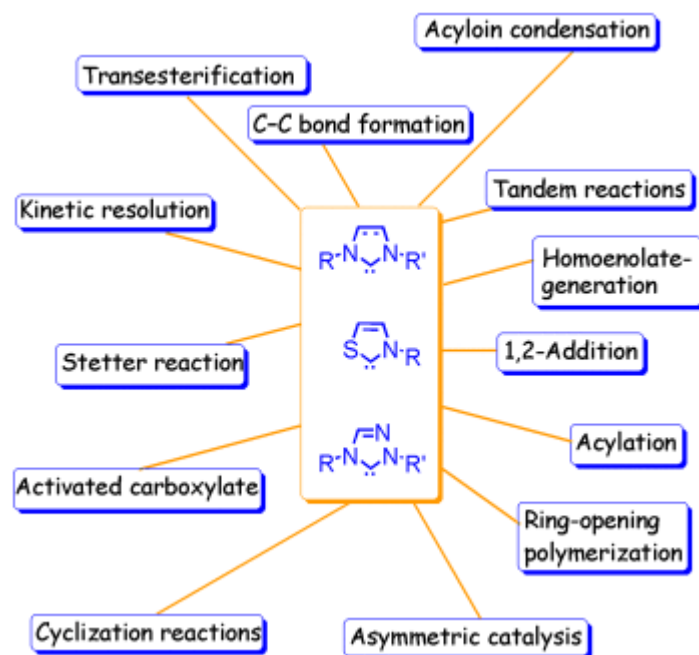


**FIGURE 2.** Time line of milestones in the development of olefin metathesis catalysts.

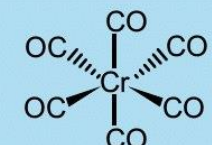
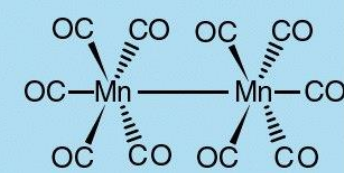
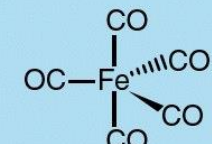
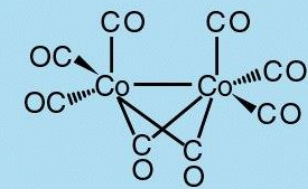
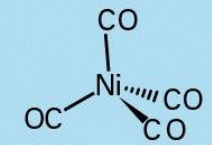
# N-Heterocyclic Carbenes as Organocatalysts

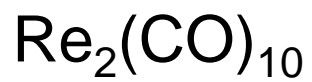
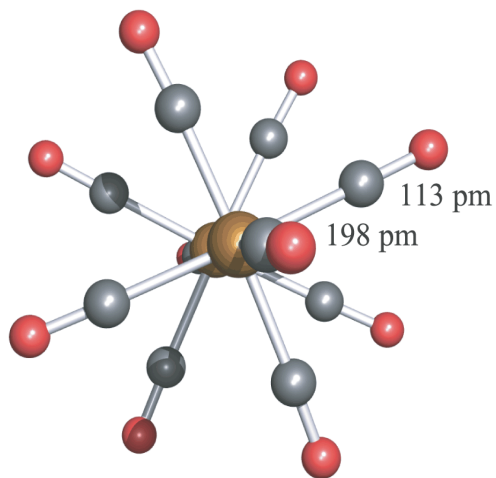
Nicolas Marion, Silvia Díez-González,\* and Steven P. Nolan\*



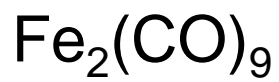
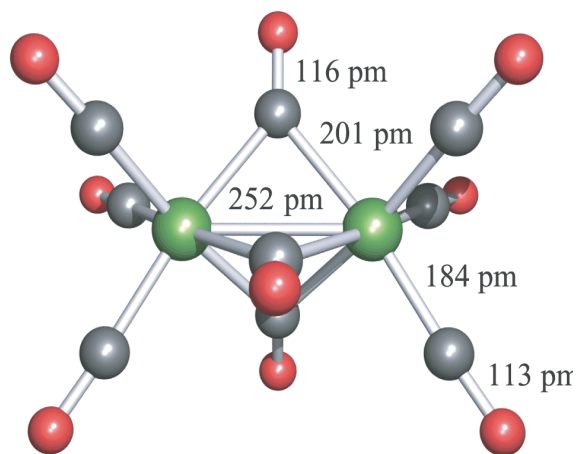
# Carbonili omoleptici

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

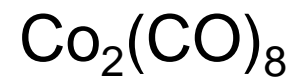
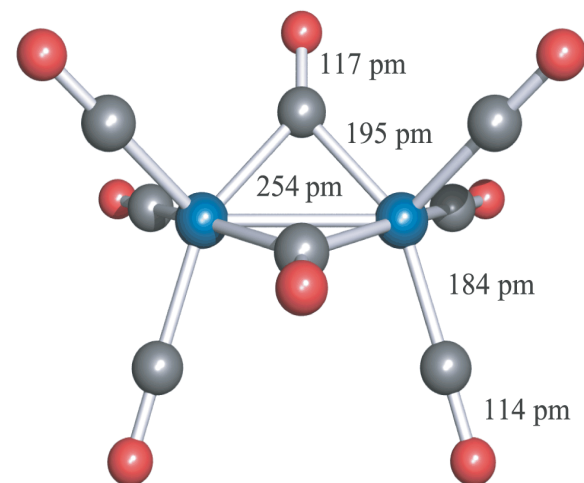
Group	Formula	Valence electrons		Structure
6	$\text{Cr}(\text{CO})_6$	Cr 6(CO)	6 <u>12</u> 18	
7	$\text{Mn}_2(\text{CO})_{10}$	Mn 5(CO) M—M	7 10 <u>1</u> 18	
8	$\text{Fe}(\text{CO})_5$	Fe 5(CO)	8 <u>10</u> 18	
9	$\text{Co}_2(\text{CO})_8$	Co 4(CO) M—M	9 8 <u>1</u> 18	
10	$\text{Ni}(\text{CO})_4$	Ni 4(CO)	10 <u>8</u> 18	



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



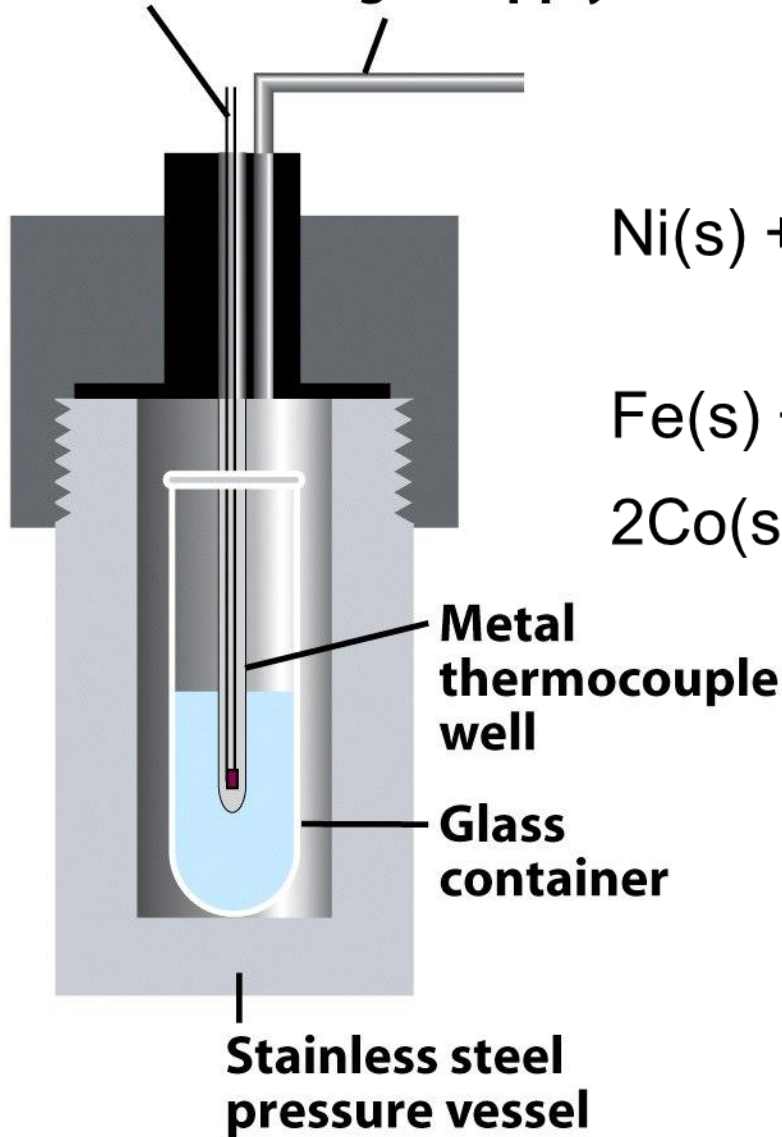
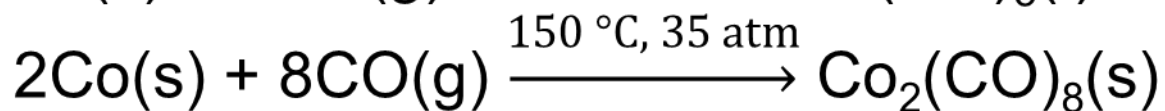
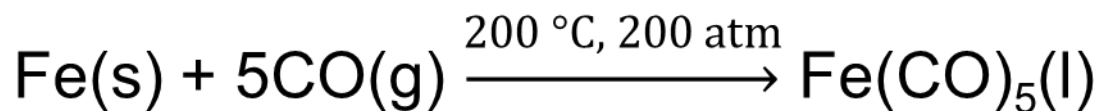
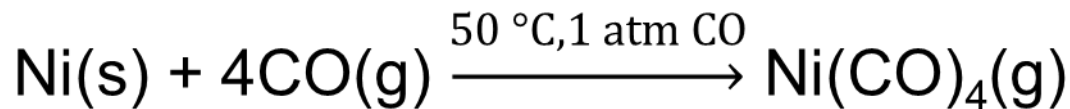
$16 + 18 + 2 = 36e^-$



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

Thermocouple  
High-pressure  
gas supply

# Reazione diretta



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  $350^{\circ}$  and  $450^{\circ}$ , 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.\*

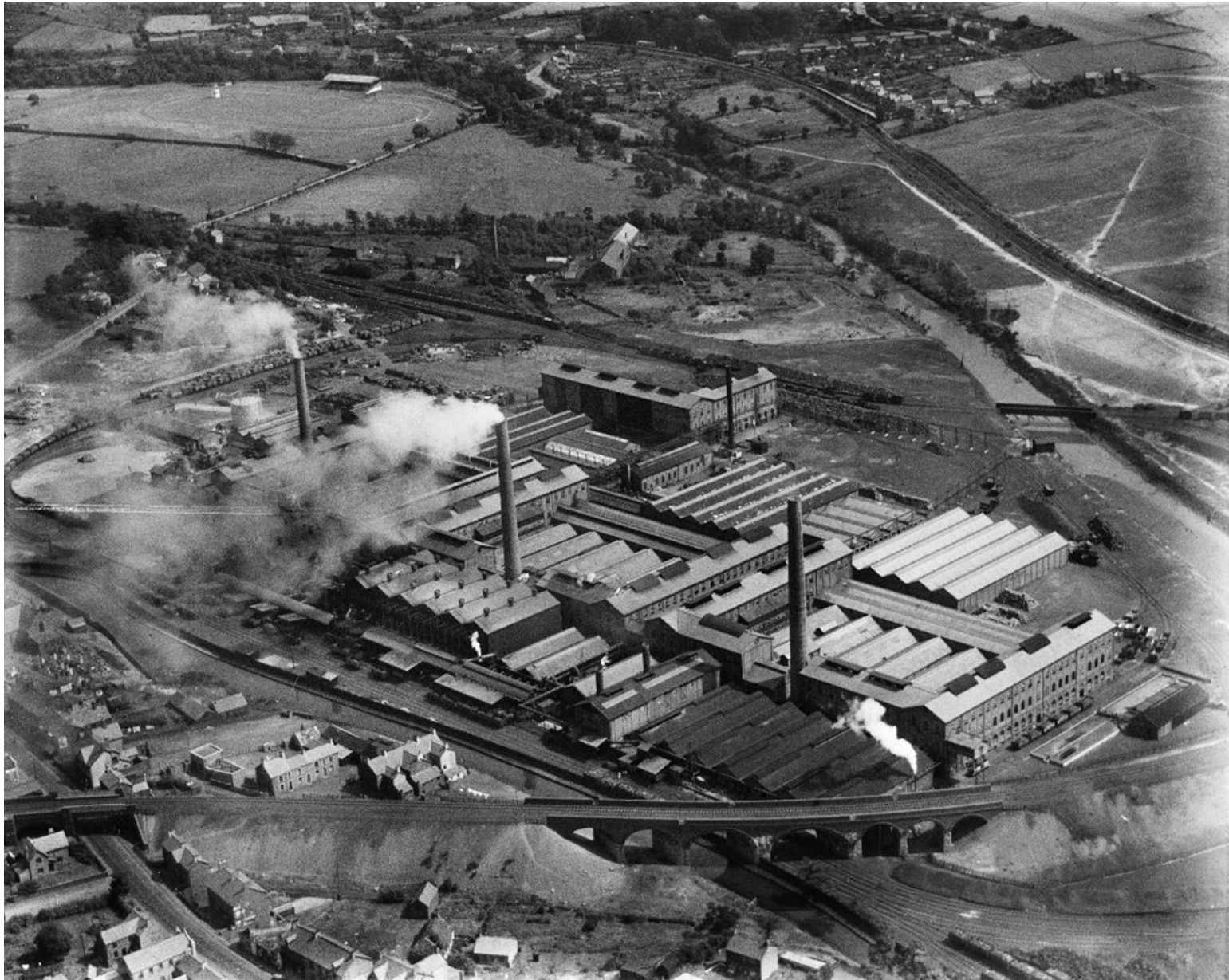
In order to determine the nickel in this substance, we have heated it with concentrated sulphuric acid to about  $200^{\circ}$ , and then added nitrate of potash in small portions to oxidise the carbon. This was the only way by which we could obtain a perfectly clear solution, and

\* 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

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  $\text{Ni}(\text{CO})_4$ .

*J. Chem. Soc. Trans.* **1890**, 57, 749–753.

