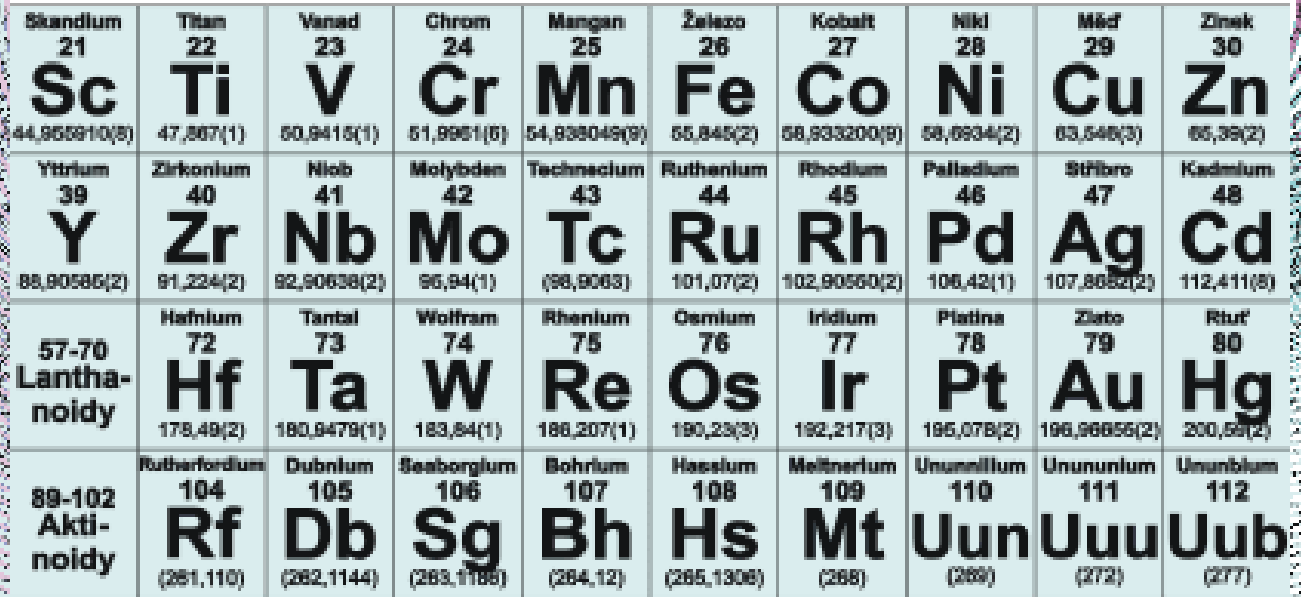
Transition metal complexes



Skandium	Titan	Vanad	Chrom	Mangan	Železo	Kobalt	Nikl	Měď	Zinek
21	22	23	24	25	26	27	28	29	30
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
44,955910(8)	47,867(1)	50,9415(1)	51,9961(6)	54,938049(9)	55,845(2)	58,933200(9)	58,6934(2)	63,546(3)	65,39(2)
Yttrium	Zirkonium	Niob	Molybden	Technecium	Ruthenium	Rhodium	Palladium	Stříbro	Kadmium
39	40	41	42	43	44	45	46	47	48
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
88,90585(2)	91,224(2)	92,90638(2)	95,94(1)	(98,9063)	101,07(2)	102,90550(2)	106,42(1)	107,8682(2)	112,411(8)
57-70 Lantha-noidy	Hafnium	Tantal	Wolfram	Rhenium	Osmium	Iridium	Platina	Zlato	Rtuť
	72	73	74	75	76	77	78	79	80
	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
	178,49(2)	180,9479(1)	183,84(1)	186,207(1)	190,23(3)	192,217(3)	195,078(2)	196,96655(2)	200,59(2)
89-102 Akti-noidy	Rutherfordium	Dubnium	Seaborgium	Bohrium	Hassium	Meitnerium	Ununnilium	Unununium	Ununbium
	104	105	106	107	108	109	110	111	112
	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub
	(261,110)	(262,1144)	(263,1186)	(264,12)	(265,1306)	(268)	(269)	(272)	(277)

Transition Metal Complexes

➢ The Nobel Prizes in Chemistry

1912 *V. Grignard* „for the discovery of the so-called Grignard reagent, which in recent years has greatly advanced the progress of organic chemistry“

1963 *K. Ziegle, G. Natta* „for their discoveries in the field of the chemistry and technology of high polymers“

1973 *E. O. Fischer, G. Wilkinson* „for their pioneering work, performed independently, on the chemistry of the organometallic, co-called sandwich compounds“

2001 *W. Knowles, R. Noyori, K. B. Sharpless* „for their work on chirally catalysed hydrogenation reactions“

2005 *Y. Chauvin, R. H. Grubbs, R. R. Schrock* „for the development of the metathesis method in organic synthesis“

2010 *R. F. Heck, E.-i. Negishi, A. Suzuki* „for palladium-catalyzed cross-couplings in organic synthesis“

