Homoleptic metal-carbonyls
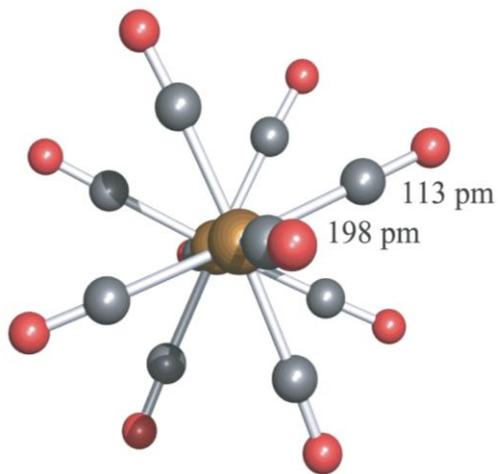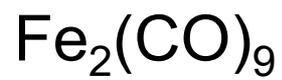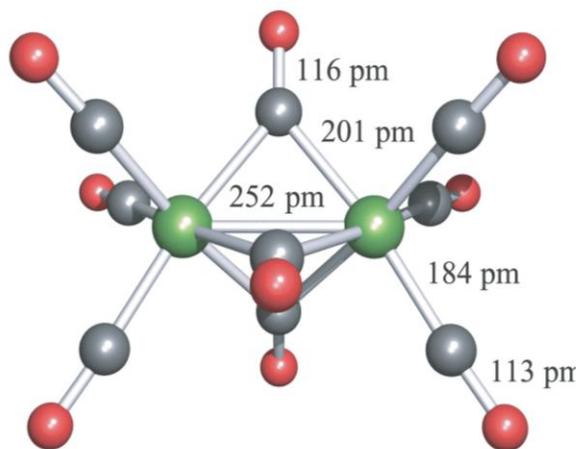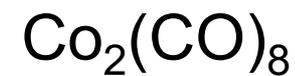
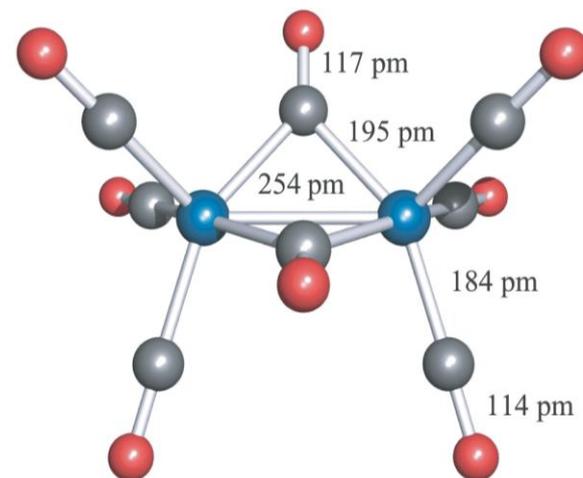**Table 21.5** Formulas and electron count for some $3d$-series carbonyls

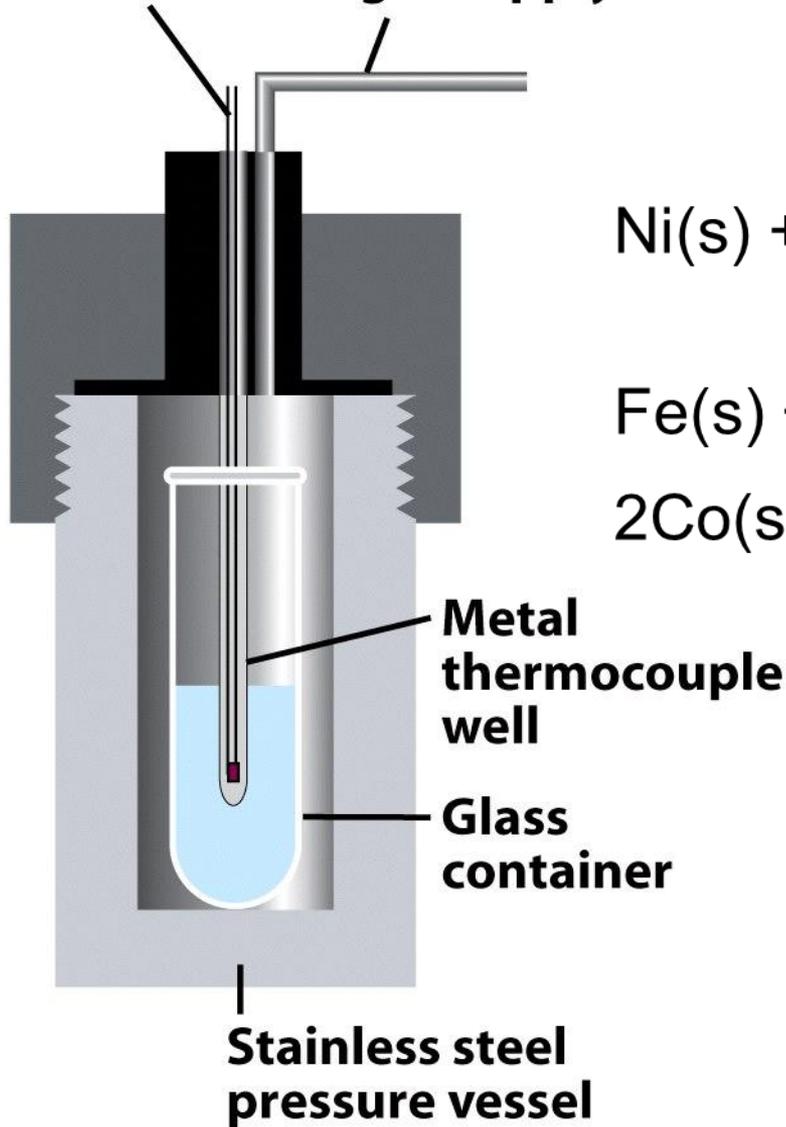| Group	Formula	Valence electrons		Structure
6	$Cr(CO)_6$	Cr	6	
		6(CO)	12	
			18	
7	$Mn_2(CO)_{10}$	Mn	7	
		5(CO)	10	
		M—M	1	
			18	
8	$Fe(CO)_5$	Fe	8	
		5(CO)	10	
			18	
9	$Co_2(CO)_8$	Co	9	
		4(CO)	8	
		M—M	1	
			18	
10	$Ni(CO)_4$	Ni	10	
		4(CO)	8	
			18	

$Re_2(CO)_{10}$

$14 + 20 + 2 = 36e^-$

$Fe_2(CO)_9$

$16 + 18 + 2 = 36e^-$

$Co_2(CO)_8$

$18 + 16 + 2 = 36e^-$

2

Direct reaction

Thermocouple

High-pressure gas supply

Metal thermocouple well

Glass container

Stainless steel pressure vessel

$$Ni(s) + 4CO(g) \xrightarrow{50\ °C,\ 1\ atm\ CO} Ni(CO)_4(g)$$

$$Fe(s) + 5CO(g) \xrightarrow{200\ °C,\ 200\ atm} Fe(CO)_5(l)$$

$$2Co(s) + 8CO(g) \xrightarrow{150\ °C,\ 35\ atm} Co_2(CO)_8(s)$$
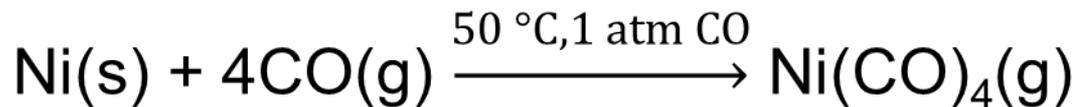
L.—*Action of Carbon Monoxide on Nickel.*
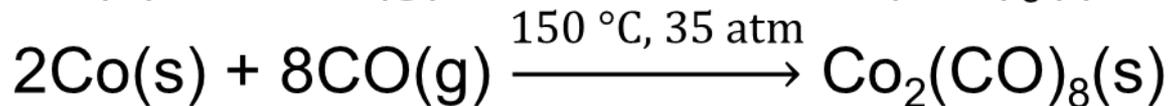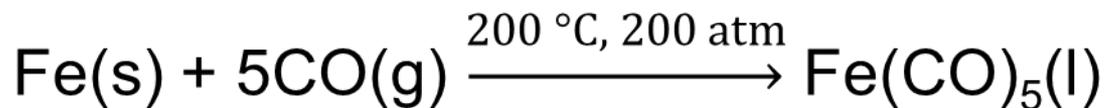
By Ludwig Mond, Dr. Carl Langer, and Dr. Friedrich Quincke.

When carbon monoxide is passed over finely-divided metallic nickel at a temperature between 350° and 450°, carbon dioxide is formed, and a black, amorphous powder is obtained consisting of nickel and carbon. The composition of this powder varies very widely with the temperature employed, and still more according to the time the operation has been carried on. A small quantity of nickel can decompose a very large amount of carbon monoxide. At the commencement, a fast current of carbon monoxide is completely changed into carbon dioxide by a comparatively small quantity of nickel. By-and-by, the change becomes less complete, but the gas may be passed for several weeks before carbon dioxide ceases to be formed.

We have in this way obtained a product containing as much as 85 per cent. carbon and 15 per cent. nickel. By treating this product with acids, a certain portion of the nickel goes into solution; but we have not been able to extract the nickel completely, the minimum quantity remaining after treatment with concentrated sulphuric acid being 5·59 per cent.; by treatment with dilute hydrochloric acid, 9·30 per cent.*

In order to determine the nickel in this substance, we have heated it with concentrated sulphuric acid to about 200°, and then added nitrate of potash in small portions to oxidise the carbon. This was the only way by which we could obtain a perfectly clear solution, and

---

* Gautier and Hallopeau (*Compt. rend.*, **108**, 1889, 1111) obtained a similar product containing 20·05 per cent. of nickel and 79·95 per cent. carbon, by acting with bisulphide of carbon on metallic nickel.

