

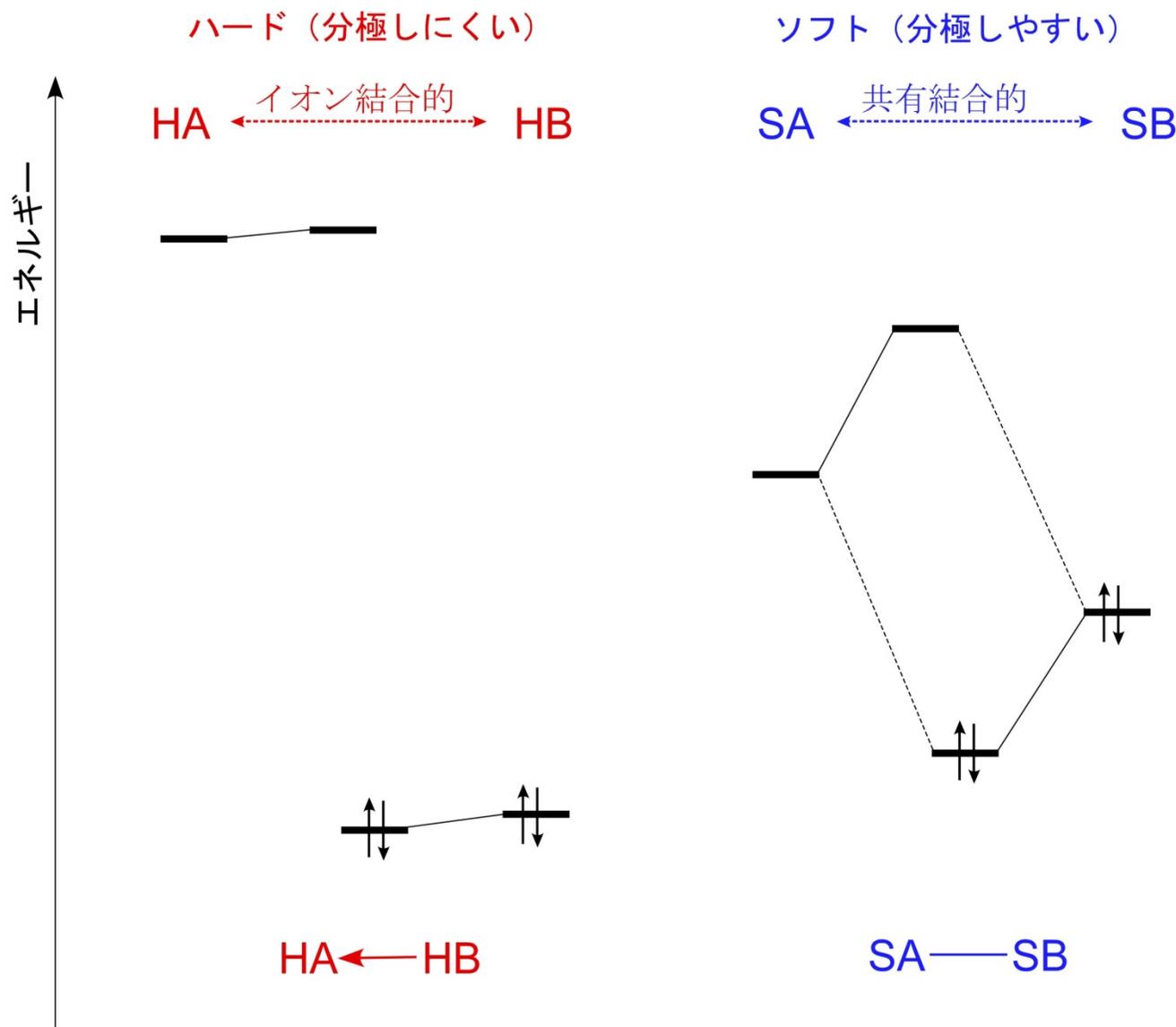
# § 1. 錯体化学の基礎

1. 金属錯体とは
2. 金属錯体の構造
3. 金属錯体の異性現象
4. 化学式と命名法



## 錯体化学におけるHSABの分類

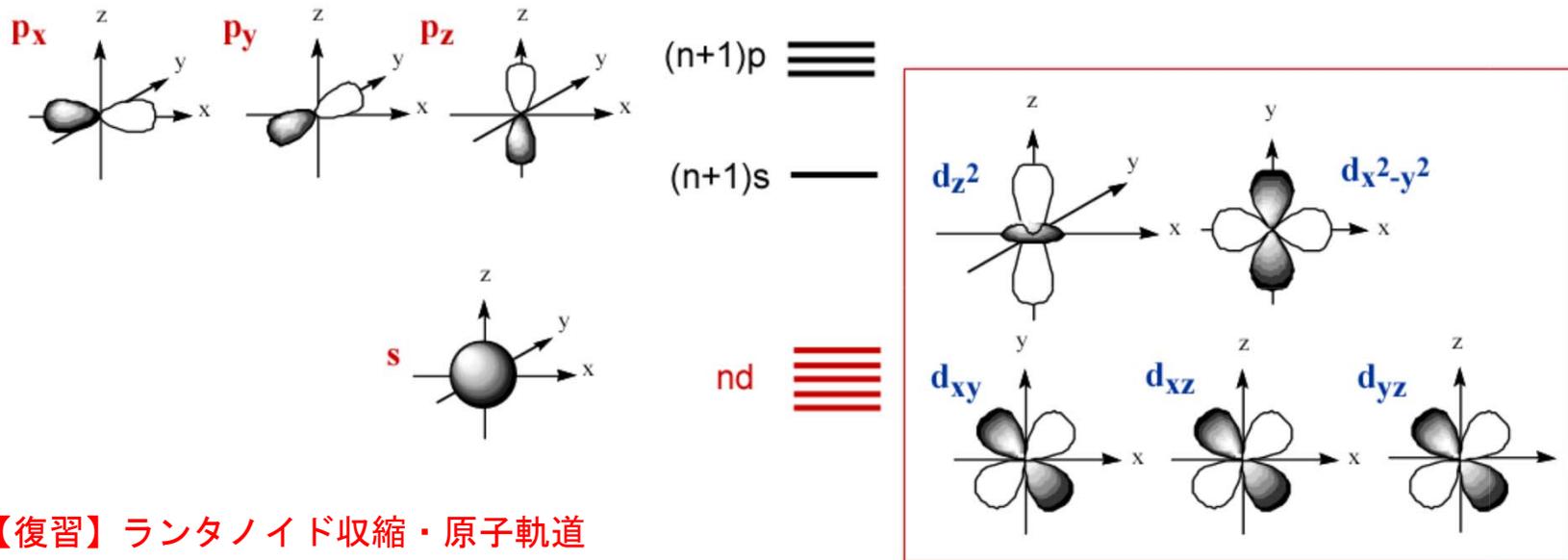
	金属 A			配位子 B			
ハード H	Mn(IV) H(I) Na(I) K(I) Mg(II)	V(V) Mn(II) Al(III) Ga(III) Ca(II)	Mo(VI) Cr(III) Co(III) Fe(III) Tl(III)	O <sup>2-</sup> NO <sub>3</sub> <sup>-</sup> RO <sup>-</sup> ROPO <sub>3</sub> <sup>2-</sup>	OH <sup>-</sup> NH <sub>3</sub> ROH (RO) <sub>2</sub> PO <sub>2</sub> <sup>-</sup>	H <sub>2</sub> O RNH <sub>2</sub> N <sub>2</sub> H <sub>4</sub>	CO <sub>3</sub> <sup>2-</sup> RCOO <sup>-</sup> PO <sub>4</sub> <sup>3-</sup> Cl <sup>-</sup>
中間	Fe(II) Cu(II)	Ni(II) Zn(II)	Co(II)	R <sub>2</sub> O N <sub>2</sub> S <sup>2-</sup>	NO <sub>2</sub> <sup>-</sup> SO <sub>3</sub> <sup>2-</sup>	Im Br <sup>-</sup>	py N <sub>3</sub> <sup>-</sup>
ソフト S	Cu(I) Pd(II) Hg(II)	Mo(II) Au(I) Pt(II)	Cd(II) Tl(I)	R <sub>2</sub> S RSH NO I <sup>-</sup>	R <sub>3</sub> P RNC (RS) <sub>2</sub> PO <sub>2</sub> <sup>-</sup> H <sup>-</sup>	RS <sup>-</sup> SCN <sup>-</sup> (RO) <sub>2</sub> P(O)S <sup>-</sup> R <sup>-</sup>	CN <sup>-</sup> CO



# 金属イオンの最外殻電子

中性遷移金属原子のd電子数

group	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
valence electron	s <sup>1</sup>	s <sup>2</sup>	d <sup>3</sup>	d <sup>4</sup>	d <sup>5</sup>	d <sup>6</sup>	d <sup>7</sup>	d <sup>8</sup>	d <sup>9</sup>	d <sup>10</sup>	d <sup>10</sup> s <sup>1</sup>	d <sup>10</sup> s <sup>2</sup>
			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
			Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
			(La)	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

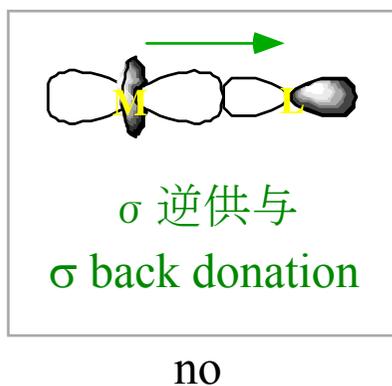
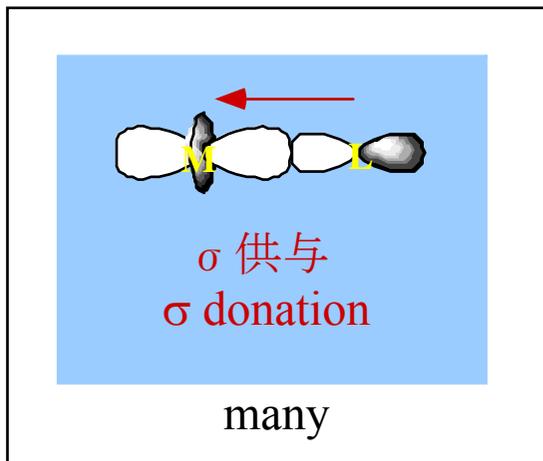


