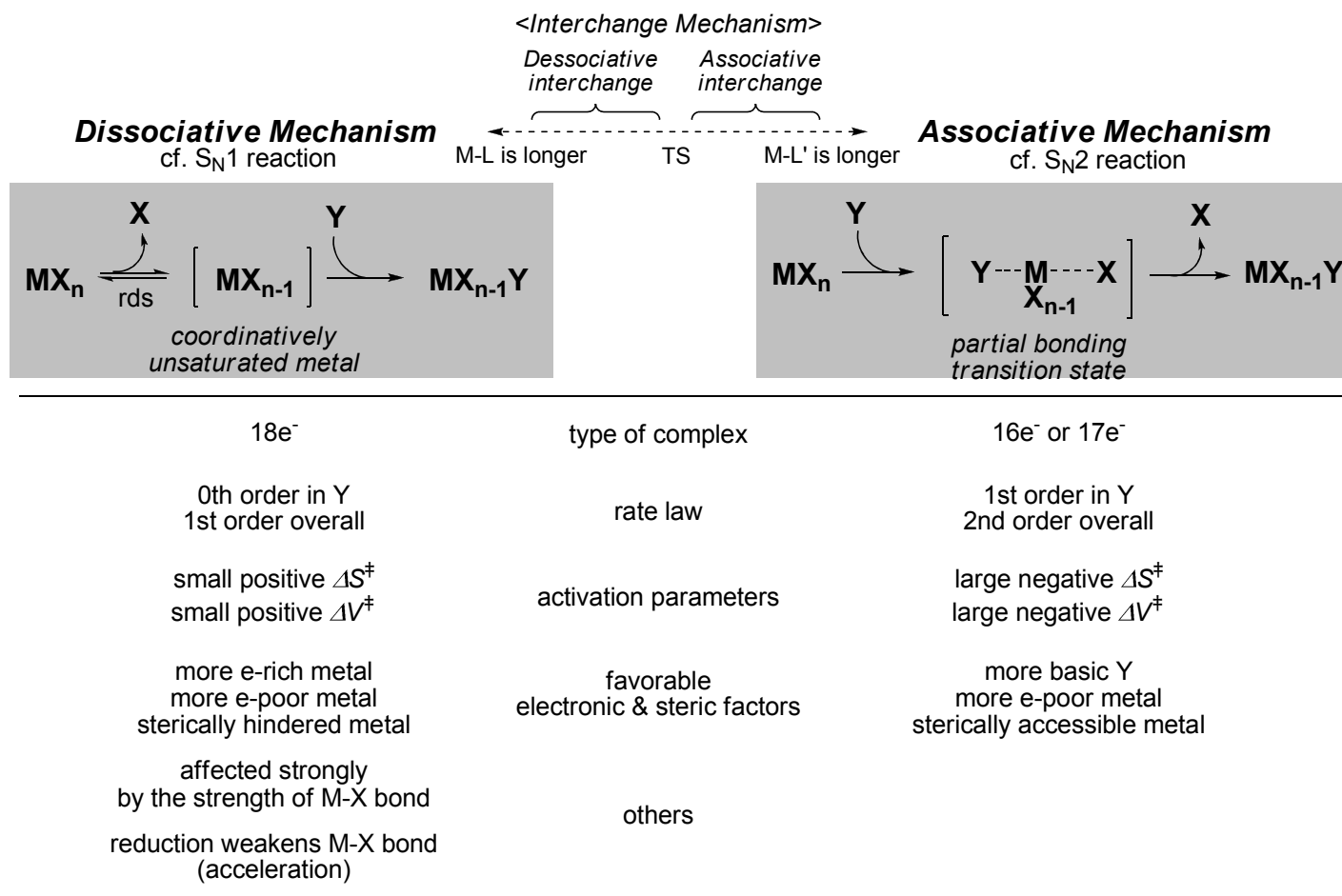
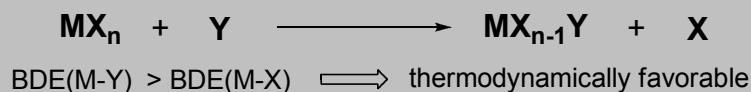