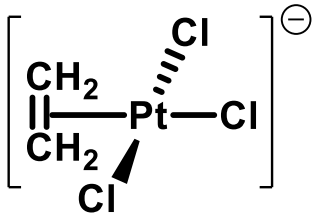
Transition Metal Complexes

➢ Milestones

- 1760 $As_2O_3 + MeCOOK \longrightarrow (Me_2As)_2O + 2\,K_2CO_3 + 2\,CO_2$

  Cadet´s fuming liquid
  red-brown liquid

- 1827 *Zeise´s* salt



- 1727 Dutch scientist *Heman Boerhaave* discovered H_2NCONH_2
- 1828 Urea was synthesized by *Friedrich Wöhler*

$$AgN{=}C{=}O + NH_4Cl \longrightarrow AgCl + \text{urea}$$

- 1852 *Franklad* prepared MeHgI $MeI + Hg \longrightarrow MeHgI$
- 1938 *O. Roelen* discovered hydroformylation
- 1951 *P. Pauson* synthesized ferrocene
- 1952 *H. Gilman* established organocuprates
- 1964 *E. O. Fischer* synthesized the first carbene complex
- 1969 *A. E. Shilov* discovered Pt^{II}-catalyzed H/D Exchange of alkene with solvents → C–H activation

Transition Metal Complexes

➢ Periodic table of the elements

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
		3	4	5	6	7	8	9	10								
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Transition Metal Complexes

- Modified periodic table of the elements

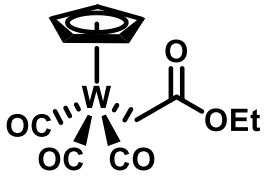
H																
Li	Be											B	C	N	O	F
Na	Mg											Al	Si	P	S	Cl
		3	4	5	6	7	8	9	10	11	12					
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi		

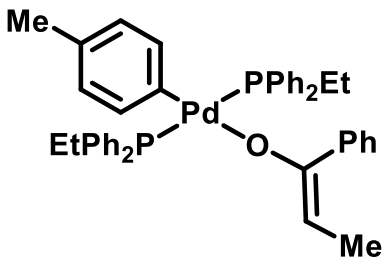
- Our periodic table of the elements

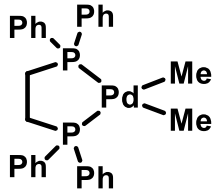
4	5	6	7	8	9	10	11	12
Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

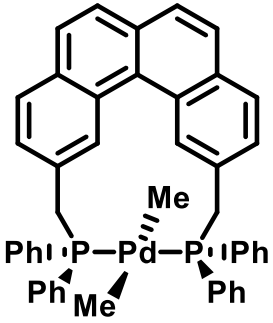
Transition Metal Complexes

- **Examples of organometallic compounds**









M—ligand

Transition Metal Complexes

➢ Properties of transition metals

M—ligand

- **Ionization potentials**

more basic
easily oxidized
more electron-rich

ionization potential increases

4	5	6	7	8	9	10	11	12
Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

more basic
easily oxidized
more electron-rich

10
Ni
Pd
Pt

ionization potential increases

- **Size**

the size of the metals decreases

4	5	6	7	8	9	10	11	12
Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

the size of the metals increases

metals from 2nd and 3rd row have similar size = Lanthanide contraction

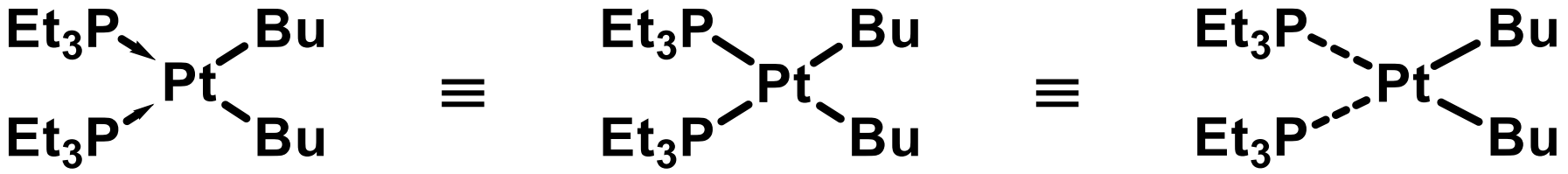
Transition Metal Complexes

➢ **Structure of transition metal complexes – Oxidation state of transition metal and number of d-electrons**

		4	5	6	7	8	9	10
		Ti	V	Cr	Mn	Fe	Co	Ni
		Zr	Nb	Mo	Tc	Ru	Rh	Pd
		Hf	Ta	W	Re	Os	Ir	Pt
		Number of d-electrons						
Oxidation state	0	4	5	6	7	8	9	10
	I	3	4	5	6	7	8	9
	II	2	3	4	5	6	7	8
	III	1	2	3	4	5	6	7
	IV	0	1	2	3	4	5	6

Transition Metal Complexes

➢ **Structure of transition metal complexes – Ligand properties**



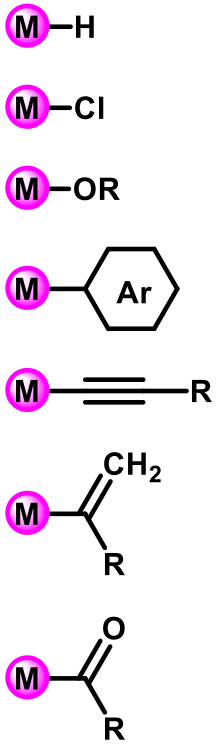
- **The 18-electron rule** – coordinatively saturated (18 electrons) or unsaturated complexes (<18 electrons)
- **Coordination number** – number of ligands bounded to the metal by σ-bonds
- **Hapticity** (η) describes how many atoms of the ligand bind to the transition metal
- **Monodentate** or **polydentate** ligands

Transition Metal Complexes

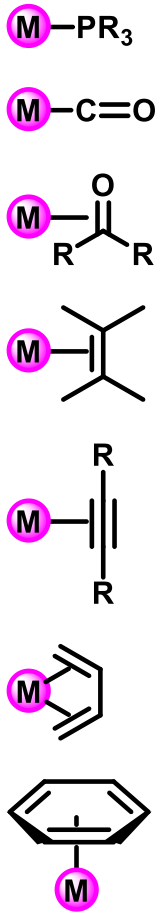
➢ Structure of transition metal complexes – 18 electron rule

