Chapter 2: Dative Ligands

2.1 Introduction

Chapters 2-4: presents illustrative summary of the types of complexes
Chapter 2: **steric and electronic properties of neutral ligands**
(Chapters 3&4: formally anionic ligands)

2.2 Carbon Monoxide and Related Ligands

2.2.1. Properties of Free Carbon Monoxide

CO

- small dipole moment with negative end located on carbon
- strong vibration in IR at 2143 cm^{-1}
- neutral ligand, commonly binds to metal C's lone pair elecrtrons
- normally binds to one metal, but bridging coordination is possible (M-C-M angle is much less than 120°)

2.2.2. Types of Metal Carbonyl Complexes

- **Preparation of metal-carbonyl complexes**

- from bulk metal

$$Ni \xrightarrow{\text{1atm } \mathbf{CO}} Ni(CO)_4$$

- from reduction of complexes in higher oxidation state

$$Re_2O_7 + 17CO \longrightarrow Re_2(CO)_{10} + 7CO_2$$

$$WCl_6 + CO + Et_3Al \longrightarrow W(CO)_6$$

- **polynuclear carbonyl complexes**

$Fe(CO)_5$	$Os(CO)_5$	$Os_3(CO)_{12}$
stable	much less stable	more stable

homoleptic carbonyl complexes
in **2nd** and **3rd row**
↓
polynuclear structure
is more favorable

Classification of metal carbonyl complexes: Figure 2.2

2.2.3. Models for CO Binding: Introduction of Backbonding

- CO binds strongly to **electron-rich**, **low valent** metals (backbonding, soft metal and soft ligand)

2.2.4. Evidnce for Backbonding in Terminal Carbonyl

IR, C-O length

2.2.5. Infrared and X-ray Diffraction Data for Complexes with Bridiging Carbonyls

2.2.6. Thermodynamics of the M-CO Bonds

dissociation of CO ligands: key step in many reactions

Table 2.3

- $Cr(CO)_6 < Mo(CO)_6 < W(CO)_6$
- $Ni(CO)_4 < Cr(CO)_6$ — higher enegy of orbitals, backdonation
- $Ir(P^iPr_3)_2Cl(CO)$ (particulary strong) — third row, electron-rich alkylphosphine

2.2.7. Isoelectronic Analogs of CO: Isocyanides and Thiocarbonyls

$C\equiv N-R$

isocyanide

- stronger σ-donor, weaker π-acceptor than CO
- weaker C-X π-bond than CO

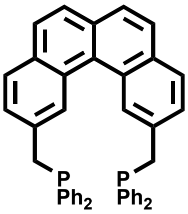
2.3 Dative Phosphorous Ligands and Heavier Congeners

2.3.1 Tertiary Phosphines and Related Ligands

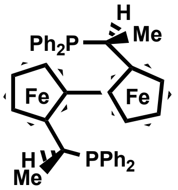
2.3.2 Chelating Phosphines

bidentate, asymmetric bisphosphine, P-M-P angle

trans coordination



Transphos



Ph-Trap

2.3.3 Properties of Free Phosphines

PR_3 vs **NR_3** ⟶

- **binding**: to transition metals more strongly (soft-soft)
- **steric effect**: less pronounced (larger atom, longer M-P)
- high inversion barrier => P-chiral phosphine

- Ar_3P, $(RO)_3P$ less sensitive to air (less electron rich)

2.3.4 Properties of Phosphine Complexes

2.3.4.1 Bonding and Electronic Properties

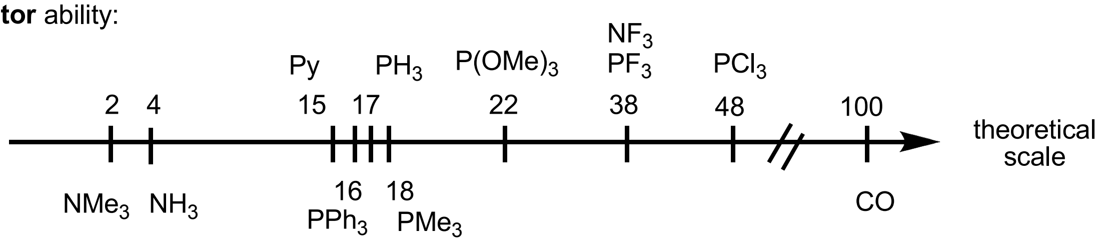
- **Electron-donating ability:** **$R_3P > Ar_3P > (RO)_3P$**

greater s-character of sp^2-hybridized orbital of aryl
=>weaker electron donor than alkyl

electron-donation: alkyl > alkoxy

- **π-acceptor orbital**: hybrid of P-X σ*-orbital and phosphorus *d*-orbital (Figure 2.9)

