

1. Crystal field theory (CFT) and ligand field theory (LFT)

CFT: interaction between positively charged metal cation and negative charge on the non-bonding electrons of the ligand

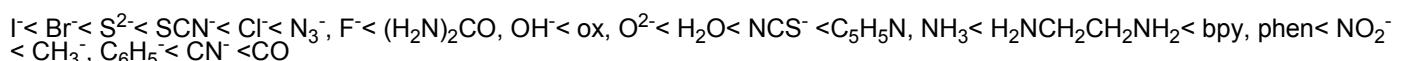
LFT: molecular orbital theory (back donation...etc)

Octahedral (figure 9-1a)

d-electrons closer to the ligands will have a higher energy than those further away which results in the d-orbitals splitting in energy.

ligand field splitting parameter (Δ_0): energy between e_g orbital and t_{2g} orbital

- 1) high oxidation state
- 2) $3d < 4d < 5d$
- 3) spectrochemical series



cf) pairing energy: energy cost of placing an electron into an already singly occupied orbital

Low spin:

If Δ_0 is large, then the lower energy orbitals(t_{2g}) are completely filled before population of the higher orbitals(e_g)

High spin:

If Δ_0 is small enough then it is easier to put electrons into the higher energy orbitals than it is to put two into the same low-energy orbital, because of the repulsion resulting from matching two electrons in the same orbital
ex) $(t_{2g})^3(e_g)^n$ (n= 1,2)

Tetrahedral (figure 9-1b), Square planar (figure 9-1c)

LFT (figure 9-3, 9-4)

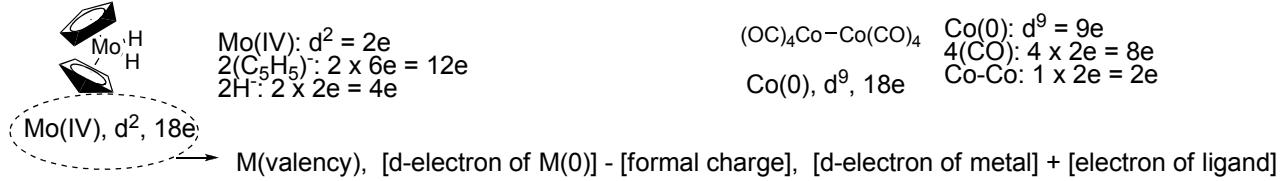
Cl^- , Br^- : lower Δ_0 (figure 9-4 a)

CO : higher Δ_0 (figure 9-4 b)

2. Ligand

metal complex	hapticity	formal charge	electron donation	metal complex	hapticity	formal charge	electron donation		
M-R	alkyl	1	-1	2		η^6 -arene	6	0	6
M-H	hydride	1	-1	2		μ -hydride	1	-1	2
M-X	halogen	1	-1	2		μ -halogen	1	-1	4
M-OR	alkoxide	1	-1	2		μ -alkoxide	1	-1	4
	acyl	1	-1	2		μ -carbonyl	1	0	2
	η^1 -alkenyl	1	-1	2		μ -alkylidene	1	-2	4
	acetylide	1	-1	2		μ^3 -carbonyl	1	0	2
	carbene	1	0	2		μ^3 -alkylidene	1	-3	6
	carbene	1	-2	4					
M-	carbyne	1	-3	6					
M-CO	carbonyl	1	0	2					
	η^2 -alkene	2	0	2					
	η^2 -alkyne	2	0	2					
	η^3 -allyl	3	-1	4					
	η^4 -diene	4	0	4					
	η^5 -cyclopentadienyl	5	-1	6					

3. d-electron



Early transition metal: smaller d-electron number (group 4, 5...)
 Late transition metal: larger d-electron number (group 9, 10...)

4. 18-electron rule

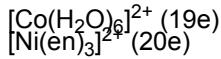
Valence shells of transition metal consists of **nine valence orbitals** (s, p, d), which collectively can accommodate **18 electrons** (same electron configuration as noble gas) either as nonbinding electron pairs or as bonding electron pairs.

18-electron complex: coordinatively saturated complex

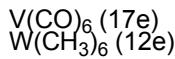
non-18-electron complex: coordinatively unsaturated complex

Violations to the 18-electron rule

Octahedral



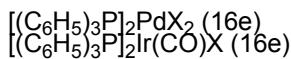
late transition metal: small Δ_0 occupation of e_g



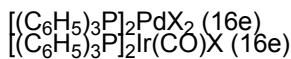
early transition metal



Square planar



instability of $d_{x^2-y^2}$

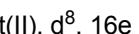
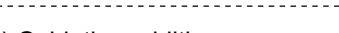
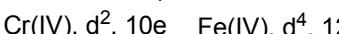
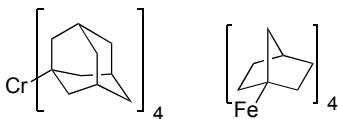
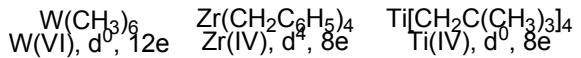