M—ligand

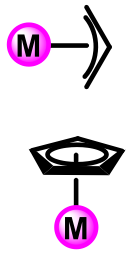
Formal charge -1



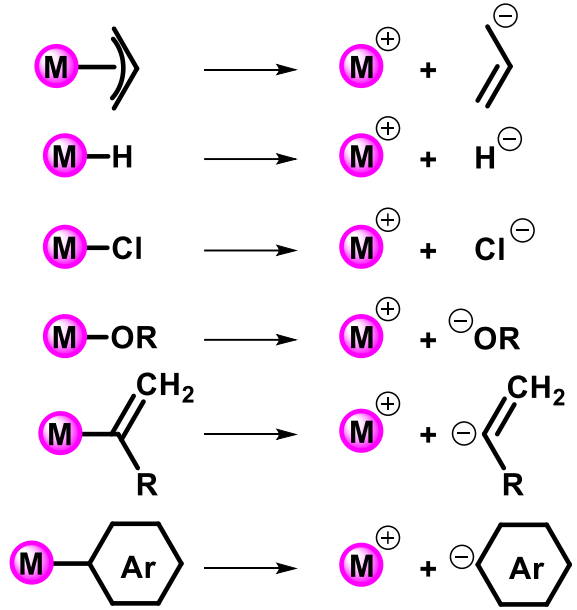
Formal charge 0



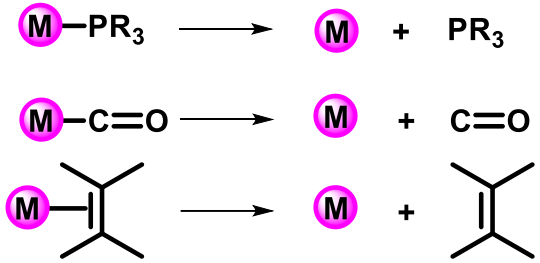
Formal charge -1 (mixed)



Formal charge -1

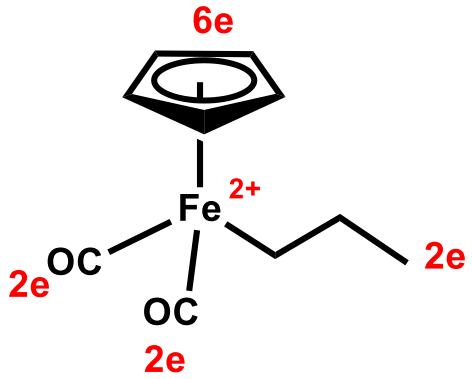


Formal charge 0

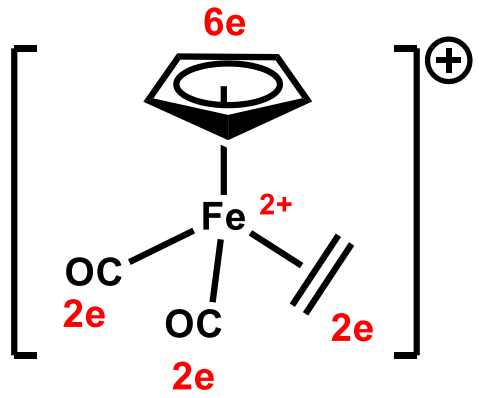


Transition Metal Complexes

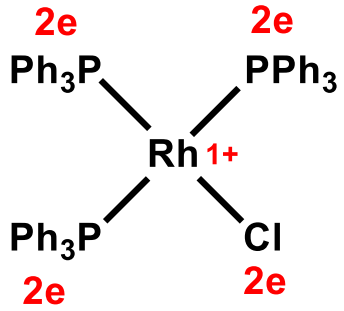
➢ Structure of transition metal complexes – 18 electron rule



total number of electrons = d^6 + 6e + 4e + 2e = 18e
coordinatively saturated complex



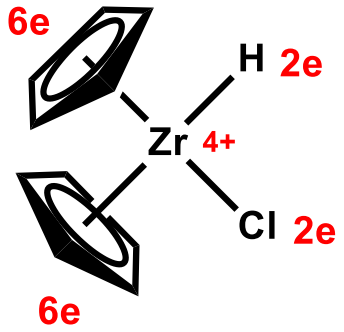
total number of electrons = d^6 + 6e + 6e = 18e
coordinatively saturated complex



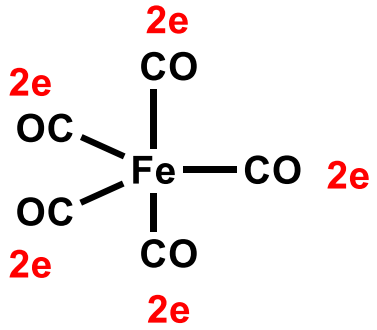
total number of electrons = d^8 + 6e + 2e = 16e
coordinatively unsaturated complex

Transition Metal Complexes

- **Structure of transition metal complexes – 18 electron rule**



total number of electrons = d^0 + 12e + 4e = 16e
coordinatively unsaturated complex



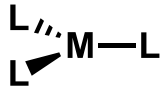
total number of electrons = d^8 + 10e = 18e
coordinatively saturated complex

Transition Metal Complexes

➢ Structure of transition metal complexes – Geometries of transition metal complexes