【復習】ランタノイド収縮・原子軌道



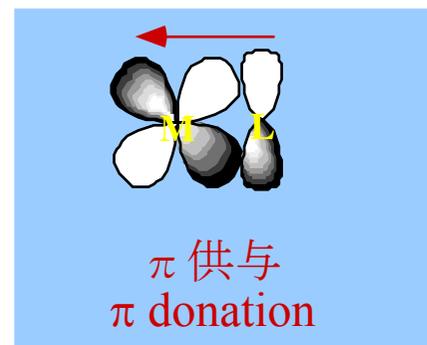
# 金属イオンと配位子との相互作用

d  $\sigma$  - p  $\sigma$  相互作用



d  $\pi$  - p  $\pi$  相互作用

Hard



Hard

$O^{2-}$ ,  $OH^-$

$NR_2^-$   $NR_2^-$

Soft



Soft

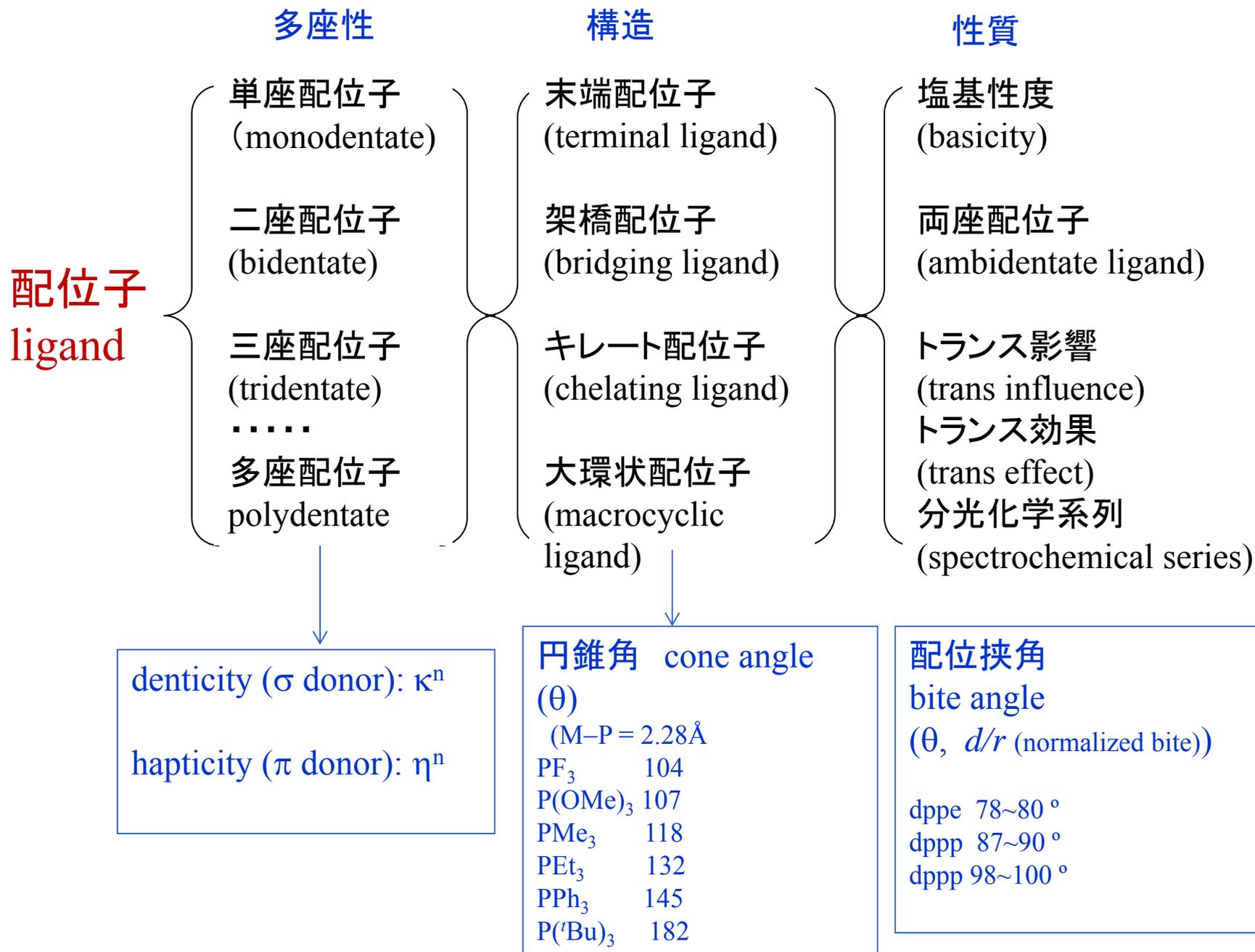
$SR_2$ ,  $SR^-$

$CO$ ,  $PR_3$

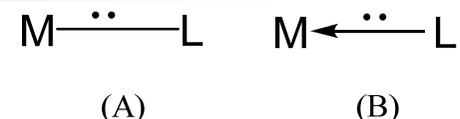
$R^-$ ,  $Ar^-$

Alkene, Alkyne

# 配位子の分類



# 代表的な配位子



厳密には(A)と(B)は異なった結合を意味するが、配位化合物では多くの場合(A)と(B)は同じ。

配位子の名称    化学式 (構造式)    略号

## 単座配位子 (monodentate ligands)

アクア (aqua)                     $\text{OH}_2$

ヒドロキシ (hydroxo)             $\text{OH}^-$

オキシ (oxo)                     $\text{O}^{2-}$

チオラト (thiolato)                 $\text{SR}^-$

スルフィド (sulfido)                $\text{S}^{2-}$

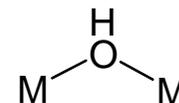
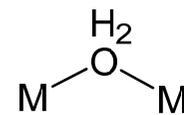
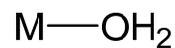
フルオロ (fluoro)                 $\text{F}^-$

クロロ (chloro)                   $\text{Cl}^-$

ブロモ (bromo)                   $\text{Br}^-$

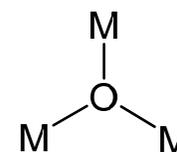
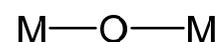
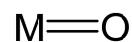
ヨード (iodo)                     $\text{I}^-$

ヒドリド (hydrido)                 $\text{H}^-$



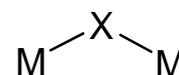
$\mu$

$\mu$

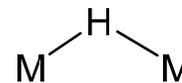


$\mu$

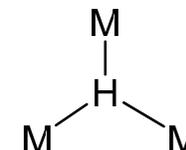
$\mu_3$



$\mu$



$\mu$

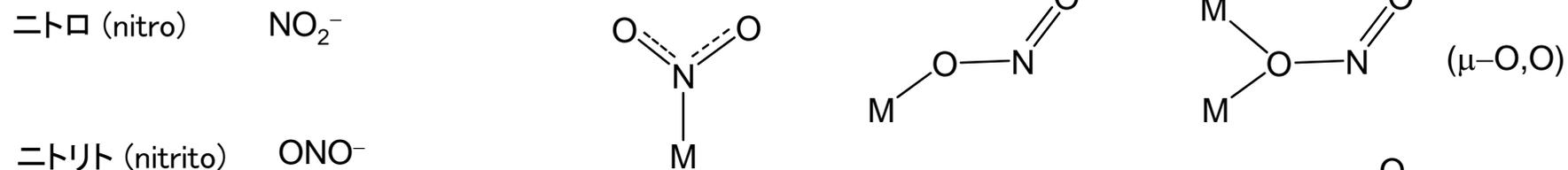
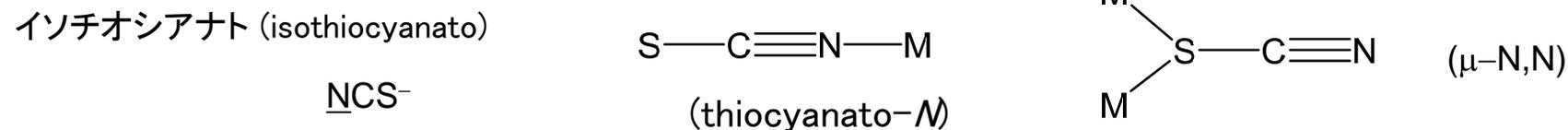
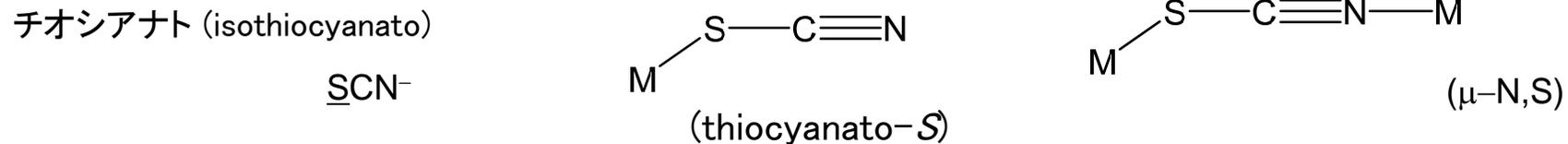
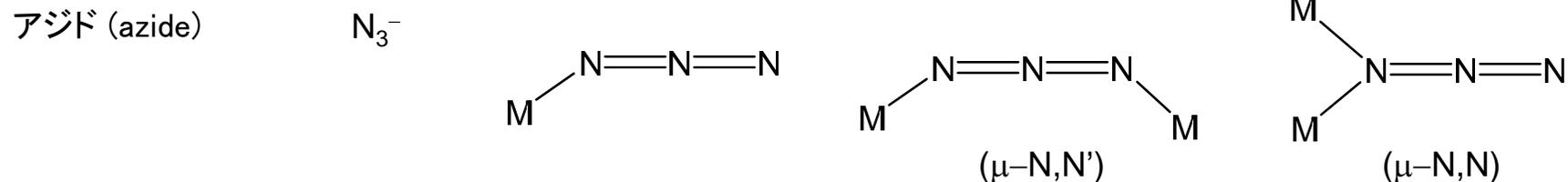
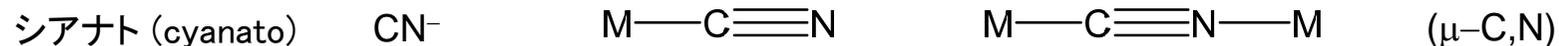