Chapter 5. Ligand Substitution Reactions

5.1 Introduction

Ligand Substitution = A reaction in which a free ligand replaces a coordinated ligand

**5.2. Thermochemical Considerations****BDE = bond dissociation energy**

energy needed for homolytic cleavage (two radical generation) for charged X-type ligand

energy needed for heterolytic cleavage (unsaturated metal + Lewis base) for neutral L-type ligand

cf) BDE (M-CO) = 25-46 kcal/mol = 50-150°C heating leads to cleave

BDE (CH₃-CH₃) = 88 kcal/mol

BDE (CH₃-H) = 104 kcal/mol

cf) BDE (polyhapto) > BDE (monohapto)

cf) BDE (M-L) tend to be first-row < second-row < third-row (but not always)

BDE(Cr(CO)₅-CO) < BDE (Mo(C)₅-CO) < BDE (W(CO)₅-CO)

37 40 46 kcal/mol

cf) BDE (M-πacidic) > BDE (M-πneutral) if M is low valent

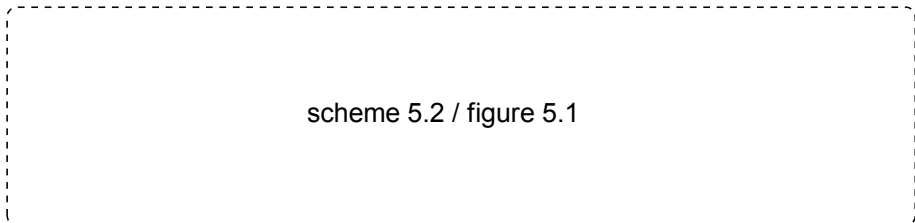
cf) BDE (less hindered) > BDE (more hindered)

5.3. Mechanisms of Ligand Substitutions of 16e- and 17e- complexes

> Associative mechanisms of square-planar d^8 complexes

"solvent assistance" = two associative substitution

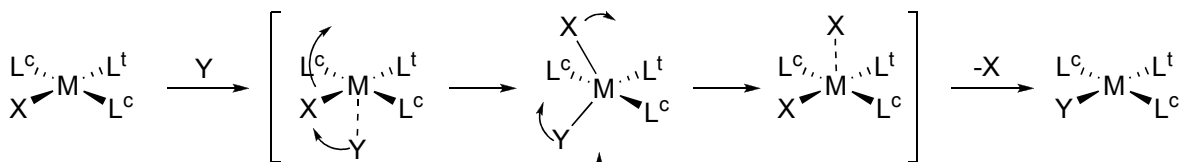
$$\text{rate} = k_{\text{obs}}[\text{L}_3\text{MX}] = (k_1 + k_2[\text{Y}])[\text{L}_3\text{MX}]$$



solvent assisted path non-solvent assisted path

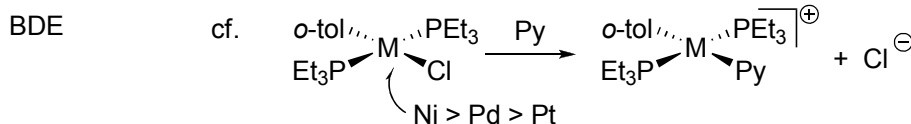
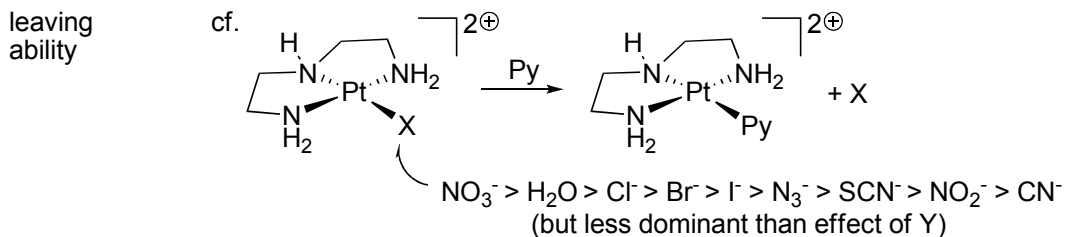
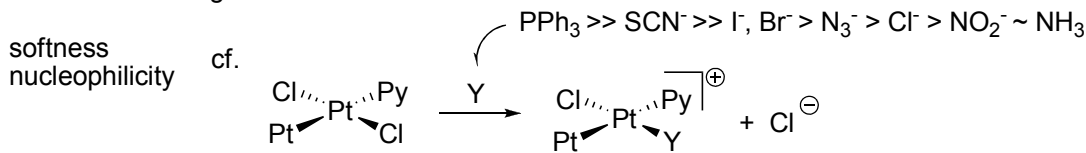
often occurs in parallel