- **π-acceptor** ability:



- **electron donating ability (ν_{CO} in $[Ni(CO)_3L]$)**

L	ν_{CO} (cm^{-1})	L	ν_{CO} (cm^{-1})
$\mathrm{P}\mathit{t}\mathrm{Bu}_3$	2056	PPh_3	2069
PCy_3	2056	$P(OMe)_3$	2079
PMe_3	2064	$P(OPh)_3$	2085
$P(C_6H_4\text{-}4\text{-}OMe)_3$	2066	PF_3	2110

2.3.4.2 Steric Properties

cone angle, solid angle (figure 2.11)

2.3.4.3 Effect of Phosphine Steric and Electronic Properties on Structure and Reactivity

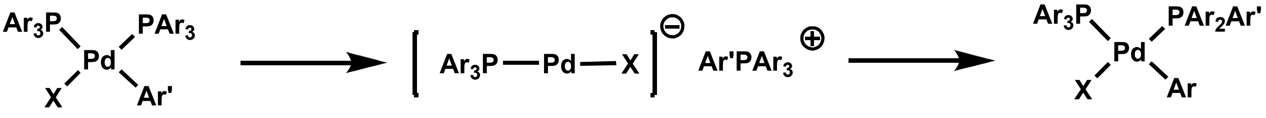
- ligand dissociation in NiL_4 (and related Pd complexes) $PMe_3 < PMe_2Ph < PMePh_2 < PEt_3 < PPh_3 < \mathrm{P}\mathit{i}\mathrm{Pr}_3 < PCy_3 < \mathrm{PPh}\mathit{t}\mathrm{Bu}_2$

- **bulky phosphines** bind **trans** to one another

- **deviation from the ideal coordination geomety** because of **bulky** phosphines
  e.g.) Wilkinson complex **$RhCl(PPh_3)_3$**=> **nonplanar** (normally, square planar for d^8 Rh(**I**))

2.3.5 Pathways for the Decomposition of Phosphorus Ligands

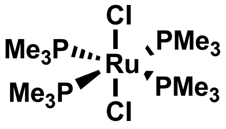
- **oxidation**: more electron rich phosphine
- **P-C bond cleavage**



- **P-X clevage** (X =OR, NR_2) by water or alcohol

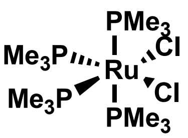
2.3.6 NMR Spectroscopic Properties of Phosphines

^{31}P: 1/2 spin, 100% abundant
relative receptivity: 0.0665 (H = 1, C = 0.000175)



trans

δ: - 6.63 (s)



cis

δ: 9.0 (t) -12.7 (t)
J = 35 Hz

2.3.7 Heavier Congeners of Phosphorus Ligands

M-L bond strength	P > As > Sb > Bi
Steric effect of substituents	P > As > Sb (M-L bond length)
P-C/As-C cleavage	P > As

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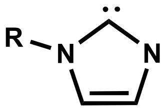
2011/5/12 Kimura

2.4 Carbenes

2.4.1. Classes of Free and Coordinated Carbenes

2.4.1.1 Properties of Free Carbenes

	more stable in
carbenes with **electron negative substituents**	**singlet** state
with **only hydrogen or alkyl groups**	**triplet** state



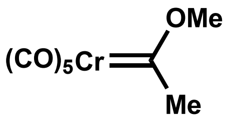
NHC

nitrogen acts as strong π-donor to unoccupied p-orbital

2.4.1.2 Properties of Carbene Complexes

Fischer Carbene

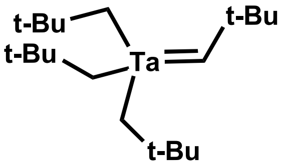
e.g.)



- **electrophilic** at carbene carbon
- carbene with **electronegative substituents**
- groups 6-8 (**late**) metal in a **low** oxdation state
- bearing π-accepting ligands such as CO
- M-C bond: not strongly polarized
- considered as **neutral** ligands
  (σ-donation and π-backdonation like CO)

Schrock Carbene

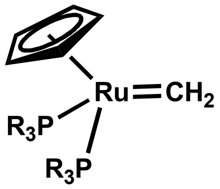
e.g.)