---

had been increased, thus proving that one volume of our compound gives 4 volumes of carbon monoxide. We give the result of several analyses, which lead to the formula $Ni(CO)_4$.
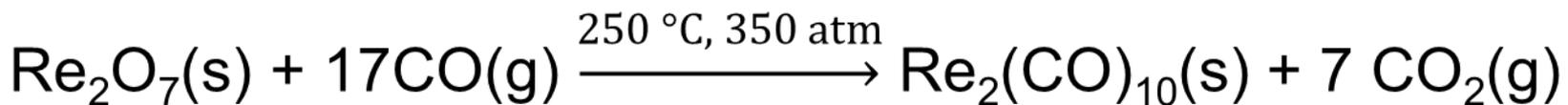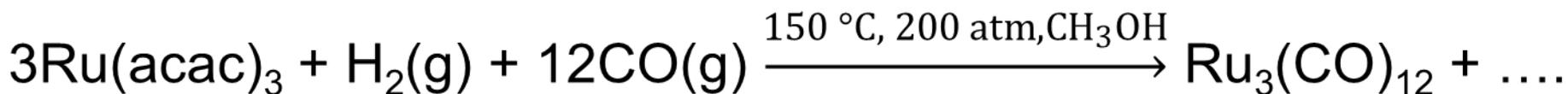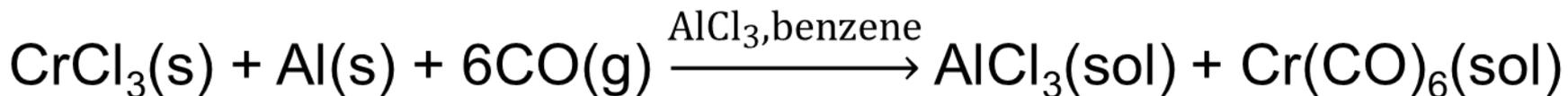
Mond Nickel Works, Clydach (Wales)
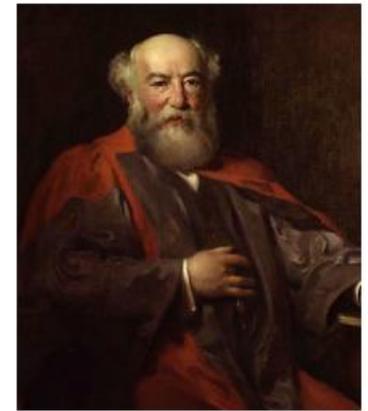
Ludwig Mond 1839-1909

Father of Metal Carbonyl Chemistry

Founder of Imperial Chemical Industry, England

'*Mond nickel company*' was making over 3000 tons of nickel in 1910 with a purity level of 99.9%

Reductive carbonylation

$$CrCl_3(s) + Al(s) + 6CO(g) \xrightarrow{\text{AlCl}_3,\text{benzene}} AlCl_3(sol) + Cr(CO)_6(sol)$$

$$3Ru(acac)_3 + H_2(g) + 12CO(g) \xrightarrow{150\ °C,\ 200\ atm,\text{CH}_3\text{OH}} Ru_3(CO)_{12} + \ldots$$

$$Re_2O_7(s) + 17CO(g) \xrightarrow{250\ °C,\ 350\ atm} Re_2(CO)_{10}(s) + 7\ CO_2(g)$$

Group number	5	6	7	8	9	10
First row metals	$V(CO)_6$ Dark blue solid; paramagnetic; dec. 343 K	$Cr(CO)_6$ White solid; sublimes *in vacuo*; dec. 403 K	$Mn_2(CO)_{10}$ Yellow solid; mp 427 K	$Fe(CO)_5$ Yellow liquid; mp 253 K; bp 376 K $Fe_2(CO)_9$ Golden crystals; mp 373 K (dec.) $Fe_3(CO)_{12}$ Dark green solid; dec. 413 K	$Co_2(CO)_8$ Air-sensitive, orange-red solid; mp 324 K $Co_4(CO)_{12}$ Air-sensitive, black solid $Co_6(CO)_{16}$ Black solid; slowly dec. in air	$Ni(CO)_4$ Colourless, volatile liquid; highly toxic vapour; bp 316 K
Second row metals		$Mo(CO)_6$ White solid; sublimes *in vacuo*	$Tc_2(CO)_{10}$ White solid; slowly dec. in air; mp 433 K	$Ru(CO)_5$ Colourless liquid; mp 251 K; dec. in air at 298 K to $Ru_3(CO)_{12}$ + CO $Ru_3(CO)_{12}$ Orange solid; mp 427 K; sublimes *in vacuo*	$Rh_4(CO)_{12}$ Red solid; >403 K dec. to $Rh_6(CO)_{16}$ $Rh_6(CO)_{16}$ Black solid; dec. >573 K	
Third row metals		$W(CO)_6$ White solid; sublimes *in vacuo*	$Re_2(CO)_{10}$ White solid; mp 450 K	$Os(CO)_5$ Yellow liquid; mp 275 K $Os_3(CO)_{12}$ Yellow solid;	$Ir_4(CO)_{12}$ Slightly air-sensitive yellow solid; mp 443 K $Ir_6(CO)_{16}$ Red solid	

Reduction of metal-carbonyls to metal-carbonyl anions (metal-carbonylates)

$$2Na + Fe(CO)_5 \xrightarrow{\text{THF}} (Na^+)_2[Fe(CO)_4]^{2-} + CO$$

ν_{CO} 1730 cm^{-1}

117 pm

175 pm

$[Fe(CO)_4]^{2-}$

$$2Na + (OC)_5Mn-Mn(CO)_5 \xrightarrow{\text{THF}} 2Na[Mn(CO)_5]$$
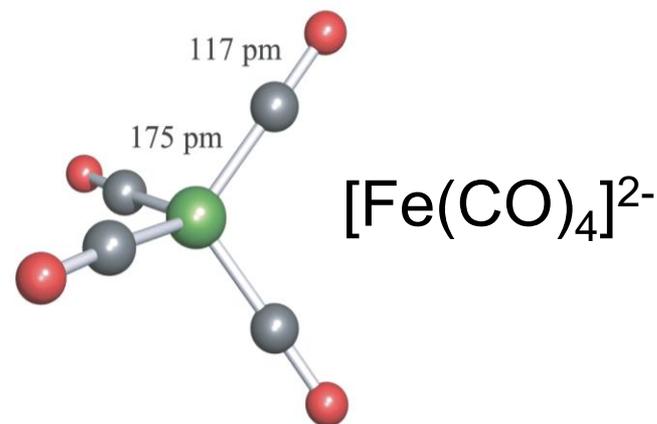
Table 21.6 Acidity constants of *d*-metal hydrides in acetonitrile at 25°C

Hydride	pK_a
$[CoH(CO)_4]$	8.3
$[CoH(CO)_3P(OPh)_3]$	11.3
$[Fe(H)_2(CO)_4]$	11.4
$[CrH(Cp)(CO)_3]$	13.3
$[MoH(Cp)(CO)_3]$	13.9
$[MnH(CO)_5]$	15.1
$[CoH(CO)_3PPh_3]$	15.4
$[WH(Cp)(CO)_3]$	16.1
$[MoH(Cp*)(CO)_3]$	17.1
$[Ru(H)_2(CO)_4]$	18.7
$[FeH(Cp)(CO)_2]$	19.4
$[RuH(Cp)(CO)_2]$	20.2
$[Os(H)_2(CO)_4]$	20.8
$[ReH(CO)_5]$	21.1
$[FeH(Cp*)(CO)_2]$	26.3
$[WH(Cp)(CO)_2PMe_3]$	26.6

Protonation of metal-carbonyl anions

$$[Mn(CO)_5]^- + H^+ \rightarrow [MnH(CO)_5]$$

9
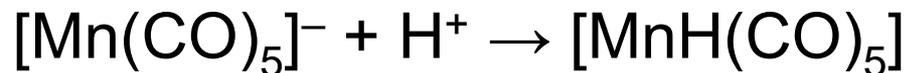
Basicity of metal-carbonyl anions
Nucleophilic attack

$[Mn(CO)_5]^- + CH_3I \rightarrow [Mn(CH_3)(CO)_5] + I^-$

$[Co(CO)_4]^- + CH_3COI \rightarrow [Co(COCH_3)(CO)_4] + I^-$

$[Mn(CO)_5]^- + [ReBr(CO)_5] \rightarrow [(OC)_5Mn{-}Re(CO)_5] + Br^-$
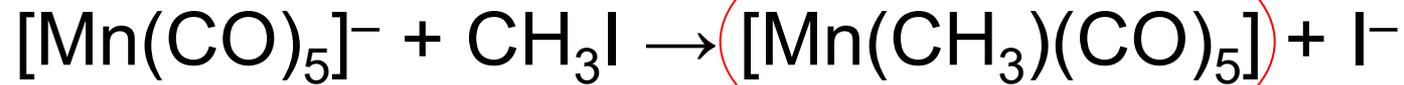
Migratory insertion

Oxidation (oxidative cleavage) of a M−M bond in metal-carbonyls

$$[(OC)_5Mn^{(0)}−Mn^{(0)}(CO)_5] + Br_2 \rightarrow 2[Mn^{(+1)}Br(CO)_5]$$
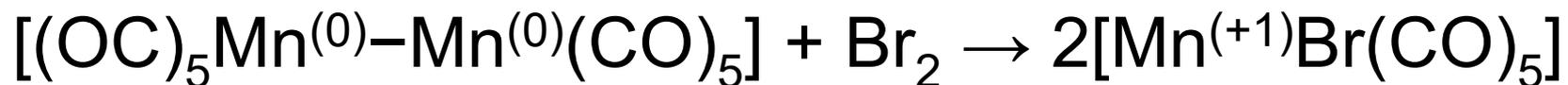
Nucleophilic and electrophilic attack to bound CO

Electron-poor metal: nucleophilic attack on the C

$$Li(CH_3) + [Mo(CO)_6] \rightarrow Li[Mo(COCH_3)(CO)_5]$$
$$[(OC)_nM(CO)] + OH^- \rightarrow [(OC)_nM(COOH)]^-$$
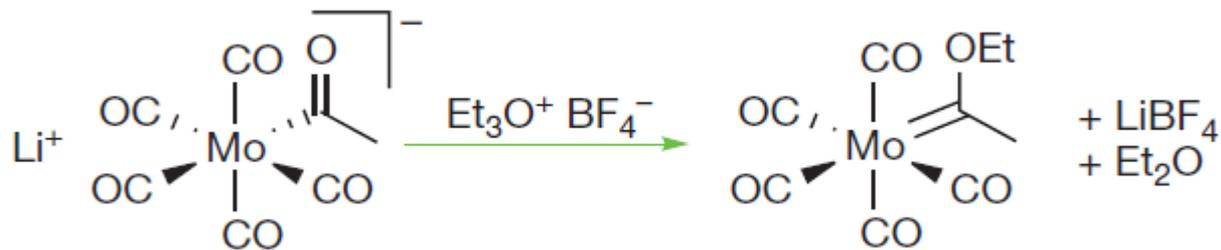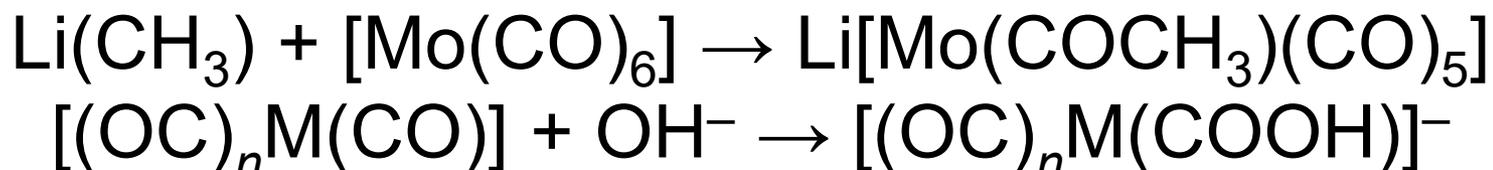
nucleophilic attack at the carbon of a metal carbonyl complex, followed by alkylation using a trialkyl oxonium salt