# Mond Nickel Works, Clydach (Wales)



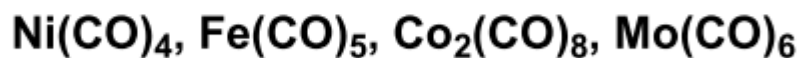
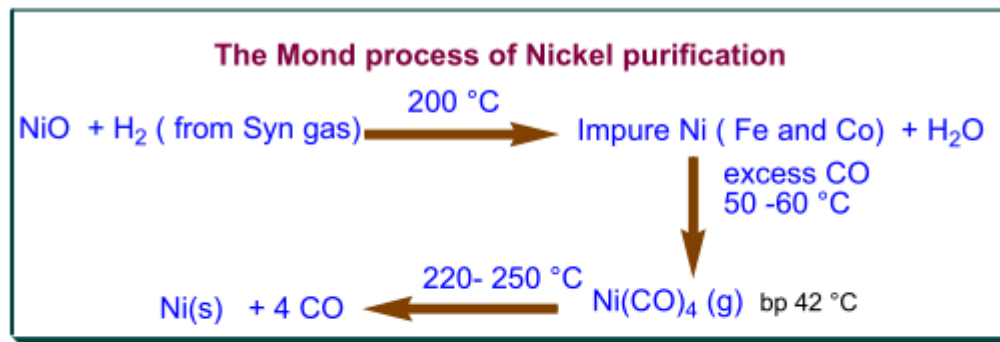




Ludwig Mond 1839-1909

Father of Metal Carbonyl Chemistry

Founder of Imperial Chemical Industry,  
England

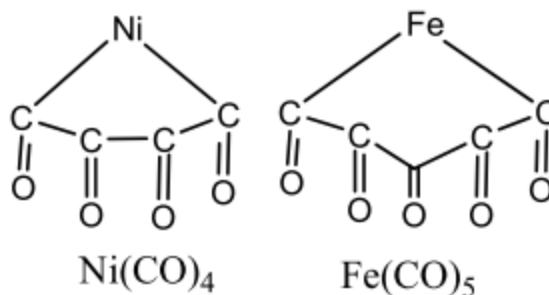


1890

1891

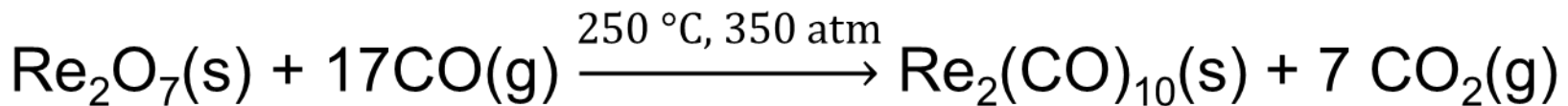
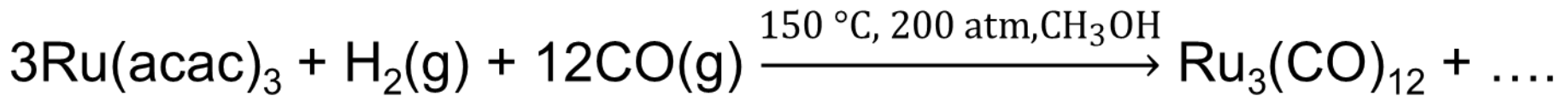
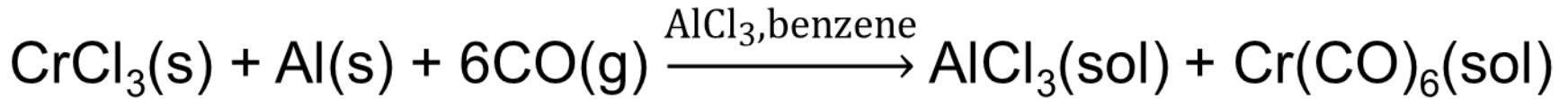
1910

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



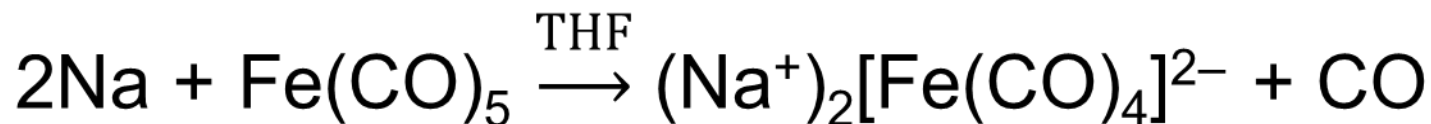
1890-1930 textbooks

# Carbonilazione riduttiva

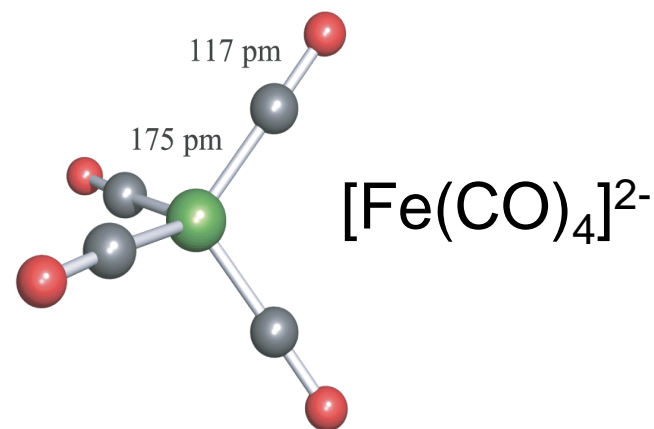


Group number	5	6	7	8	9	10
First row metals	<b>V(CO)<sub>6</sub></b> Dark blue solid; paramagnetic; dec. 343 K	<b>Cr(CO)<sub>6</sub></b> White solid; sublimes <i>in vacuo</i> ; dec. 403 K	<b>Mn<sub>2</sub>(CO)<sub>10</sub></b> Yellow solid; mp 427 K	<b>Fe(CO)<sub>5</sub></b> Yellow liquid; mp 253 K; bp 376 K  <b>Fe<sub>2</sub>(CO)<sub>9</sub></b> Golden crystals; mp 373 K (dec.) <b>Fe<sub>3</sub>(CO)<sub>12</sub></b> Dark green solid; dec. 413 K	<b>Co<sub>2</sub>(CO)<sub>8</sub></b> Air-sensitive, orange-red solid; mp 324 K  <b>Co<sub>4</sub>(CO)<sub>12</sub></b> Air-sensitive, black solid <b>Co<sub>6</sub>(CO)<sub>16</sub></b> Black solid; slowly dec. in air	<b>Ni(CO)<sub>4</sub></b> Colourless, volatile liquid; highly toxic vapour; bp 316 K
Second row metals		<b>Mo(CO)<sub>6</sub></b> White solid; sublimes <i>in vacuo</i>	<b>Tc<sub>2</sub>(CO)<sub>10</sub></b> White solid; slowly dec. in air; mp 433 K	<b>Ru(CO)<sub>5</sub></b> Colourless liquid; mp 251 K; dec. in air at 298 K to Ru <sub>3</sub> (CO) <sub>12</sub> + CO  <b>Ru<sub>3</sub>(CO)<sub>12</sub></b> Orange solid; mp 427 K; sublimes <i>in vacuo</i>	<b>Rh<sub>4</sub>(CO)<sub>12</sub></b> Red solid; >403 K dec. to Rh <sub>6</sub> (CO) <sub>16</sub>  <b>Rh<sub>6</sub>(CO)<sub>16</sub></b> Black solid; dec. >573 K	
Third row metals		<b>W(CO)<sub>6</sub></b> White solid; sublimes <i>in vacuo</i>	<b>Re<sub>2</sub>(CO)<sub>10</sub></b> White solid; mp 450 K	<b>Os(CO)<sub>5</sub></b> Yellow liquid; mp 275 K  <b>Os<sub>3</sub>(CO)<sub>12</sub></b> Yellow solid;	<b>Ir<sub>4</sub>(CO)<sub>12</sub></b> Slightly air-sensitive yellow solid; mp 443 K  <b>Ir<sub>6</sub>(CO)<sub>16</sub></b> Red solid	

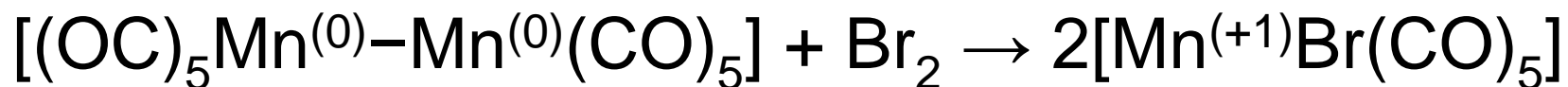
# Riduzione dei metallocarbonili a metallocarbonilati



$\nu_{\text{CO}} 1730 \text{ cm}^{-1}$



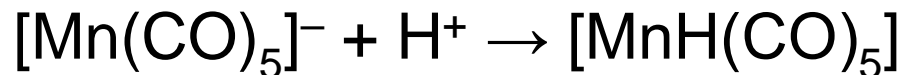
# Ossidazione (rottura ossidativa) di un legame M–M in metallo-carbonili



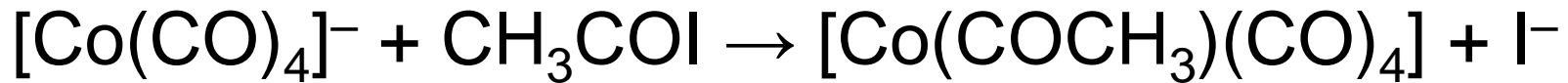
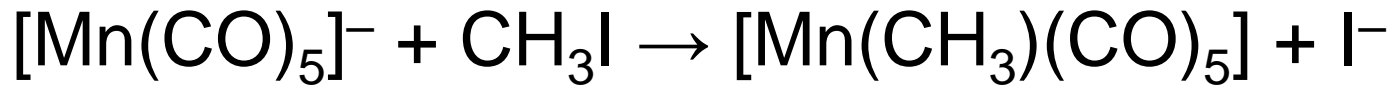
**Table 21.6** Acidity constants of *d*-metal hydrides in acetonitrile at 25°C

Hydride	p <i>K</i> <sub>a</sub>
[CoH(CO) <sub>4</sub> ]	8.3
[CoH(CO) <sub>3</sub> P(OPh) <sub>3</sub> ]	11.3
[Fe(H) <sub>2</sub> (CO) <sub>4</sub> ]	11.4
[CrH(Cp)(CO) <sub>3</sub> ]	13.3
[MoH(Cp)(CO) <sub>3</sub> ]	13.9
[MnH(CO) <sub>5</sub> ]	15.1
[CoH(CO) <sub>3</sub> PPh <sub>3</sub> ]	15.4
[WH(Cp)(CO) <sub>3</sub> ]	16.1
[MoH(Cp*)(CO) <sub>3</sub> ]	17.1
[Ru(H) <sub>2</sub> (CO) <sub>4</sub> ]	18.7
[FeH(Cp)(CO) <sub>2</sub> ]	19.4
[RuH(Cp)(CO) <sub>2</sub> ]	20.2
[Os(H) <sub>2</sub> (CO) <sub>4</sub> ]	20.8
[ReH(CO) <sub>5</sub> ]	21.1
[FeH(Cp*)(CO) <sub>2</sub> ]	26.3
[WH(Cp)(CO) <sub>2</sub> PMe <sub>3</sub> ]	26.6

## Protonazione di metallocarbonilati

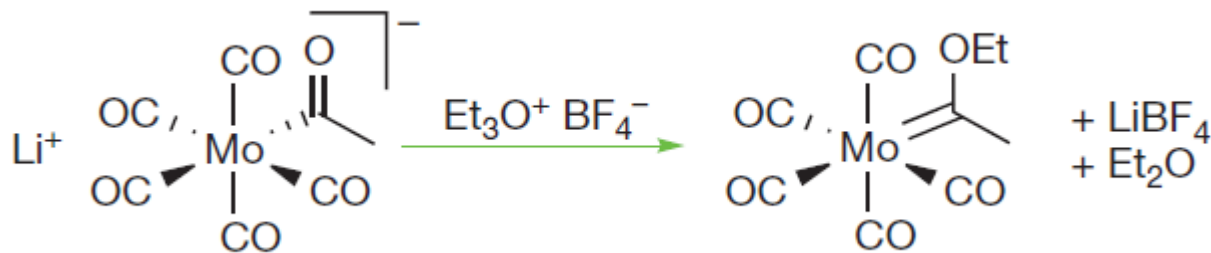
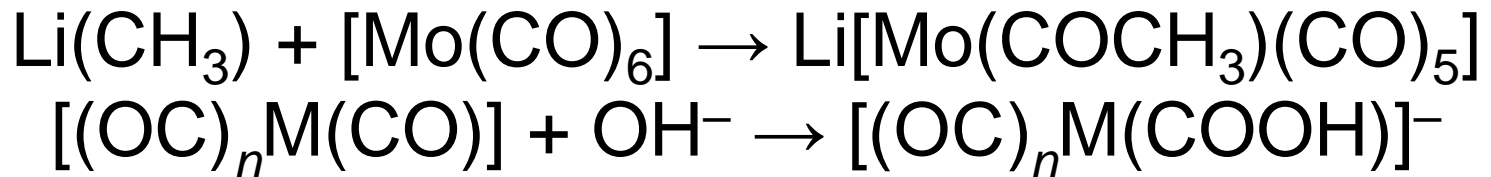


# Basicità dei metallocarbonilati: Attacco nucleofilo

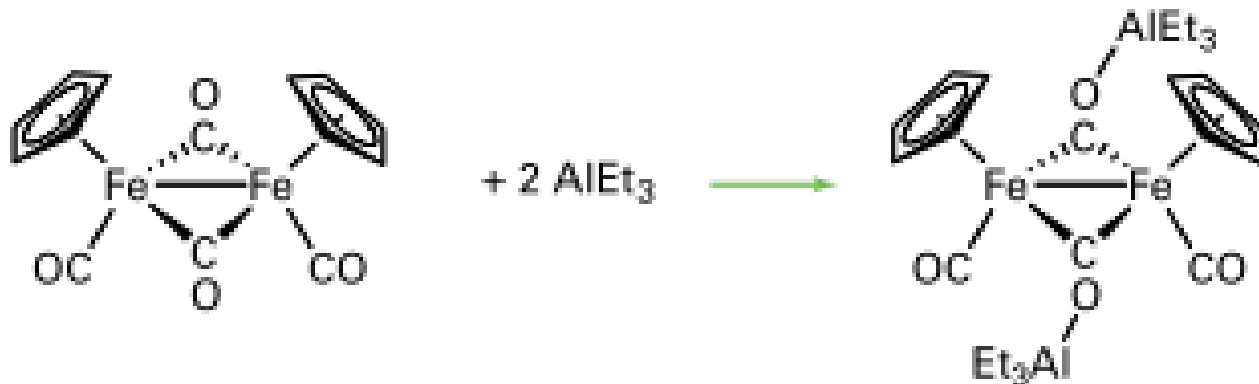


# Attacchi nucleofili ed elettrofilii a carbonili

Metallo elettron-povero: attacco nucleofilo su C



Metallo elettron-ricco: attacco elettrofilo su 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 <sup>†</sup>	$M(CO)_5$	<i>ax</i>		$C_{3v}$	3 <sup>§</sup>
$M(CO)_4L_2$	<i>trans</i>		$D_{4h}$	1	$M(CO)_4L$	<i>eq</i>		$C_{2v}$	4
$M(CO)_4L_2$	<i>cis</i>		$C_{2v}$	4 <sup>‡</sup>	$M(CO)_3L_2$	<i>trans</i>		$D_{3h}$	1
$M(CO)_3L_3$	<i>mer</i>		$C_{2v}$	3 <sup>‡</sup>	$M(CO)_3L_2$	<i>cis</i>		$C_s$	3
$M(CO)_3L_3$	<i>fac</i>		$C_{3v}$	2	$M(CO)_4$			$T_d$	1