- **nucleophilic** at carbene carbon
- carbene with **hydrogen** or **alkyl groups**
- groups 4-6 (**early**) metal, **high** oxidation state
- more polar M-C bond
- considered as **dianionic** ligands

Hybrid of Fischer and Schrock Carbene

e.g.)

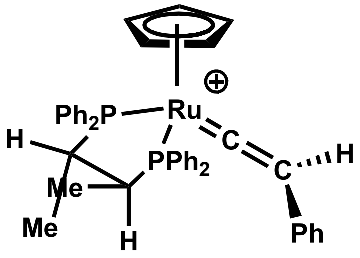


- **late metal, low oxidation state**
- carbane ligand **lacking heteroatom substituent**
- with **strongly donating ligand** inatead of CO

- **unsaturated hydrocarbyl group**
  such as phenyl or vinyl
- considered as **neutral ligand**

Vinylidene complex

e.g.)

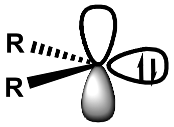


- one methylene substituent at carbene carbon
- free vinyldene: **electrophilic** (like dihalocarbene)
  : prone to rearrange to alkyne

- tautomers of alkyne and vinylidene (eq. 2.10a,b)
  (relative stability depends on
  the number and identity of ligand)
- **electrophilic** at carbene carbon (**C**α)
  nucleophilic at **metal** and **C**β

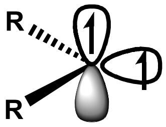
2.4.2. Bonding of Carbenes

siglet carbene



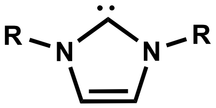
- closely related with CO
- donate two electrons to metal through a dative bond
- accept d-electrons in π-backbonding
- often have **weak p-bonds** (large ΔE bet. d_M and p_π)
- low rotation barrier (8~10 kcal/mol)

triplet carbene



- considered as dianionic
- donation of two electron pairs to metal (σ, π)

NHC



- **strong σ-donor**, weak π-acceptor
- σ: carbon is soft and less electronegative than most heteroatom Lewis base
- π: p-orbital of carbene carbon participates in strong π-bonding with amino subsituents
- like phosphine, but stronger σ-donor
- two fold symmetry ("fences rather than cones")

2.4.3. Spectroscopic Characteristics of Carbene Complexes

^{13}C	Fischer	X = O	290 ~ 365 ppm
		X = N	185 ~ 280 ppm
	Schrock		240 ~ 330 ppm
^{1}H			10 ~ 20 ppm

2.5 Transition Metal Carbyne Complexes

$M\equiv C-R$

carbyne

General Preparation Method
(1) via metathesis of M-M or M-L triple bond with alkyne
(2) transformation of existing ligand (carbene) into carbyne
(3) modification of existing carbyne to exchange substituents at carbyne C

Reactivity

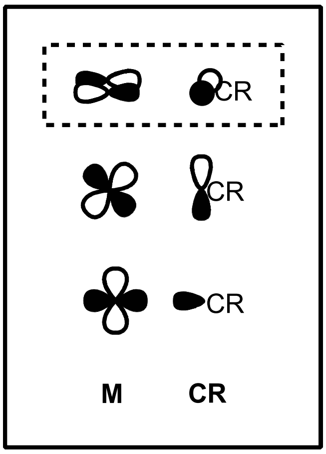
- [2+2] cycloaddition (Chapters 13 and 20)
- attack by nucleophiles (Chpter 11)
- by electrophiles (Chapter 12)

2.5.1.Bonding and Structure of Carbyne Comlexes

$M\equiv C-R$

carbyne

- mostly, **group 5~7** metal complexes
- carbene is typically considered **trianionic** (cf. monocationic like linear nitrosyl)
- bonding interaction: carbene + additional π-bond



- in the case of **heteroatom-substituted carbyne**
  - HOMO: metal
  - LUMO: one of the π*-orbitals of M-C bond
  - => nuclephiles attack carbyne carbon

- R = NR_2 (π-donor group): decrease π-acidity
- R = R_3Si (electropositive group): increase π-acidity