$\mu_3$

## Coordination Chemistry

### 単座～2座配位子 (mono-, bidentate ligands)

### Pseudohalides

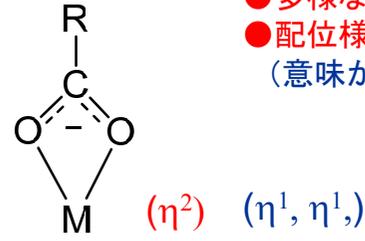
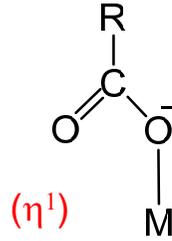
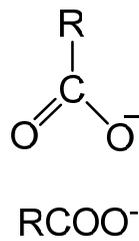


$[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]^{2+}$  O (red), N (yellow) linkage isomer

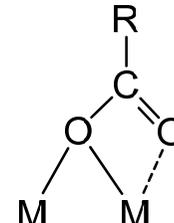
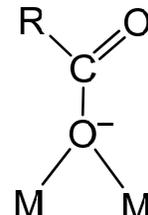
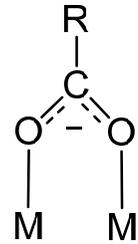
dmsolに注意 (その他配位性の溶媒: dmf, nitrile, ROH, H<sub>2</sub>O)

## 単座～2座配位子 (monodentate~bidentate ligands)

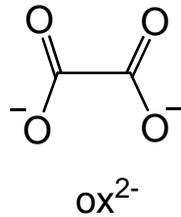
カルボキシラト (carboxylato)



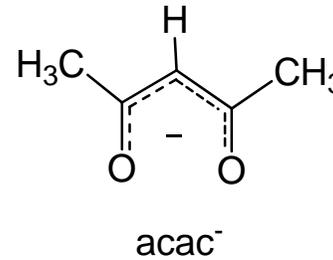
- 多様な配位様式 (カルボキシラトシフト)
- 配位様式の記号  $\eta^n$  に注意 (意味が異なる場合有)



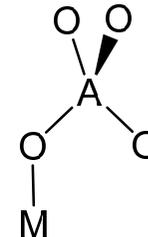
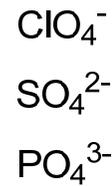
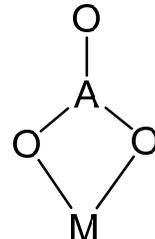
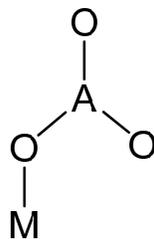
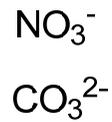
オキサラト (ox)



アクアク (acac)

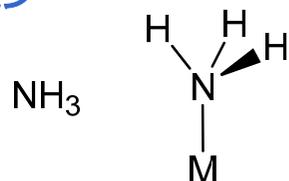


オキソアニオン



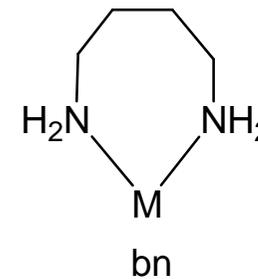
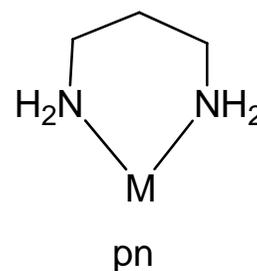
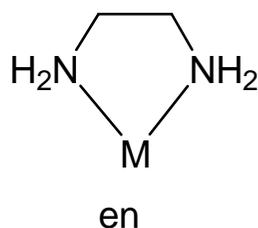
## アミン系配位子(単座～多座配位子)

### アンミン

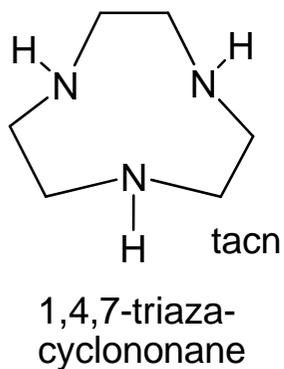
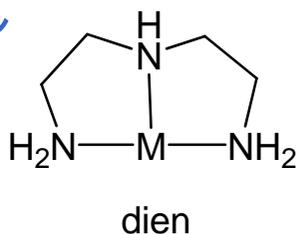


### ジアミン

diamine

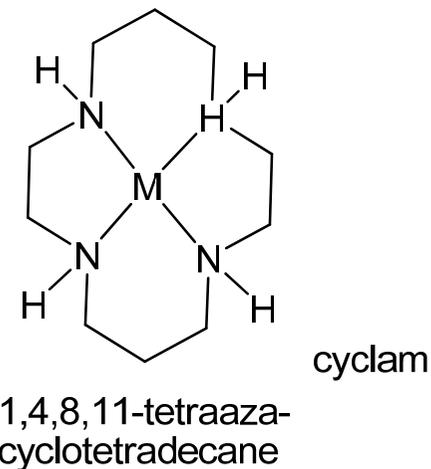
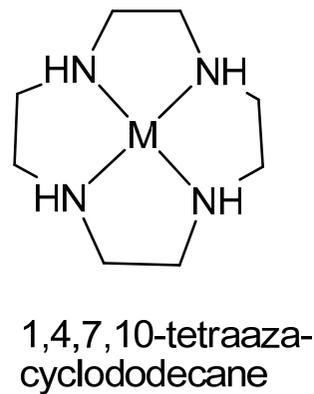
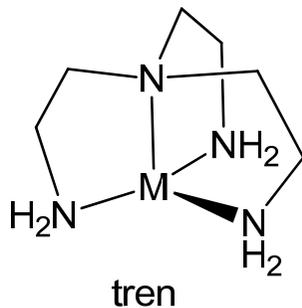
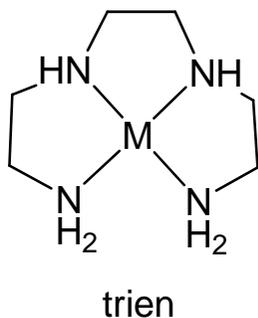


### トリアミン



キレート配位子(chelate ligand)

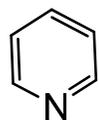
### テトラミン



大環状配位子(macrocyclic ligand)

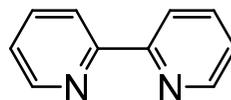
## イミン系配位子 (単座～多座配位子)

ピリジン  
pyridine

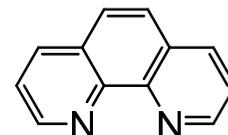


py

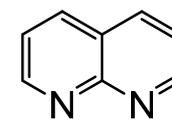
ジイミン  
diimine



2,2'-bpy

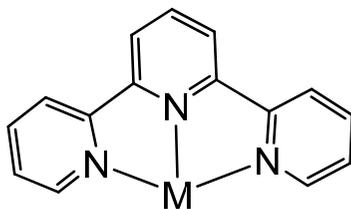


1,10-phen

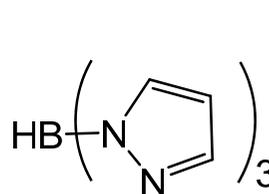


1,8-nap

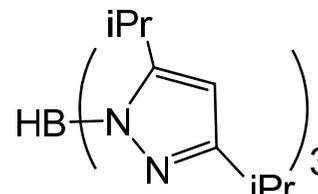
トリイミン



terpy

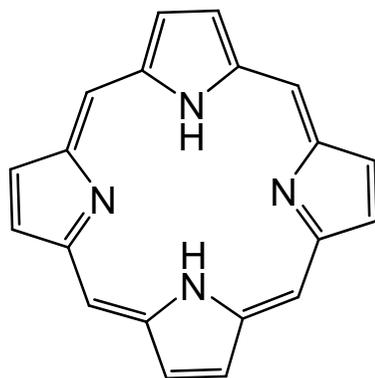


Tp<sup>-</sup>

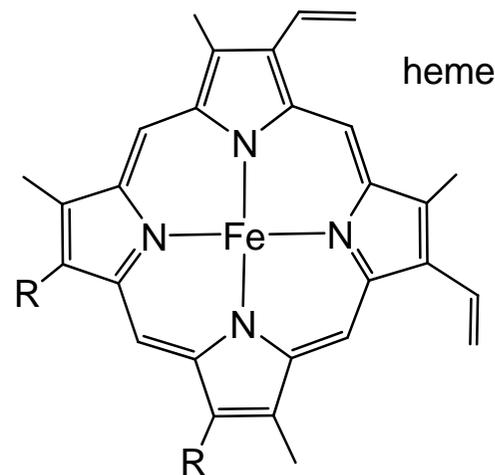


Tp<sup>\*-</sup>

ポルフィリン  
porphyrin



H<sub>2</sub>por



heme

R = CH<sub>2</sub>CH<sub>2</sub>COOH  
proto porphyrine IX

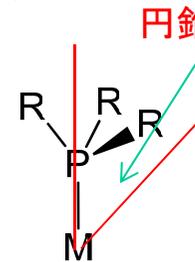
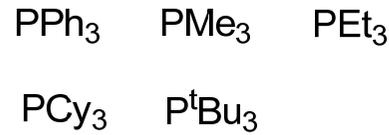
生体関連配位子  
(macrocyclic ligand)

# 代表的な配位子

## ホスフィン系配位子(単座~多座配位子)

### 単座ホスフィン

monophosphine

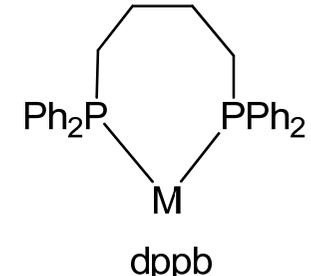
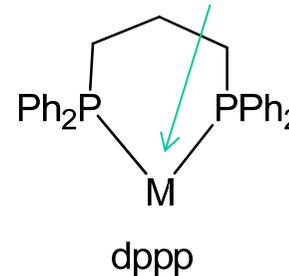
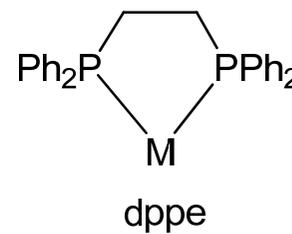
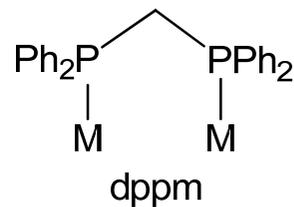