stereochemistry = **retentive** (but not always) // cf. analogy of S_N2

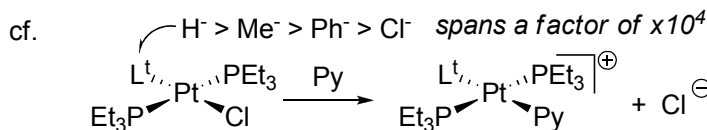


if pentacoordinate intermediate is long-lived, stereochemistry is lost via Berry pseudorotation.

other factors affecting to rate



trans effect = trans ligand affect the rate of ligand substitutions = transition state/dynamism/kinetic (cf. **trans influence** = related to bond length = ground state/structure/thermodynamic)



cis effect = similar effect by cis ligand, but usually smaller contribution

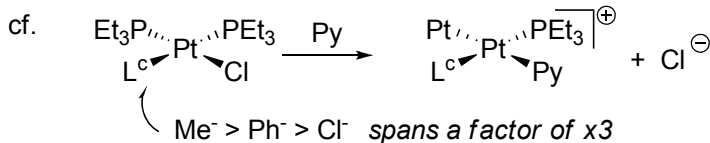
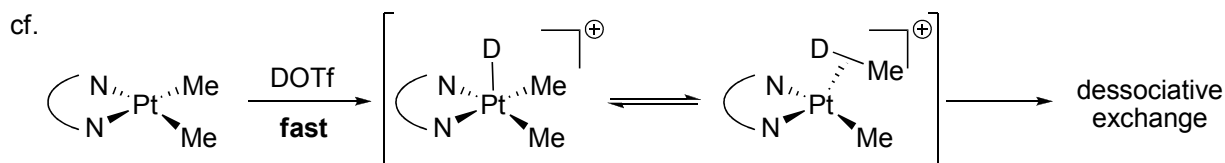
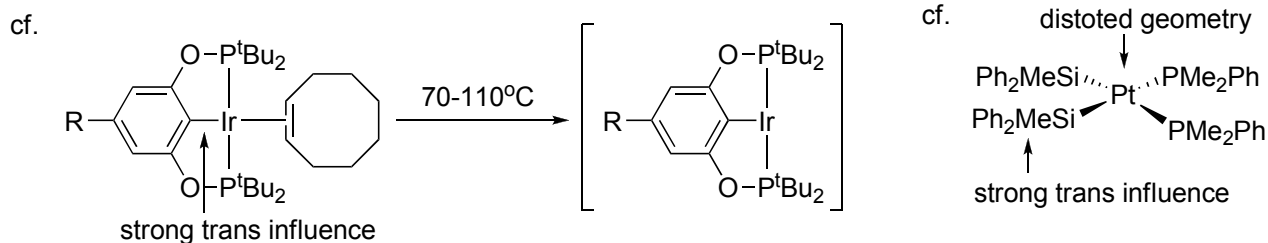
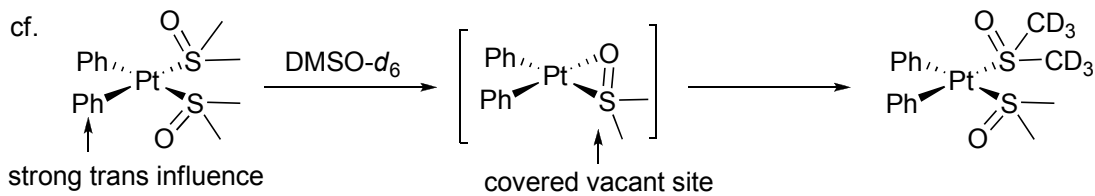


Fig 5.2

larger when L^t is σ -donating (weakens M-X bond), or π -accepting (stabilizing 5-coordinate intermediate).