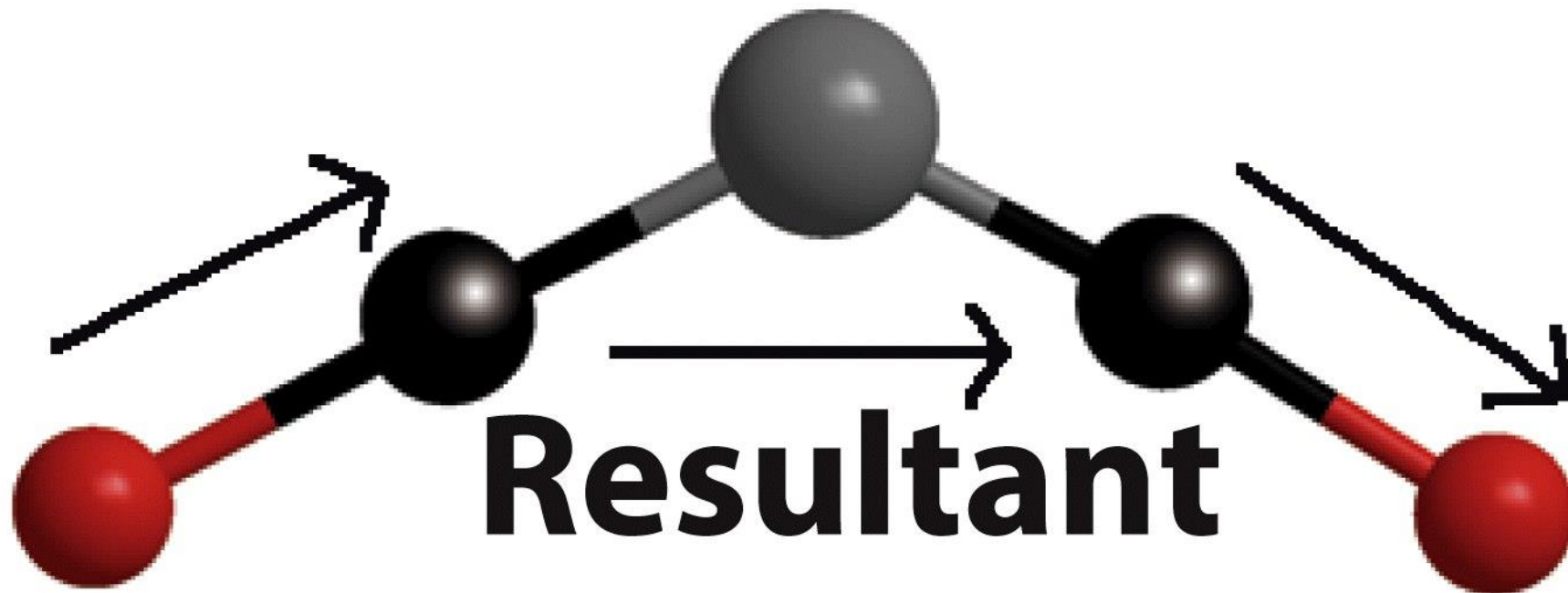
\* The number of IR bands expected in the CO stretching region is based on formal selection rules, and in some cases fewer bands are observed, as explained below.

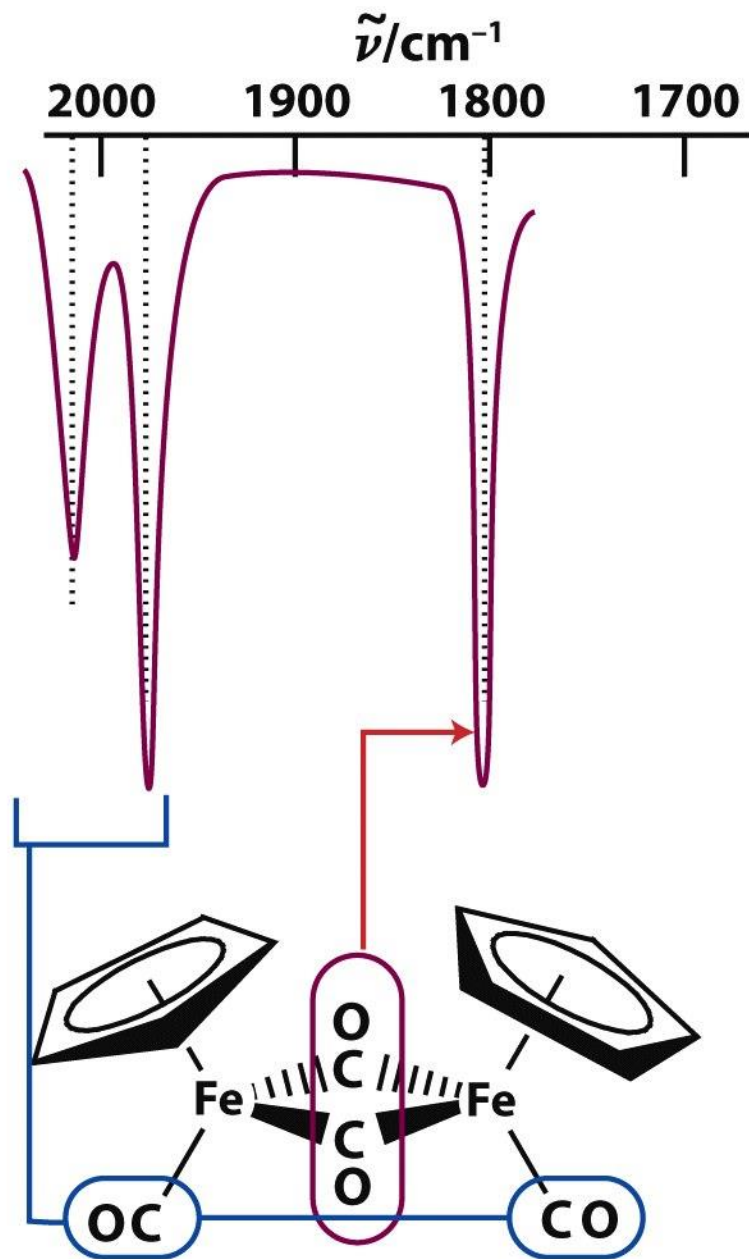
† If the fourfold array of CO ligands lies in the same plane as the metal atom, two bands will be observed.

‡ If the *trans* CO ligands are nearly collinear, one fewer band will be observed.

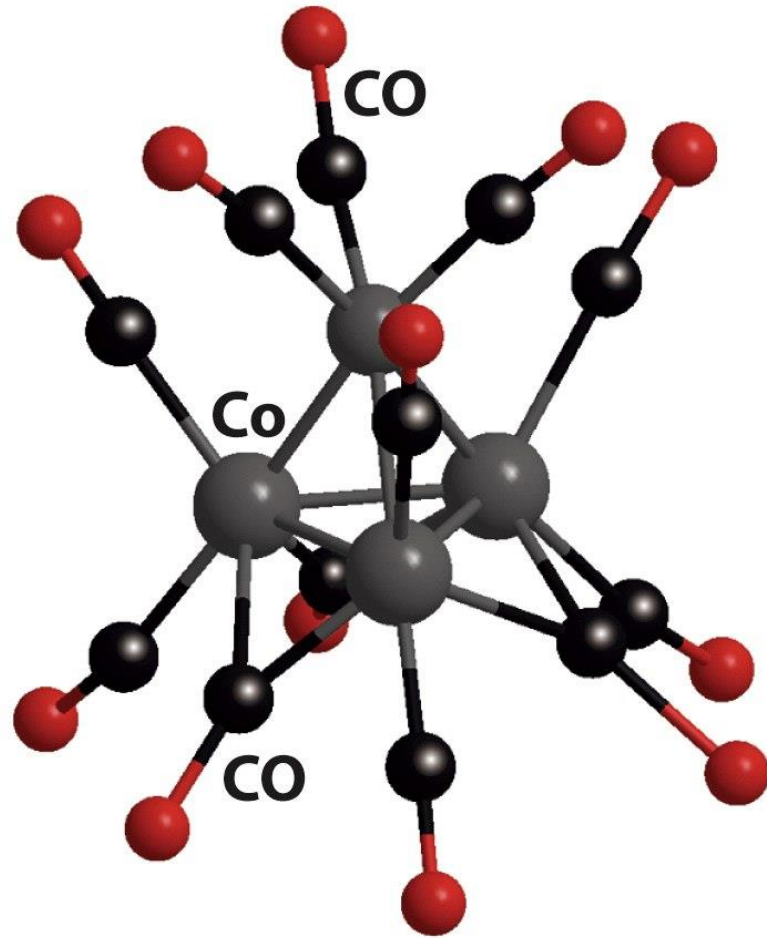
§ If the threefold array of CO ligands is nearly planar, only two bands will be observed.

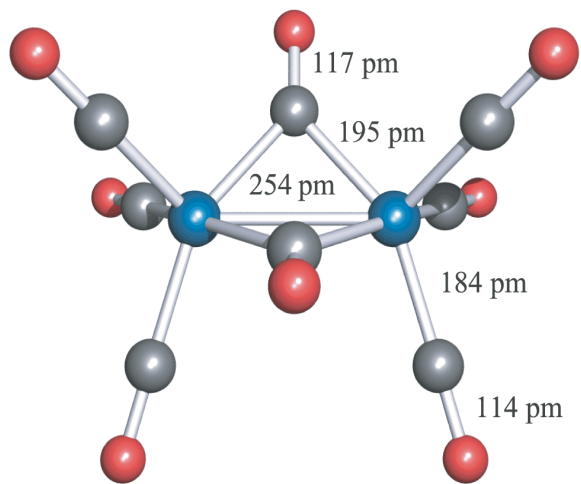




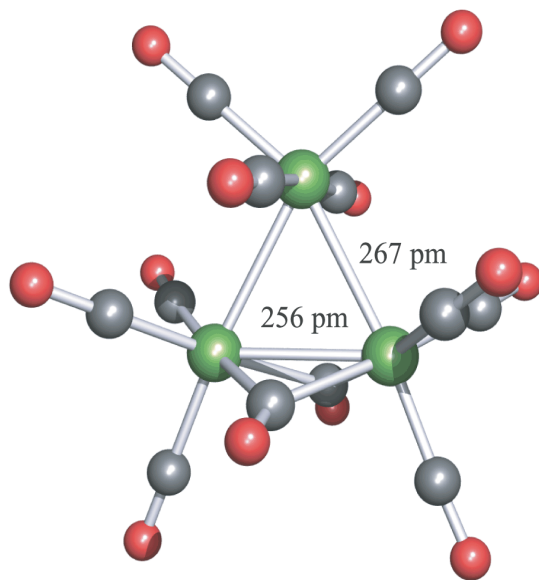
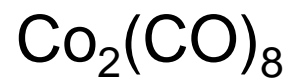


# Cluster carbonilico

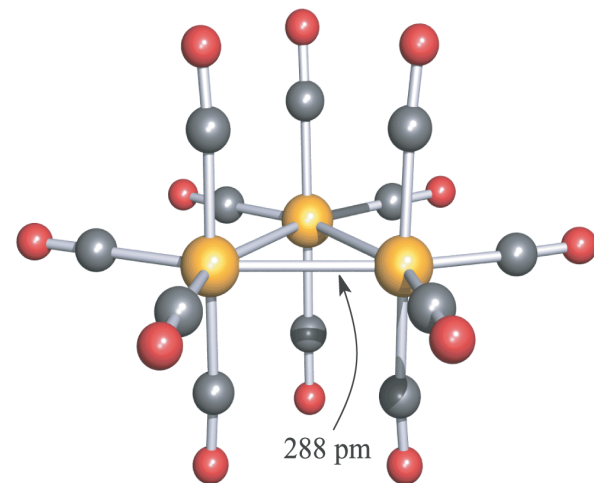




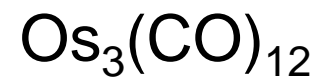
(d)

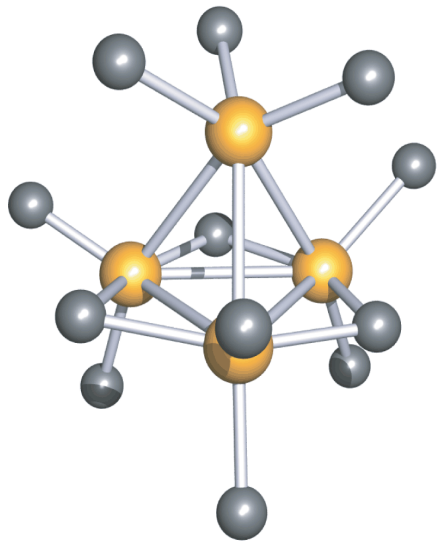


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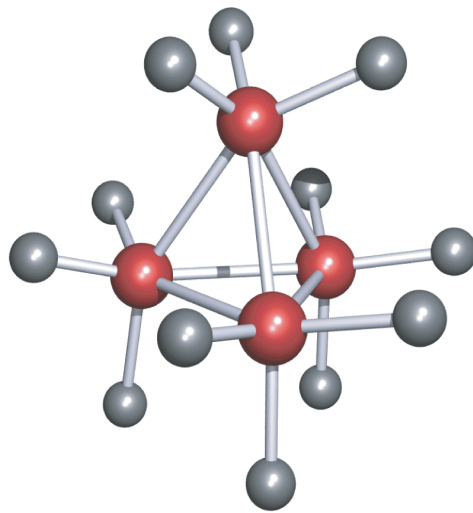
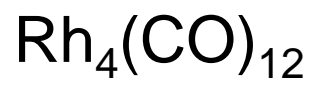