円錐角(cone angle)

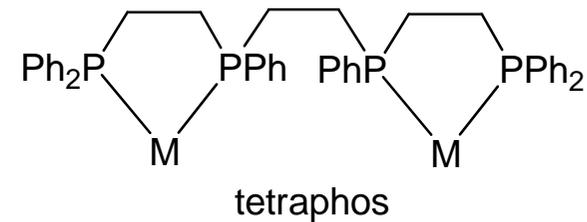
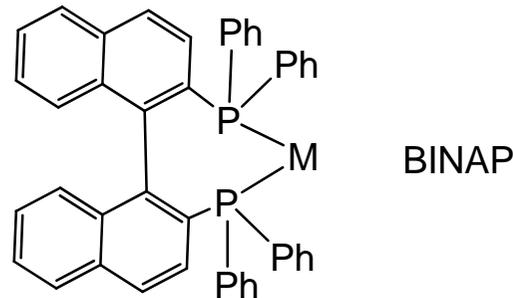
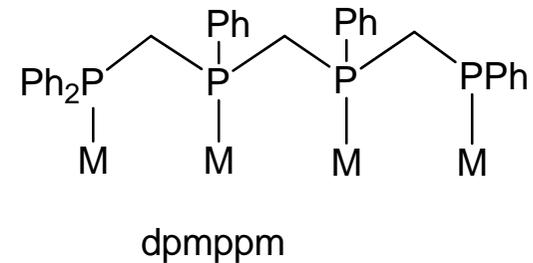
キレート角(配位挟角)  
bite angle (normalized bite)

### 二座ホスフィン

diphosphine

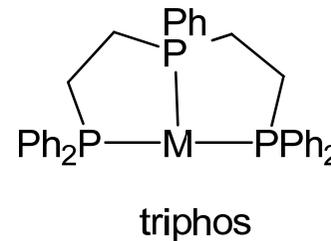
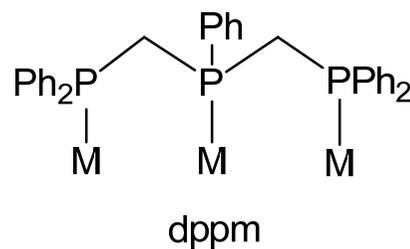


tetraphosphine



### 三座ホスフィン

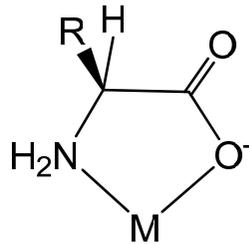
triposphine



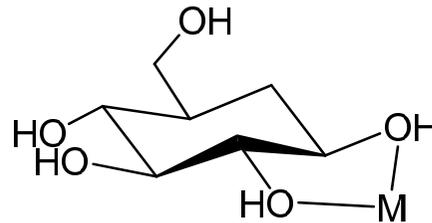
### 四座ホスフィン

多座性(denticity):  $\kappa^n$

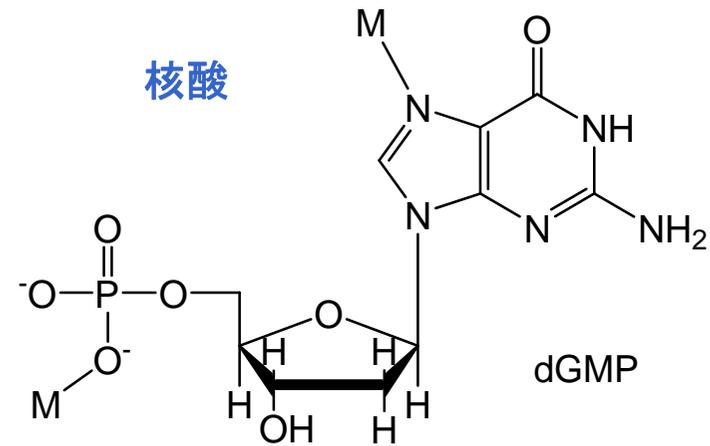
# 代表的な配位子



アミノ酸



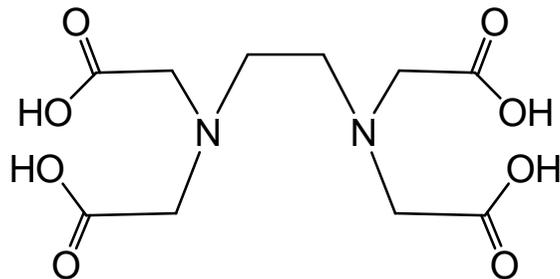
糖



核酸

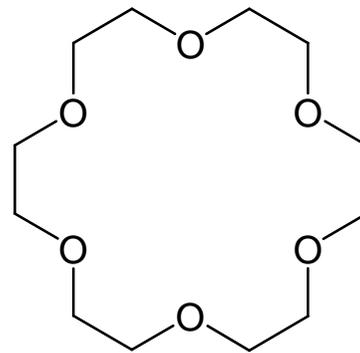
dGMP

## 生体関連配位子



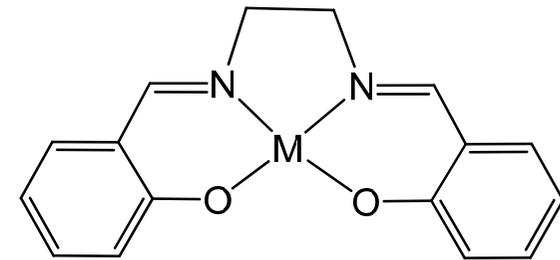
H<sub>4</sub>edta

エチレンジアミン四酢酸



18-crown-6

クラウンエーテル



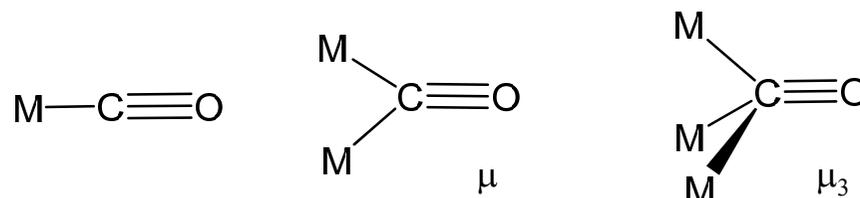
salen

Schiff塩基

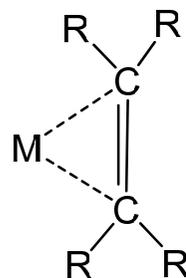
## キレート剤(金属を取り込む配位子)

## 有機金属配位子(単座～多座配位子)

カルボニル

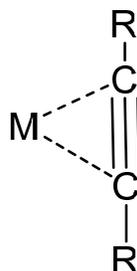


多座性(hapticity):  $\eta^n$

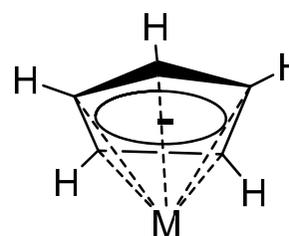


アルケン

( $\eta^2$ )

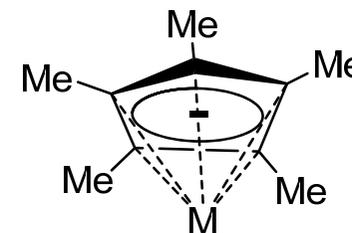


アルキン

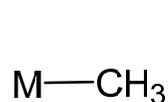


Cp

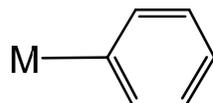
( $\eta^5$ )



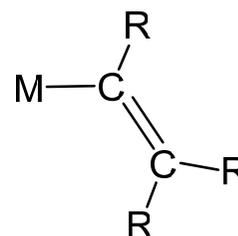
Cp\*



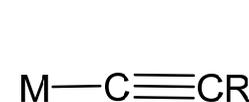
アルキル



アリール



ビニル



アルキニル

# 金属錯体の立体構造

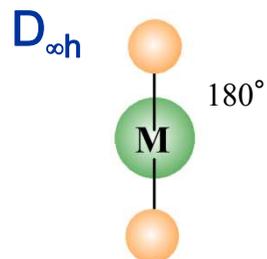
配位数 N = 2

3

4

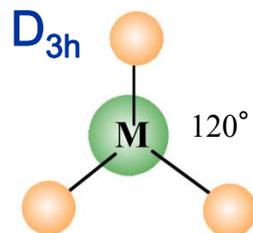
5

6



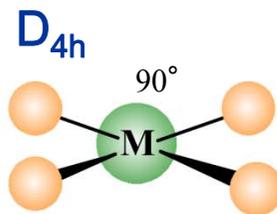
直線  
linear

Au(I), Ag(I)  
Cu(I), Hg(II)



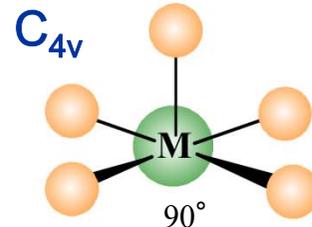
平面三角形  
trigonal  
planar

Cu(0), Pd(0)  
Pt(0)



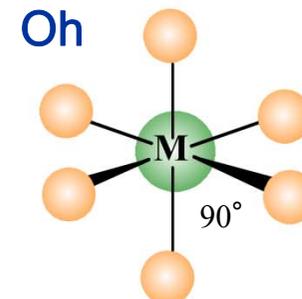
平面四角形  
square planar

Pt(II), Pd(II), Ni(II)  
Ir(I), Rh(I)