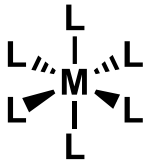
- **Depends on coordination number**

linear

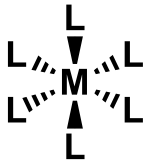


trigonal planar

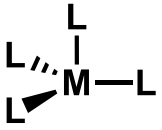
pyramidal



octahedral

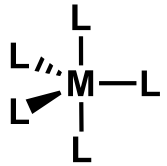


trigonal prismatic

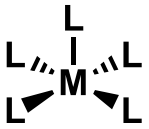


tetrahedral

square planar



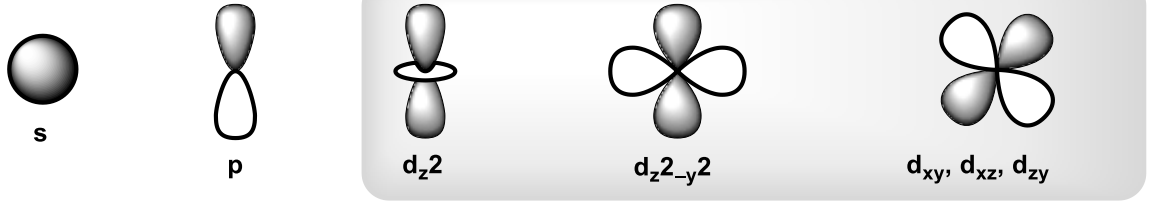
trigonal bipyramidal

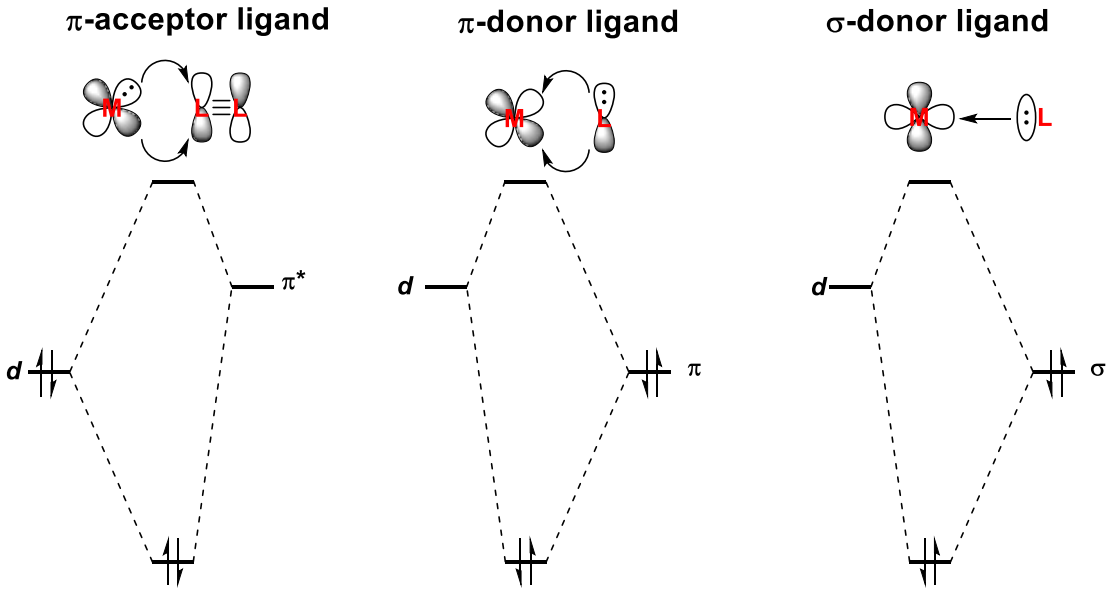


square-based pyramid

Transition Metal Complexes

➢ Structure of transition metal complexes – Bindings in transition metal complexes





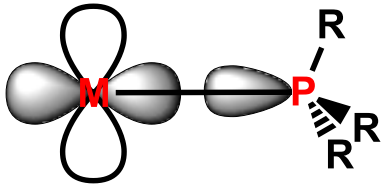
π-acceptor ligand: R_3P, R_3As, R_2S, CO, alkeny
π-donor ligand: RO^-, RS^-, F^-, Cl^-, Br^-, I^-, R_2N^-, RCO_2^-
σ-donor ligand: NH_3, H_2O, H^-

Transition Metal Complexes

➢ Structure of transition metal complexes – Phosphine ligands

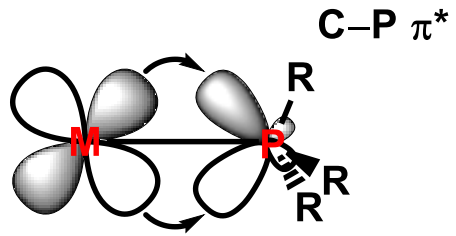
$M—PR_3$

Binding through σ-donation



unoccupied
d-orbital

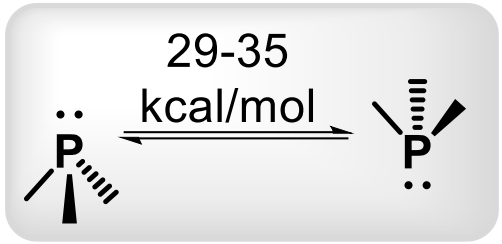
π-Backbonding



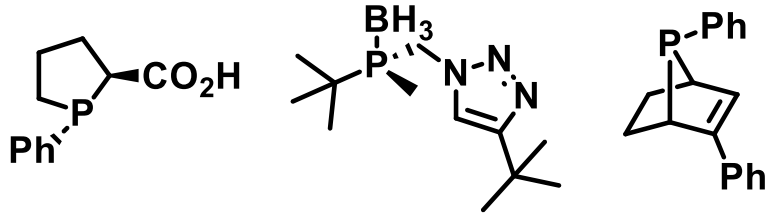
filled
d-orbital

Transition Metal Complexes

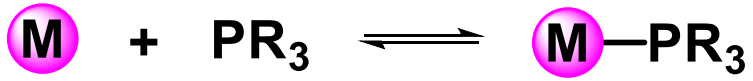
➢ Structure of transition metal complexes – Phosphine ligands