5. σ -bonding ligand

5.1 alkyl complex

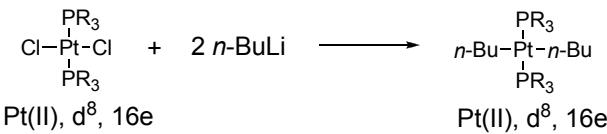
M-C bond: 130~300 kJmol⁻¹
 β -hydride elimination

stable alkyl complexes

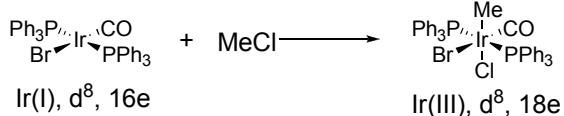


synthesis of alkyl complexes

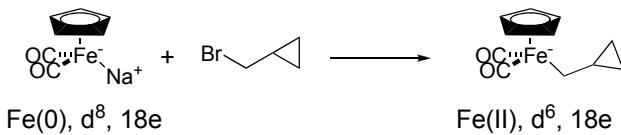
1) Metathetical exchange using a carbon nucleophile



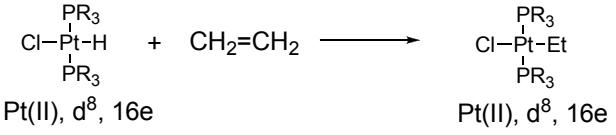
3) Oxidative addition



2) Metal centered nucleophile



4) Insertion

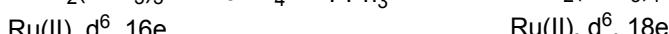
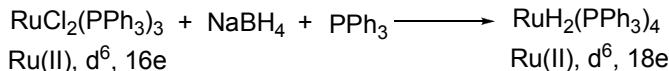


5.2 hydride complex

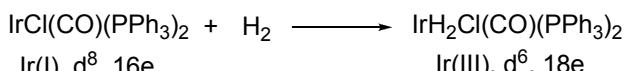
M-H bond: 240~350 kJmol⁻¹

synthesis of hydride complexes

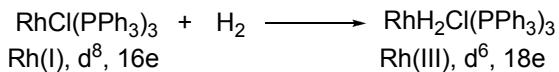
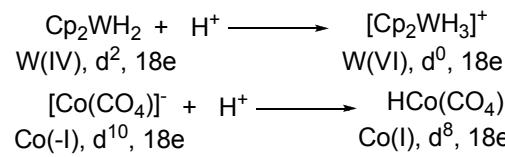
1) Metal halide + reductant



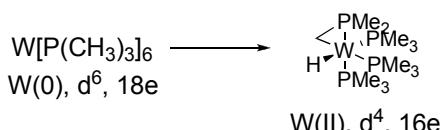
3) Oxidative addition



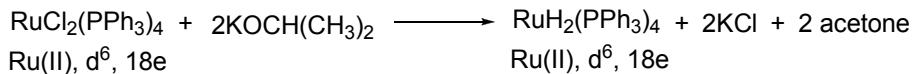
2) Protonation



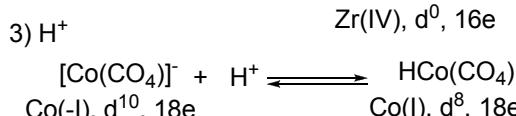
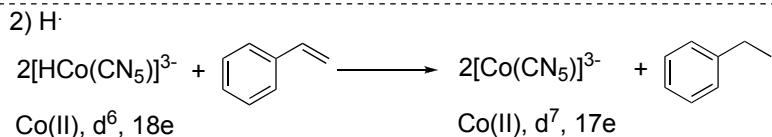
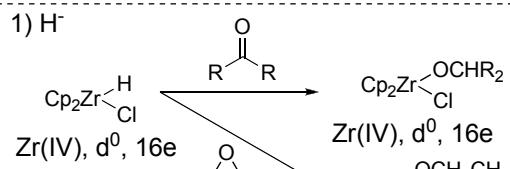
4) Ortho metallation, cyclo metallation



5) β -hydride elimination

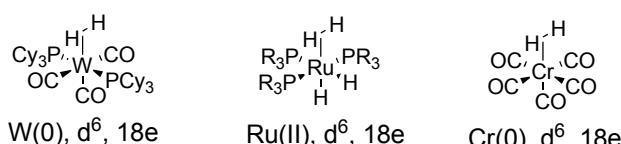


Reactivity of hydride complex



4) insertion to alkene and alkyne
5) H_2 elimination

5.3 molecular hydrogen complex



weak back donation to hydrogen

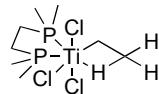
5.4 agostic interaction

agostic interaction: interaction of a coordinately-unsaturated transition metal with a C-H bond (two electrons involved in the C-H bond enter the empty d-orbital of a transition metal, resulting in a two electron three center bond)

ex)