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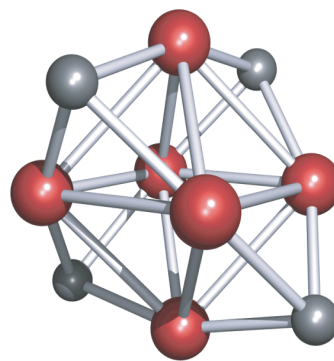




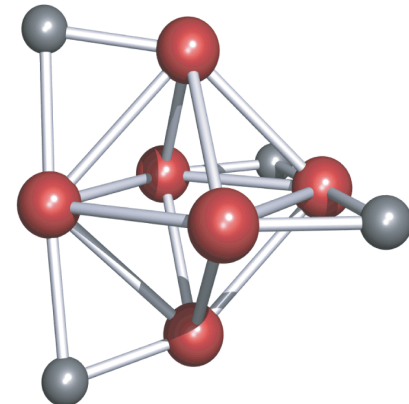
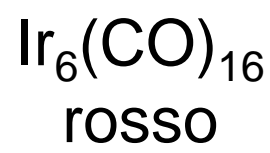
(a)



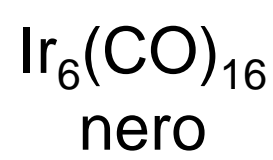
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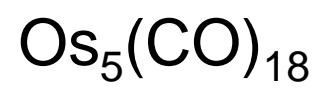
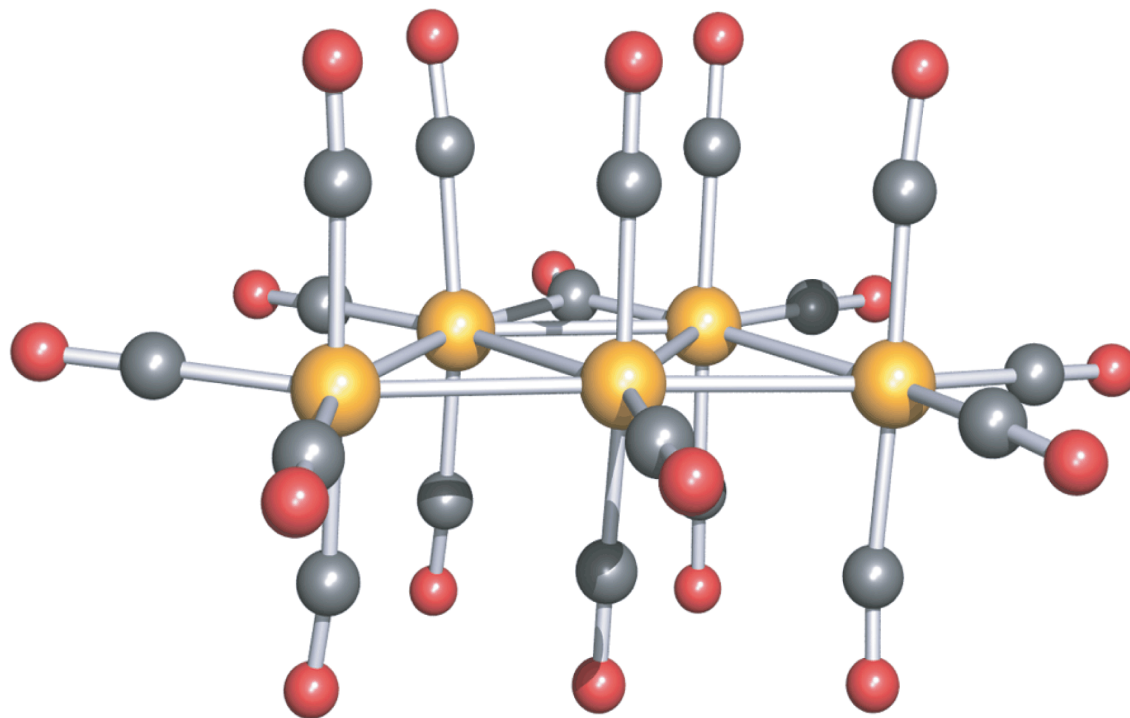


(c)



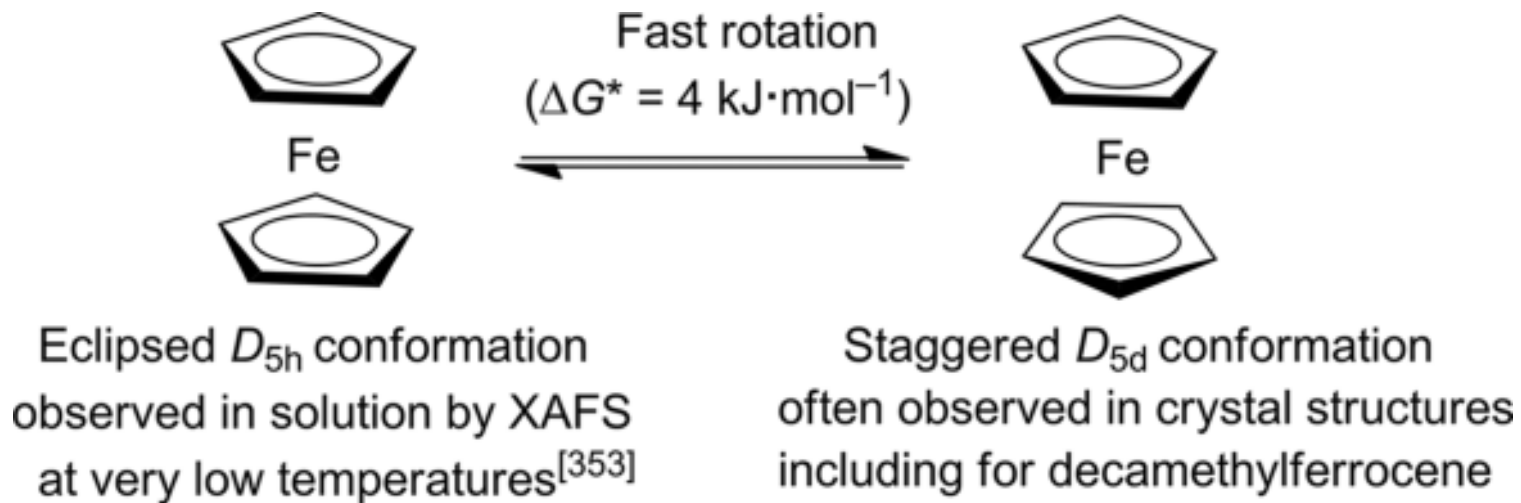
(d)







# Ferrocene e Metalloceni



- 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.

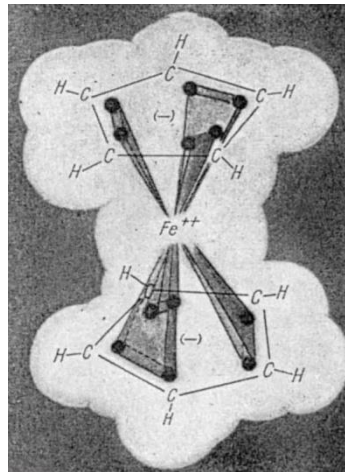
*Nel 2017 si contavano più di 18000 pubblicazioni sui ferroceni*

1973

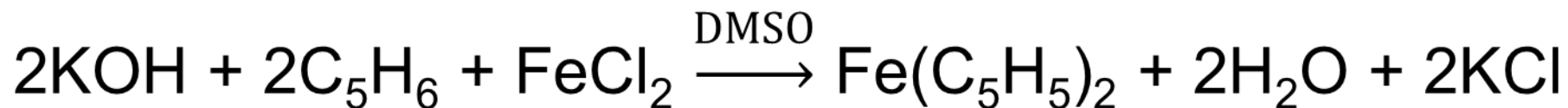
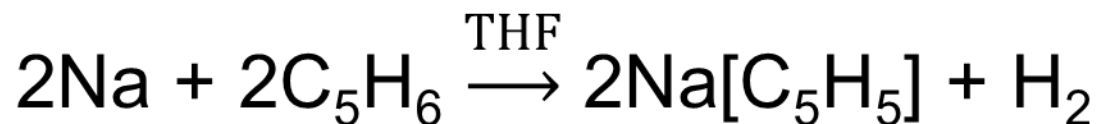
## Premio Nobel

Ernst-Otto Fisher (Monaco di Baviera)

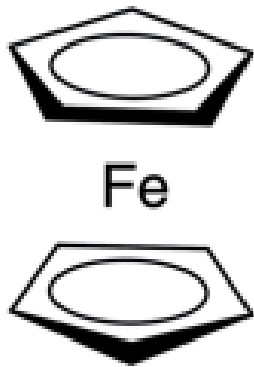
Geoffrey Wilkinson (Londra)



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

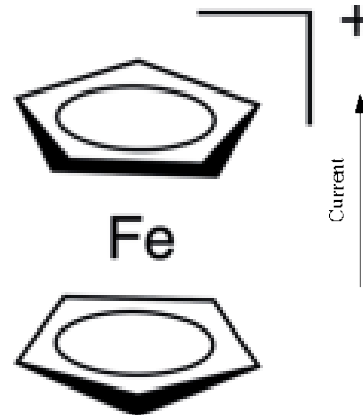
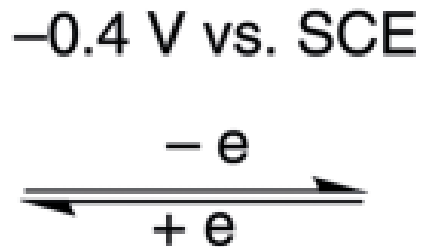


- Stabile fino a 400 °C (fonde a 172 °C)
- Stabile all'aria e solubile in molti solventi organici
- Reattività di un super-elettrofilo aromatico
- Ossidazione reversibile a +0.4 V vs SCE



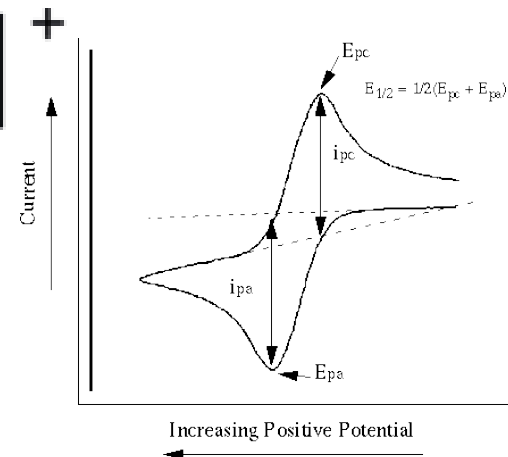
Ferrocene, orange  
 $d^6$ ,  $Fe^{II}$ , 18e

Functionalization with  
 non-oxidizing electrophiles

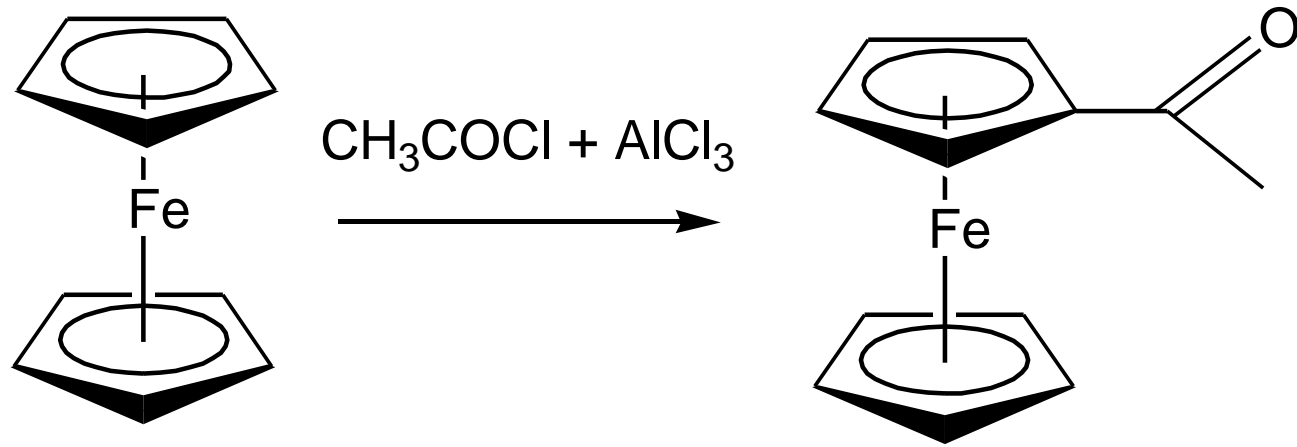


Ferricinium, deep-blue  
 $d^5$ ,  $Fe^{III}$ , 17e

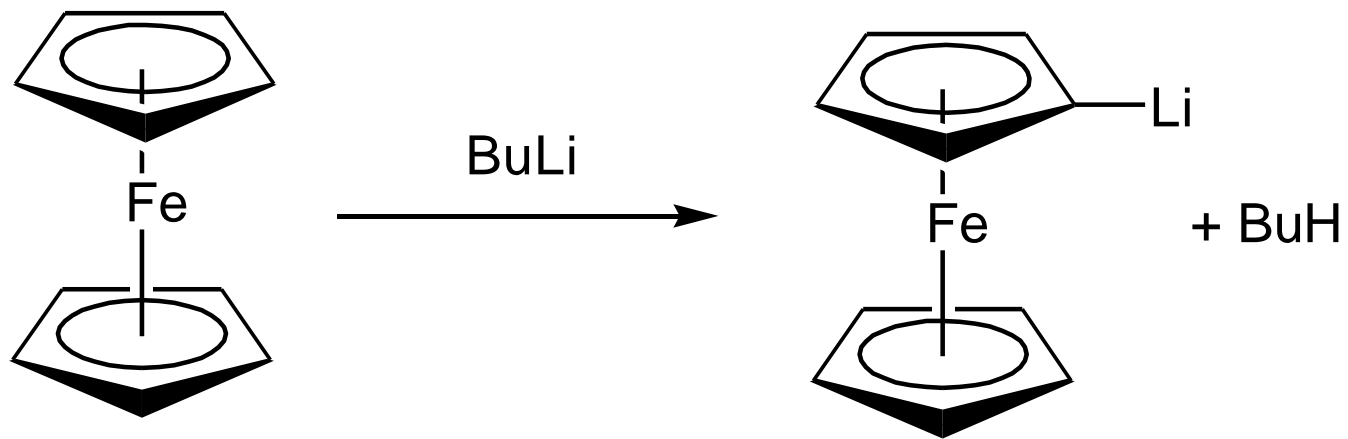
Isolable as  $BF_4^-$  or  $PF_6^-$  salt, etc.  
 Sensitive to  $O_2$  and nucleophiles