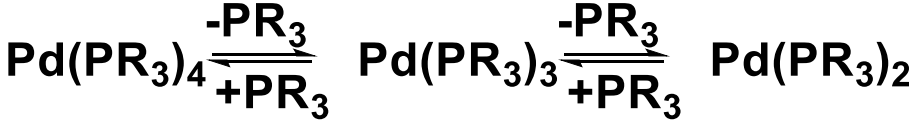


- **Chiral phosphines**



- **Behaviour of phosphine–metal complexes in solution**

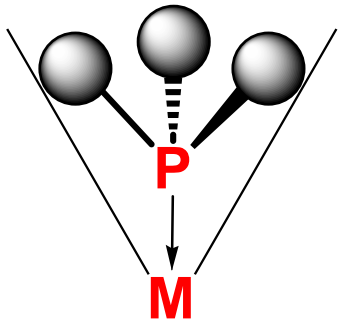




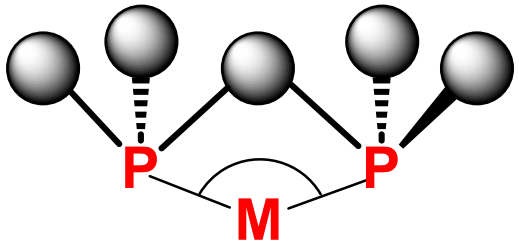
Transition Metal Complexes

➢ Structure of transition metal complexes – Phosphine ligands

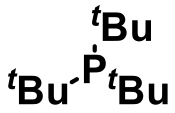
- Tolman cone angle (Bite angle)

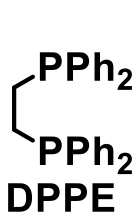


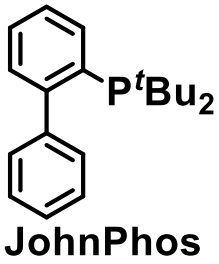
Θ = Cone angle

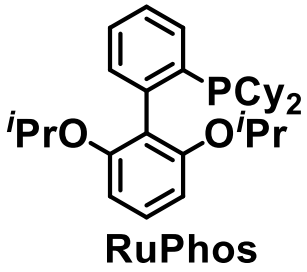


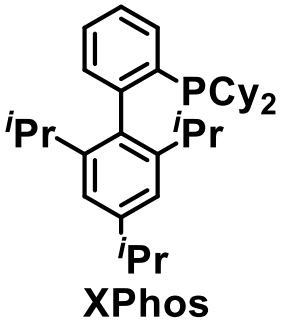
Bite angle

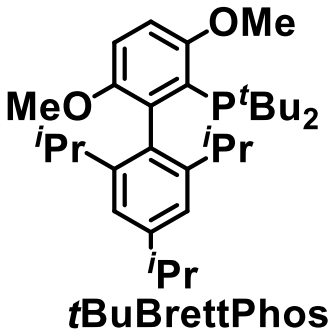


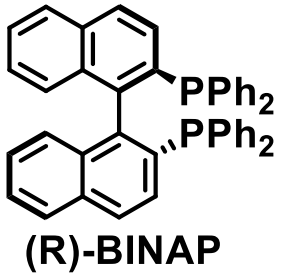


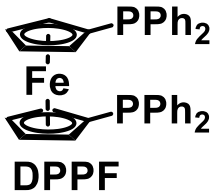


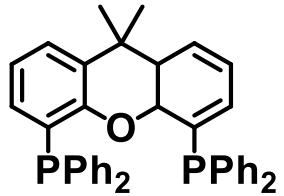










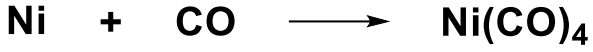


Phosphorus ligand	Cone angle (°)
PH_3	87
$P(OMe)_3$	107
PMe_3	118
PPh_3	145
PCy_3	170
P^tBu	182
$P(mesityl)_3$	212

Transition Metal Complexes

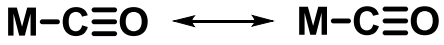
➢ Structure of transition metal complexes – Carbon monoxide

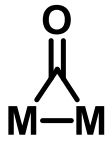
- **Carbon monoxide as ligand**
  - **Complexes are available by direct synthesis**

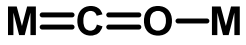


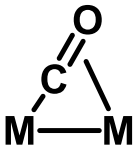
  - **Complexes are available by reductive carbonylation**