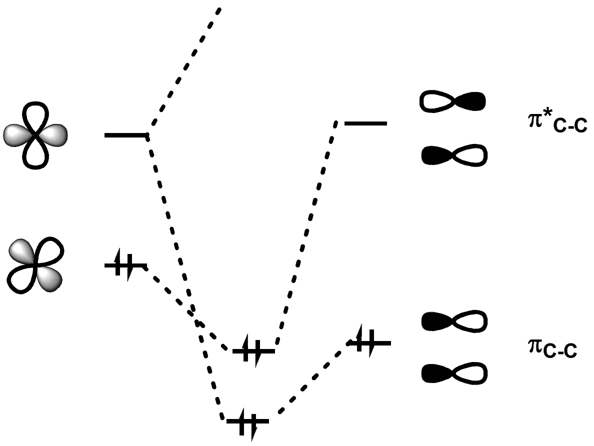
- R = alkyl (σ-donor group): increase the enegies of all the orbitals => more polarized M-C bond, **C** becmes more nucleophlic

2.5.2.Spectroscopic Characteristics of Carbyne Comlexes

^{13}**C**: 200 ~ 350 ppm, **triple bond vibration**: 1250 ~ 1400 cm^{-1}

2.6 Organic Ligands Bound Through More than One Atom

2.6.1 Olefin Comlexes



Chatt-Dewar-Duncanson
model

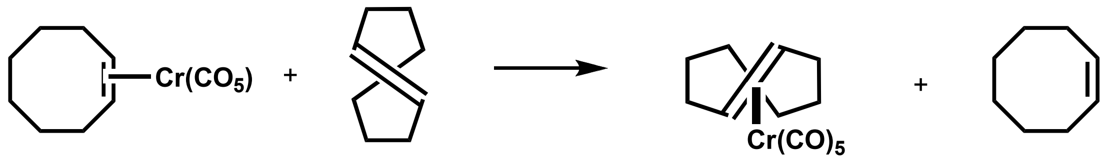
2.6.1.1 Stability of Metal-Olefin Comlexes

- **electron-rich** metal => olefin bering **EWG** (e.g. Ni(0))
- **M** in higer oxdation state (with charges greater than +1 and d^0): olefin complexes are **less common** (cf. olefin polymerization)
- also sensitive to **steric effects** (binding: ethylene > α-olefins)

2.6.1.2 Structures of Metal-Olefin Comlexes

2.6.1.2.1 Structural Changes Upon Binding

* backbonding: sp^2 => sp^3



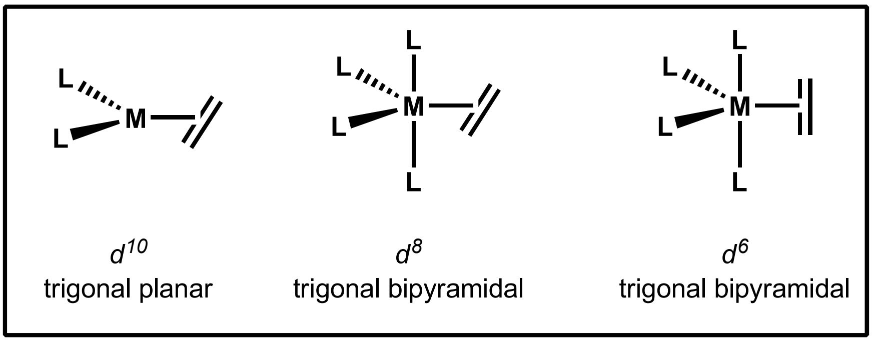
trans-cycloctene

cis-cycloctene

2.6.1.2.2 Structural Changes Upon Binding

σ-donor + **π-acceptor** ⟶ electronic **preference for orientaion** about M-olefin axis

orientation of olefin:
controlled by **metal HOMO** ⟶



d^{10}
trigonal planar

d^8
trigonal bipyramidal

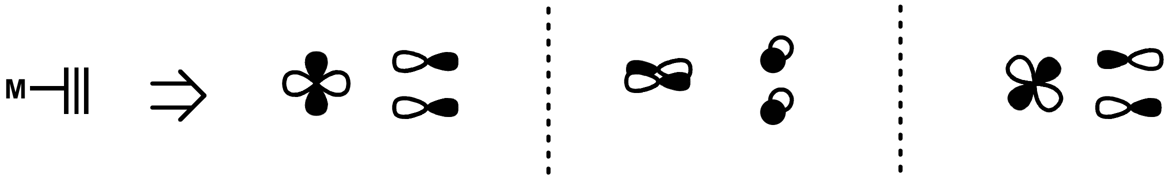
d^6
trigonal bipyramidal

2.6.1.3. Spectral Properties of Metal-Olefin Comlexes

NMR

- electron-poor metal complex: close to free olefin
- electron-rich metal complex: upfield shift