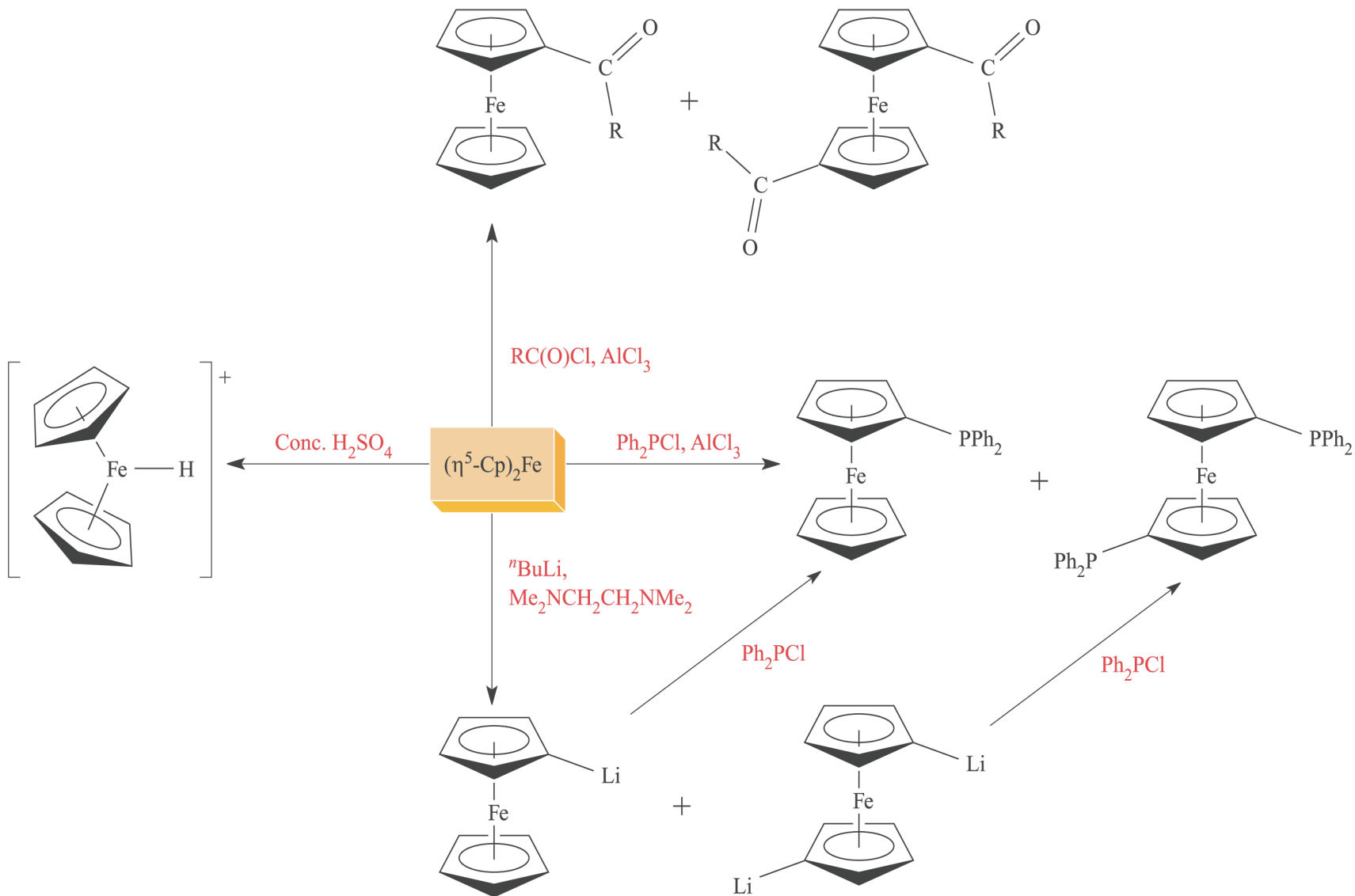


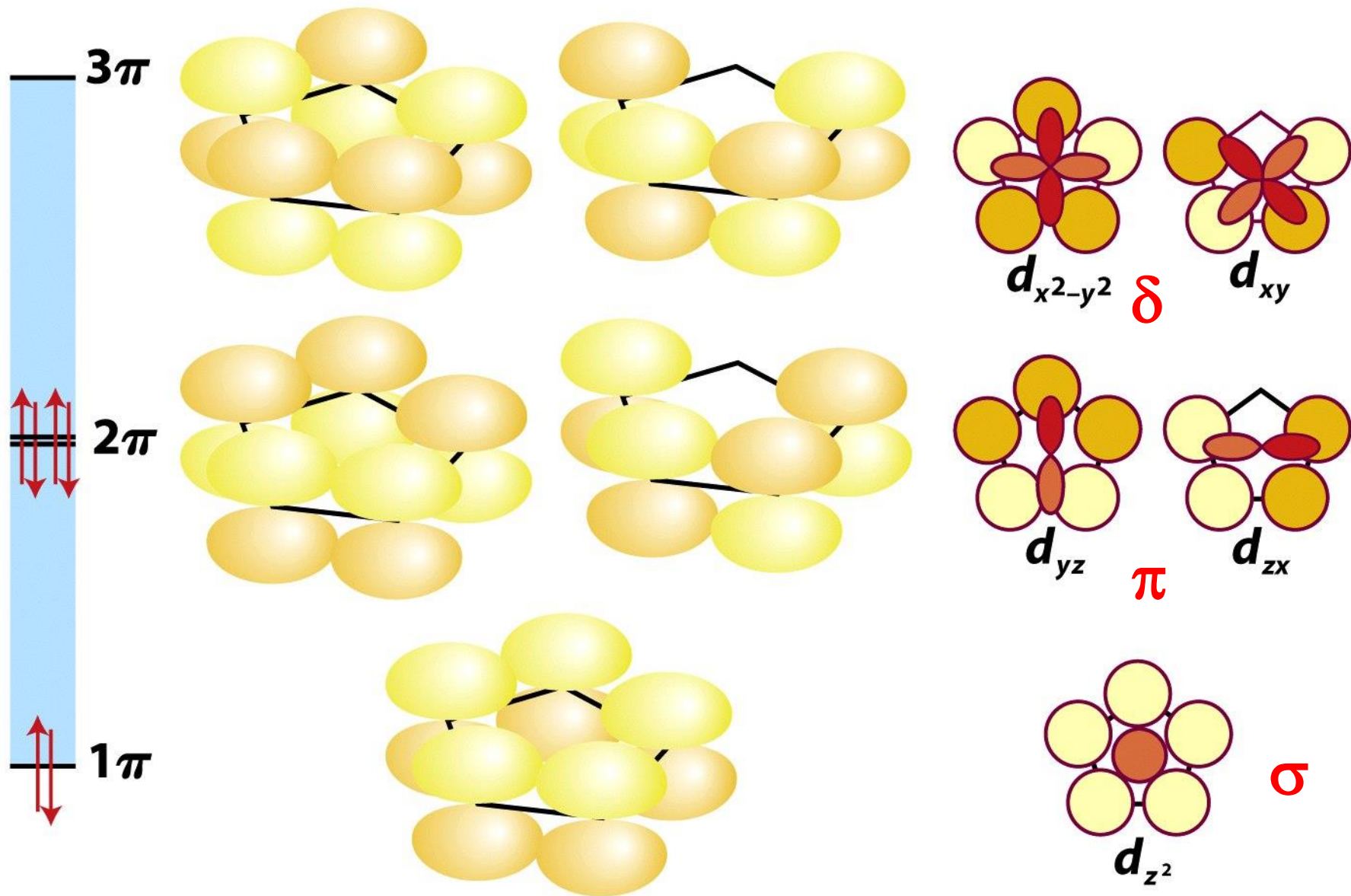
*L'ossidazione è perfettamente reversibile, tanto che il ferrocene è usato come standard in voltammetria ciclica. Di conseguenza il ferricinio ( $17e^-$ ) deve essere piuttosto stabile.*



acilazione di Friedel – Crafts







$(C_5H_5)_2^{2-}$  ( $D_{5h}$ )

Ferrocene ( $D_{5h}$ )