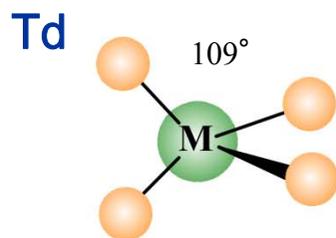
四角錐  
square  
pyramidal

$[\text{VO}(\text{H}_2\text{O})_4]^{2+}$   
 $[\text{Ni}(\text{CN})_5]^{3-}$



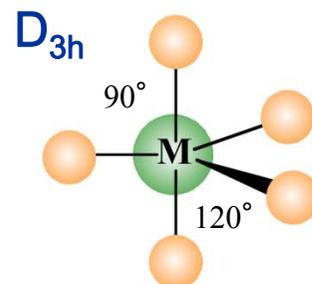
正八面体  
octahedral

Co(III), Rh(III), Ir(III)  
Pt(IV), Fe(II),  $d^6$ ,  $d^3$



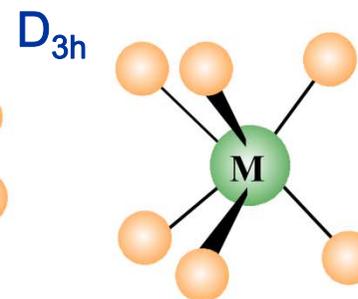
正四面体  
tetrahedral

Ni(0), Pd(0), Pt(0)  
Zn(II), L = X



三方両錐  
trigonal  
bipyramidal

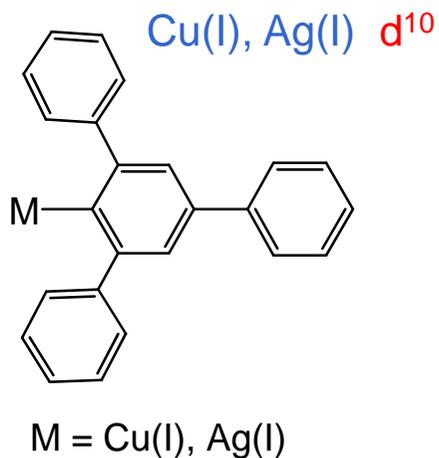
$[\text{Fe}(\text{CO})_5]$   
 $[\text{CoH}(\text{N}_2)(\text{PPh}_3)_3]$



三角柱  
trigonal prism

$[\text{Re}\{\text{SC}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{S}\}_3]$

## 一配位錯体 (極めて稀)



## 二配位錯体

Cu(I), Ag(I), Au(I), Hg(II)  
(Pd(0), Pt(0))  $d^{10}$

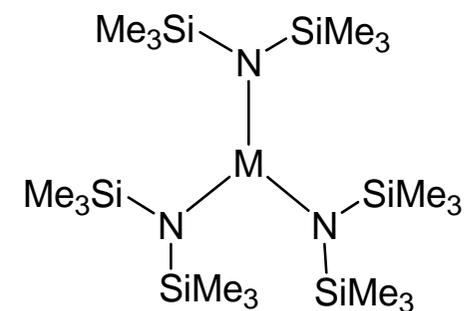
$[\text{CuCl}_2]^-$ ,  $[\text{Ag}(\text{NH}_3)_2]^+$ ,  $[\text{Au}(\text{CN})_2]^-$   
 $[\text{AuClL}]$  (L =  $\text{PR}_3$ ,  $\text{R}_2\text{S}$ ),  $[\text{Au}(\text{PR}_3)_2]^+$   
 $\text{Hg}(\text{CN})_2$ ,  $\text{Hg}(\text{CH}_3)_2$

低配位錯体(1  
~3配位)はほとん  
どが $d^{10}$ 閉殻金属  
である。それ以外  
は嵩高い配位子を  
含む。

## 三配位錯体

Cu(I), Ag(I), Au(I), Hg(II)  
(Pd(0), Pt(0))  $d^{10}$

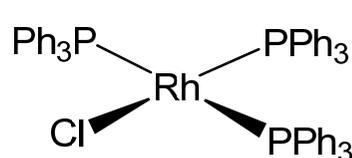
$[\text{Cu}(\text{CN})_2]^-$ ,  $[\text{Ag}(\text{PPh}_3)_3]^+$ ,  $[\text{Au}(\text{PPhCy}_2)_3]^+$   
 $[\text{HgI}_3]^-$ ,  $[\text{Hg}(\text{SPh})_3]^-$   
 $[\text{M}(\text{PPh}_3)_3]$  (M = Pd, Pt),  $[\text{Pt}(\text{PCy}_3)_3]$



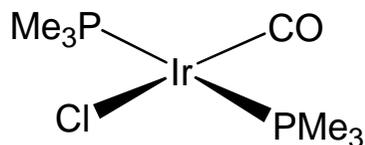
M = Fe(III), (Sc(III), Y(III))

## 平面正方形錯体

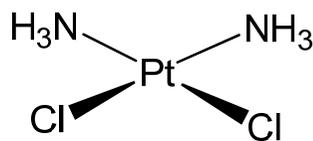
Pt(II), Pd(II), Ni(II)

Ir(I), Rh(I), Au(III)  $d^8$  $[\text{RhCl}(\text{PPh}_3)_3]$  Wilkinson錯体 (1) $\text{trans-}[\text{IrCl}(\text{CO})(\text{PMe}_3)_2]$  Vaska錯体 (2) $[\text{M}(\text{CN})_4]^{2-}$  (M = Ni, Pd, Pt), $[\text{MCl}_4]^{2-}$  (M = Pd, Pt) $[\text{Pt}(\text{NH}_3)_4]^{2+}$ ,  $\text{cis-}[\text{PtCl}_2(\text{NH}_3)_2]$  シスプラチン (3) $[\text{AuCl}_4]^-$ 

(1)

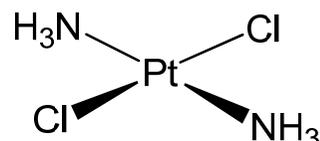


(2)



cis

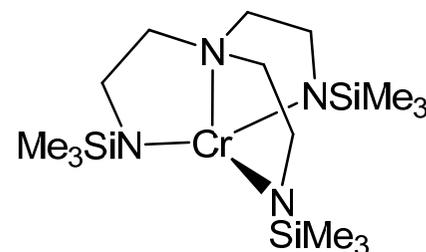
(3)



trans

 $[\text{CoCl}_4]^{2-}$  ( $d^7$ の平面正方形錯体では数少ない例)

## 四面体形錯体

多くの $\text{MX}_4$  アニオン (X = F, Cl, Br, I)高原子価の $\text{MO}_4$ アニオン $d^0$ :  $[\text{VO}_4]^{3-}$ ,  $[\text{CrO}_4]^{2-}$ ,  $[\text{MnO}_4]^-$  $[\text{MoS}_4]^{2-}$ ,  $[\text{WS}_4]^{2-}$  $d^1$ :  $[\text{MnO}_4]^{2-}$ ,  $[\text{TcO}_4]^{2-}$ ,  $[\text{ReO}_4]^{2-}$  $[\text{RuO}_4]^-$  $d^2$ :  $[\text{FeO}_4]^{2-}$ ,  $[\text{RuO}_4]^{2-}$  $d^5$ :  $[\text{FeCl}_4]^-$ ,  $[\text{MnCl}_4]^{2-}$  $d^6$ :  $[\text{FeCl}_4]^{2-}$ ,  $[\text{FeI}_4]^{2-}$  $d^7$ :  $[\text{CoCl}_4]^{2-}$  $d^8$ :  $[\text{NiCl}_4]^{2-}$ ,  $[\text{NiBr}_4]^{2-}$  $d^9$ :  $[\text{CuCl}_4]^{2-}$  (distorted) $d^{10}$ :  $[\text{Ni}(\text{CO})_4]$ ,  $[\text{Cu}(\text{CN})_4]^{3-}$  $[\text{ZnCl}_4]^{2-}$ ,  $[\text{Zn}(\text{OH})_4]^{2-}$  $[\text{CdCl}_4]^{2-}$ ,  $[\text{HgBr}_4]^{2-}$  $(d^3, d^4)$ の四配位錯体は稀である

## 四角錐形錯体

## 三方両錐形錯体

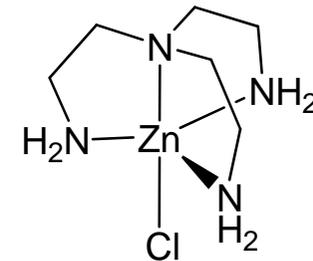
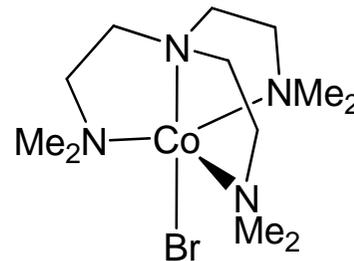
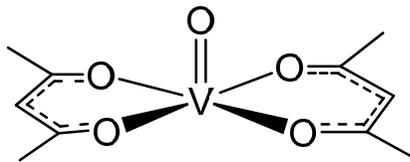


これらのエネルギー差は小さい  
(Berry擬回転)

5配位構造指標  
( $\tau$  value =  $(\theta_{\max} - \theta_{2\text{nd}})/60$   
= 1 (tbp), 0 (sp))

- d<sup>0</sup>: [Nb(=O)Cl<sub>4</sub>]<sup>-</sup>  
 d<sup>1</sup>: [V(=O)(acac)<sub>2</sub>], [W(=O)Cl<sub>4</sub>]<sup>-</sup>  
 [Tc(≡N)Cl<sub>4</sub>]<sup>-</sup>, [Tc(≡N)Br<sub>4</sub>]<sup>-</sup>  
 d<sup>2</sup>: [Tc(=O)Cl<sub>4</sub>]<sup>-</sup>, [Re(=O)Cl<sub>4</sub>]<sup>-</sup>  
 d<sup>8</sup>: [Ni(CN)<sub>5</sub>]<sup>3-</sup>

- d<sup>8</sup>: [Fe(CO)<sub>5</sub>],  
 [CoH(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>3</sub>]  
 [Ni(CN)<sub>5</sub>]<sup>3-</sup>

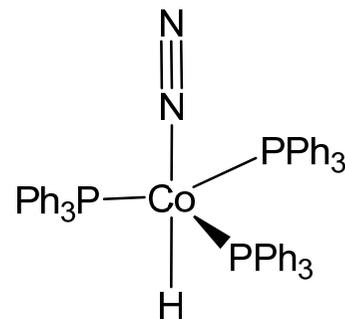
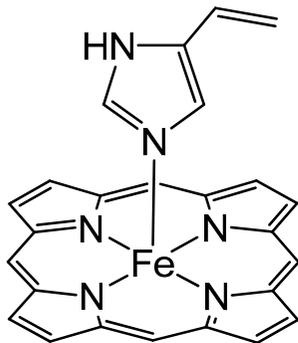


tripodal ligandsは  
tbpを安定化

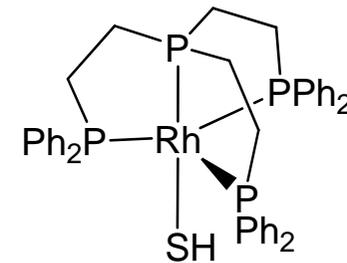
[CoBr(Me<sub>6</sub>tren)]