Electron-rich metal: electrophilic attack on the O
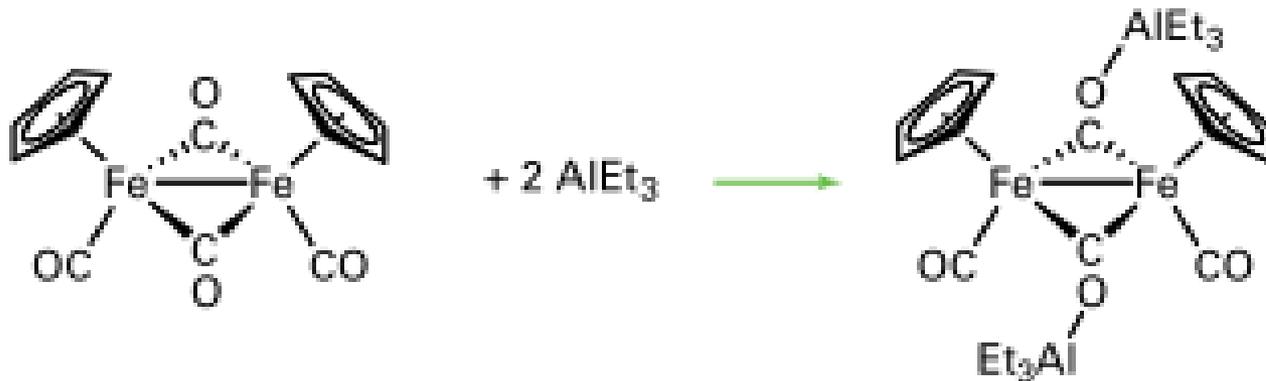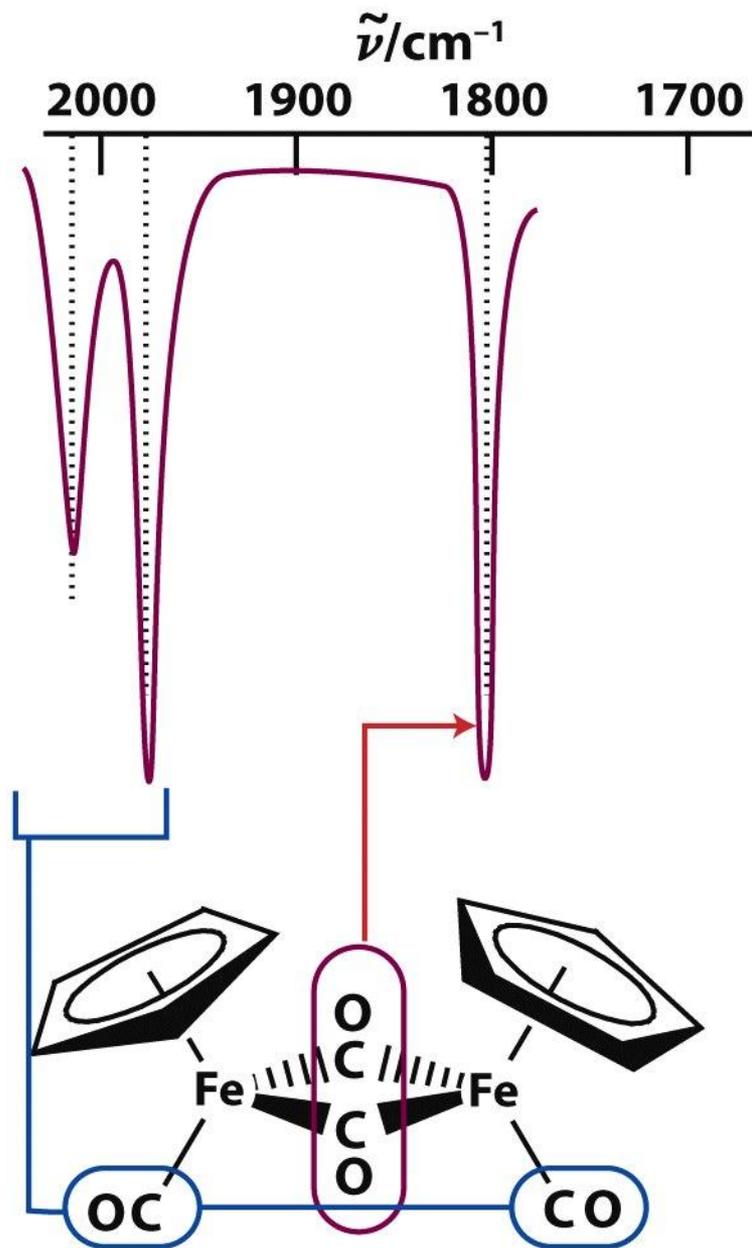
Table 21.7 Relation between the structure of a carbonyl complex and the number of CO stretching bands in its IR spectrum

Complex	Isomer	Structure	Point group	Number of bands*	Complex	Isomer	Structure	Point group	Number of bands*
$M(CO)_6$			O_h	1	$M(CO)_5$			D_{3h}	2
$M(CO)_5L$			C_{4v}	$3^\dagger$	$M(CO)_5$	ax		C_{3v}	$3^\S$
$M(CO)_4L_2$	trans		D_{4h}	1	$M(CO)_4L$	eq		C_{2v}	4
$M(CO)_4L_2$	cis		C_{2v}	$4^\ddagger$	$M(CO)_3L_2$	trans		D_{3h}	1
$M(CO)_3L_3$	mer		C_{2v}	$3^\ddagger$	$M(CO)_3L_2$	cis		C_s	3
$M(CO)_3L_3$	fac		C_{3v}	2	$M(CO)_4$			T_d	1

* The number of IR bands expected in the CO stretching region is based on formal selection rules, and in some cases fewer bands are observed, as explained below.
† If the fourfold array of CO ligands lies in the same plane as the metal atom, two bands will be observed.
‡ If the *trans* CO ligands are nearly collinear, one fewer band will be observed.
§ If the threefold array of CO ligands is nearly planar, only two bands will be observed.