$Fe^{2+}$



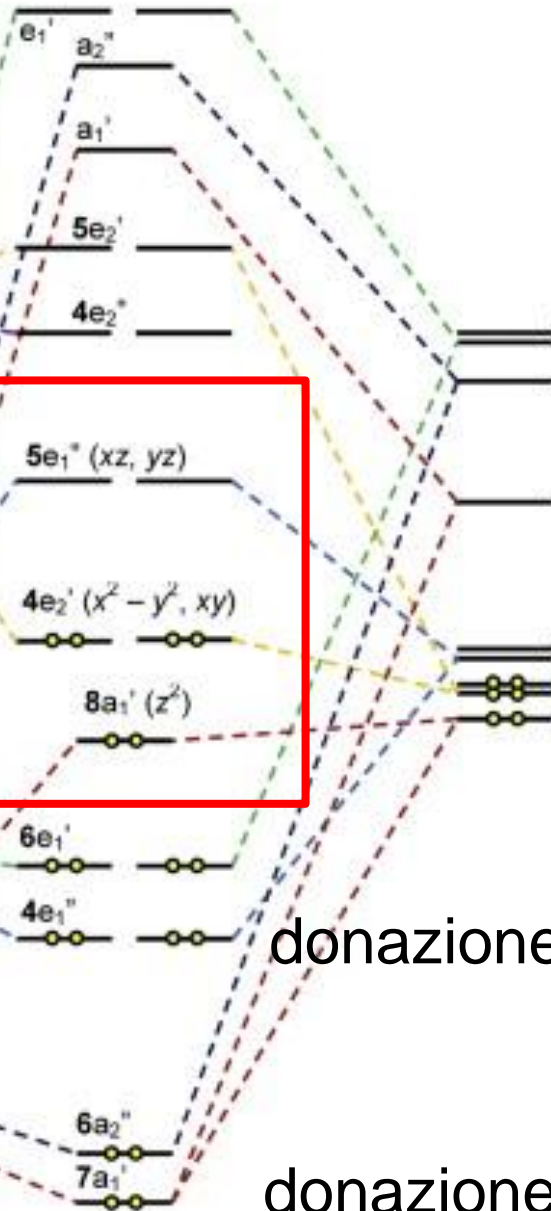
$e_2^*$   
 $e_2'$



$e_1^*$   
 $e_1'$



$a_2^*$   
 $a_1'$



$e_1'$



$a_2^*$

4p



$a_1'$

4s



$xz, yz$

$e_1^*$



$xy$   
 $x^2 - y^2$

$e_2'$



$a_1'$

3d

retrodonazione  $\delta$

LUMO

HOMO

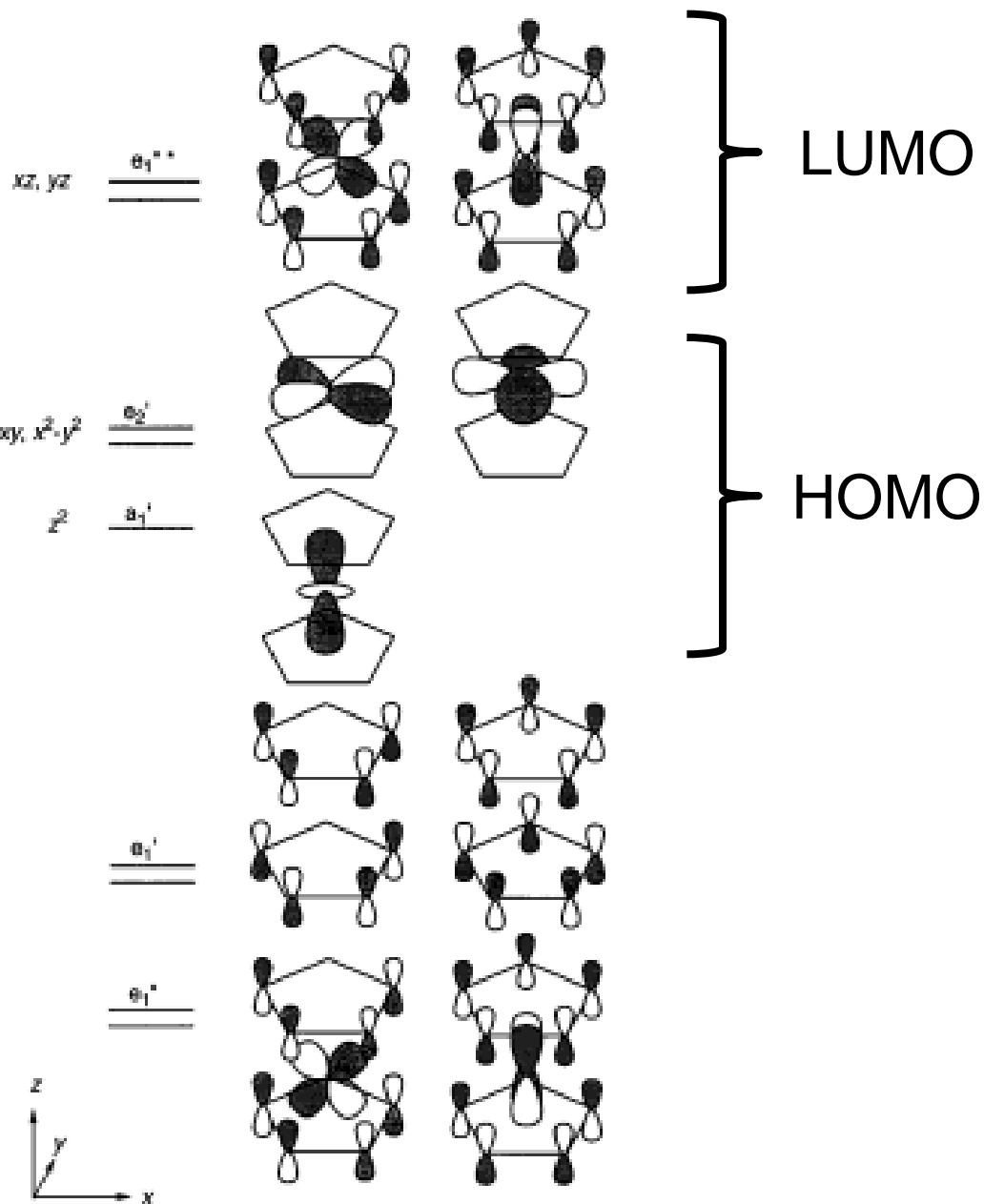
donazione  $\pi$

donazione  $\sigma$



retrodonazione  $\delta$   
non legame

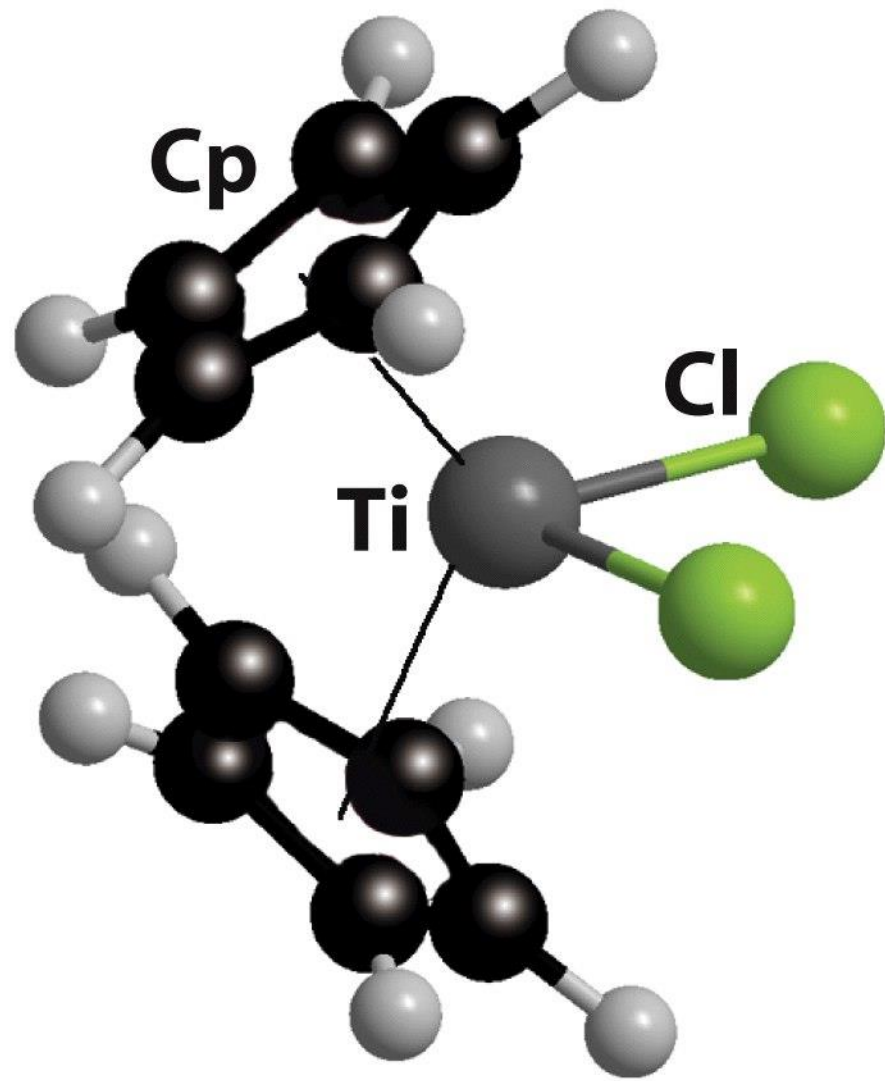
donazione  $\pi$



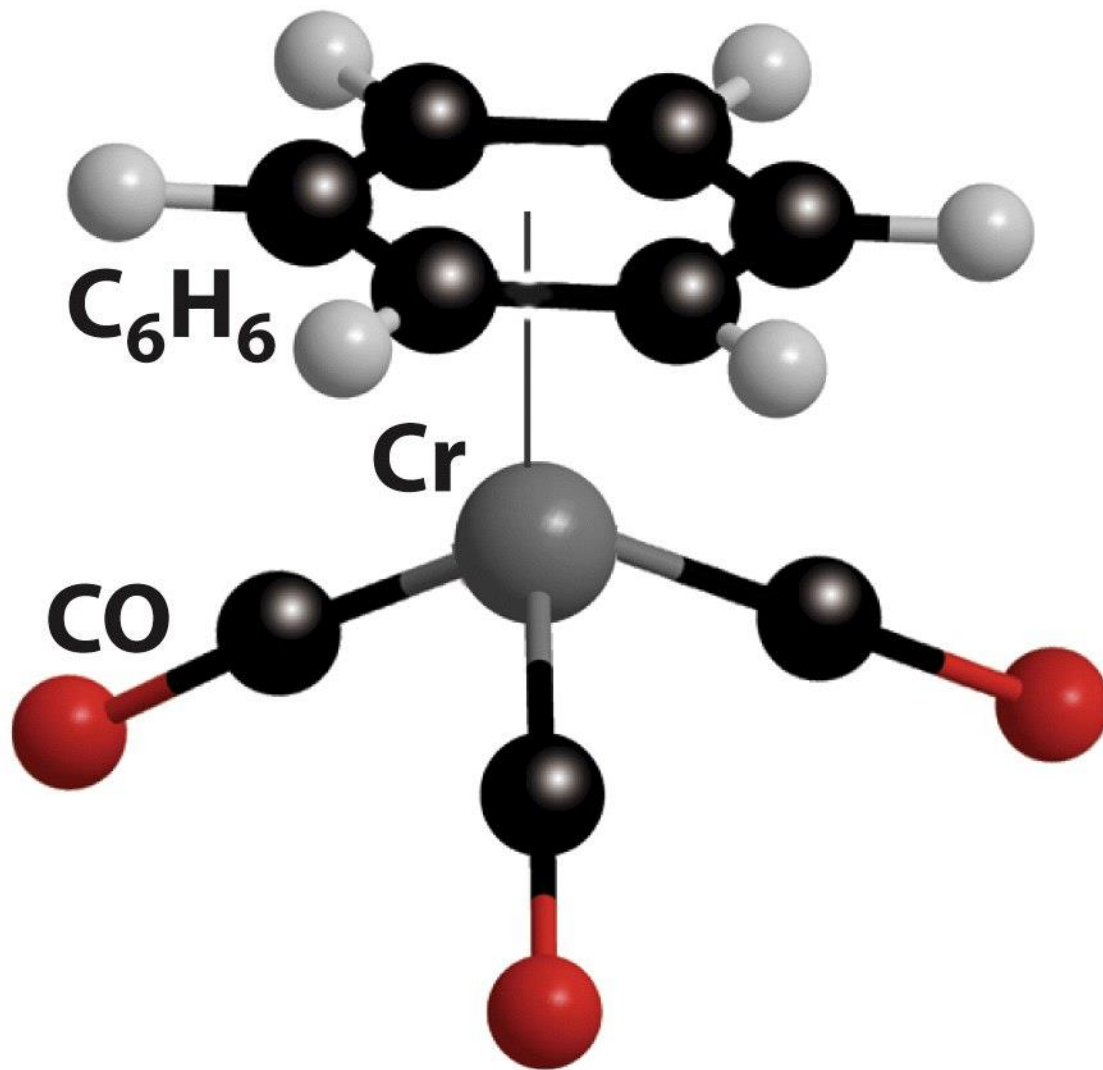
**Table 21.8** Electronic configuration and M—C bond length in  $[M(\eta^5\text{-Cp})_2]$  complexes

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

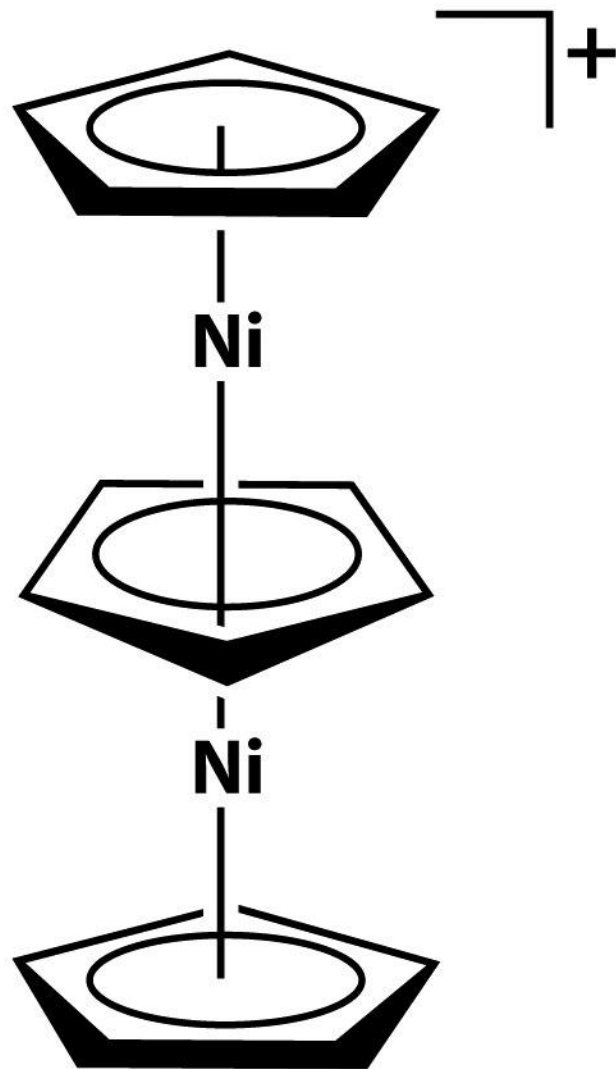
\*Data are quoted for this complex because  $[\text{Mn}(\eta^5\text{-Cp})_2]$  has a high-spin configuration and hence an anomalously long M—C bond (238 pm).



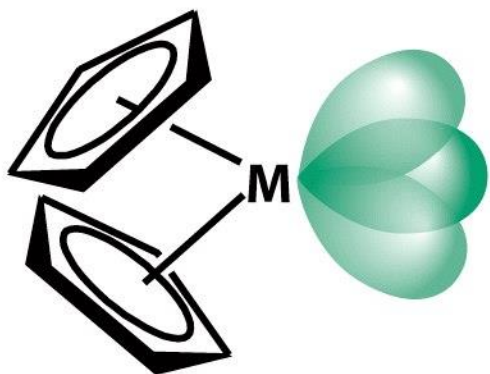
*Bent sandwich*



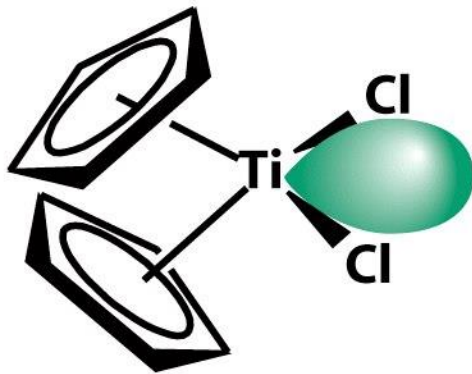
*Half sandwich o Piano stool*



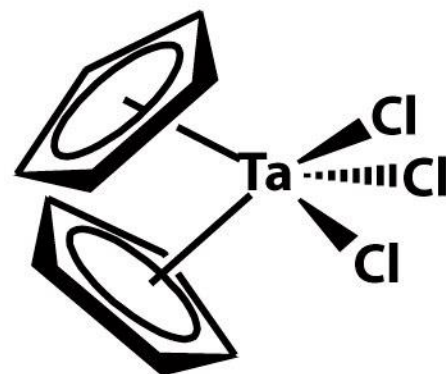
*Triple decker o doppio sandwich*



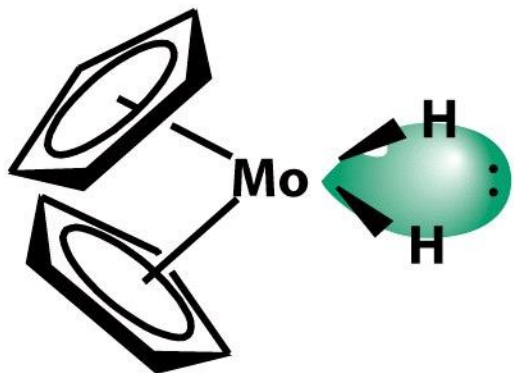
General form



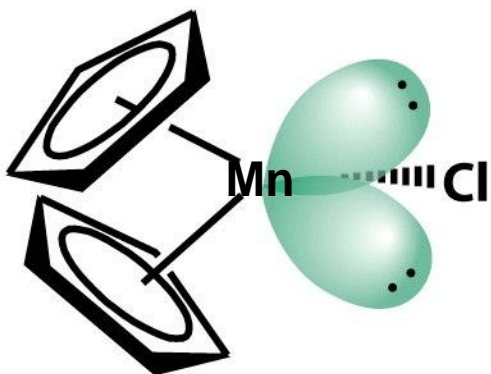
16-electron



18-electron



18-electron

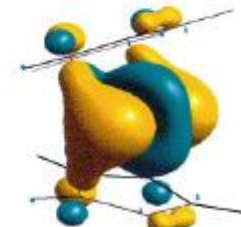
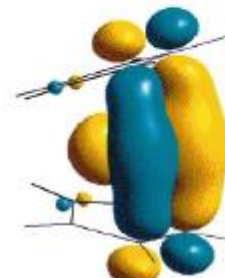
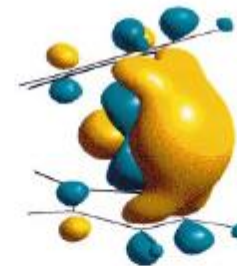
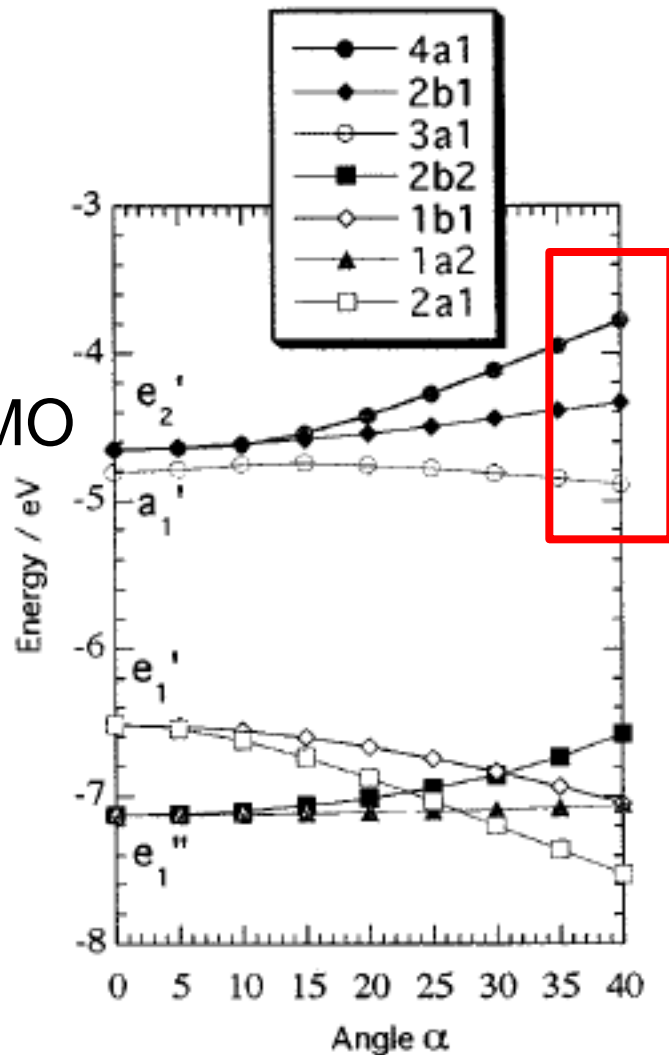