[ZnCl(tren)]

Hb model

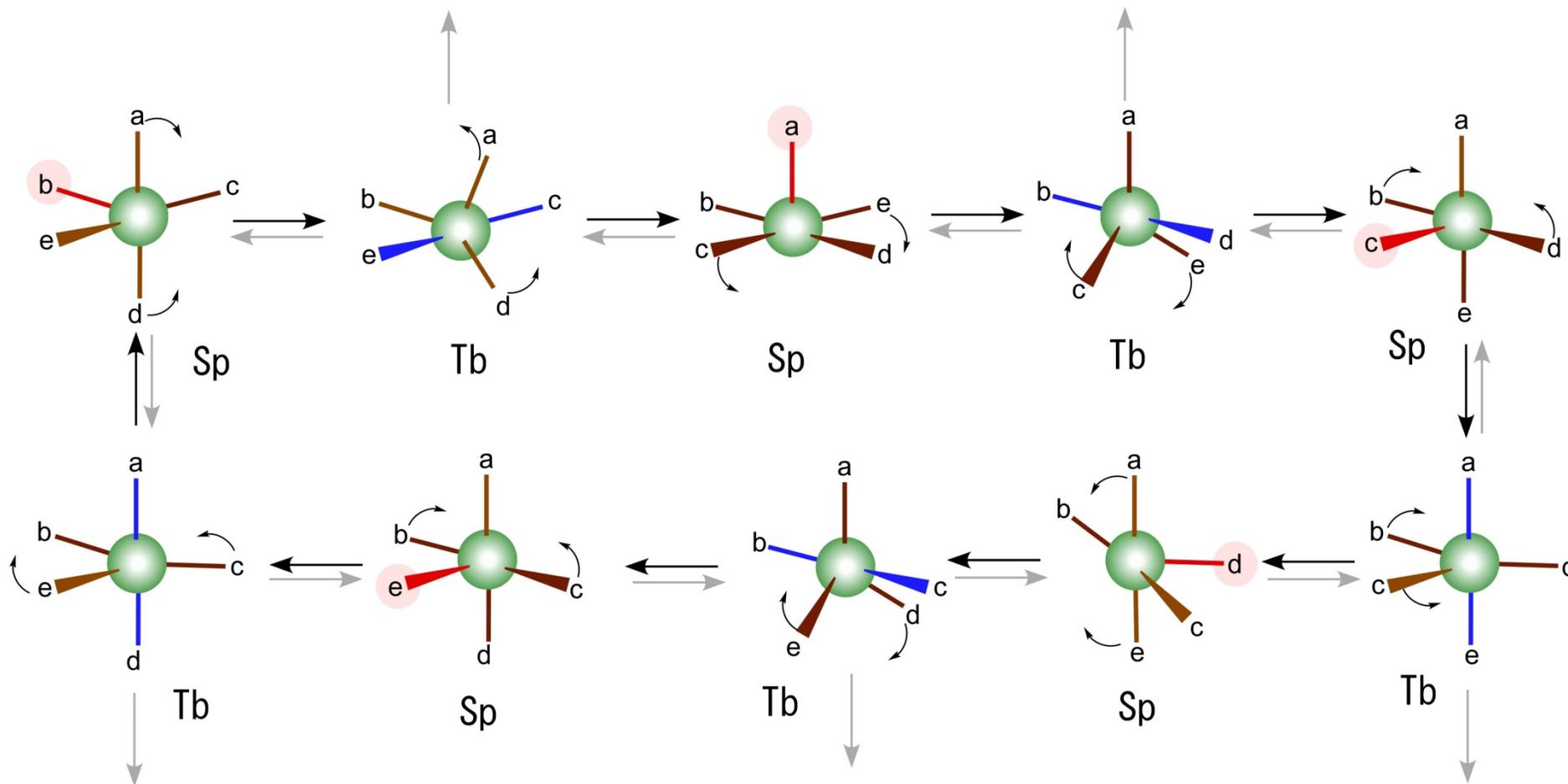


[CoH(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>3</sub>]



[Rh(SH)(P(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>)]

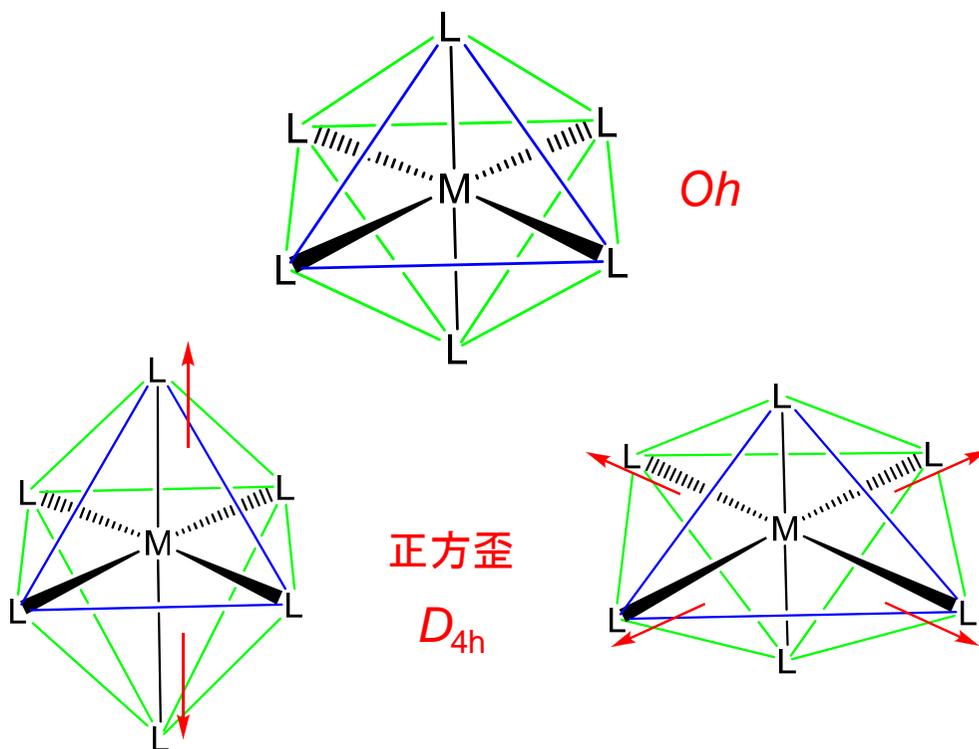
ベリ-擬回転  
(Berry Pseudorotation)



## 八面体形錯体

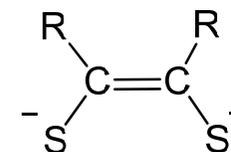
多くの  $d^3$ ,  $d^6$  錯体 (これ以外も多い)  
 Cr(III), Fe(II), Co(III), Rh(III)  
 Ir(III), Pd(IV), Pt(IV)  
 $[M(H_2O)_6]^{2+}$  (M = Fe, Co, Ni, Cu, Zn)  
 $[M(H_2O)_6]^{3+}$  (M = Ti, V, Cr, Mn)

$d^4$  (Mn(III)),  $d^9$  (Cu(II)) は Jahn-Teller 正方歪

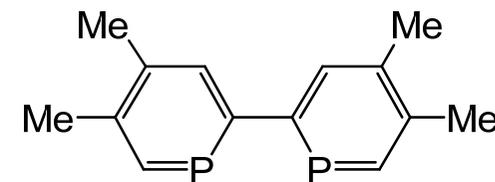


## 三角柱形錯体

数少ない  
 $[Zr(CH_3)_6]^{2-}$ ,  
 $[M(S_2C_2R_2)_3]$  (M = Mo, R = H; M = Re, R = Ph)  
 $[WL_3]$ ,  $[ML_3]^{2-}$  (M = Ti, Zr, Hf, L =  $P_2C_{14}H_{16}$ )



$S_2C_2R_2^{2-}$  (ジチオレン)  
 R = H, Ph,  $CF_3$   
 small normalized bite (d/r)

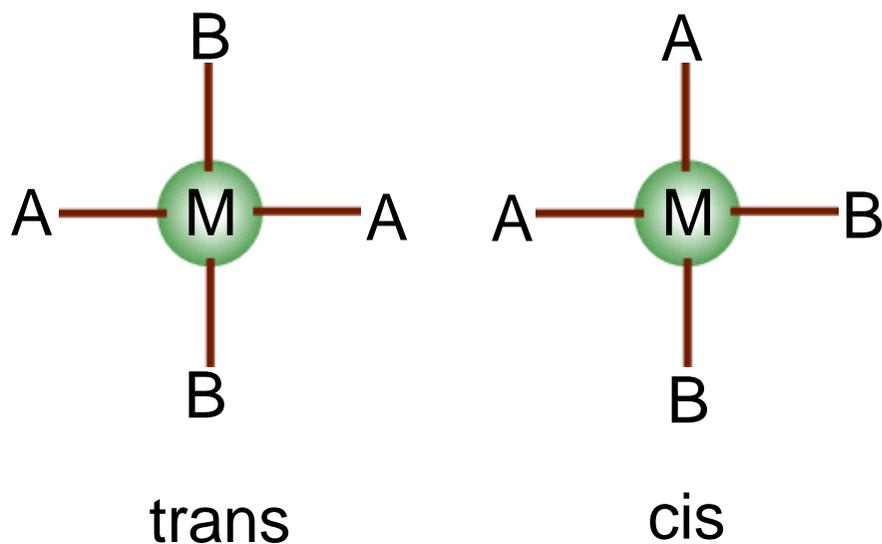


$P_2C_{14}H_{16}$  (phosphinine)

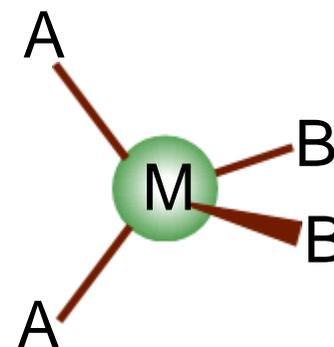
## 幾何異性体 (Geometrical Isomers)