2.6.2 Alkyne Comlexes

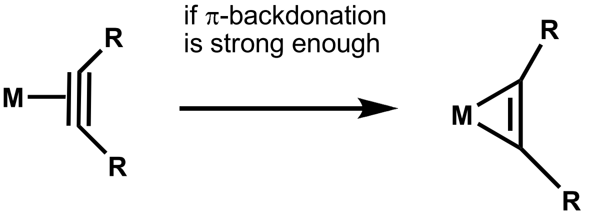


σ-Bonding

π-Donation

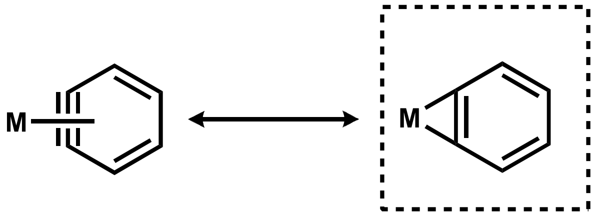
π-Backbonding

2.6.2.1 Structural Characteristics of Alkyne Complexes



distorted to the
geometry of cis-olefin

"metallacyclopropene"



strained alkynes stabilized upon
coordinationto the metal

2.6.2.2 Physical and Chemical Properties of Alkyne Complexes

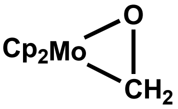
2.6.3 Complexes of Organic Carbonyl Compounds

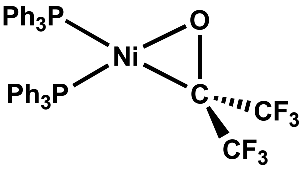
- **electron-rich** metal fragments
  (low-valent late metal)

⇓

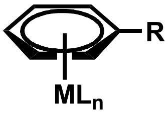
bind to aldehyde/ketone
in η^2-**fassion**

e.g.)



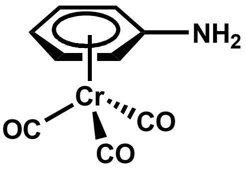


2.6.4 η^{6-} Arene and Related Complexes

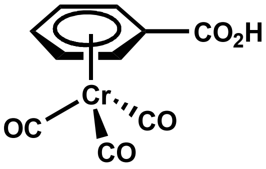


- arene is **stronger** electron donor than three CO ligands
- **electron-releasing substituents** on aromatic ring invariably stabilize η^6-arene ligand
- steric interactions counteract this electronic effect
- coordination with TM **depletes arene of much of its π-electron density**

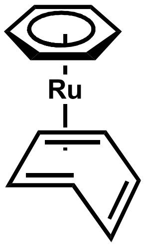
↓



less basic than aniline



more acidic than benzoic acid

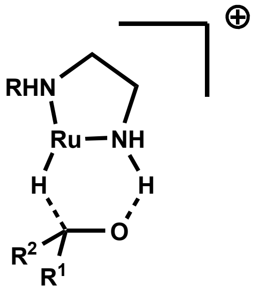


- η^4-arene complexes
- distortion from planarity, large loss of aromaticity
- prepared by reduction of (η^6-arene) dication

2.7 Complexes of Ligands Bound Through N, O and S

2.7.1 Neutral Nitrogen Donor Ligands

2.7.1.1 Amine Complexes



- ammonia, amines: classic ligand in coordination chemistry
- these Lewis bases are **less commonly** used
- **NH proton** of coordinated amine tend to be **reactive**

- tertiary amines bind weakly (hard-soft mismatch)
- tertiary amins are morer sterically congested than tertially phosphine
  (shorter C-N bond, larger C-N-C angle)

2.7.1.2 Pyridine and Imine Complexes

* examples: figure 2.39

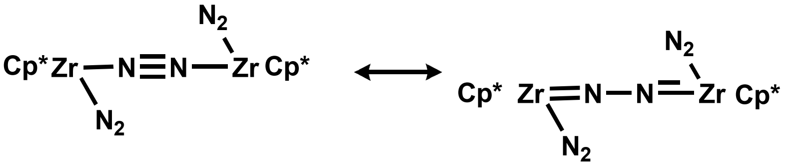
- nitrogens in pyridine, imine, oxazoline are softer
- heteroarenes can act as π-acceptors
- they lack reactive N-H bond
- monoimines tend to be reactive species

