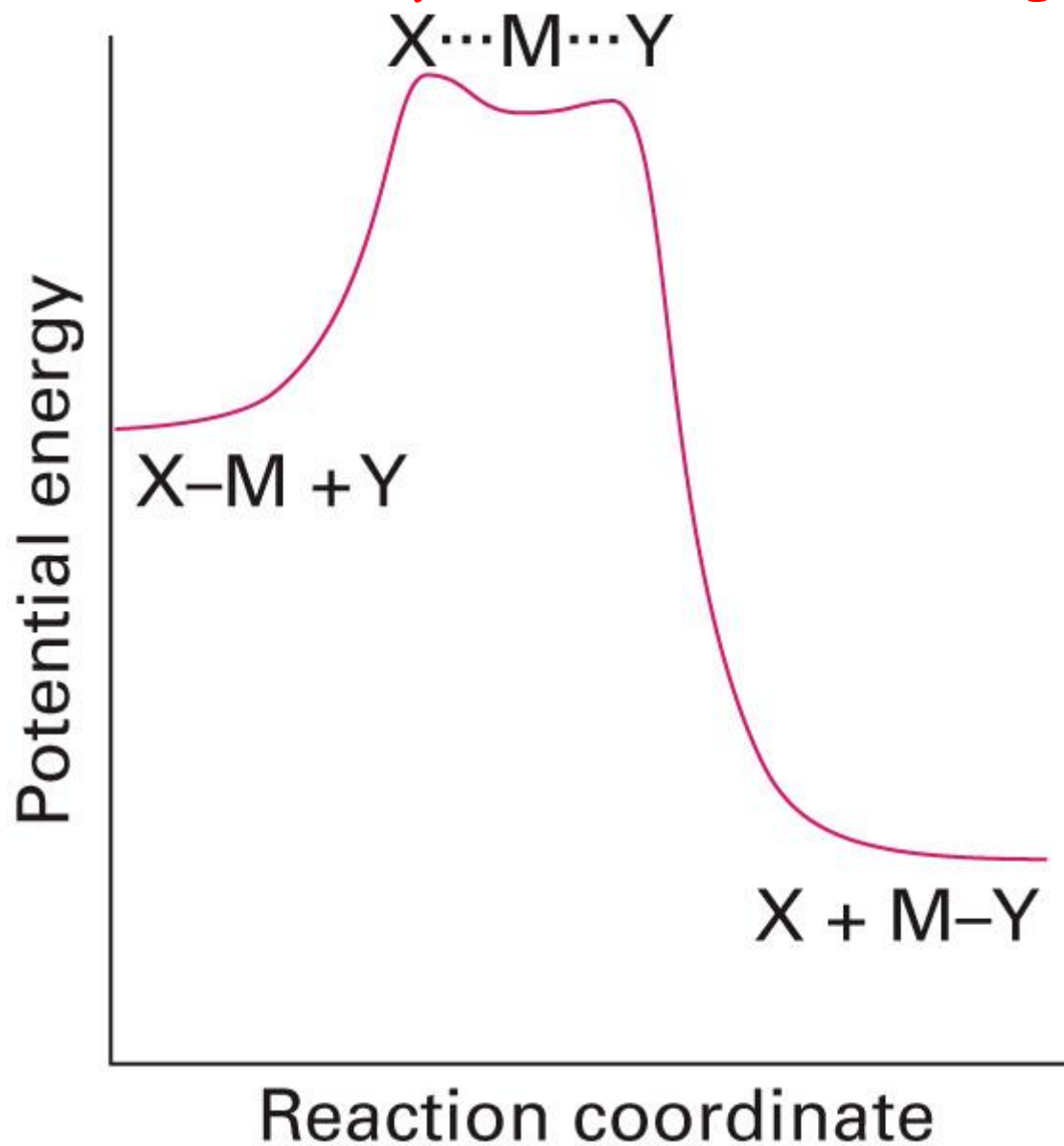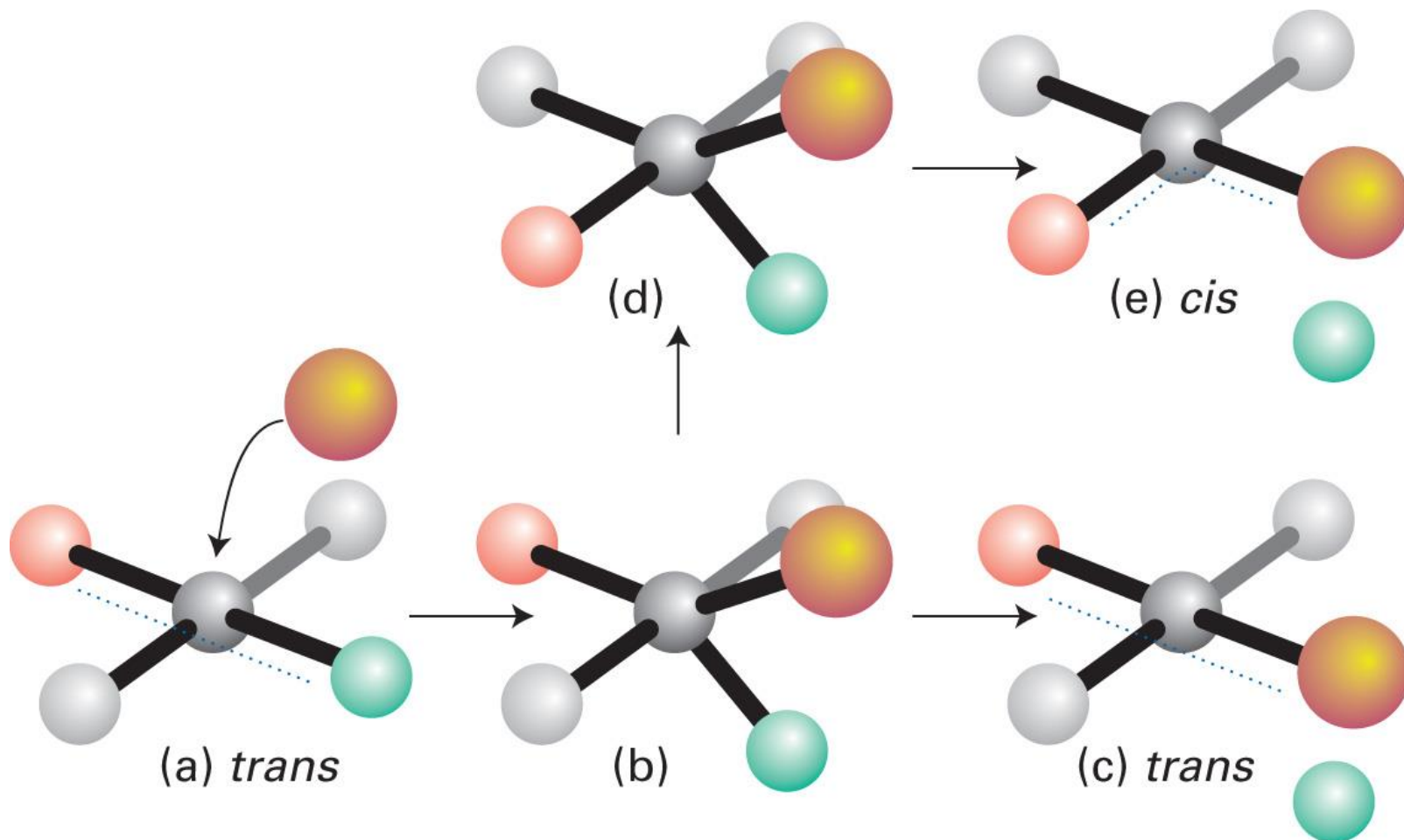
(c) *trans*