    - **CO binding modes**



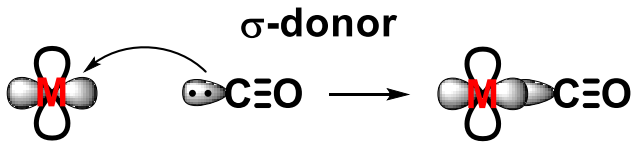


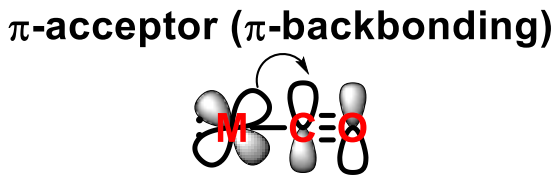


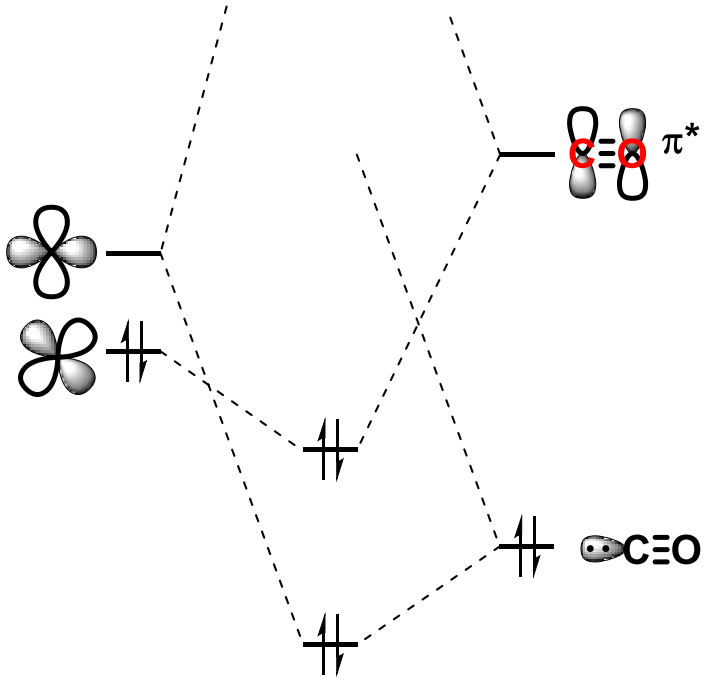


Transition Metal Complexes

➢ Structure of transition metal complexes – Carbon monoxide







Transition Metal Complexes

➢ Structure of transition metal complexes – Carbon monoxide

- **Carbon monoxide as a tool to determine the scope of π-backbonding**

CO	$Ph_3P_{Cl}Ir_{PPh_3}^{CO}$	$Ph_3P_{Cl}Pt^{\oplus}_{PPh_3}CO$	$Ni(CO)_4$	$Co(CO)_4^{1-}$	$Fe(CO)_4^{2-}$
ν_{CO} = 2143	ν_{CO} = 1860	ν_{CO} = 2100	ν_{CO} = 2057	ν_{CO} = 1886	ν_{CO} = 1785
		decreased π-backbonding		increased π-backbonding	

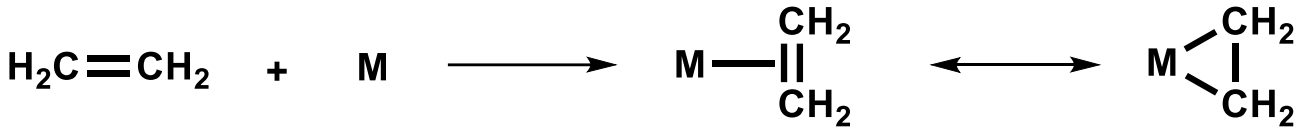
- **Carbon monoxide and electronic properties of *P*-ligand**

$Ni(CO)_3L$ CO ν_{CO} = 2143 $Ni(CO)_4$ ν_{CO} = 2057

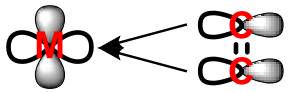
$P(t\text{-Bu})_3$	$P(Cy)_3$	$P(Me)_3$	$P(Ph)_3$	$P(4\text{-}OMeC_6H_4)_3$	$P(OMe)_3$	$P(OPh)_3$	PF_3
ν_{CO} = 2056	ν_{CO} = 2056	ν_{CO} = 2064	ν_{CO} = 2069	ν_{CO} = 2069	ν_{CO} = 2079	ν_{CO} = 2085	ν_{CO} = 2110 weakest donor

Transition Metal Complexes

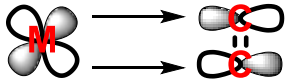
➢ Structure of transition metal complexes – Alkenes

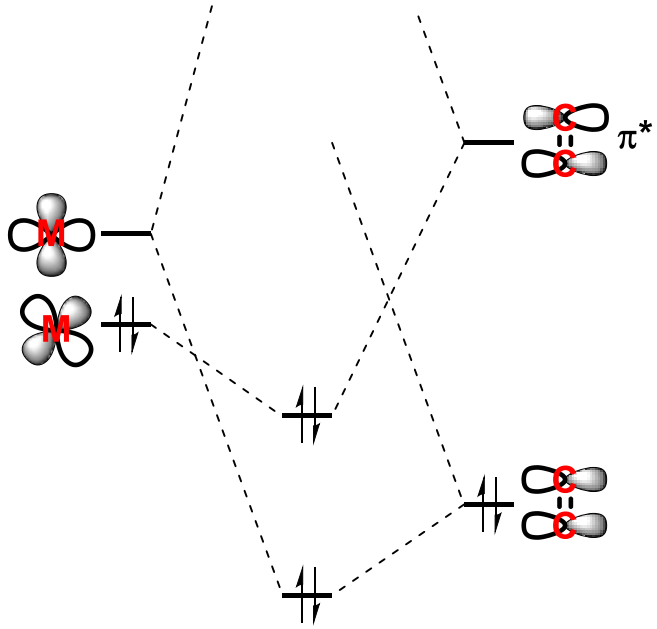


δ-donor ligand



π-acceptor ligand (π-backbonding)

