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Organometálicos, Catálise e Clusters



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Organometálicos

ORGANOMETALLICS

<http://pubs.acs.org/journal/orgnd7>

- *For the purposes of this journal, an “organometallic” compound will be defined as one in which there is a bonding interaction (ionic or covalent, localized or delocalized) between one or more carbon atoms of an organic group or molecule and a main group, transition, lanthanide, or actinide metal atom (or atoms).*



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Analogia isolobal

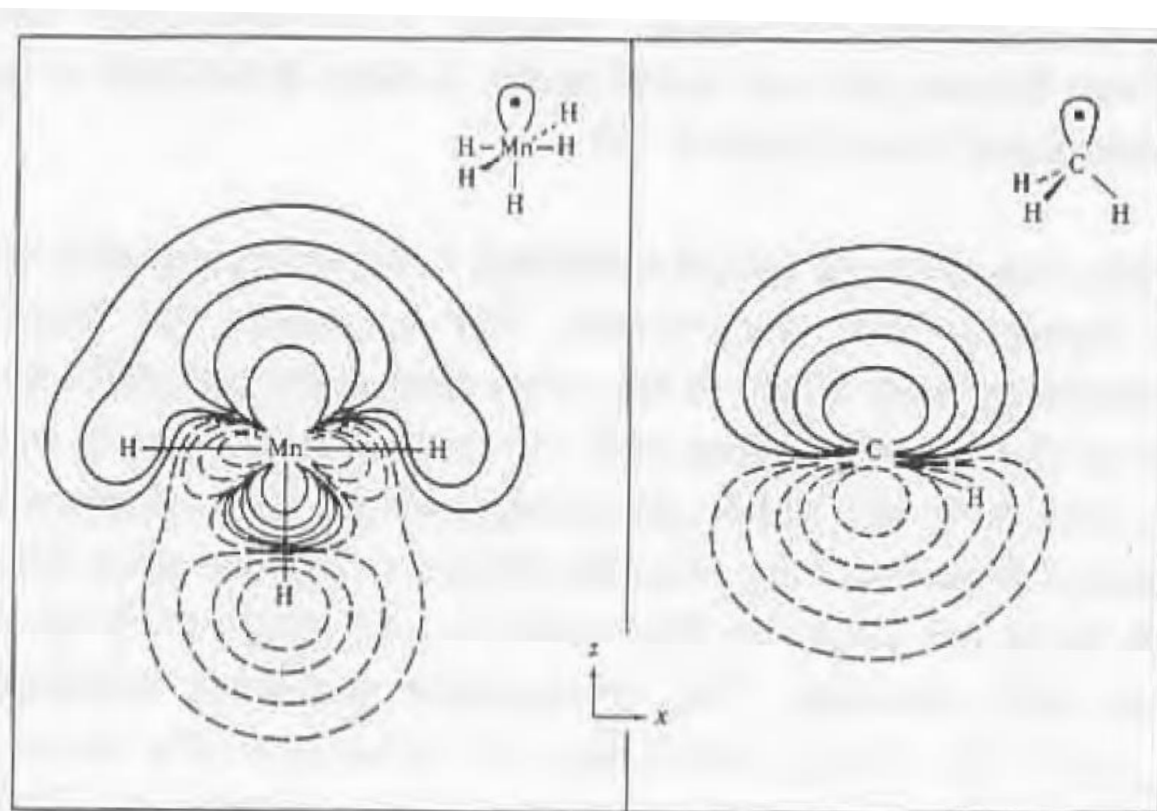


Fig. 15.12 Calculated contour diagrams for the isolobal a_1 orbitals of $[MnH_5]^{3-}$ (left) and $(CH_3)^\bullet$ (right). The contours are plotted in a plane passing through manganese and three hydrogen atoms and through carbon and one hydrogen. [From Hoffmann, R. *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 711-724. Reproduced with permission.]



Analogia isolobal

Fragmentos isolobais			
Espécies orgânicas			
CH_3	CH_2	CH	C
CH_2^-	CH^-	CH_2^+	CH^+
	CH_3^+		
Fragmento organometálico			
$\text{Co}(\text{CO})_4$	$\text{Fe}(\text{CO})_4$	$\text{Co}(\text{CO})_3$	$\text{Fe}(\text{CO})_3$
$\text{Mn}(\text{CO})_5$	$\text{Cr}(\text{CO})_5$	$\text{Mn}(\text{CO})_4$	$\text{Cr}(\text{CO})_4$
$\text{CpFe}(\text{CO})_2$	$\text{CpCo}(\text{CO})$	CpNi	CpCo
$\text{CpCr}(\text{CO})_3$	$\text{CpMn}(\text{CO})_2$	$\text{CpFe}(\text{CO})$	$\text{CpMn}(\text{CO})$
	$\text{Ni}(\text{CO})_2$	$\text{CpCr}(\text{CO})_2$	
	$\text{Ni}(\text{CO})_3$		