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Carbonyl Clusters
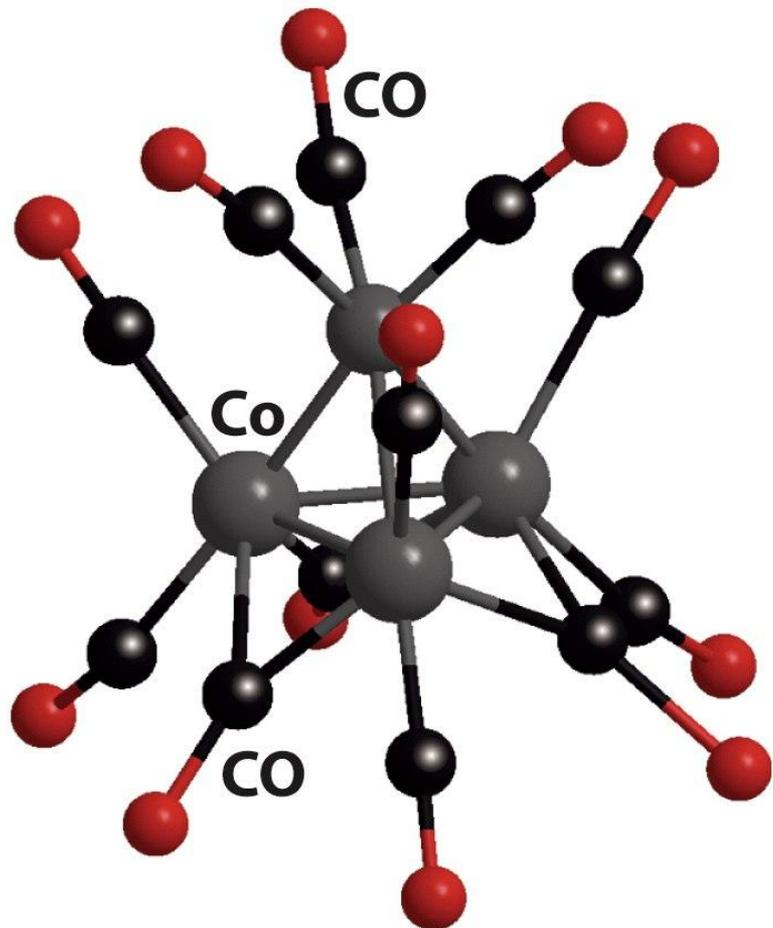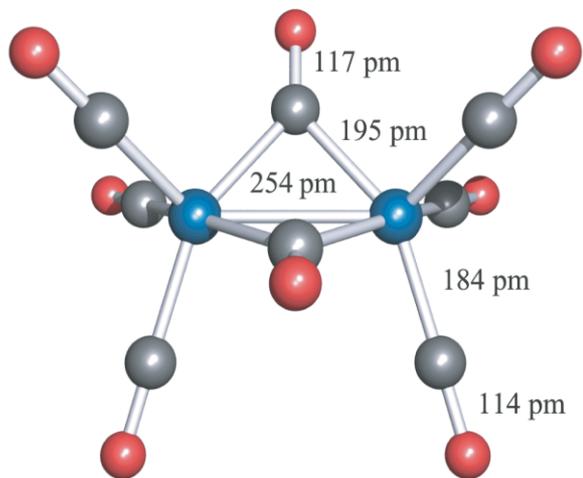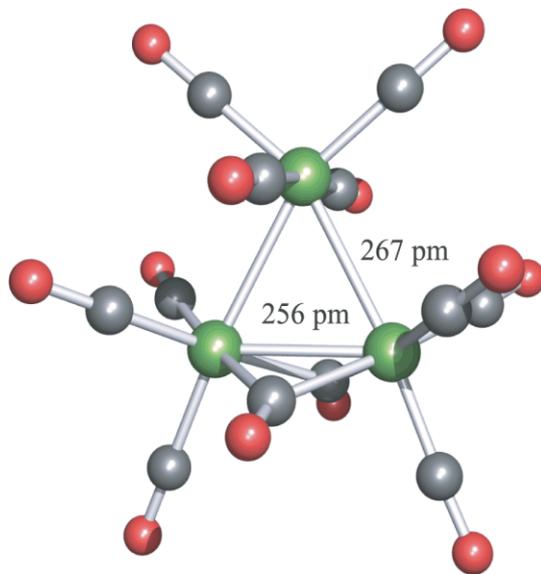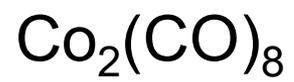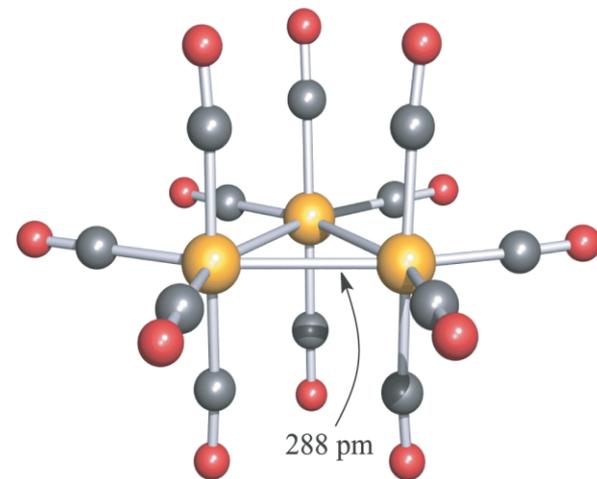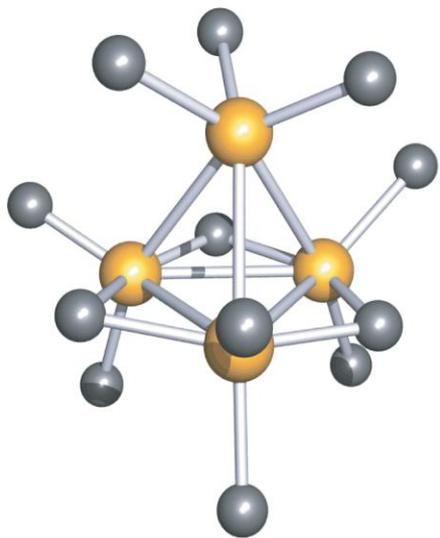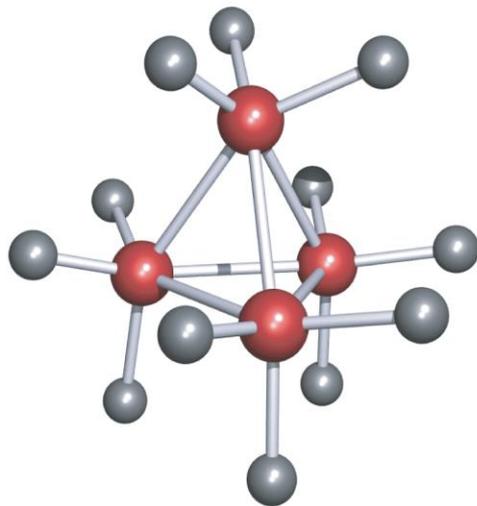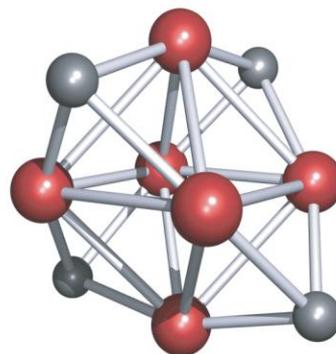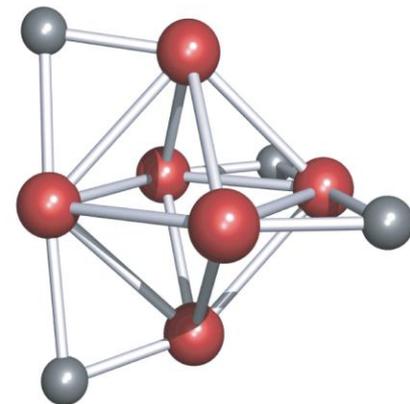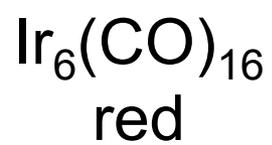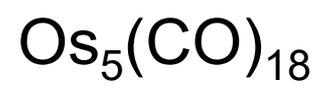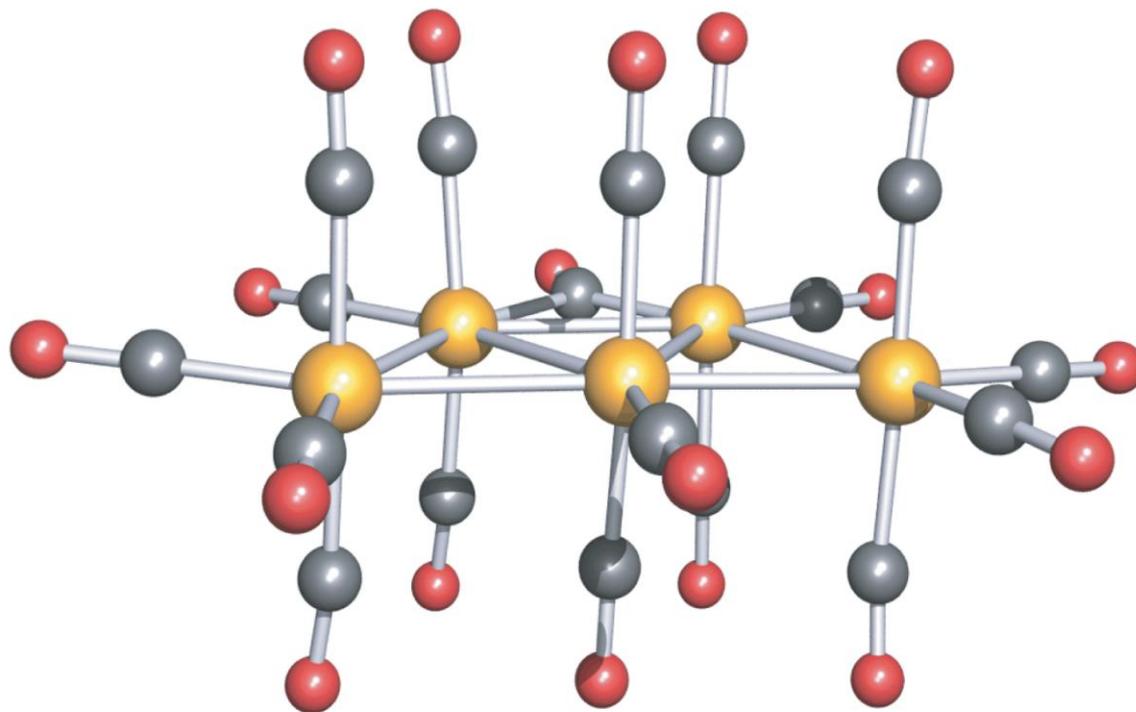
$[Co_4(CO)_{12}]$

117 pm
195 pm
254 pm
184 pm
114 pm

267 pm
256 pm

288 pm

(d)

(e)

(f)

$Co_2(CO)_8$

$Fe_3(CO)_{12}$

$Os_3(CO)_{12}$

(a)

$Rh_4(CO)_{12}$

(b)

$Ir_4(CO)_{12}$

(c)

$Ir_6(CO)_{16}$
red

(d)

$Ir_6(CO)_{16}$
black

17

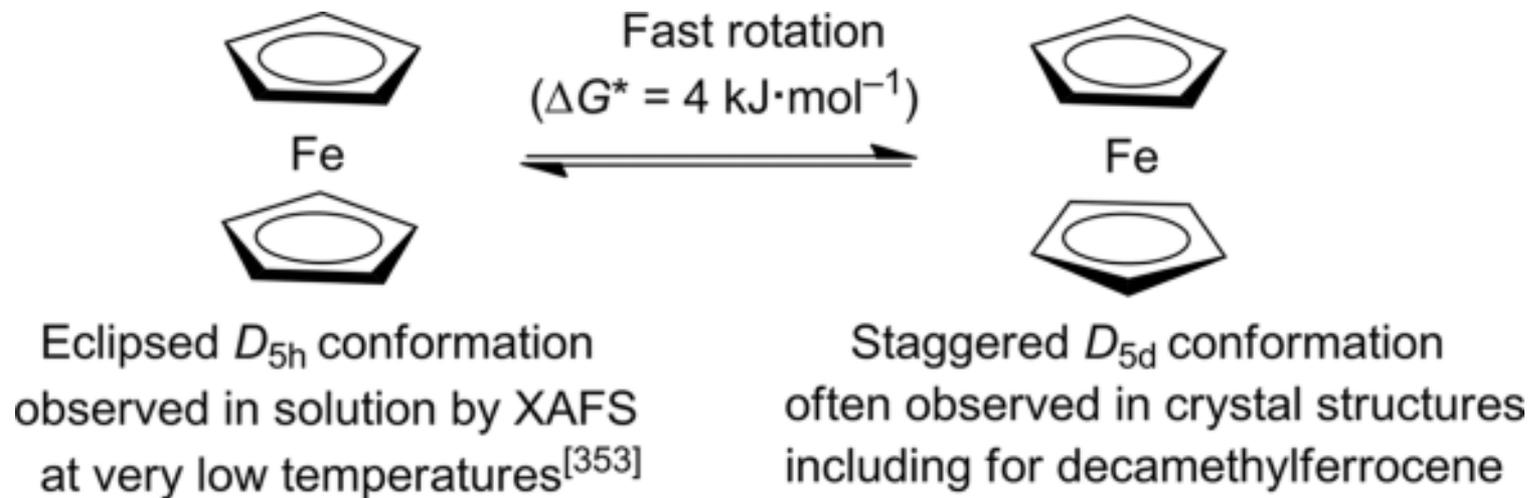$Os_5(CO)_{18}$

Ernst Otto Fischer

Geoffrey Wilkinson
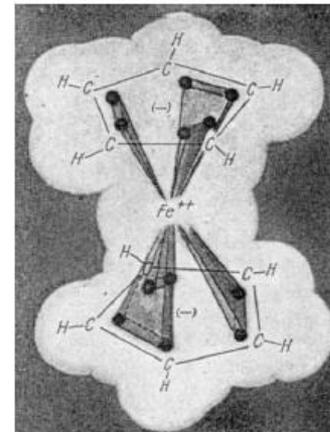
1973 – **Nobel Prize** for Organometallic Chemistry of the *d-block* elements

"for their pioneering work, performed independently, on the chemistry of the organometallic, so called sandwich compounds"

Ferrocene and Metallocenes

Fast rotation
$(\Delta G^* = 4\ kJ \cdot mol^{-1})$

Eclipsed D_{5h} conformation observed in solution by XAFS at very low temperatures[353]

Staggered D_{5d} conformation often observed in crystal structures including for decamethylferrocene

- G. Wilkinson, M. Rosenblum, M. C. Whiting, R. B. Woodward, *J. Am. Chem. Soc.* **1952**, *74*, 2125–2126.