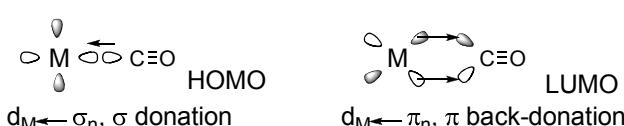
α -agostic interaction



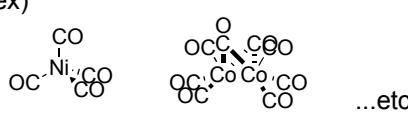
β -agostic interaction

6. σ donation, π back-donation

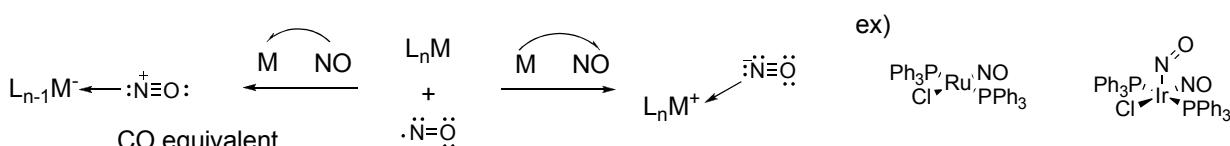
6.1 carbonyl complex



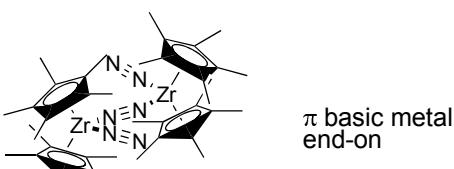
ex)



6.2 nitrocyt complex

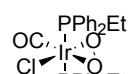
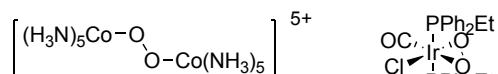


6.3 molecular nitrogen complex

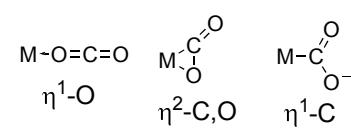


π basic metal end-on

6.4 molecular oxygen complex



6.5 molecular carbon dioxygen complex

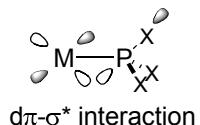


6.6 phosphine complex

basicity: $\text{PR}_3 > \text{PR}_2\text{Ar} > \text{PAr}_2 > \text{PAr}_3$

π acceptor ability: $\text{NO} > \text{CO} > \text{RNC} > \text{PF}_3 > \text{PCl}_3 > \text{PCl}_2\text{R} > \text{PBr}_2\text{R} > \text{P(OR)}_3 > \text{PR}_3 > \text{RCN} > \text{RNH}_2 > \text{NH}_3$

→ $d\pi-\sigma^*$ interaction



a. Structural factor

Tolman cone angle: measure of size of ligand

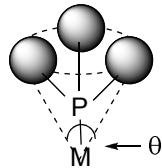


Table 9-7

bite angle: bidentate ligand

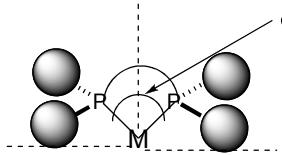


Table 9-8

b. electronic factor

$(\text{R}_3\text{P})\text{Ni}(\text{CO})_3$: there is a strong correlation between ν_{CO} and electron donating ability of phosphine ligand. Table 9-9

6.7 carbene complex

Schrock carbene: nucleophilic carbene

high oxidation state

early transition metal

π -donor ligand

hydrogen and alkyl substituents on carbenoid carbon

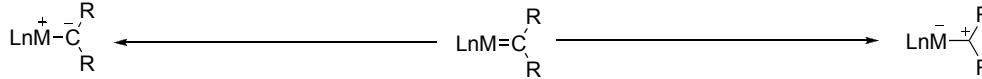
Fisher carbene: electrophilic carbene

low oxidation state

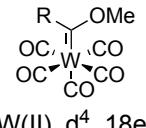
middle and late transition metal

π -acceptor ligand

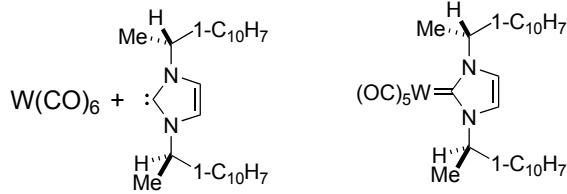
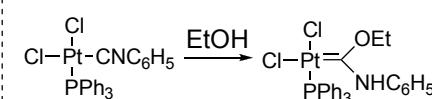
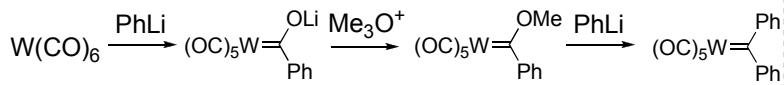
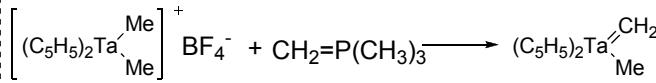
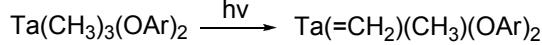
π -donor substituents on methylene