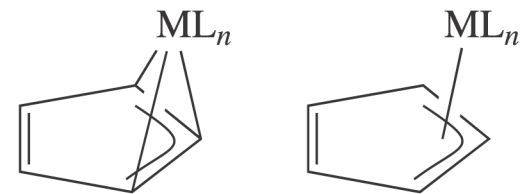


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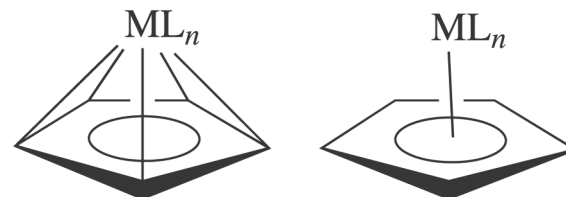
Hapticidade



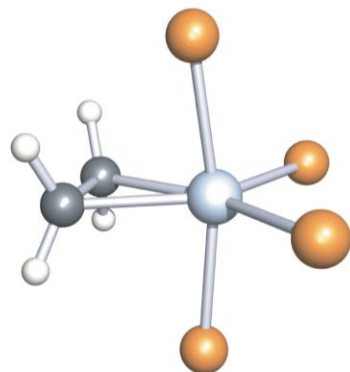
η^1 -mode



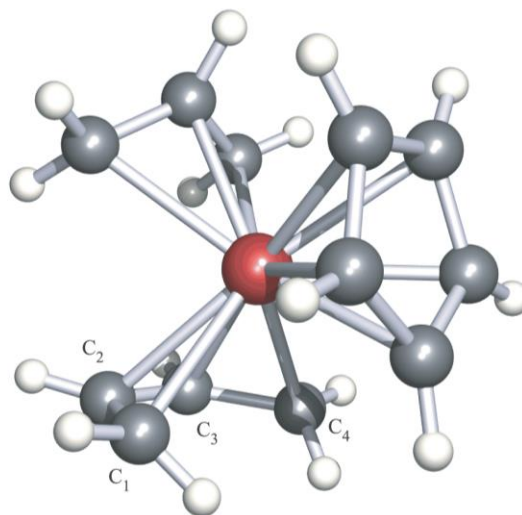
η^3 -mode



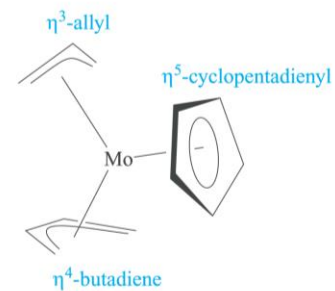
η^5 -mode



$\text{Ru}(\eta^2\text{-C}_2\text{H}_4)(\text{PMe})_4$



(b)

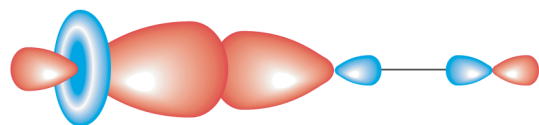
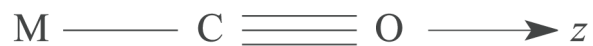


(c)



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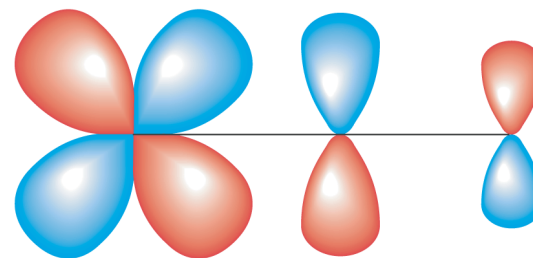
M-CO



Vacant
metal
orbital, e.g.
 $sp_z d_{z^2}$ hybrid

HOMO
of CO;
 σ -donor MO

CO-to-M donation
(a)



Filled
metal
 d_{xz} or d_{yz}

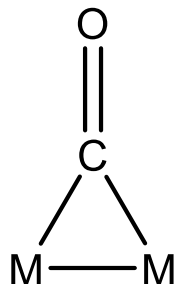
Vacant
 π^* of CO

M-to-CO back-donation
(b)

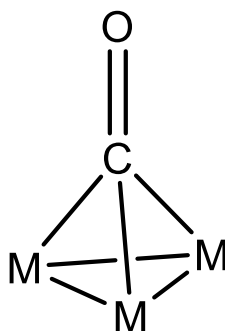


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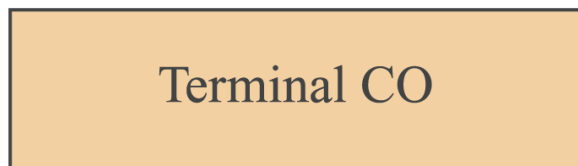
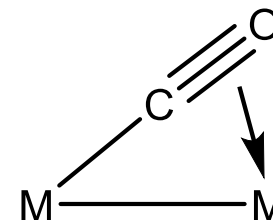
M-CO