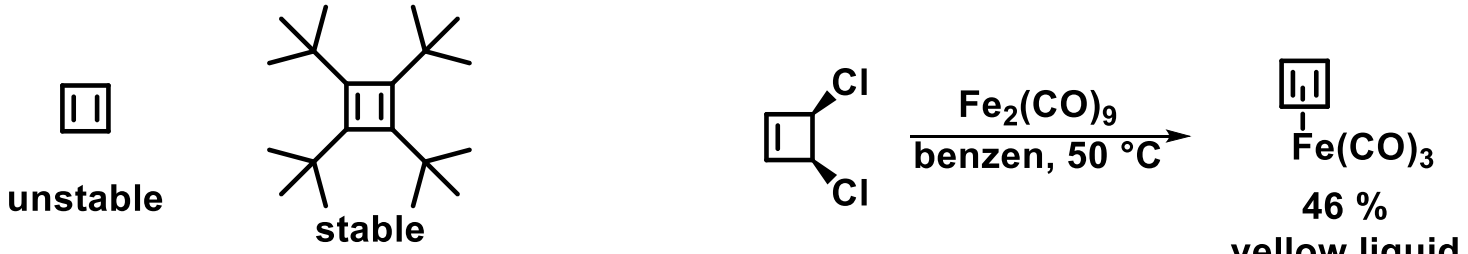


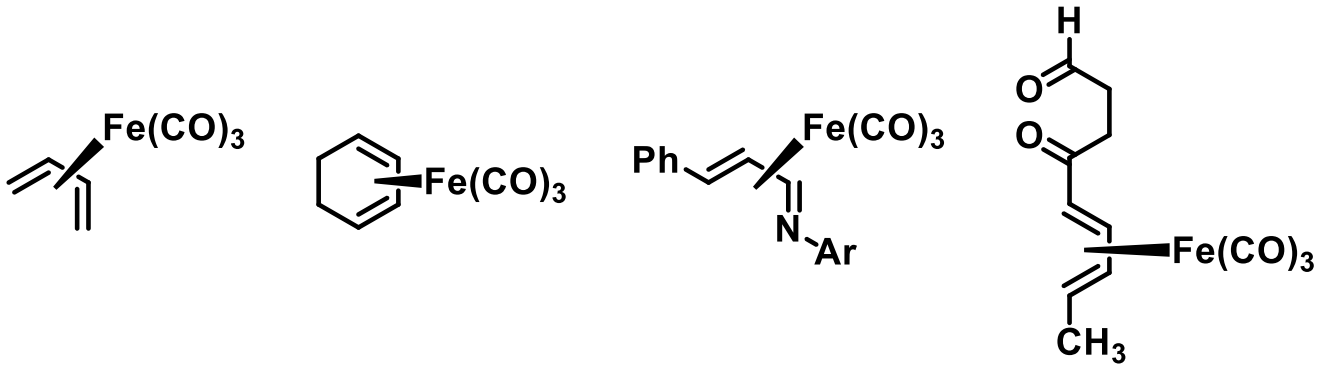


Transition Metal Complexes

➢ Structure of transition metal complexes – Alkenes

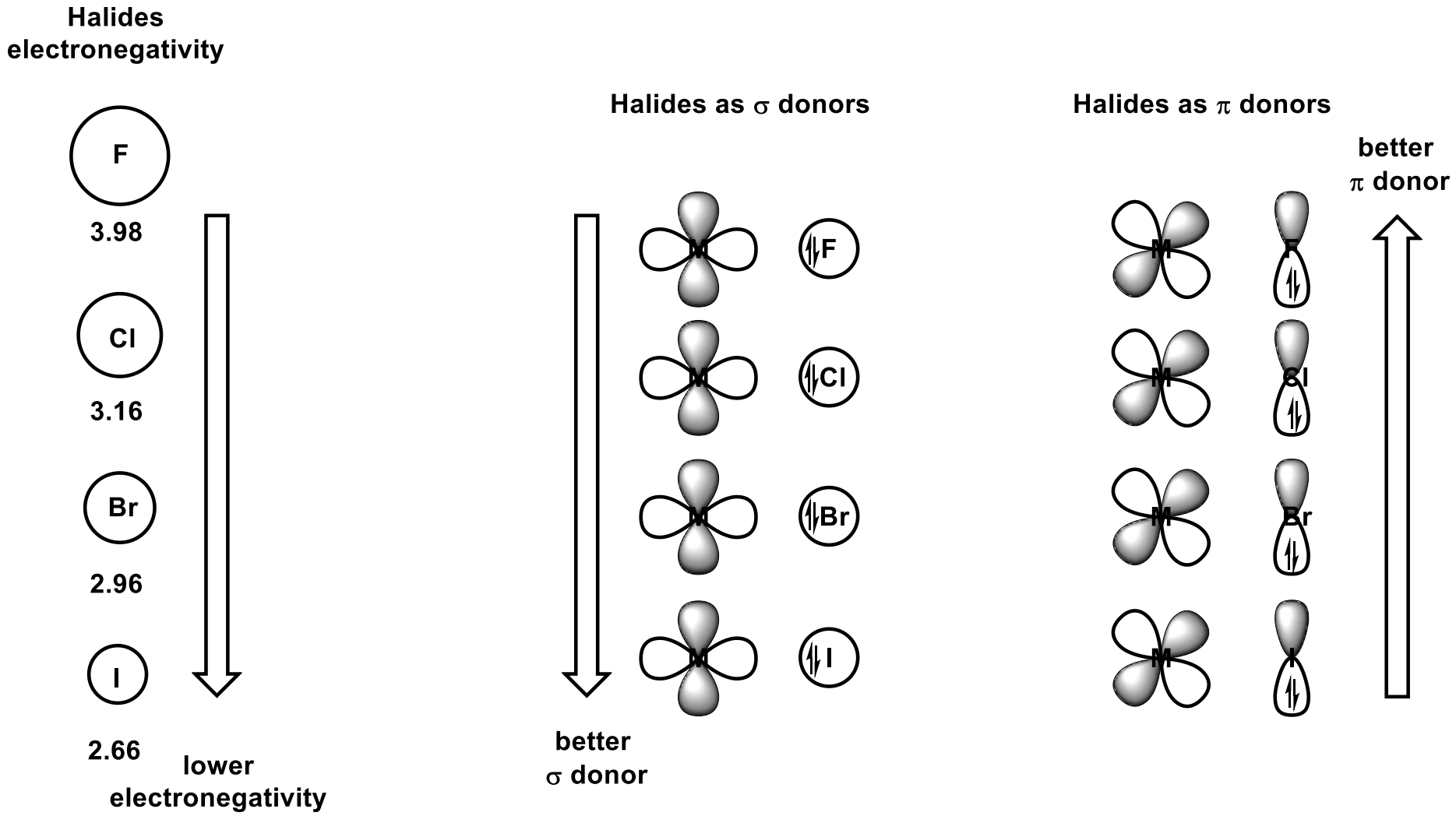
- **Examples of stable alkene complexes**