Ta(V), d^0 , 18e

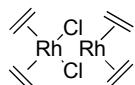
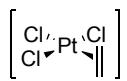


synthesis of carbene complex

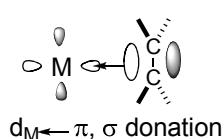


7. π -bonding ligand

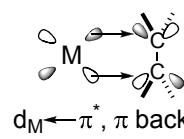
7.1 alkene complex



Dewar-Chatt-Duncanson model



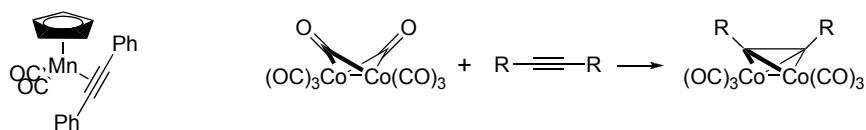
high oxidation state



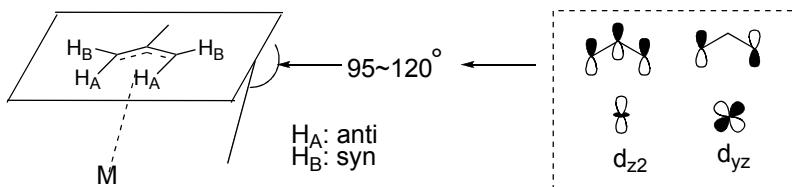
anionic complex
electron donating ligand

7.2 alkyne complex

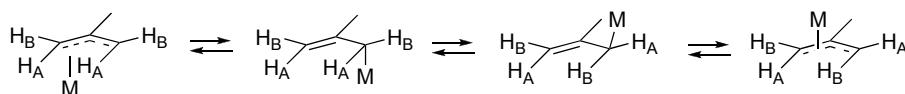
Dewar-Chatt-Duncanson model can be applied to alkyne complex.