- E. O. Fischer, W. Pfab, *Z. Naturforsch. B* **1952**, *7*, 377–379.

In 2017 more than18000 publications about ferrocenes

$$2Na + 2C_5H_6 \xrightarrow{\text{THF}} 2Na[C_5H_5] + H_2$$

$$2KOH + 2C_5H_6 + FeCl_2 \xrightarrow{\text{DMSO}} Fe(C_5H_5)_2 + 2H_2O + 2KCl$$
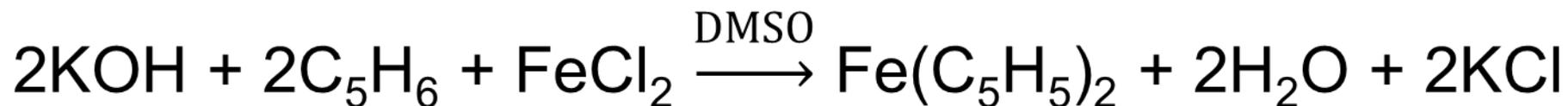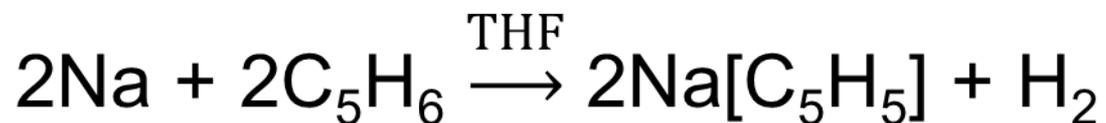
- Stable up to 400 ºC (melts at 172 ºC)
- Stable to air and soluble in most organic solvents
- Reactivity similar to a super-aromatic elecrophile
- Reversible oxidation at +0.4 V vs SCE
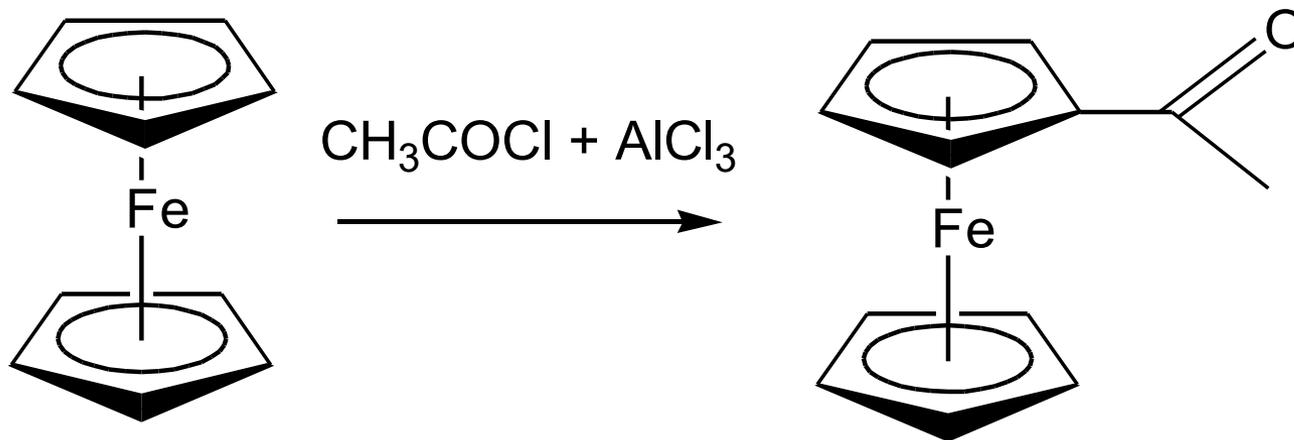
Friedel – Crafts acylation

RC(O)Cl, AlCl$_3$

Conc. H$_2$SO$_4$

$(\eta^5\text{-Cp})_2$Fe

Ph$_2$PCl, AlCl$_3$

^{n}BuLi,
Me$_2$NCH$_2$CH$_2$NMe$_2$

Ph$_2$PCl

Ph$_2$PCl

23

−0.4 V vs. SCE

$$\xrightarrow[+e]{-e}$$

Fe

Fe
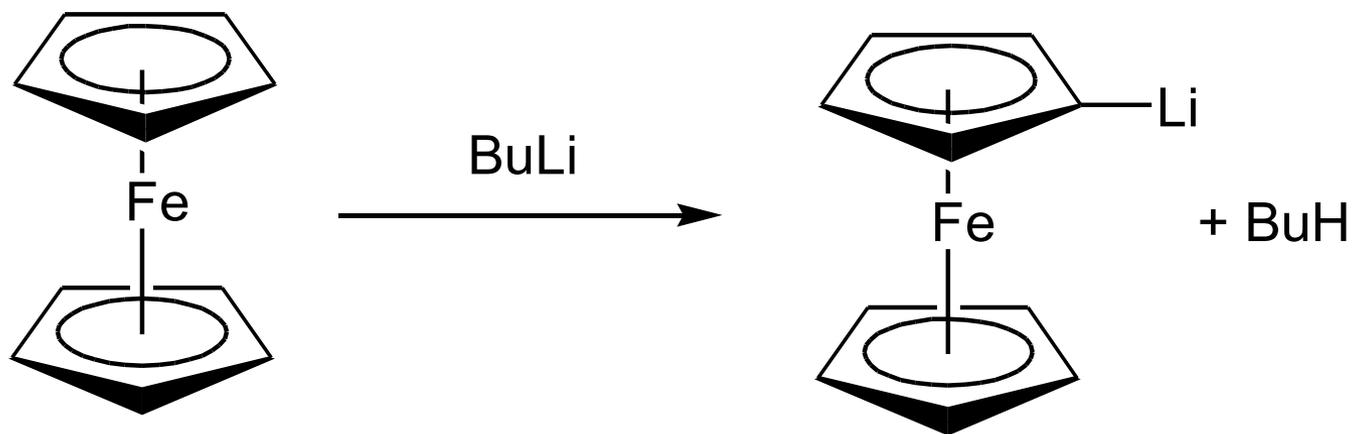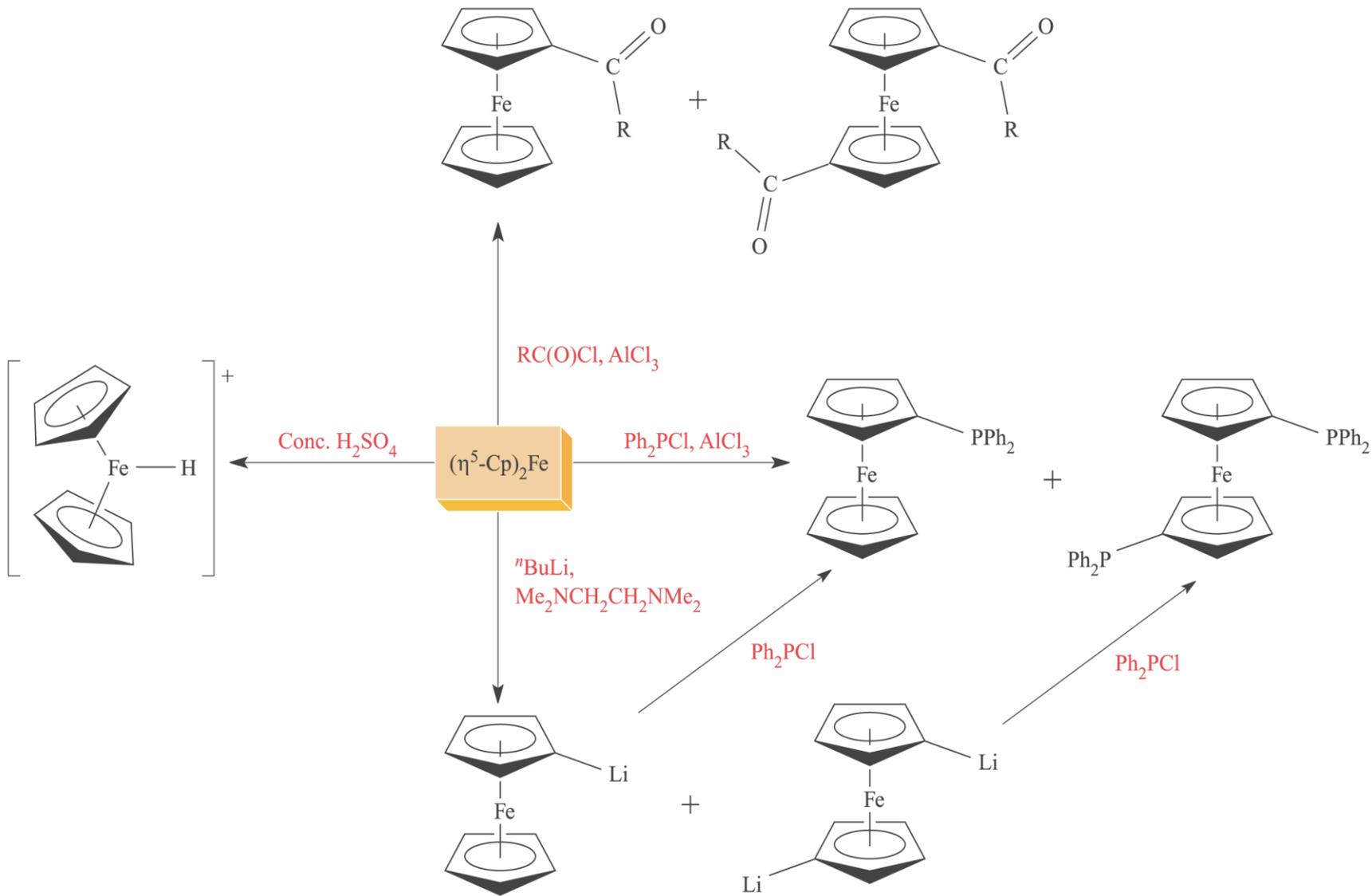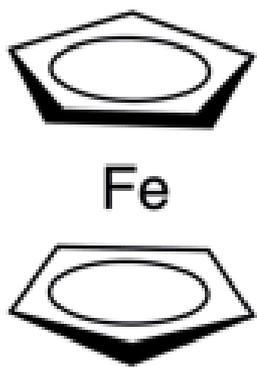
Ferrocene, orange
d^6, Fe^{II}, 18e
Functionalization with
non-oxidizing electrophiles
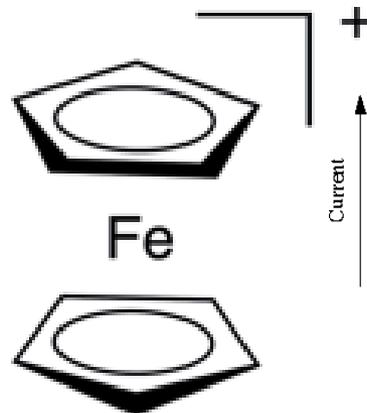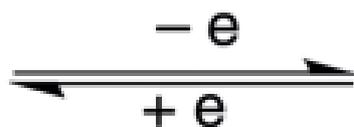
Ferricinium, deep-blue
d^5, Fe^{III}, 17e
Isolable as BF_4^- or PF_6^- salt, etc.
Sensive to O_2 and nucleophiles
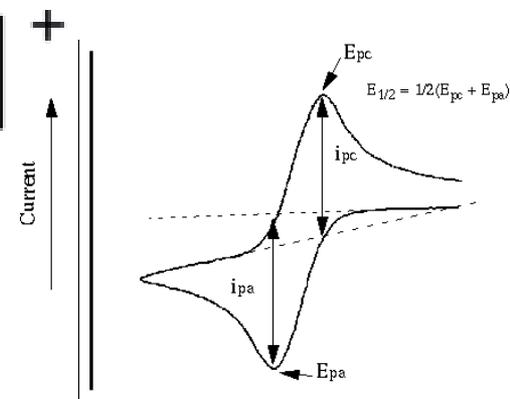
The oxidation is fully reversible - Ferrocene used as standard in CV. This means that Fericcinium (17e$^-$) is also rather stable.
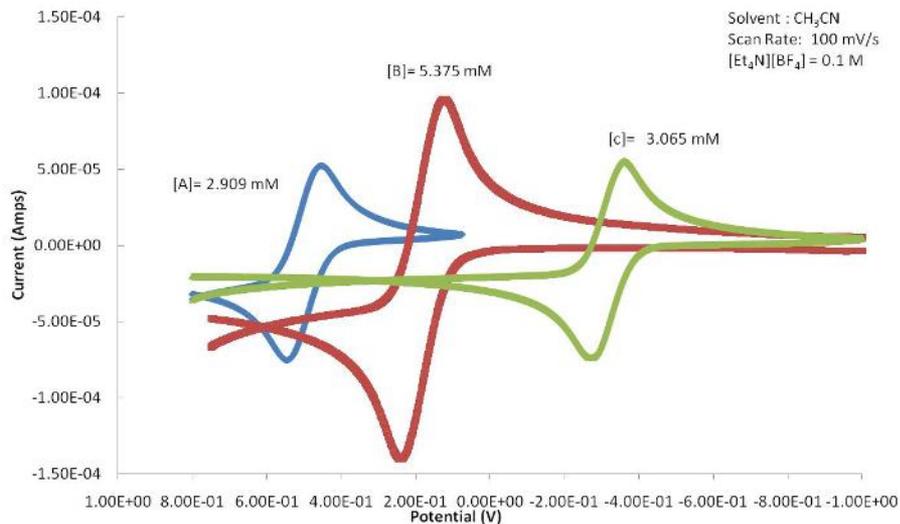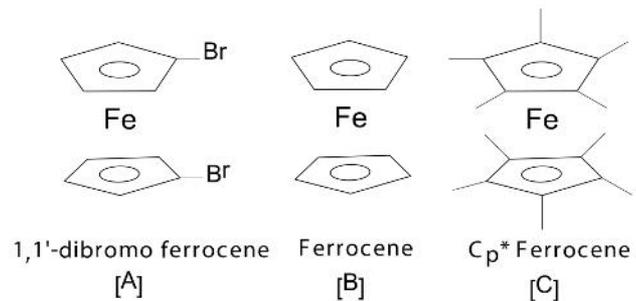
The electron withdrawing halide results in the $E_{1/2}$ value of this complex to be shifted to more positive potentials because the oxidized form is destabilized by the electron withdrawing ligand. The electron donating methyl groups of compound C result in the $E_{1/2}$ to shift to more negative potentials as the oxidized species is stabilized.