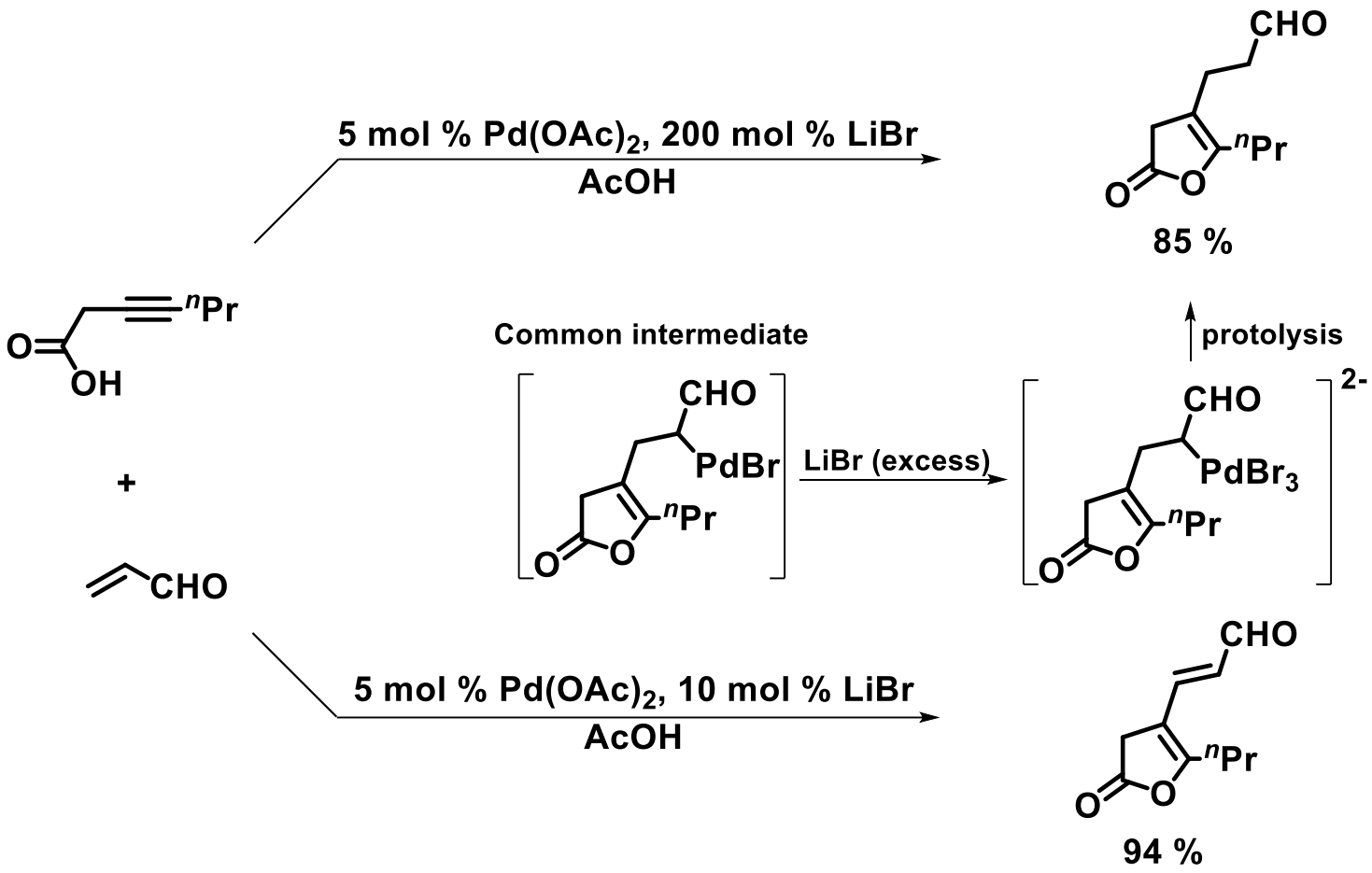
Transition Metal Complexes

➢ Structure of transition metal complexes – Halides M–X



Transition Metal Complexes

➢ Structure of transition metal complexes – Halides binding in organic synthesis



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