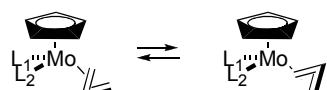
7.3 π -allyl complex



syn-anti isomerization



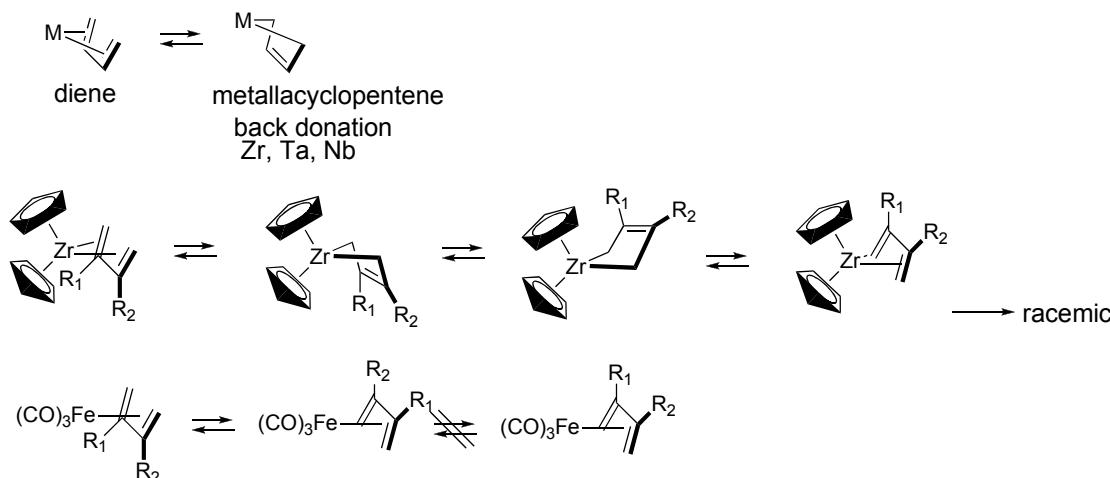
allylic rotation



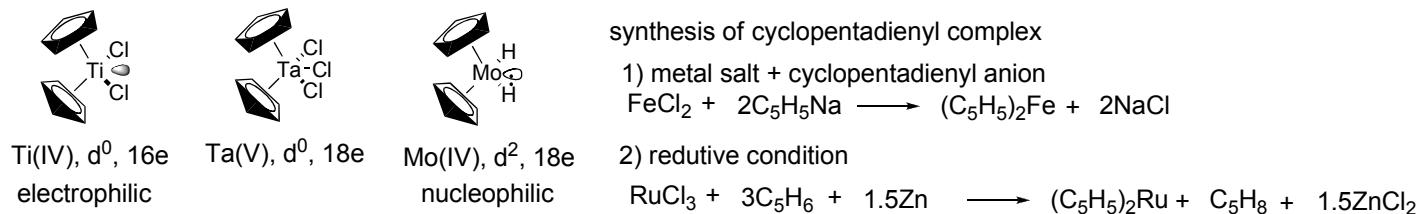
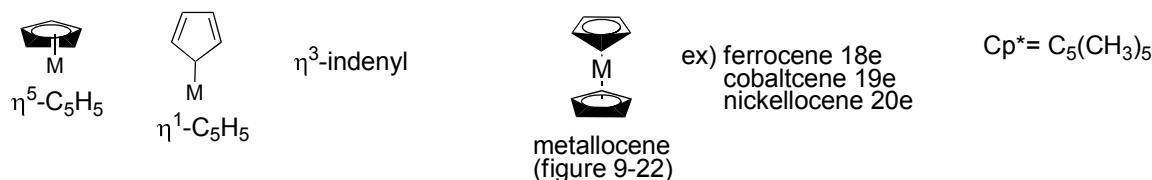
cf) crotyl complex: racemization, 1,3-disubstituted allylic complex: syn-anti isomerization

7.4 diene complex

molecular orbital (figure 9-20)



7.5 cyclopentadienyl complex



7.5 π benzene complex

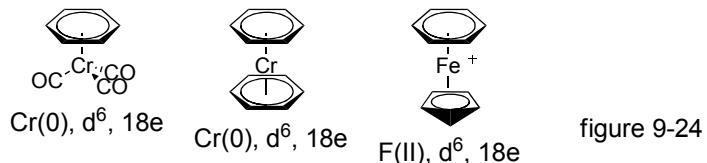
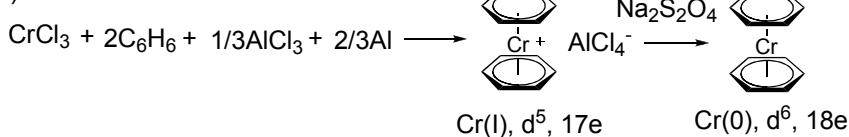


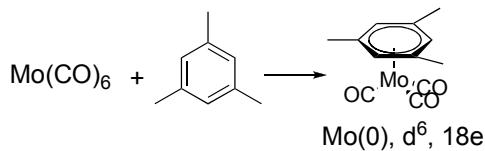
figure 9-24

synthesis of arene complex

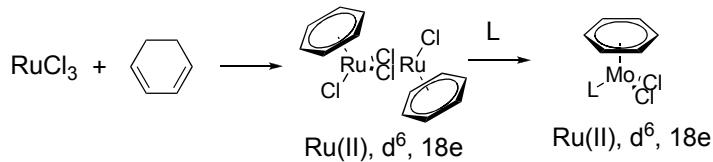
1) arene + metal salt



2) ligand exchange



3) hydrogen extraction from cyclohexadiene



Appendix

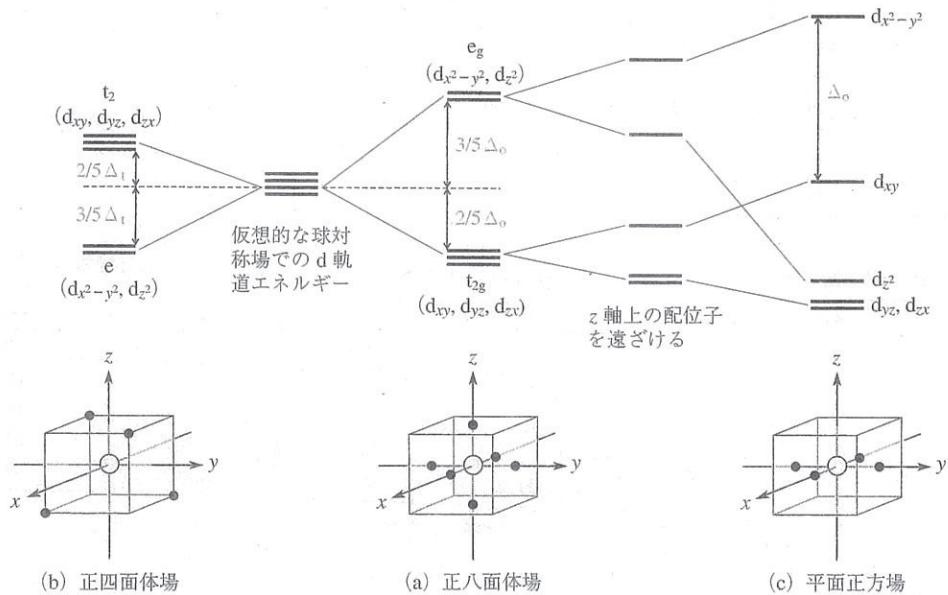


図 9・1 結晶場中の d 軌道の分裂. ●は点電荷.