3π
(e_2)

2π
(e_1)

1π
(a_1)

d_{x2-y2} d_{xy} δ

d_{yz} d_{zx} π

d_{z^2} σ

26
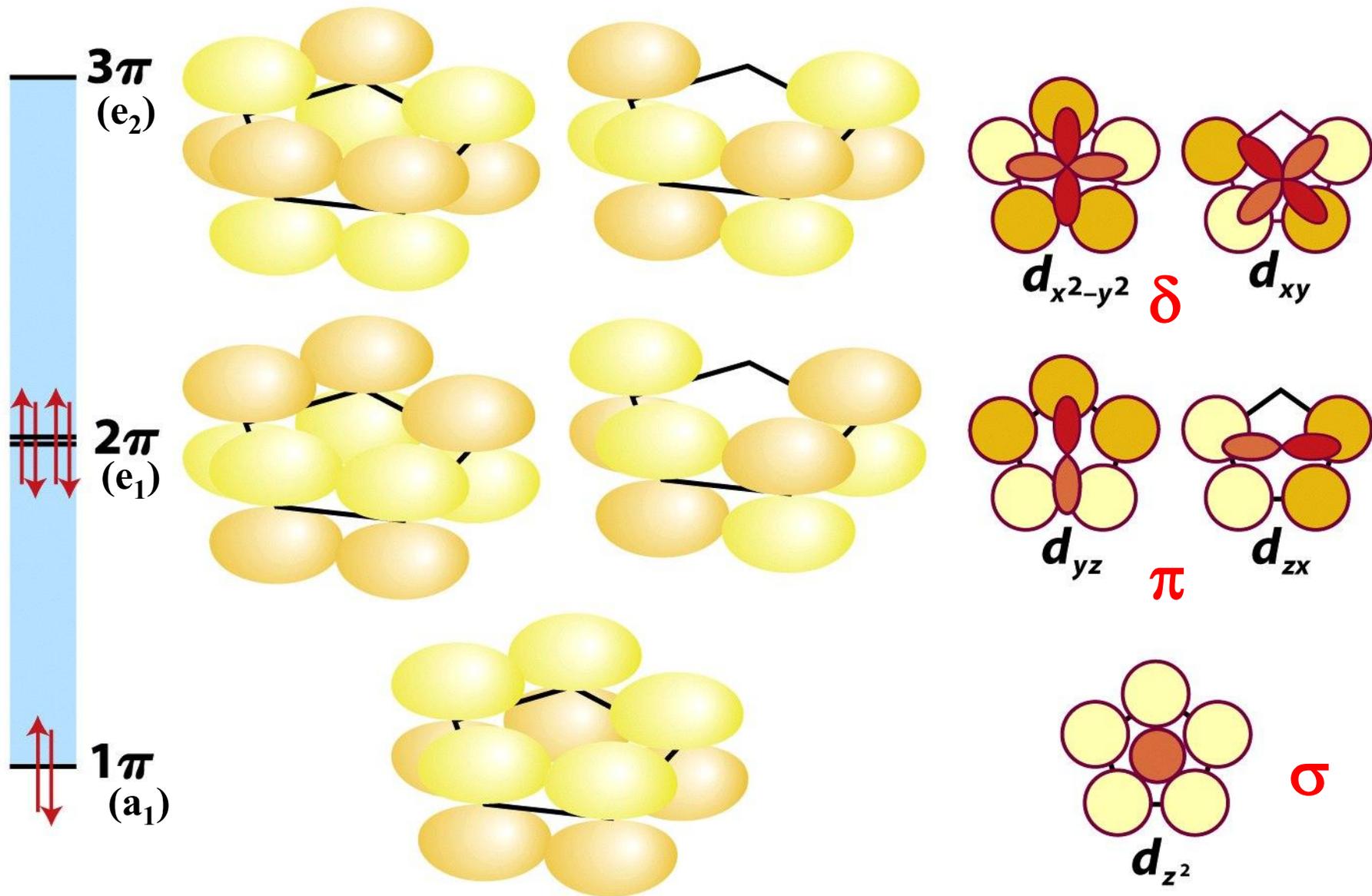
$(C_5H_5)_2^{-2-}$ (D_{5h}) Ferrocene (D_{5h}) Fe^{2+}

e_1'
a_2''
a_1'
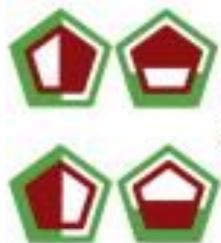
e_2''
e_2'

$5e_2'$
$4e_2''$

4p

LUMO

$5e_1''$ (xz, yz)

a_1'

4s

δ-backdonation

HOMO

$4e_2'$ $(x^2 - y^2, xy)$

$8a_1'$ (z^2)

xz, yz

e_1''

e_1''
e_1''

$6e_1'$

$4e_1''$

π-donation

xy
x^2-y^2

e_2'

a_2''
a_1'

$6a_2''$

$7a_1'$

σ-donation

a_1'

3d

27
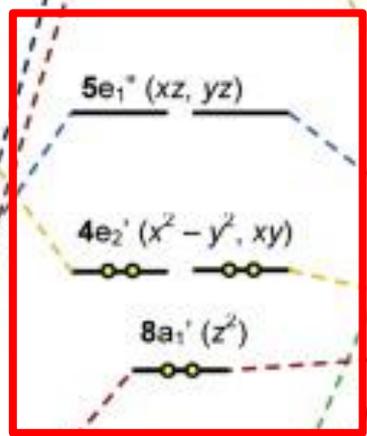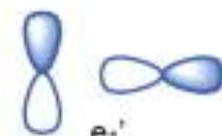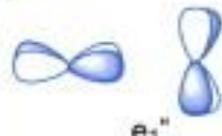
Table 21.8 Electronic configuration and M—C bond length in $[M(\eta^5\text{-Cp})_2]$ complexes

Complex	Valence electrons	Electron configuration	M—C bond length/pm
$[V(\eta^5\text{-Cp})_2]$	15	$e_2'^2 a_1'^1$	228
$[Cr(\eta^5\text{-Cp})_2]$	16	$e_2'^3 a_1'^1$	217
$[Mn(\eta^5\text{-Me-C}_5\text{H}_4)_2]*$	17	$e_2'^3 a_1'^2$	211
$[Fe(\eta^5\text{-Cp})_2]$	18	$e_2'^4 a_1'^2$	206
$[Co(\eta^5\text{-Cp})_2]$	19	$e_2'^4 e_1''^1 a_1'^2$	212
$[Ni(\eta^5\text{-Cp})_2]$	20	$e_2'^4 e_1''^2 a_1'^2$	220

*Data are quoted for this complex because $[Mn(\eta^5\text{-Cp})_2]$ has a high-spin configuration and hence an anomalously long M—C bond (238 pm).