> When dissociative mechanism of square-planer d^8 complexes is dominant ?

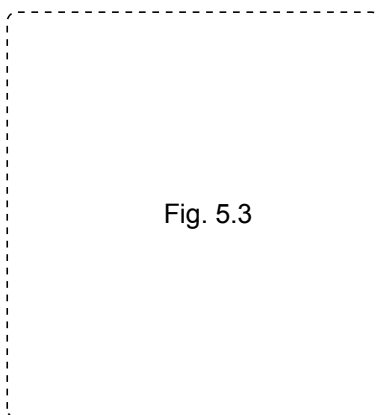
- # weakly bound X
- # strong trans influence ligand
- # unsaturated metal site is covered by polydentate coordination
- # axial association of Y is prohibited
- # metal geometry is distorted from square planer
- # coordination number > 4
- # very fast association generate super leaving group



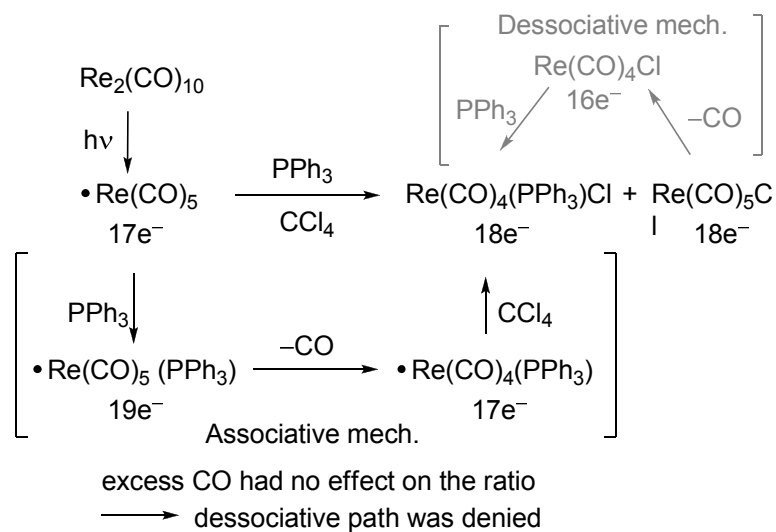
> Associative mechanism of 17e- complexes

substitution rate:
17e complexes > 18e complexes

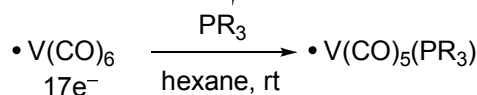
associative mech. leads to energetic gains.



cf.) Poe's experiment ref)



cf.

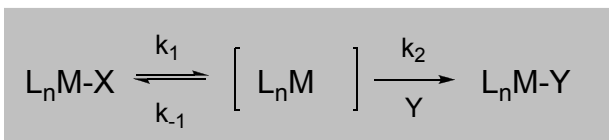


$$\text{rate} = k[\text{V}(\text{CO})_6][\text{PR}_3]$$

negative ΔS^\ddagger

5.4. Mechanisms of Ligand Substitutions of 18e- complexes

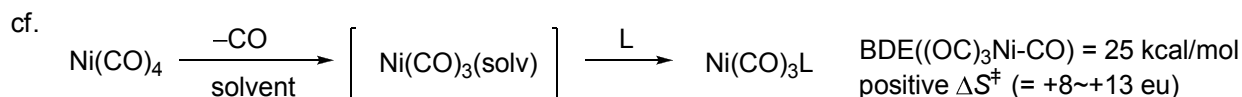
> Dissociative mechanism



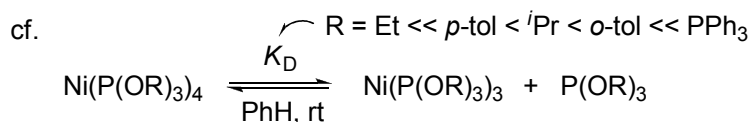
$$\text{rate} = \frac{k_1 k_2 [L_nMX][Y]}{k_{-1}[X] + k_2[Y]} \doteq k_1 [L_nMX]$$