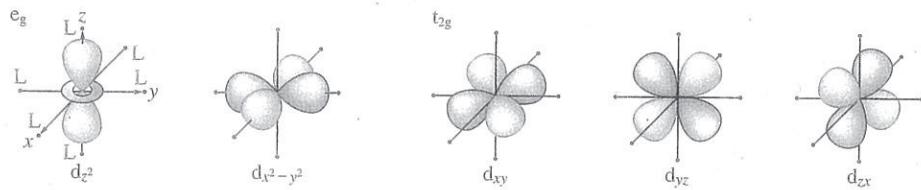


図 9・2 正八面体錯体における配位子 L と d 軌道との関係

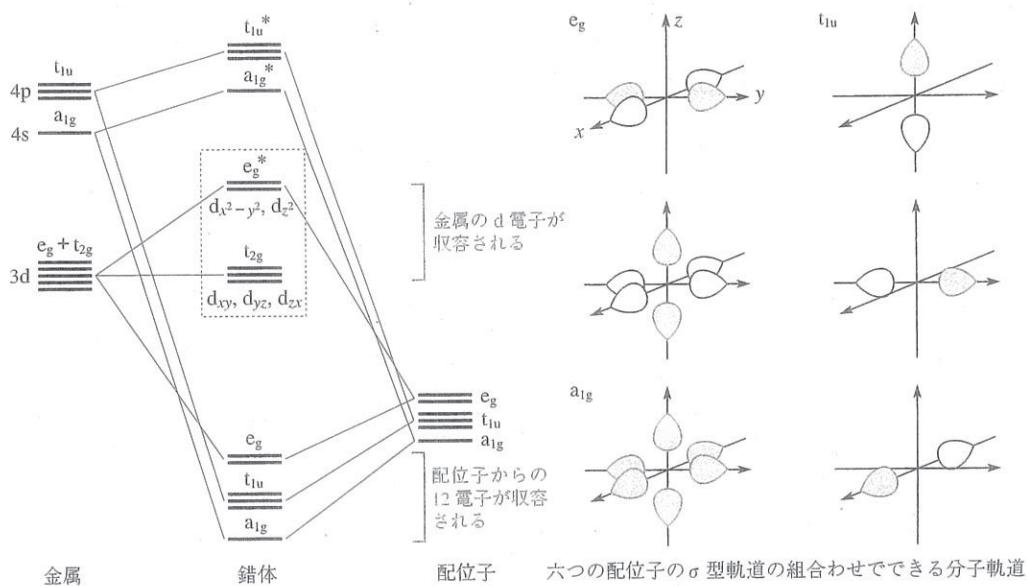


図 9・3 正八面体形錯体の分子軌道エネルギー準位

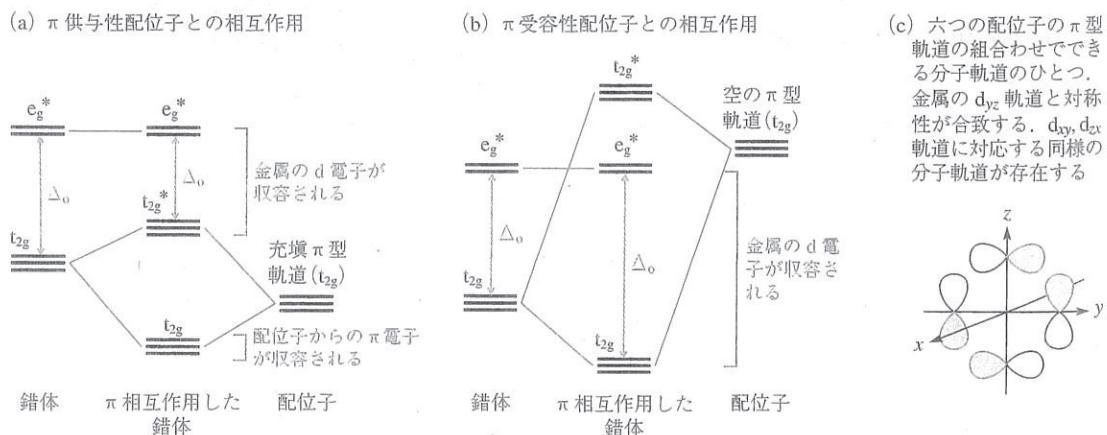


図 10・4 π 型結合と反結合の電子供与性配位子と金属との結合によるトスメル結合アントラゼン結合のモデル

表 9・7 ホスフィン、ホスファイト配位子類の円錐角

PR ₃	円錐角 [†]	PR ₃	円錐角 [†]	PR ₃	円錐角 [†]
P(<i>o</i> -CH ₃ C ₆ H ₄) ₃	194	P(O- <i>o</i> -C ₆ H ₄ CH ₃) ₃	141	P(OC ₆ H ₅) ₃	128
P(C ₆ H ₅) ₃	184	P(C ₂ H ₅) ₂ (C ₆ H ₅)	140	P(CH ₃) ₂ (C ₆ H ₅)	122
P(<i>t</i> -C ₄ H ₉) ₃	182	P(<i>n</i> -C ₃ H ₇) ₃	139	P(CH ₃) ₃	118