Bent sandwich

C_6H_6

Cr

CO
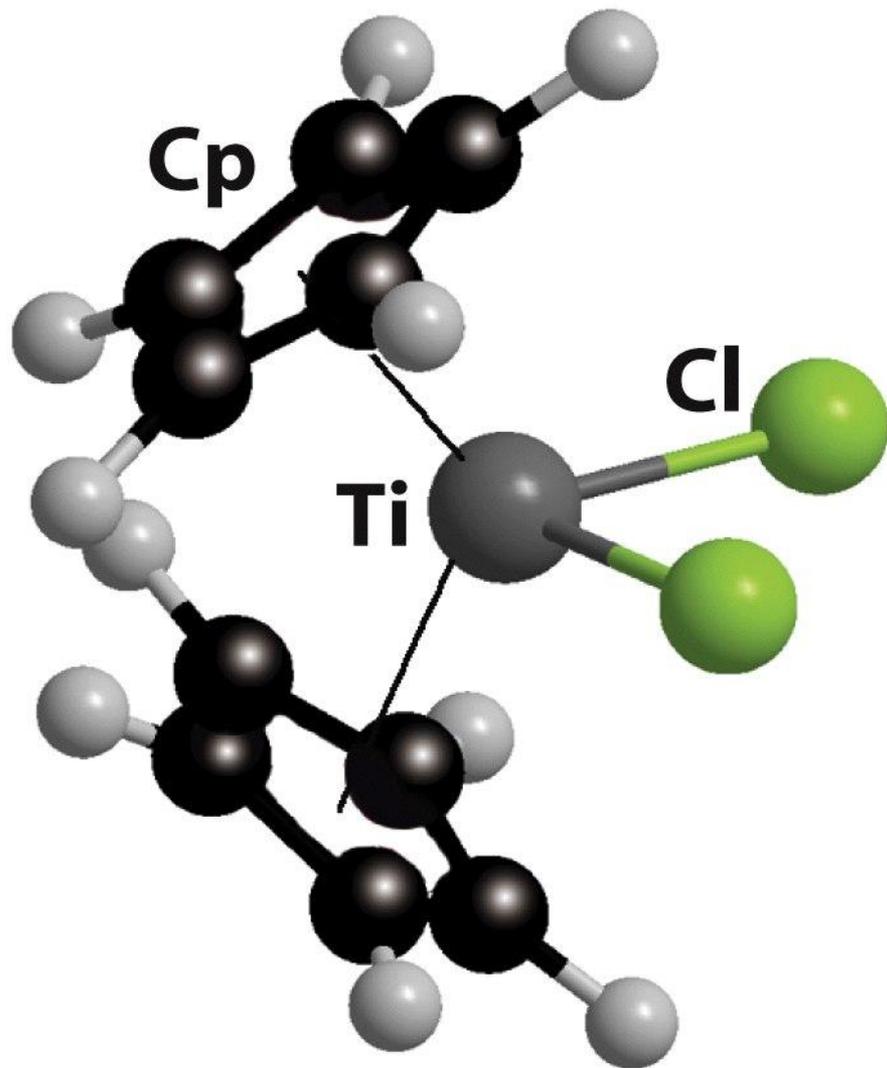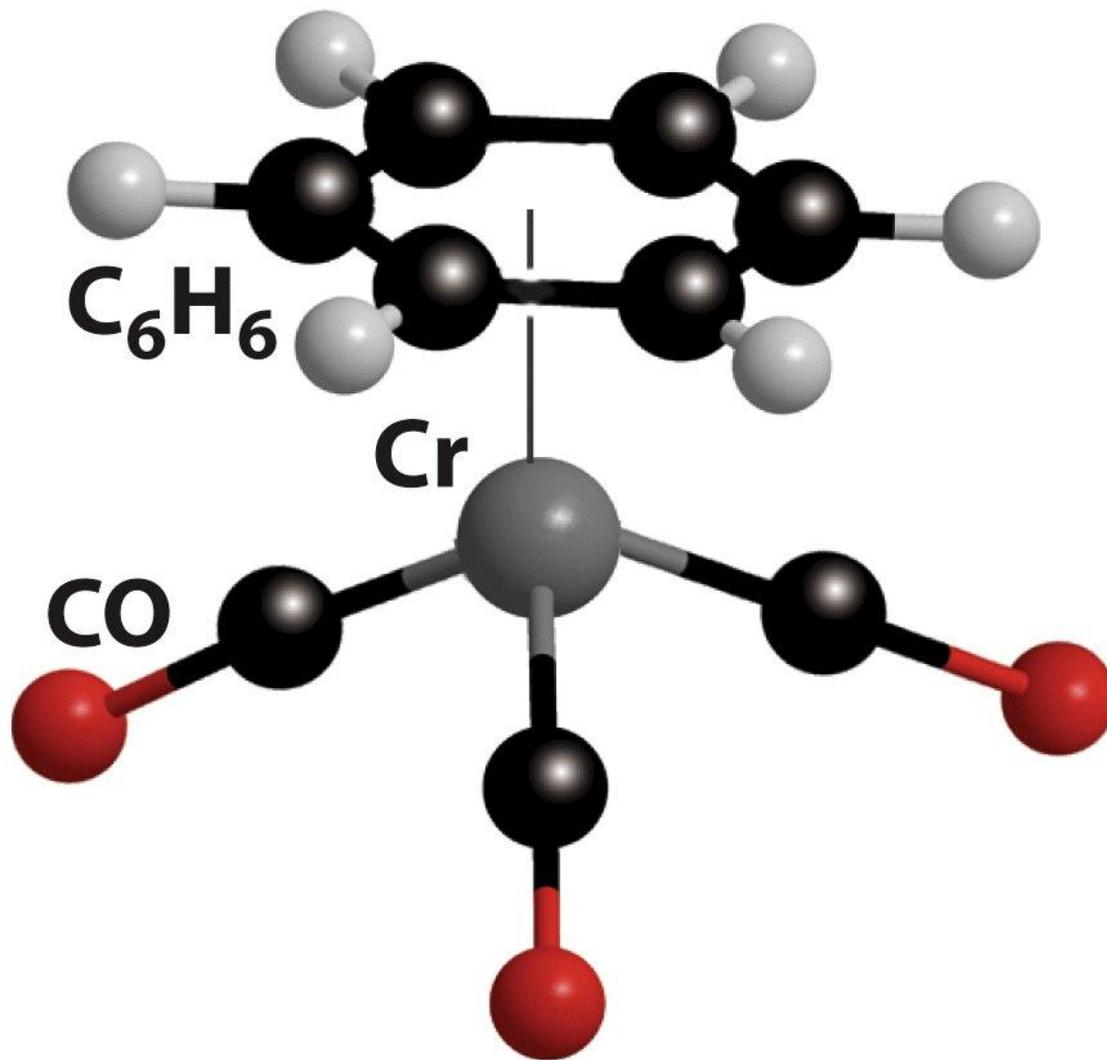
Half sandwich or *Piano stool*
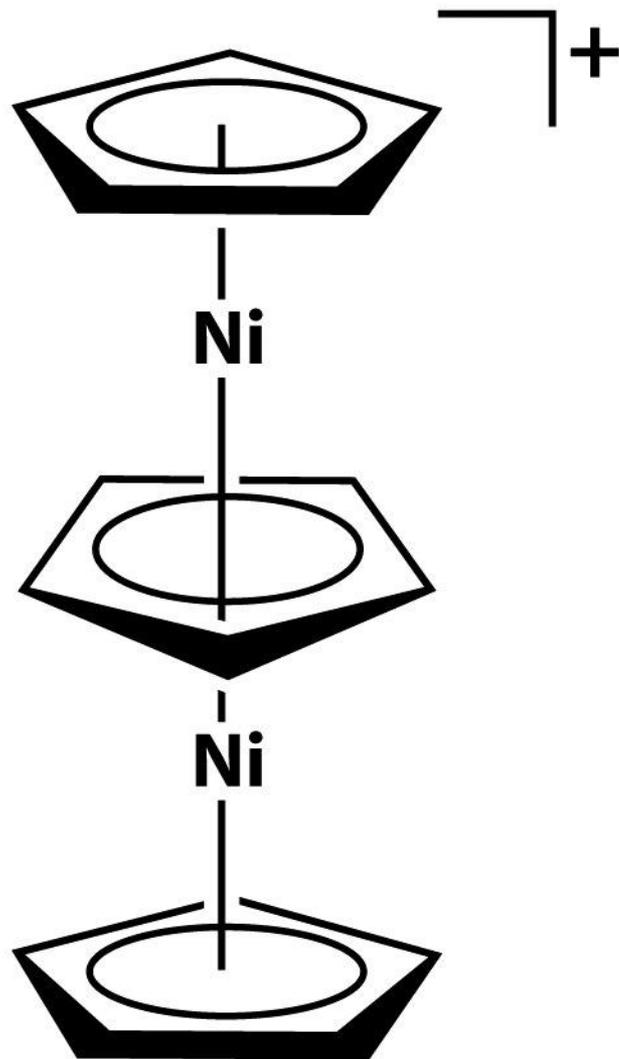
Triple decker or *double sandwich*
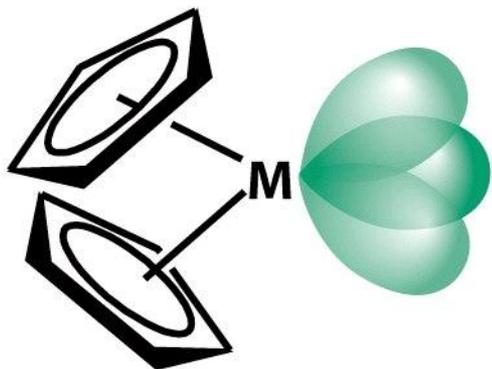
General form
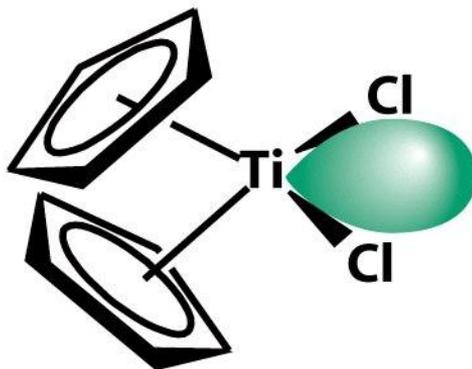
16-electron   M (0)
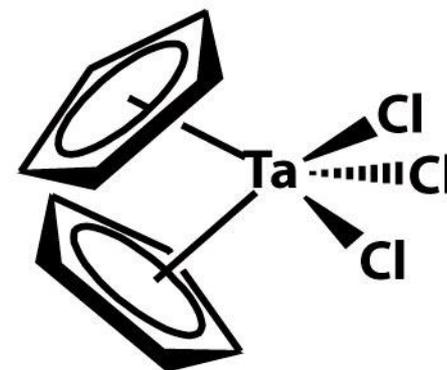
18-electron
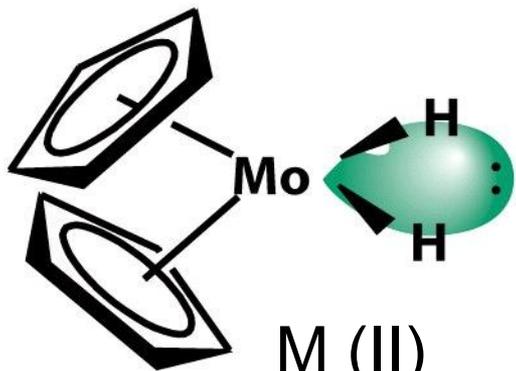
18-electron   M (II)
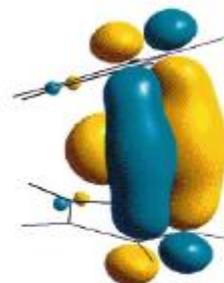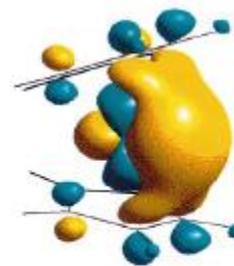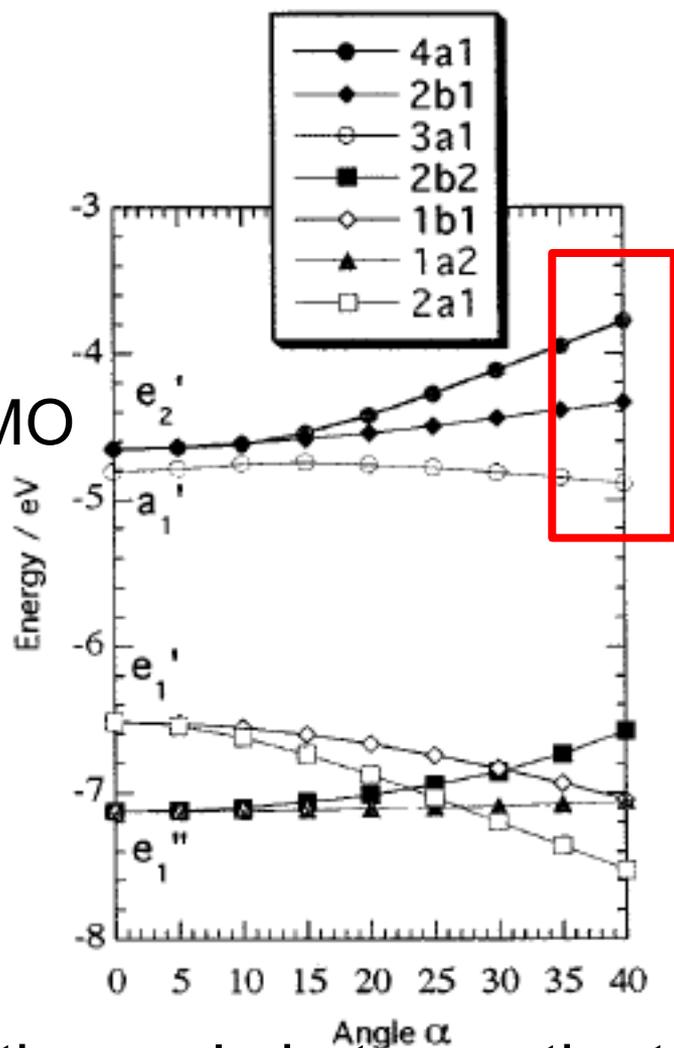
18-electron   M (III)