18-electron

# Diagramma di Walsh

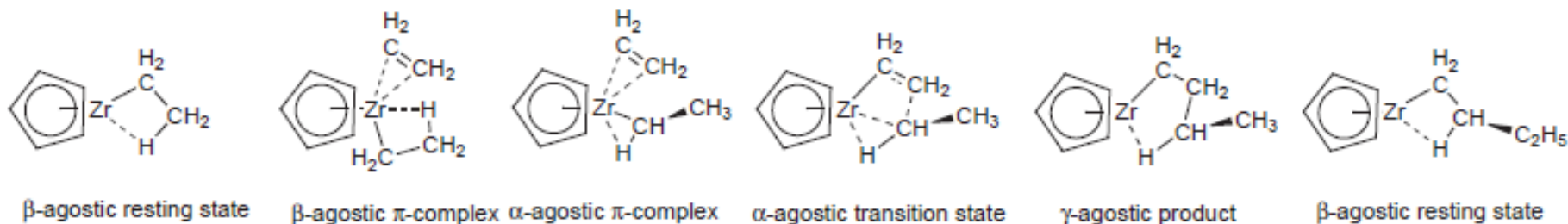
*la geometria più stabile dipende sostanzialmente da quanti elettroni porta il metallo*

HOMO



$\alpha$  è l'angolo fra i Cp;  $\alpha = 0$  corrisponde al ferrocene

# $\text{Cp}_2\text{ZrCl}_2$ : catalizzatore tipo Ziegler-Natta per la polimerizzazione di olefine



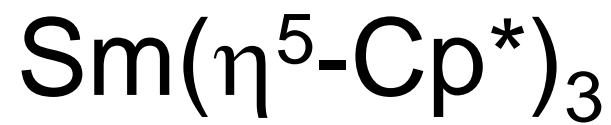
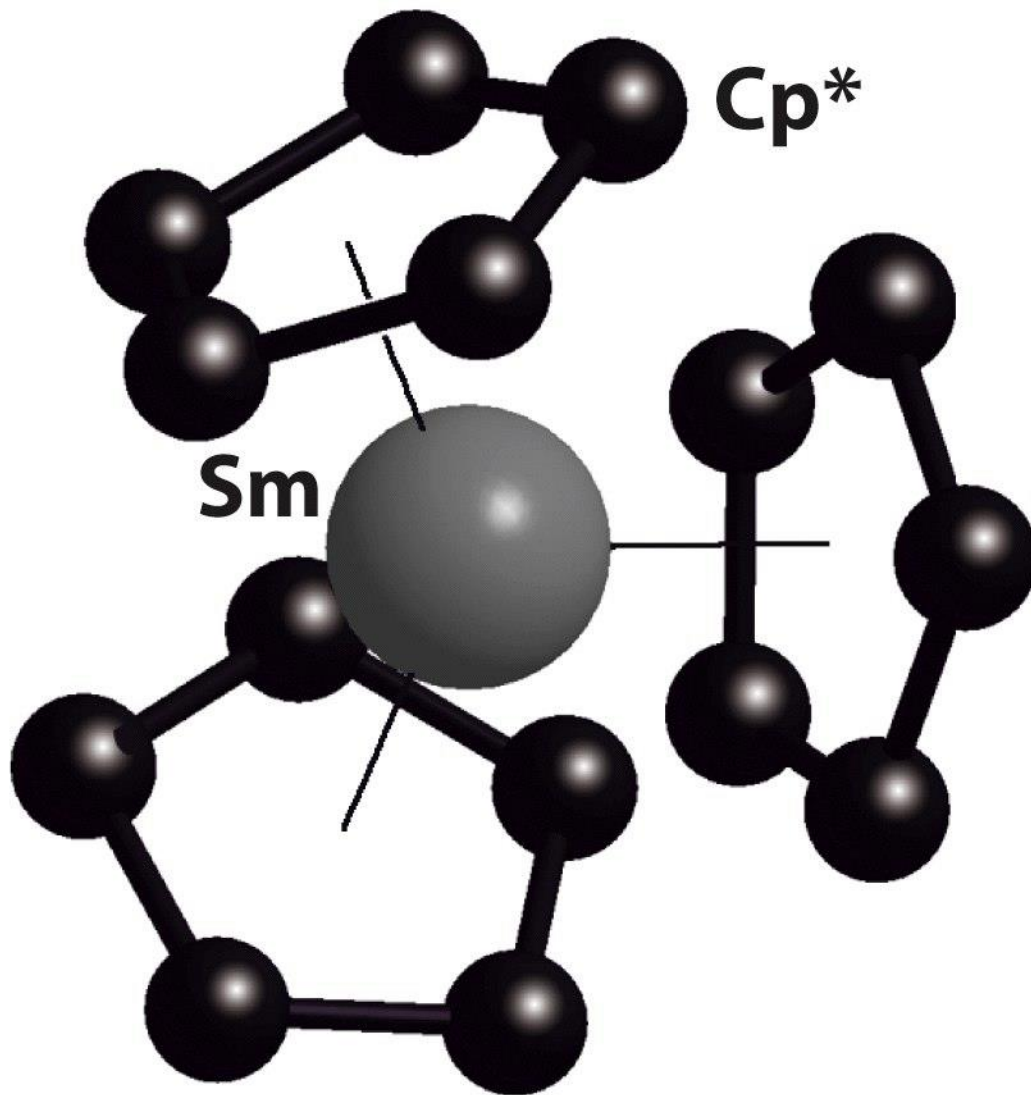


# Elementi del blocco f

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

Lantanide generico =  $Ln, 4f^n 5d^1 6s^2$

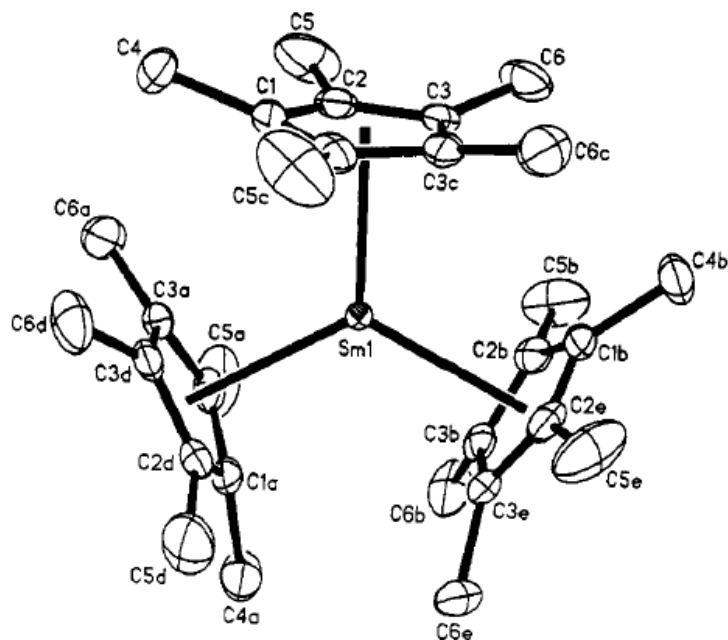
Attinide generico =  $An, 5f^n 6d^1 7s^2$



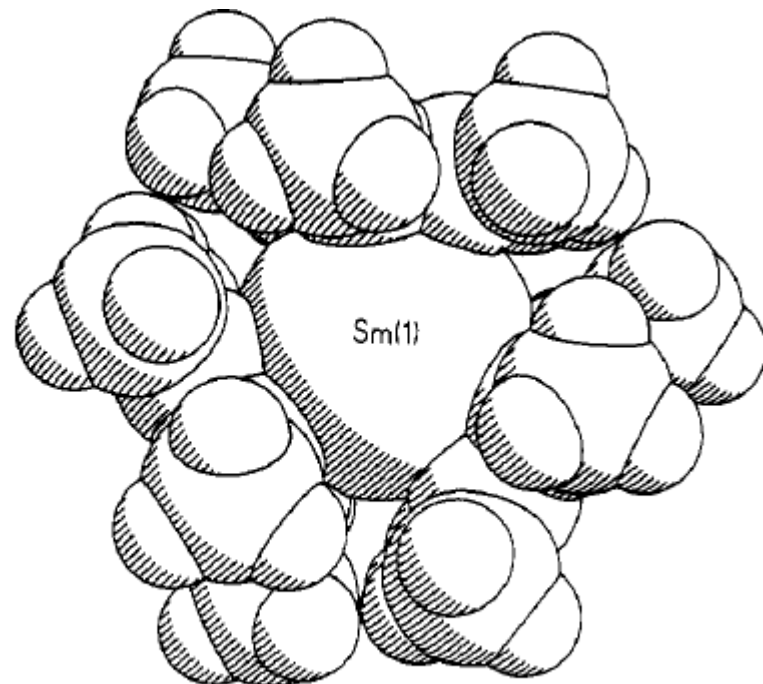
# Synthesis and X-ray Crystal Structure of the First Tris(pentamethylcyclopentadienyl)-Metal Complex: ( $\eta^5\text{-C}_5\text{Me}_5$ )<sub>3</sub>Sm

William J. Evans,\* Shirley L. Gonzales, and Joseph W. Ziller

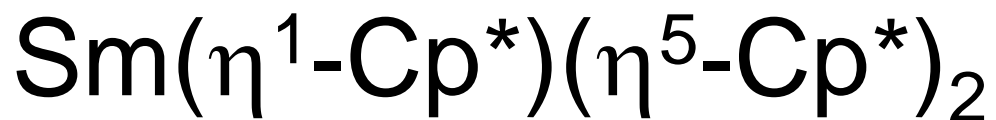
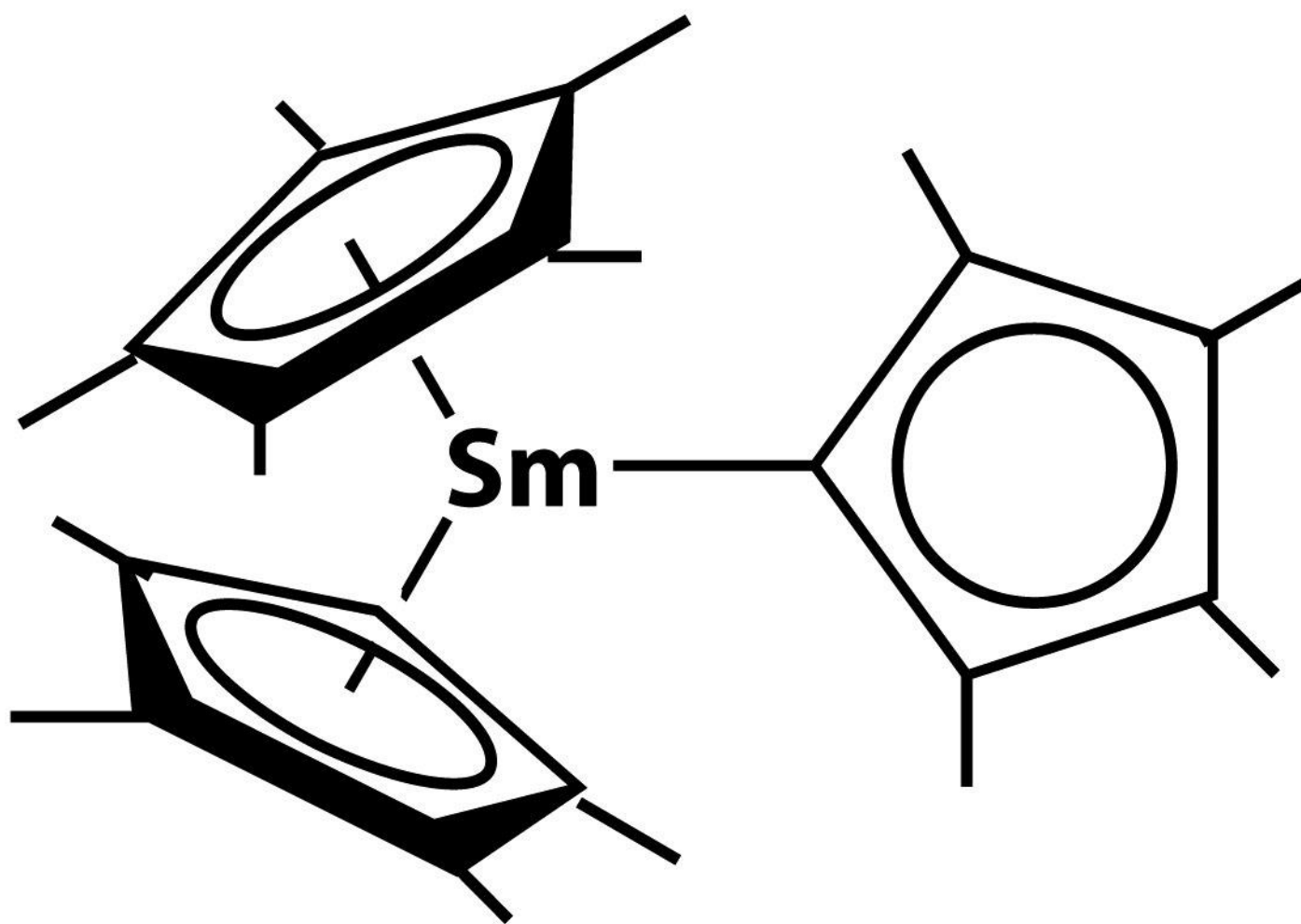
*J. Am. Chem. Soc.* 1991, 113, 7424-7426