P(<i>c</i> -C ₆ H ₁₁) ₃	179	P(<i>n</i> -C ₄ H ₉) ₃	136	P(O- <i>i</i> -C ₃ H ₇) ₃	114
P(<i>t</i> -C ₄ H ₉)(<i>i</i> -C ₃ H ₇) ₂	167	P(C ₂ H ₅) ₂ (C ₆ H ₅)	136	P(OC ₂ H ₅) ₃	109
P(<i>i</i> -C ₃ H ₇) ₃	160	P(OC ₂ H ₅)(C ₆ H ₅) ₂	133	P(OCH ₃) ₃	107
P(CH ₂ C ₆ H ₅) ₃	160	P(C ₂ H ₅) ₃	132	P(OCH ₂) ₃ CC ₂ H ₅	101
P(C ₆ H ₅) ₃	145	P(OC ₆ H ₅) ₂ (C ₆ H ₅)	129		

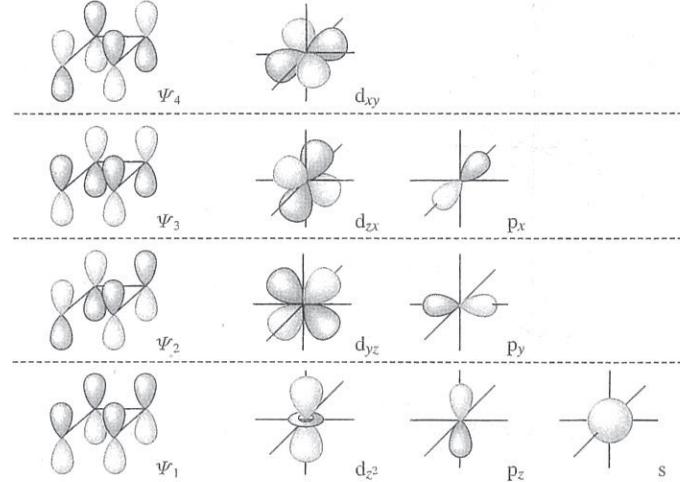
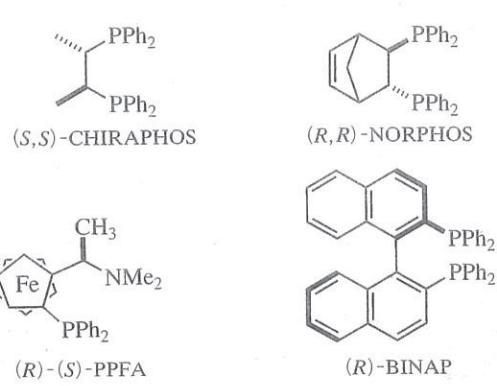
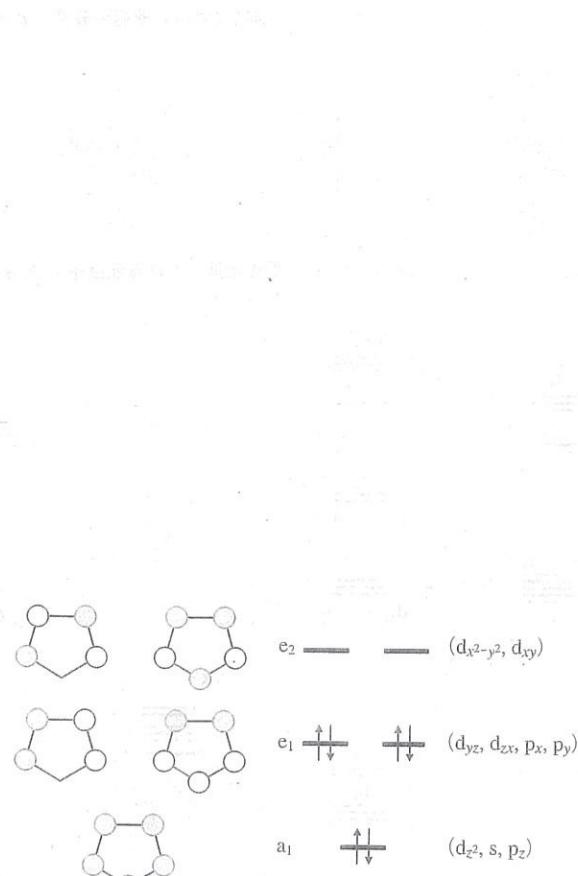
[†] degree.