32
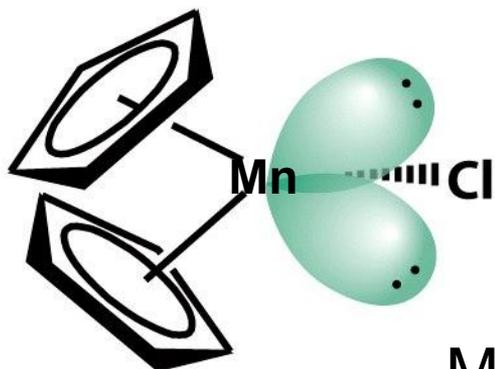
Walsh diagram

The most stable geometry depends on the metal electrons number

HOMO
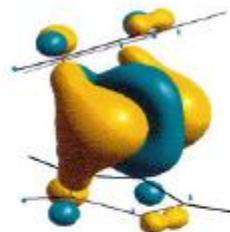
α is the angle between the two Cp ligands; $\alpha = 0$ corresponds to Ferrocene

33

f-block elements

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Rf

General lanthanide = Ln, $4f^{n}5d^{1}6s^{2}$

Synthesis and X-ray Crystal Structure of the First Tris(pentamethylcyclopentadienyl)–Metal Complex: $(\eta^5\text{-}C_5Me_5)_3Sm$

William J. Evans,* Shirley L. Gonzales, and
Joseph W. Ziller
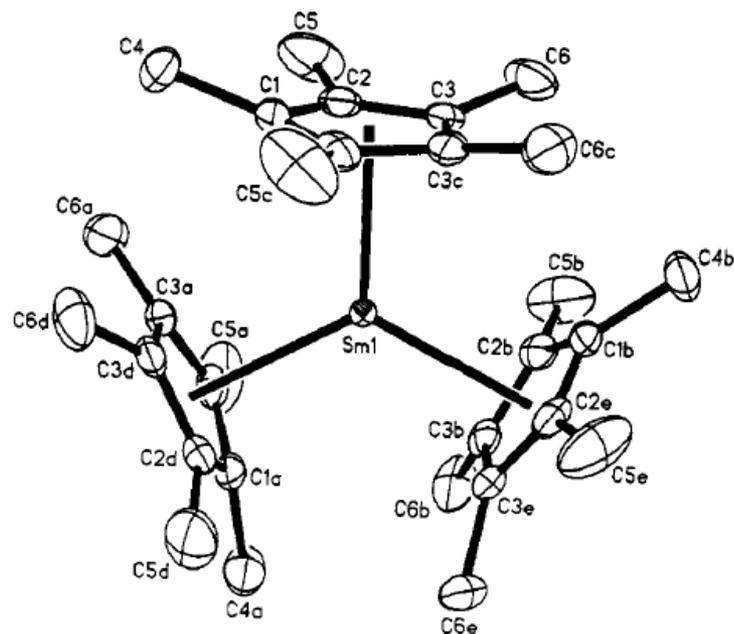
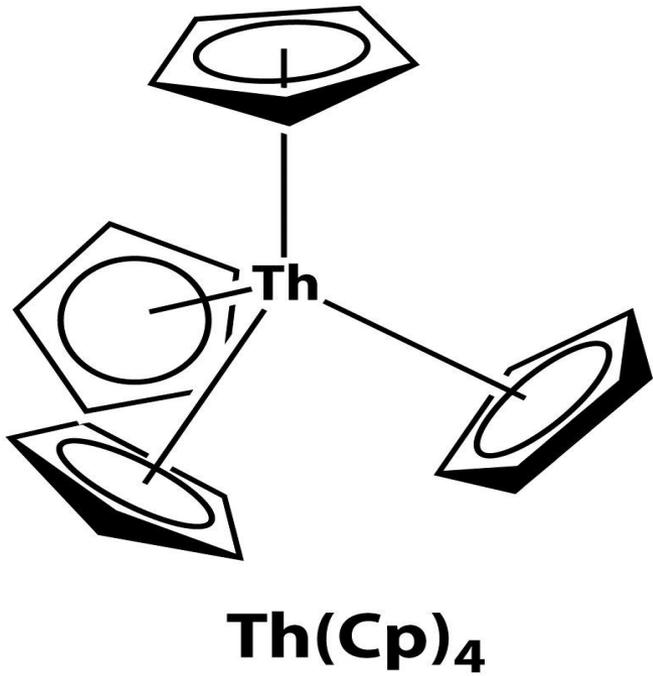**Figure 1.** Molecular structure of $(C_5Me_5)_3Sm$ (2) with probability ellipsoids drawn at the 50% level.
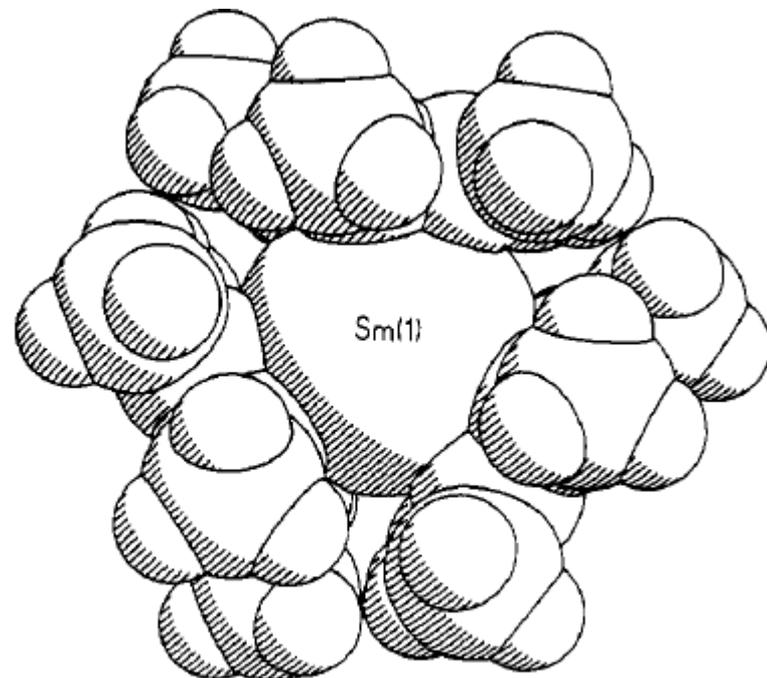
Figure 2. Space-filling model of $(C_5Me_5)_3Sm$ (2). 35

$$Sm(\eta^1\text{-}Cp^*)(\eta^5\text{-}Cp^*)_2$$

$$Sm(\eta^5\text{-}Cp^*)_3 \rightleftharpoons Sm(\eta^1\text{-}Cp^*)(\eta^5\text{-}Cp^*)_2$$

f-block elements

General actinide = An, $5f^n6d^17s^2$

Th(Cp)₄

U(Cp)₄

U(Cp*)₃Cl

Th(C$_8$H$_8$)$_2$

Thorocene

U(C$_8$H$_8$)$_2$

Uranocene