平面四角形錯体



四面体形錯体

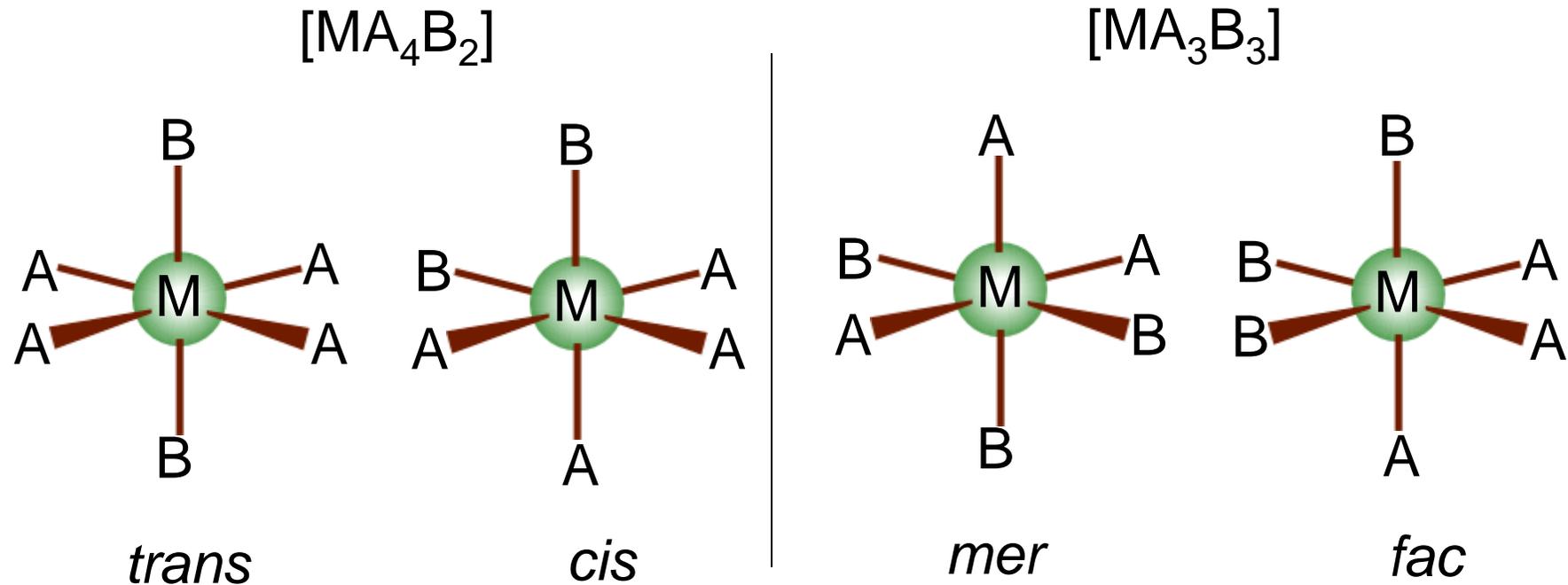


【練習】  $[PdClBr(PPh_3)_2]$ ,  $[PtClBr(PPh_3)_2]$  の幾何異性体構造について  $^{31}P\{^1H\}$  NMR スペクトルで考察せよ。

【参考】核スピンに関するデータ:  $^1H$  100%,  $I = \frac{1}{2}$  100 MHz,  $^{19}F$  100%,  $I = \frac{1}{2}$  94 MHz,  $^{31}P$  100%  $I = \frac{1}{2}$  40.5 MHz,  $^{195}Pt$  34%  $I = \frac{1}{2}$  24.1 MHz,  $^{103}Rh$  100%  $I = \frac{1}{2}$  3.2 MHz

## 幾何異性体 (Geometrical Isomers)

## 八面体形錯体



【練習1】  $[MA_2B_2C_2]$ の幾何異性体構造について考察せよ。(鏡像異性体も考慮する)

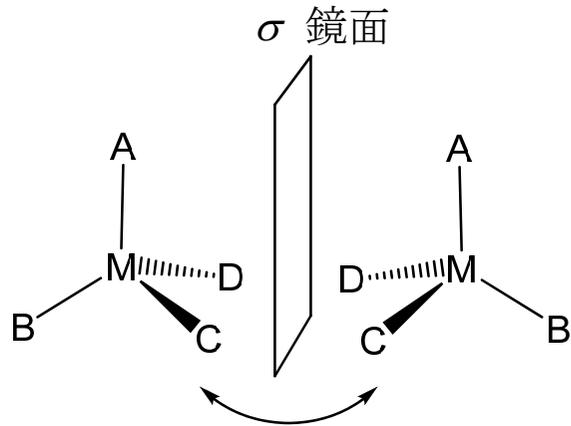
【練習2】  $[M(\text{gly})_2(\text{H}_2\text{O})_2]$ の幾何異性体構造について考察せよ。(glyのN-Oキレート  
の立体配座については考えなくてよい)

【練習3】 A, B, C 3種類の単座配位子を含む  $[MA_nB_mC_l]$  ( $n+m+l=6$ ;  $n, m, l \geq 1$ )の幾何異性体は全部でいくつか。(鏡像異性体は考えなくてよい)

# 鏡像異性体 (Enantiomeric Isomers)

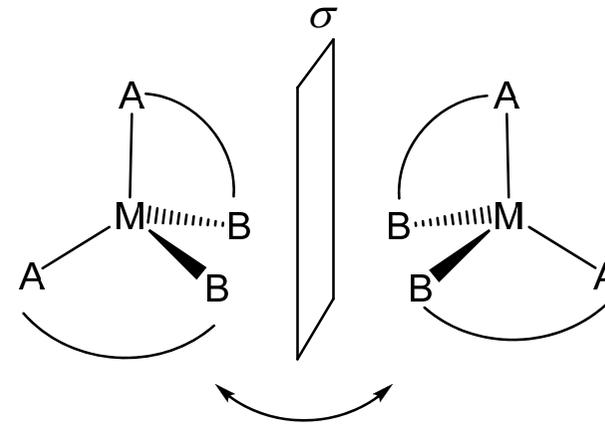
## 四面体形錯体

[MABCD]  $C_1$  Chiral (中心性不斉)



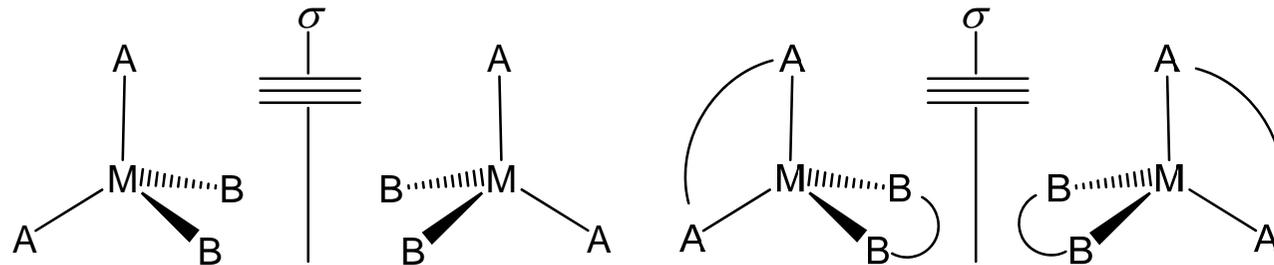
鏡像異性体 (enantiomer)

[M(A-B)<sub>2</sub>]  $C_2$  Chiral (軸性不斉)



鏡像異性体 (enantiomer)

金属周りの絶対配置 (Absolute Configuration)  
R/S (Cahn, Ingold, Prelog)



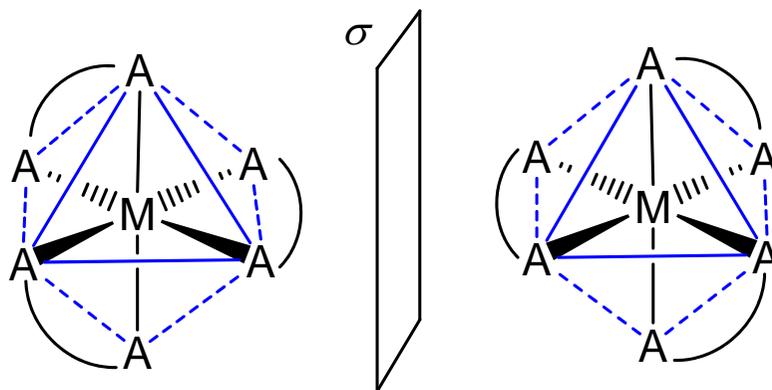
【注意】これらは同一。cis, transの幾何異性体もない

# 鏡像異性体 (Enantiomeric Isomers)

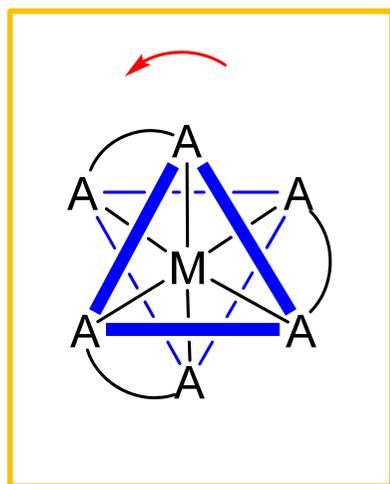
## 八面体形錯体



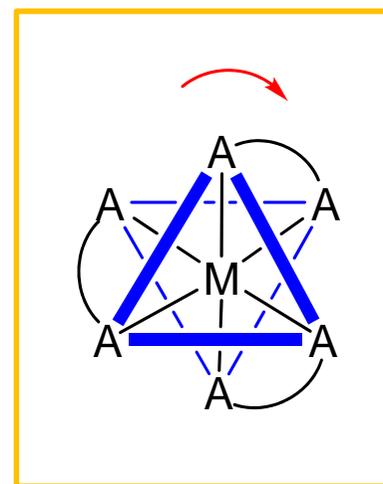
$C_3$  Chiral (軸性不斉)



鏡像異性体 (enantiomer)



金属周りの絶対配置  
(Absolute Configuration)