表 9・8 キラルな二座ホスフィン配位子をもつ錯体の配位挾角

錯体	キレート環員数	配位挾角, degree
[Rh(CHIRAPHOS)(cod)]ClO ₄	5	83.8
[Rh(NORPHOS)(nbd)]ClO ₄	5	86.4
[Rh(DIPAMP)(cod)]PF ₆	5	84.0
[Rh(PPFA)(nbd)]PF ₆	6	95.5
[Rh(BINAP)(nbd)]ClO ₄	7	91.8
[Rh(DIOP)(nbd)]ClO ₄	7	98
Fe(DIOP)(Cp)I	7	99.1
Ir(DIOP)(cod)Cl	7	92.4

表 9・9 (*R*₃P)Ni(CO)₃におけるカルボニル伸縮振動 ν_{CO} の基準値[†]からのシフト値

配位子	シフト (χ, cm^{-1})	配位子	シフト (χ, cm^{-1})
P(<i>i</i> -C ₃ H ₇) ₃	3.1	P(C ₆ H ₅) ₃	12.9
P(<i>n</i> -C ₃ H ₇) ₃	4.9	P(O- <i>n</i> -C ₄ H ₉) ₃	19.5
P(C ₂ H ₅) ₃	5.6	P(OCH ₃) ₃	23.4
P(CH ₂ C ₆ H ₅) ₃	10.3	P(OC ₆ H ₅) ₃	29.2

[†] (*t*-C₄H₉)₃PNi(CO)₃ の $\nu_{CO} = 2056.1 \text{ cm}^{-1}$.図 9・20 *s-cis*-ブタジエンの分子軌道と対称性が対応する金属の原子軌道図 9・21 シクロペンタジエニルアニオンの分子軌道と η^5 配位に対応する金属の原子軌道 (括弧内)

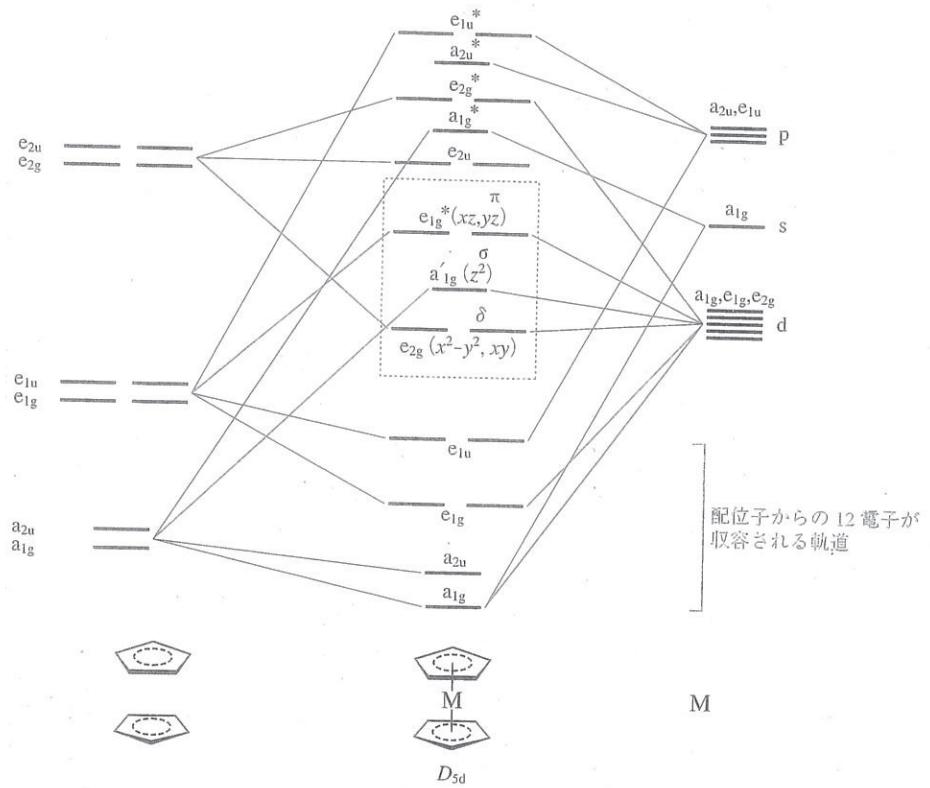


図 9・22 D_{5d} 対称 $(C_5H_5)_2M$ における C_5H_5 と金属の軌道相互作用

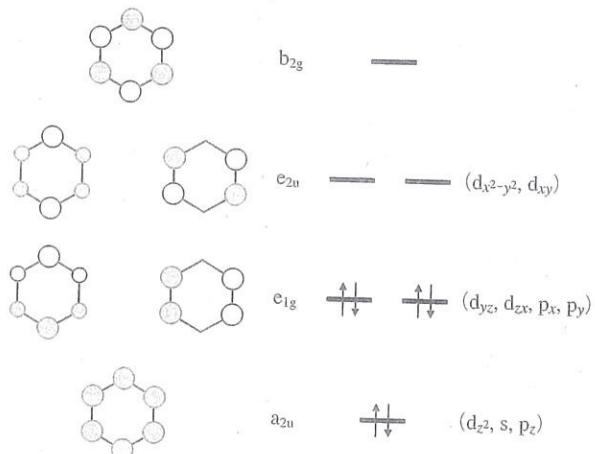


図 9・24 ベンゼンの分子軌道と
 η^6 配位に対応する金属の原子軌道 (括弧内)