2.7.1.3. Dinitrogen Complexes

M—N$_2$

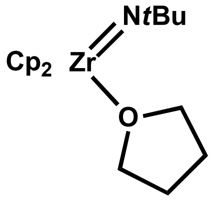
- N_2 is isoelctronic with CO, binds most often as an **η^1-ligand**
- less basic than CO, less π-acidic than CO

- π–**accepting ability of N_2 is stronge**r than σ-donating propety
- N_2 is generally **more electron-accepting** than it is electron-donating
- most dinitrogen complexes contain electron-rich metal center
- mostly, mononuclear complex, weak interaction



- dinuclear complex
- N-N bond is much longer
- much more activated N_2 in **side on** complex

2.7.1.4. Complexes of Neutral Oxygen Donors

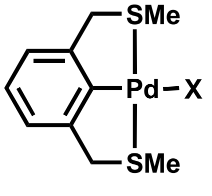


- H_2O, MeOH, THF, DME, acetone DMSO, Ar_3PO etc.

- even **dessociate readily** from more-oxophilic high-valent transition metals
- **R_3PO** tend to bind more **strongly** than **R_2O**
- despite of weak bindings, these can influence reaction chemistry (without forming stable complexes)

- THF, DME, phosphine oxides are common (Figure 2.44)
- dissociate readily => temporaly masking of reactive intermediate
- bindentate ligand with mixture of P and OR (figure 2.45)

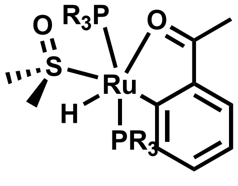
2.7.1.5. Complexes of Neutral Sulfur Donors



- neutral **sulfur** donors: **softer** and more polarizable than neutral oxygen donors
- **thioethers** and **sulfoxides** are most common

- **trans influence** of neutral sulfur donor is **greater than** neutral **oxygen donor**

  compatible with amine
- **M-SR$_2$** is stronger than **M-NR$_3$** bond, but weaker than **M-PR$_3$** bond
- spectrochemical series: $PR_3 > SR_2 > Cl^-$



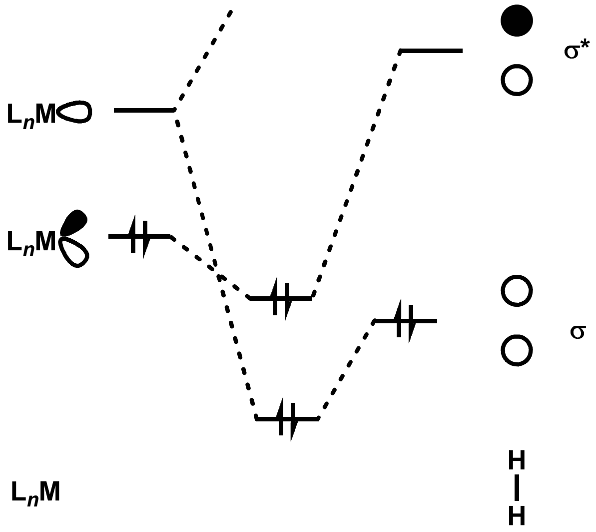
DMSO

- to **low-valent** late metals: through electron pair on **sulfur**
- to harder **high-valent** metals: through electron pairs on **oxygen**

- DMSO can **induce isomerization** of square-planar complexes to nonrigid five-coordinate intermediate

2.8 Sigma Complexes

2.8.1. Overview of Sigma Complexes



- dihydrogen, alkanes, silane, boranes (X-H bond)

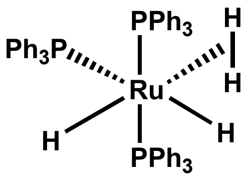
- electron donation from X-H σ-bonding orbital
- backdonation from metal to X-H σ*-orbital

- like olefin's Chatt-Dewar-Duncanson model (σ–**donation** from π-bonding and **backbonding** to π*-orbital)
- bonding intercation is much weaker than olefin
- σ-bonding enegy is in lower (**less basic**)
- σ*-bonding is higher in enegy (**less π-acidic**)