(usually $k_2[Y] \gg k_{-1}[X]$)

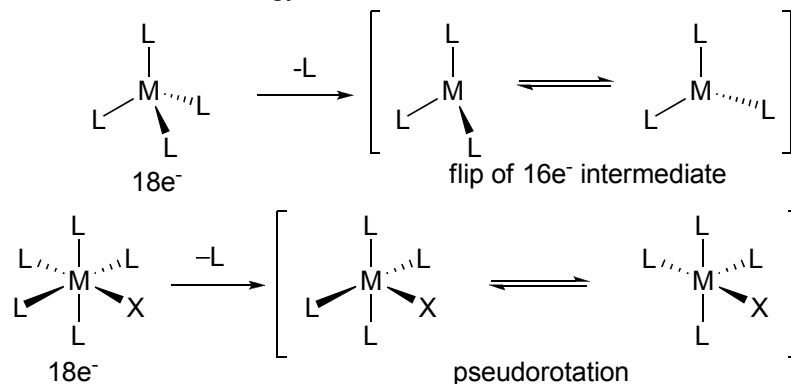
fig 5.4



Steric bulkiness of ligand (Tolman's cone angle) largely affects the rate.

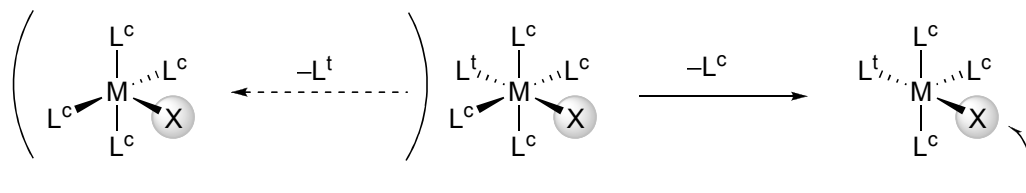


stereochemistry = **easily lost** //cf. analogy to S_N1

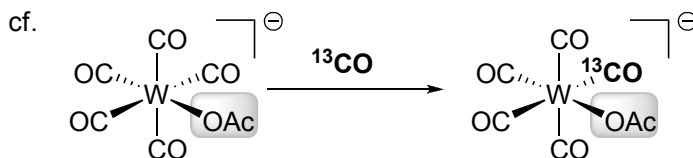


cis effect in (pseudo)octahedral complexes

= X makes dissociation of L^{cis} faster than that of L^{trans}

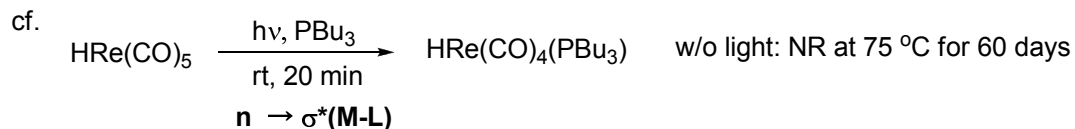


$NO_3^- > OAc^-$, HCO_2^- , $RC(O)^- > NHR > SH^- > OR > Cl^- > Br^- > I^- >$ carbene $>$ PPh₃ $>$ H⁻, CO
 larger in case of **chelating**, **π -donating**, **less σ -donating** ligand \longrightarrow stabilization of unsaturated metal