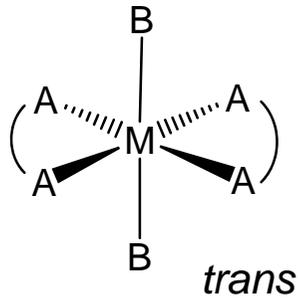


【練習】  $[M(A-B)_3]$  の (立体配置) 異性体について考察せよ。

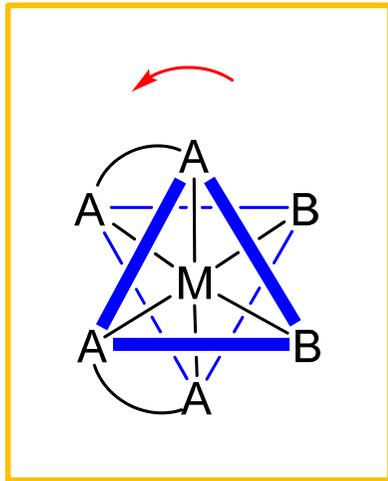
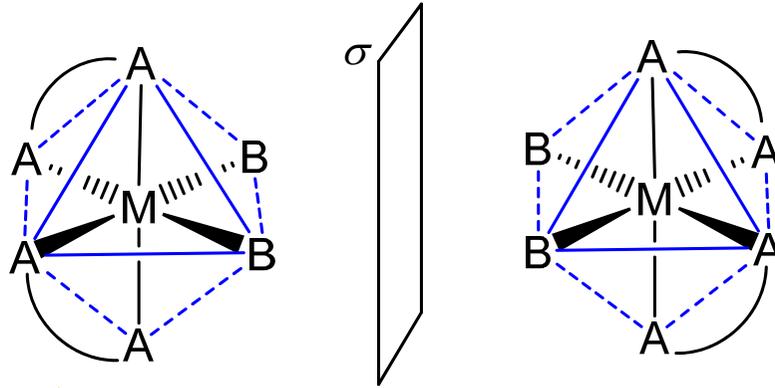
# 鏡像異性体 (Enantiomeric Isomers)

## 八面体形錯体

【参考】対象要素  $i(S_2)$ ,  $\sigma(S_1)$ ,  $S_n$ があるとアキラル



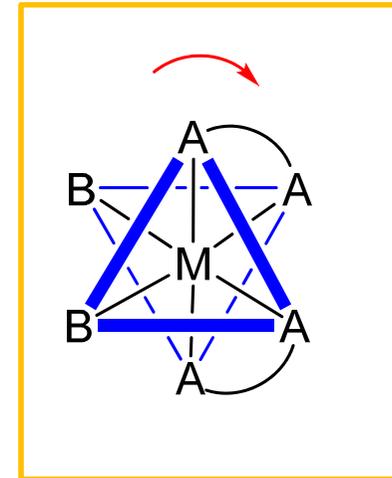
Helical chirality (らせん不斉)



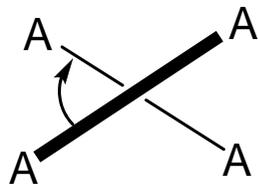
$\Lambda$

鏡像異性体 (enantiomer)

金属周りの絶対配置  
(Absolute Configuration)



$\Delta$



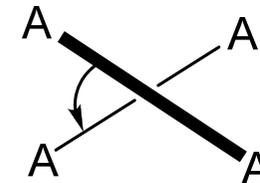
$\lambda$

左巻き螺旋

Skew-line convention

$\delta$

右巻き螺旋

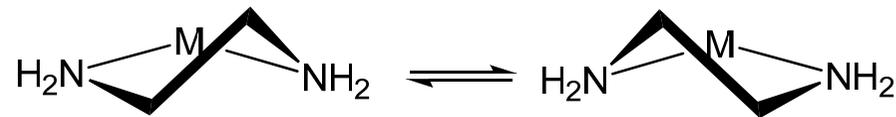
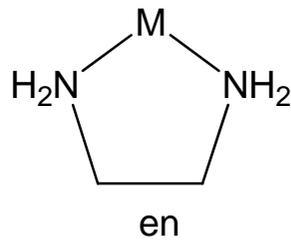


【参考】  $trans-[CoCl_2(en)_2]Cl$  (緑),  $cis-[CoCl_2(en)_2]Cl$  (紫)

# 立体配座異性体 (Conformational Isomers)

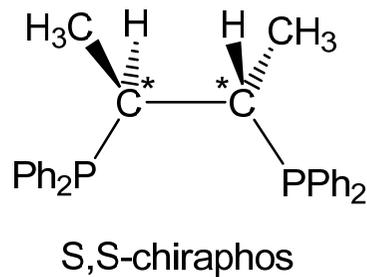
結合を切断することなく、単結合周りの自由回転によって発生する立体配座 (conformation) の中で安定な構造を立体配座異性体という。

5員環キレート構造



λ ゴーシュ (gauche)

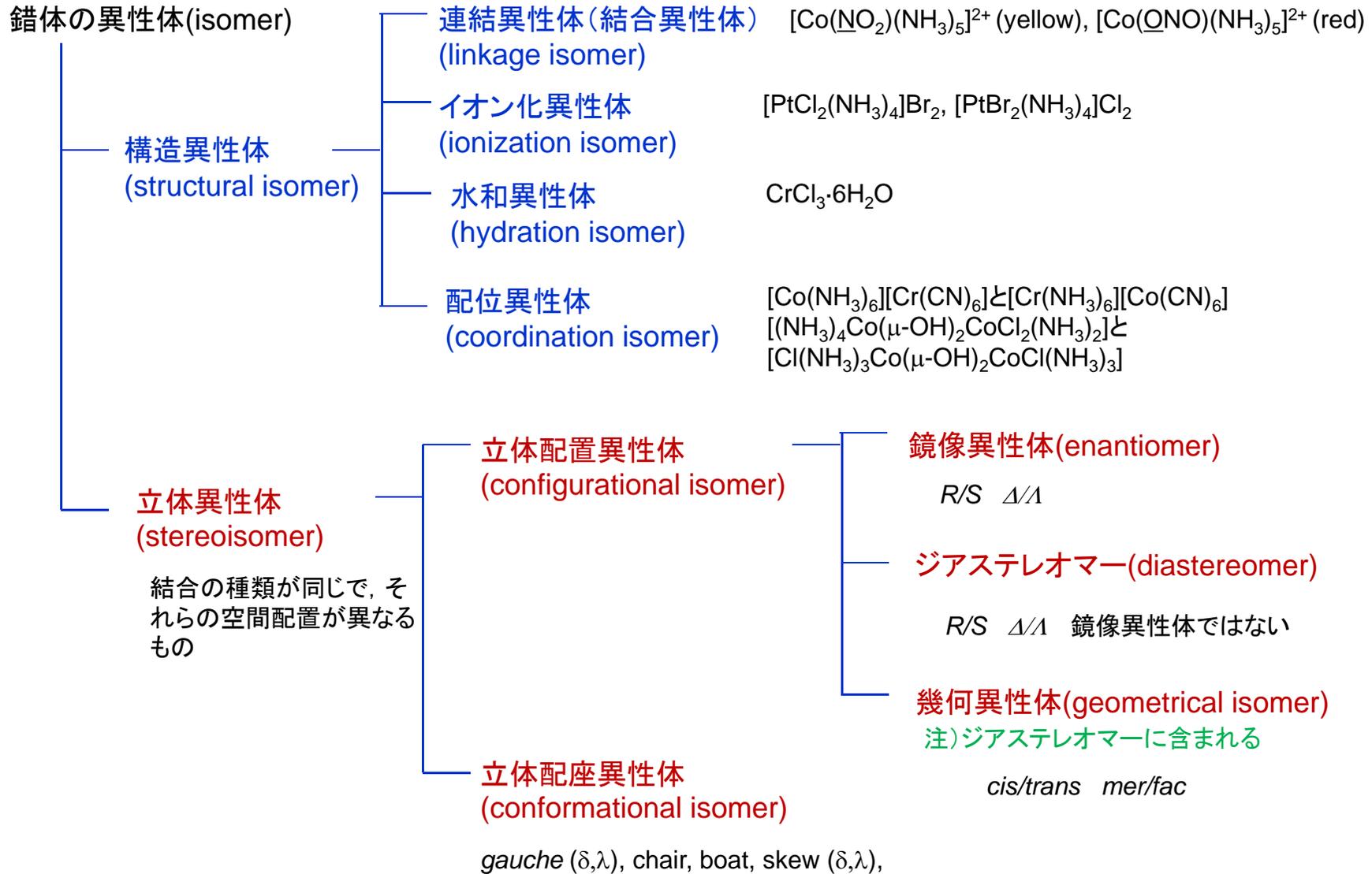
δ ゴーシュ (gauche)



【練習1】1,3-プロパンジアミン (pn) の6員環キレートの立体配座について考察せよ。

【練習2】S,S-chiraphos (左図) の5員環キレートの立体配座について考察せよ。

# 錯体の異性現象



# 錯体の命名法 nomenclature



配位子はアルファベット順  
(倍数接頭語は別)

 錯イオン(カチオン)の場合: トリ( A )ジ( B )(金属)(酸化数)イオン

 錯イオン(アニオン)の場合: トリ( A )ジ( B )(金属)(酸化数)酸イオン

 化学式の場合:  $[M(\text{アニオン配位子})_n(\text{中性配位子})_m]^{p+ \text{ or } q-}$  中性錯体は0を書かない  
配位子はそれぞれで配位原子のアルファベット順

【例】:  $[\text{Co}(\text{NH}_3)_6]^{3+}$  ヘキサアンミンコバルト(III)イオン

$[\text{Re}_2\text{Cl}_8]^{3+}$  オクタクロロ二レニウム(III)酸イオン  
(二は漢字)

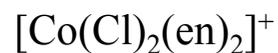
$[\text{Cr}_2(\mu\text{-O})(\text{NH}_3)_{10}]^{4+}$   $\mu$ -オキソビス[ペンタアンミンクロム(III)]イオン

$[\text{Co}(\text{en})_3]^{2+}$  トリス(エチレンジアミン)コバルト(II)イオン

$[\text{Fe}(\underline{\text{NCS}})(\text{OH}_2)_5]^{2+}$  ペンタアクア(チオシアナト-N)鉄(II)イオン

【参考】mono, di (bis), tri (tris), tetra (tetrakis), penta (pentakis), hexa (hexakis), hepta (heptakis)  
octa (octakis), nona (nonakis), deca (decakis), undeca, dodeca, trideca, ...

【練習問題 1】以下の錯体に名前を付け，構造を書け。



【練習問題 2】以下の錯体の化学式と構造を書け。

ジアクアジクロロ白金(II)

ジアンミンテトラ(チオシアナト-*N*)クロム(III)酸イオン

トリス(エチレンジアミン)ロジウム(II)

ブロモペンタカルボニルマグネシウム(I)

クロロトリス(トリフェニルホスフィン)ロジウム(I)