- ΔE between σ and σ* is too large?
  -> complexation => longer X-H bond => less ΔE

2.8.2 Dihydrogen Complexes

2.8.2.1 Properties that Lead to Stable H_2 Complexes



- H_2-complexes: arrested oxidative addition of dihidrogen
- metal backbonds to H_2 σ*, but cleaves H-H **only partially**

- most metal: **in low oxidation stat**e (backbonding)
- many of these low-valent complexes are **cationic** (neutral, low-valent metal is too much electron-rich)
- **neutral H_2** complexes have **π-accepting carbonyl group**

[**Mo**(**H_2**)(CO)(dppe)$_2$] : **dihydroge**n complex

[**WH_2**(CO)(dppe)$_2$] : **dihydride** complex

second-row metals: **dihydrogen** complex

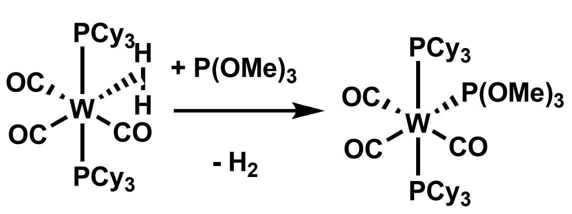
third-row metals: **dihydride** complex

2.8.2.2 Spectroscopic Signatures of H_2 Complexes

2.8.2.3 Reactivity of H_2 Complexes

*** reactivity** →

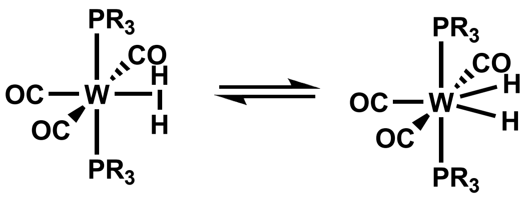
- dissociation of dihydrogen
- addition of dihydrogen to form dihydride
- deprotonation of hydrogen by external base



Dissociation of H_2

- H_2 is replaced by **CO, PR_3, nitriles**
- not replaced by H_2O nor ethers
- binding entropic term is surprizingly large

- rate of substitution reaction => **0 order** in incoming ligand
- rate of displacement = **rate of dissociation of H_2**



Addition of H_2 to form dihydride

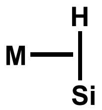
- oxidative addition to cleave H-H bond
- in many cases. **equibrium** between H_2 and dyhydride

- barrier: **structural change** to accomodate two hydrides
- in some cases: **dihydrogen as kinetic produc**t at low temp.

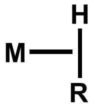
2.8.3 Alkane and Silane Comlexes

- property and reactivity: closely **related to those of dihydrogen complexes**
- **silane** complexes: similar stability to dihydrogen-comlex (or slightly unstable)
- **alkane** complexes: not so much study (too unstable in solution)

2.8.3.1 Stability Relative to H_2 Complexes



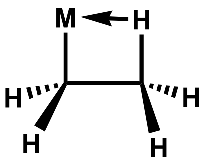
- **silane** complexes: **simila**r stabiliy to **dihydrogen complexes** (despite greater steric effect)
  ⇐ Si-H bond is **more basi**c than H-H or R-H bond
  ⇐ Si-H bond is much longer weaker, has **lower energy σ*-orbital**



- **alkane** complexses: **less stable** than H_2 or Si-H complexes
  ⇐ steric effect is **not compensated** by smaller ΔE between σ and σ*-orbitals

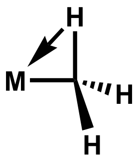
2.8.3.2 Evidence for Alkane Complexes

2.8.3.3 Intramolecular Coordination of Aliphatic C-H Bonds (Agostic Interactions)



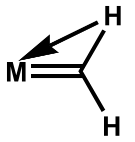
β-agostic

intermediate to
β-hydrogen elimination
(Chapte 10)



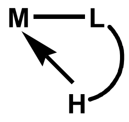
α-agostic

electrophilic
metal



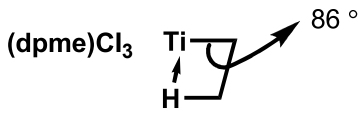
α-agostic

carbene in high
oxidation state



**agostic interaction
with a dative ligand**

unsaturated metal



severe distortion
from agostic
interaction

agostic interaction: dynamic

C-H in methyl: single peak in NMR