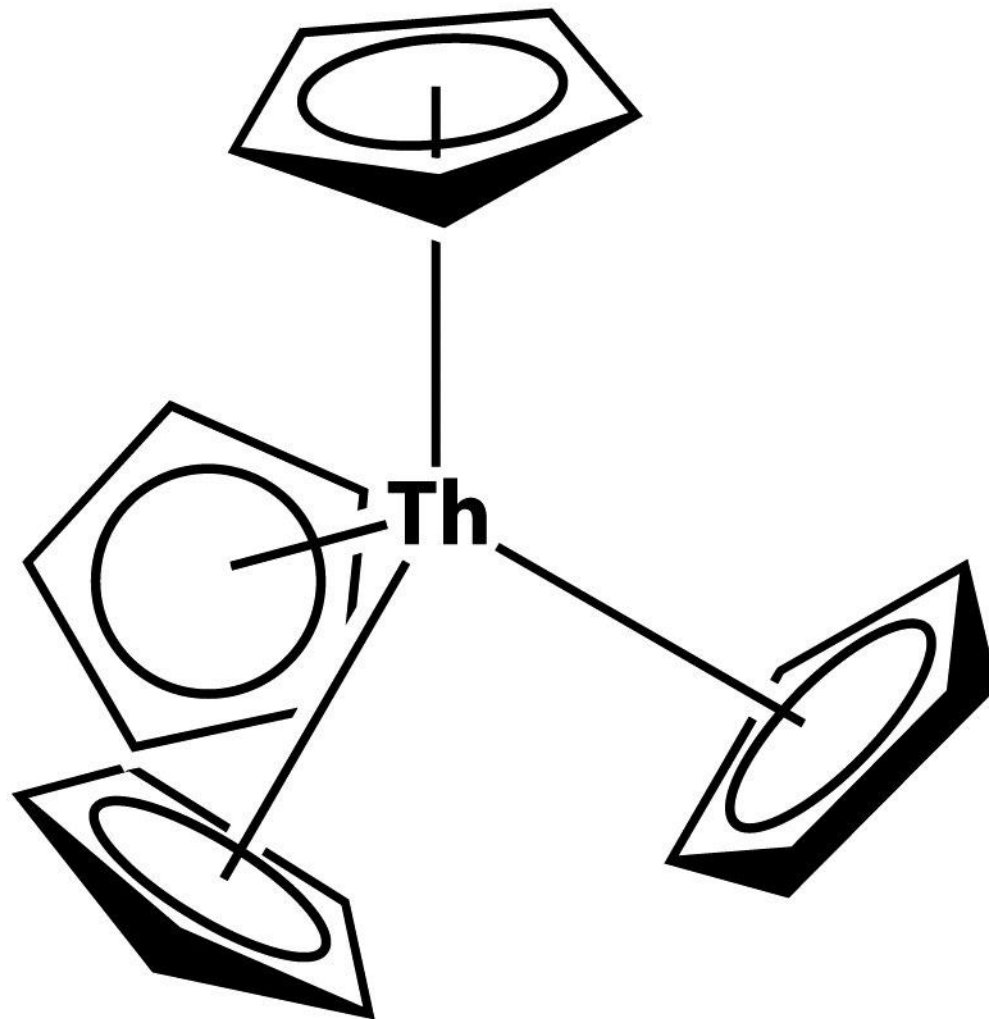


**Figure 1.** Molecular structure of ( $\text{C}_5\text{Me}_5$ )<sub>3</sub>Sm (2) with probability ellipsoids drawn at the 50% level.

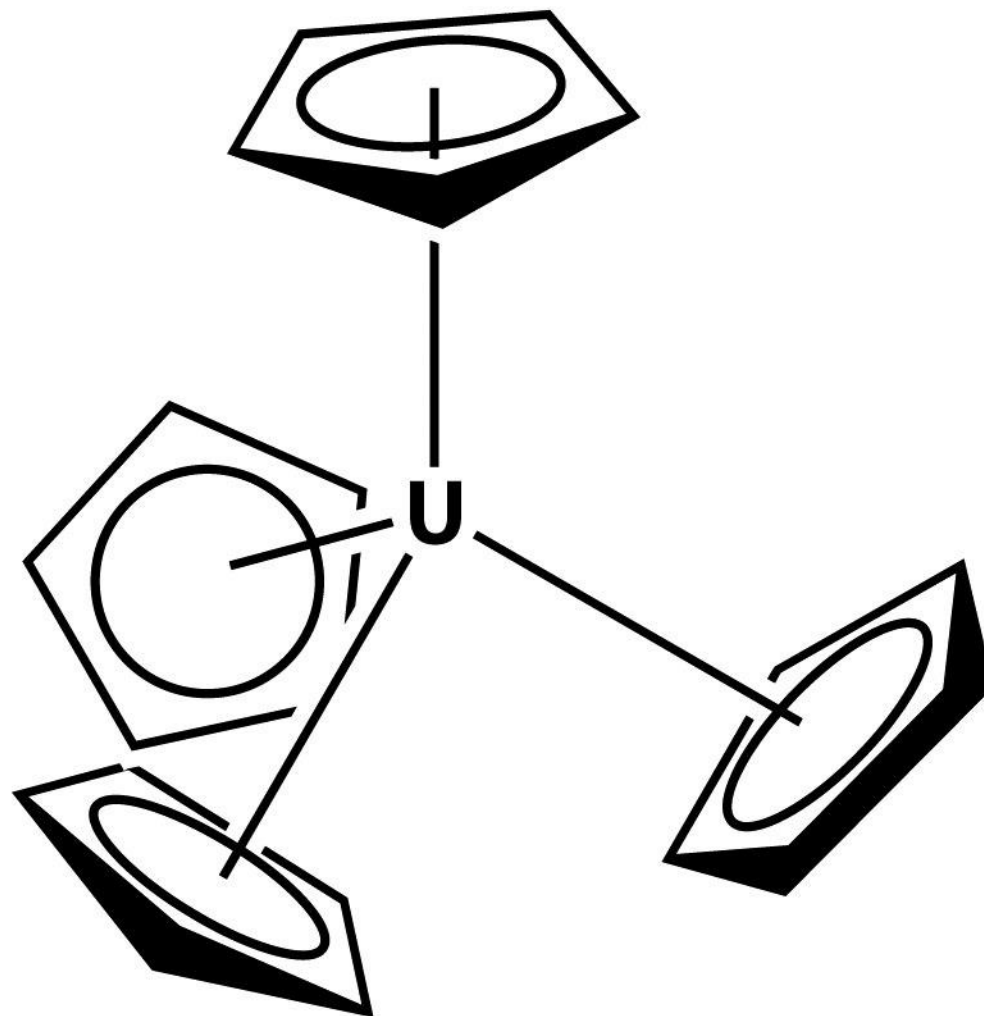


**Figure 2.** Space-filling model of ( $\text{C}_5\text{Me}_5$ )<sub>3</sub>Sm (2).

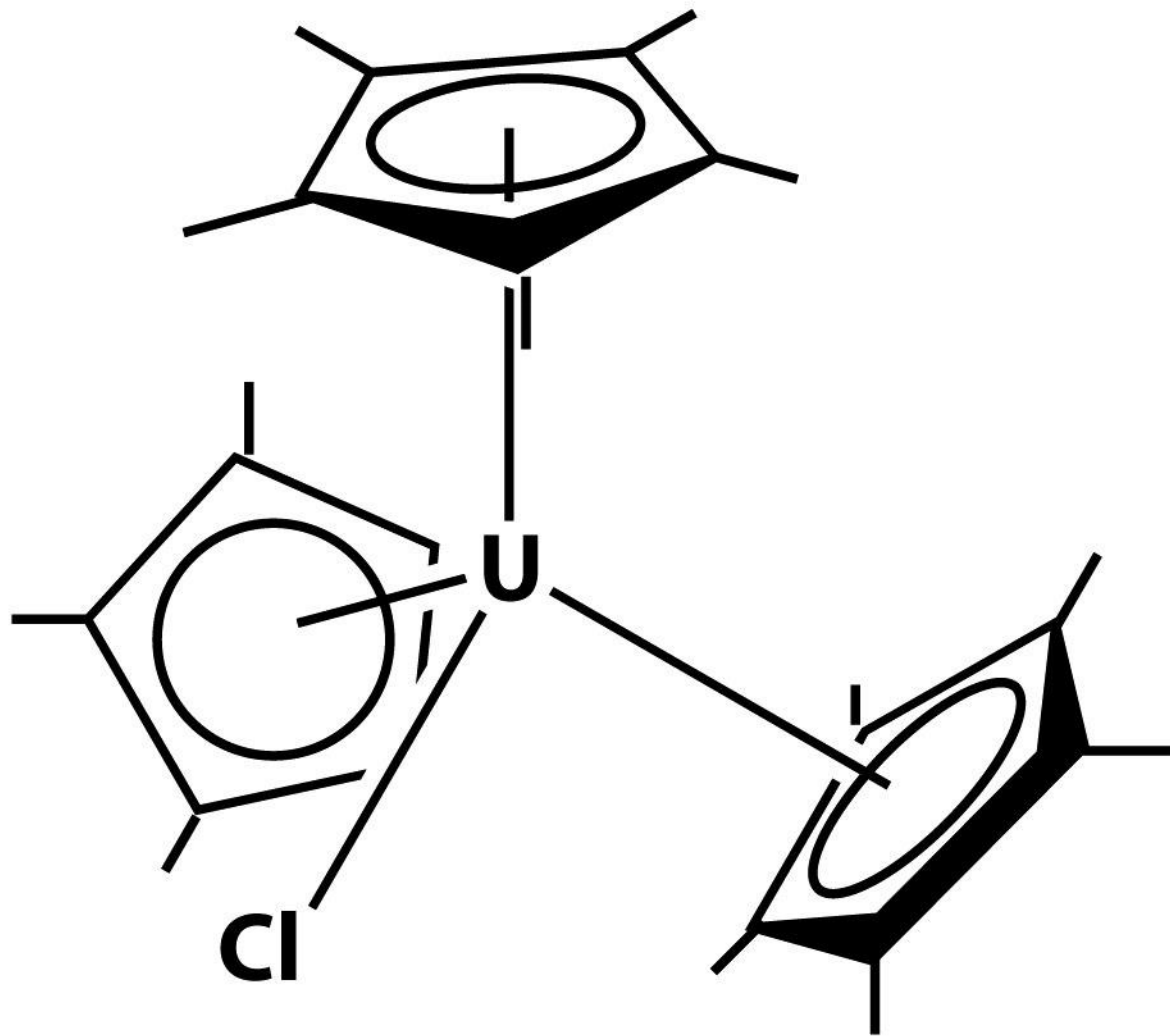


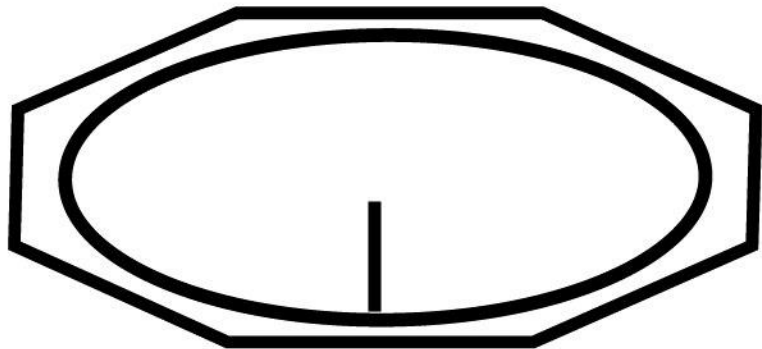


**$\text{Th}(\text{Cp})_4$**

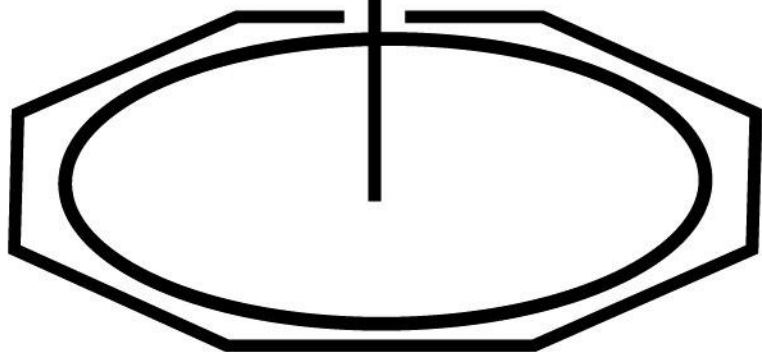


**$U(Cp)_4$**

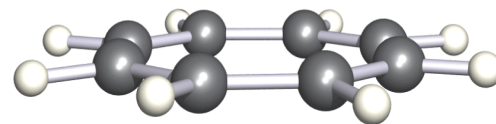
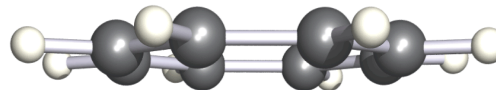




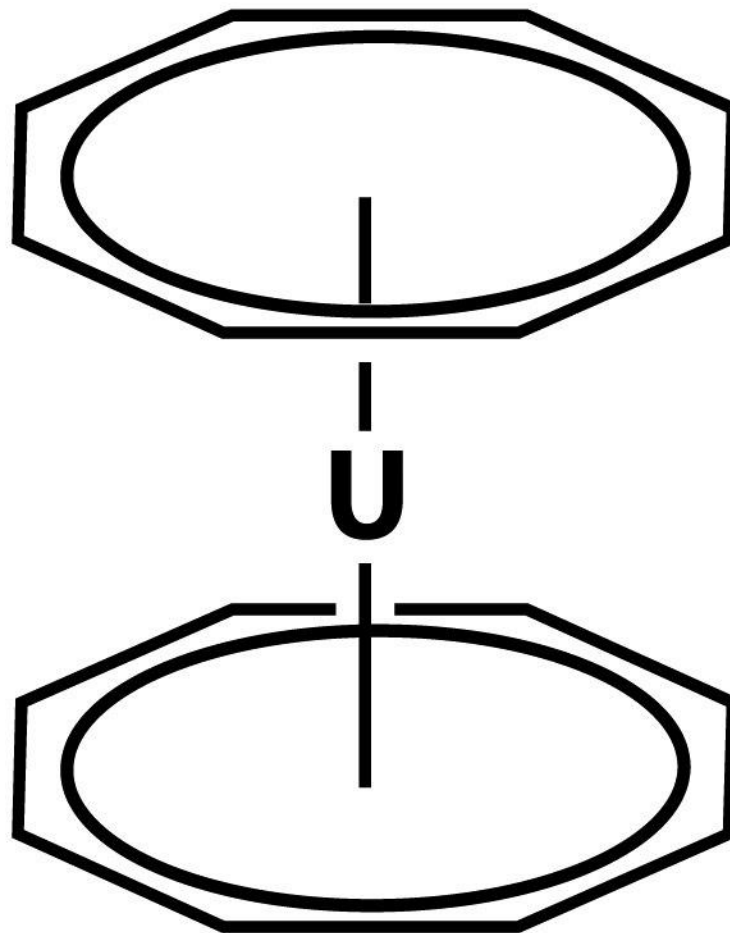
**Th**



Torocene







Uranocene