Use of trans-effect in synthesis:

Trans Effect vs. Trans Influence

- **Trans effect**: A strong σ-donor or π-acceptor ligand greatly accelerates substitution of a ligand that lies in the position trans to it.

- **Trans Influence**: Extent to which the ligand T weakens the bond trans to itself in the ground state of the complex. Correlates with σ-donating ability.

The *trans* effect

- ◆ The rates of substitution in square planar complexes depend strongly on the nature of the ligand *trans* to the leaving group

- ◆ Rates are enhanced by good σ donors and π acceptors

Table 14.4 The effect of the *trans* ligand in reactions of *trans*-[PtCl(PEt$_3$)$_2$L]

L	k_1/s^{-1}	$k_2/(L\ mol^{-1}\ s^{-1})$
CH_3^-	1.7×10^{-4}	6.7×10^{-2}
$C_6H_5^-$	3.3×10^{-5}	1.6×10^{-2}
Cl^-	1.0×10^{-6}	4.0×10^{-4}
H^-	1.8×10^{-2}	4.2
PEt_3	1.7×10^{-2}	3.8

- T σ donor: $OH^- < NH_3 < Cl^- < Br^- < CN^-, CO, CH_3^- < I^- < SCN^- < PR_3 < H^-$
- T π acceptor: $Br^- < I^- < NCS^- < CN^- < CO, C_2H_4$

Substitution in square planar complexes

- ◆ Stereochemistry is typically preserved during substitution suggesting that there is no long lived intermediate capable of rearranging
- ◆ The substitution reactions of square planar complexes are usually associative (a)
  - – rates are strongly influenced by the nucleophile
    - » suggests an associative mechanism
  - – rates are also strongly influenced by the group trans to the leaving group
    - » implies that the trans group somehow stabilizes the transition state or destabilizes/stabilizes the starting material
  - – leaving group also has some effect

Is there a cis effect?