> Reagent and catalyst induced dissociation of CO

photo-induced

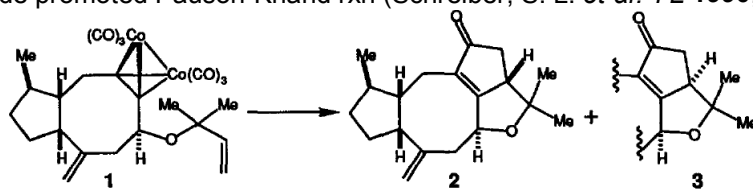
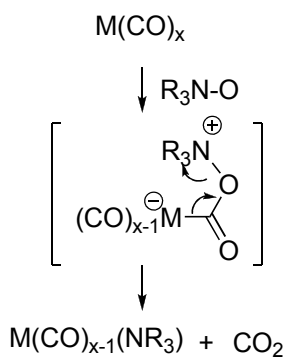


redox, SET-induced cf. analogous to radical chain rxn

scheme 5.8

ligand oxidation-induced (review: *Coord. Chem. Rev.* **1984**, 53, 227.)

cf. N-oxide promoted Pauson-Khand rxn (Schreiber, S. L. *et al.* *TL* **1990**, 31, 5289)



Conditions	Yield (%)	Selectivity (2 : 3)
NMO, CH ₂ Cl ₂ , RT	68	11 : 1
CH ₃ CN, 82 °C	75	4 : 1
CH ₃ CN, 45 °C	45	3 : 1

(faster if CO is more electrophilic)

5.4. Mechanisms of Substitutions Involving Polyhapto Ligands

> Diene and Triene

18e- complex + strong dative L = competitive pathways



$$\text{rate} = (k_1 + k_2[\text{L}])[\text{M}(\text{CO})_4(\text{diene})]$$

dissociative path

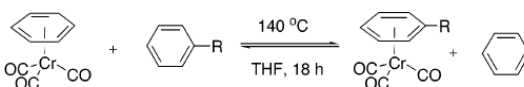
associative path

> Arene

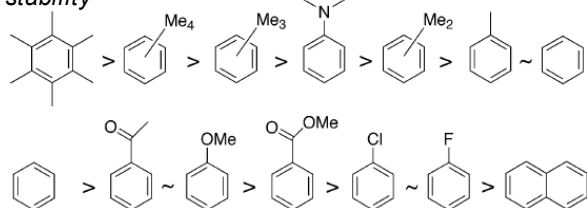
stepwise ring slip ($\eta^6 - \eta^4 - \eta^2$) occurs on the occasion when solvent or ligand income.

→ faster in case of **donor solvent, weakly binding arenes**

cyclohexanone (1300) > PhCN (600) > THF (30)
 ~ Cr(CO)₃(C₆Me₆) (30) > uncatalyzed (1)



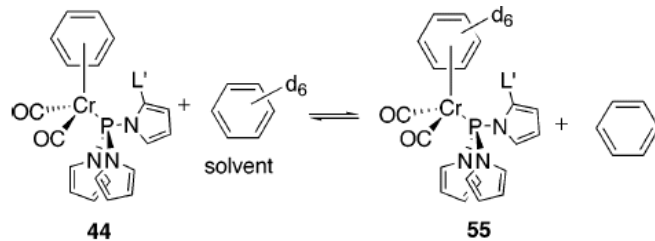
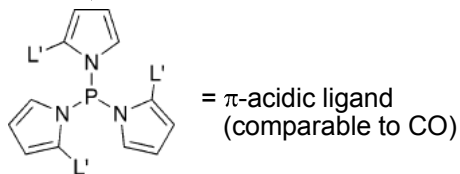
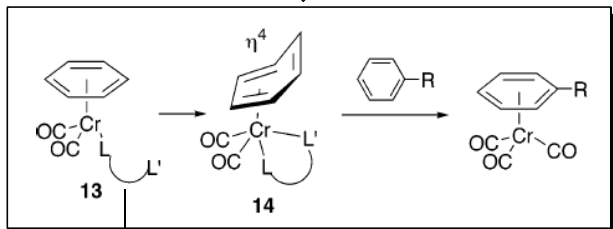
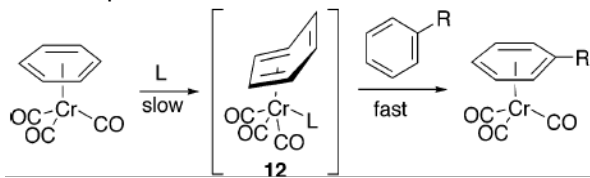
stability



photoirradiation, redox, SET also accelerate the process.

cf.) acceleration by ligand design (Semmelhack, M. F. *et al.* *JACS* **2001**, 123, 8438, *JACS* **2005**, 127, 7759.)

<concept>

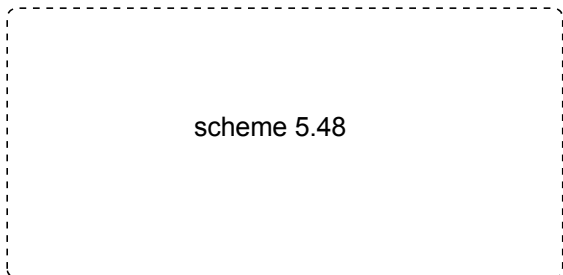


complex	half life at 70.0 °C
44a L = SMe	8.7 h
44b L = SCF ₃	<5% conversion/12 h
44c L = SPh	30.6 h
44d L = CH ₂ SMe	28.7 h
44e L = CH ₂ SPh	very slow (decomp)
44f L = CONMe ₂	9 h at 22 °C ^a
44g L = St-Bu	9.91 h
44h L = CO ₂ Me	0.5 h (~115 h at 23 °C)
44j L = 2-Py	8 h at 22 °C ^a

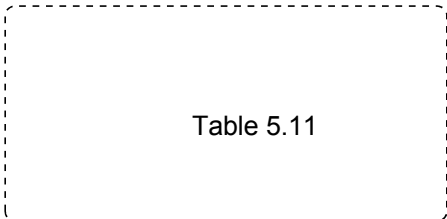
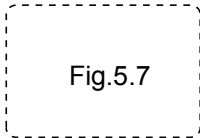
^a Too fast to measure at 70 °C.

> Cp ligand

associative substitution of ligand other than Cp ring



stepwise **ring slip** ($\eta^5 - \eta^3$) occurs on the occasion when solvent or ligand income.



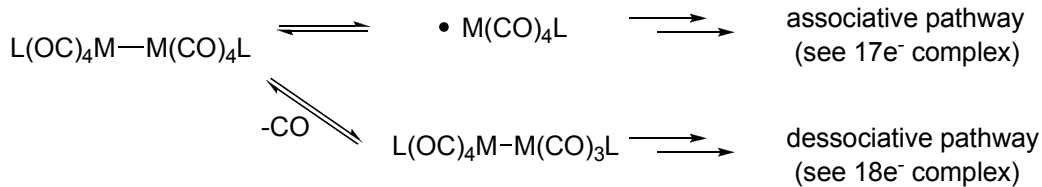
aromaticity is not preserved during ring slip, in case of rightside Cp families.

as other rationalization, ground state energy of η^5 -indenyl is higher (because of ring dissymmetry) than η^5 -Cp.

5.6 Ligand Substitutions in Multimetallic Clusters

All associative, d dissociative, reagent-induced substitutions are allowed as mononuclear complexes.

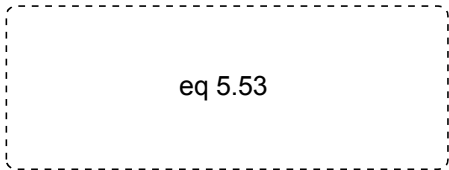
> Complex possessing metal-metal bond



depends relative strength between $\text{BDE}(\text{M-M})$ and $\text{BDE}(\text{M-CO})$

↓
weaker in case of first-row transition metals

cf.)



1st: associative
2nd: dissociative
3rd: dissociative

relative rate, 1st : 2nd : 3rd = 1 : 30 : 920
presence of **bridging CO ligand** affects largely.