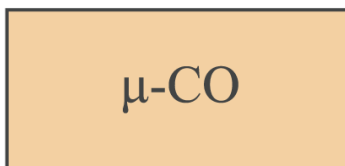
μ -CO



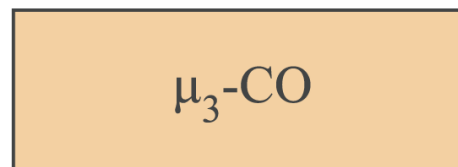
μ_3 -CO



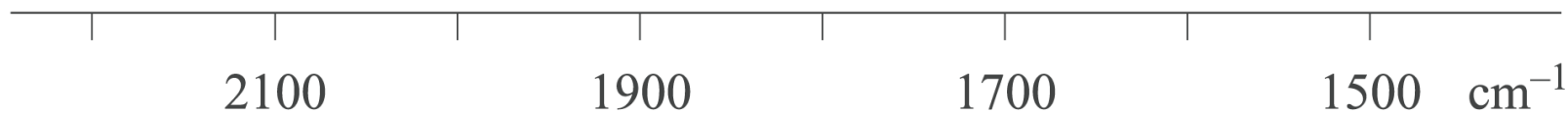
Terminal CO



μ -CO



μ_3 -CO





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Metal-hidretos

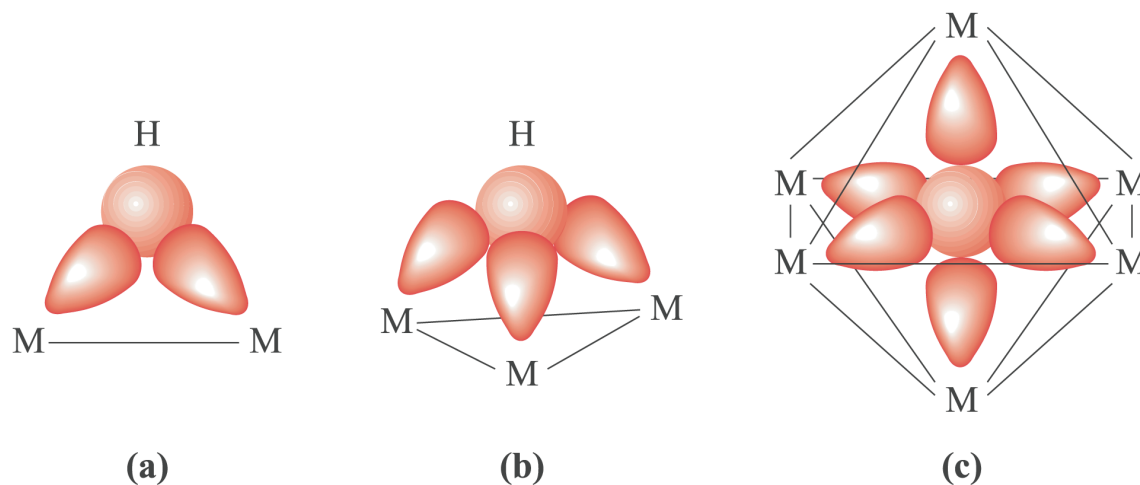
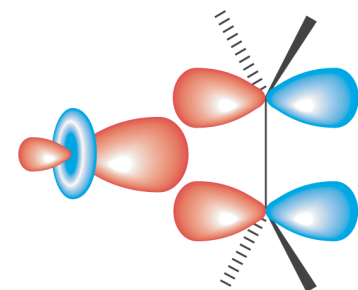
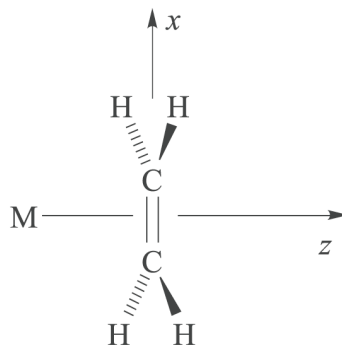


Fig. 24.3 Overlap of the H $1s$ atomic orbital with (a) two or (b) three appropriate metal hybrid orbitals to form $\mu\text{-H}$ and $\mu_3\text{-H}$ bridges. (c) For an interstitial H atom within an octahedral M_6 -cage, a delocalized description involves the overlap of the H $1s$ atomic orbital with six appropriate metal orbitals to give a $7c\text{-}2e$ interaction.



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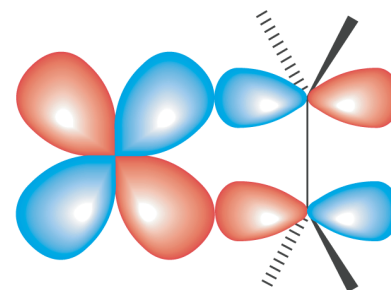
Metal alcenos



Vacant metal orbital, e.g. $sp_z d_{z^2}$ hybrid

Filled π -MO of C_2H_4

Alkene-to-M donation
(a)



Filled metal d_{xz}

Vacant π^* -MO of C_2H_4

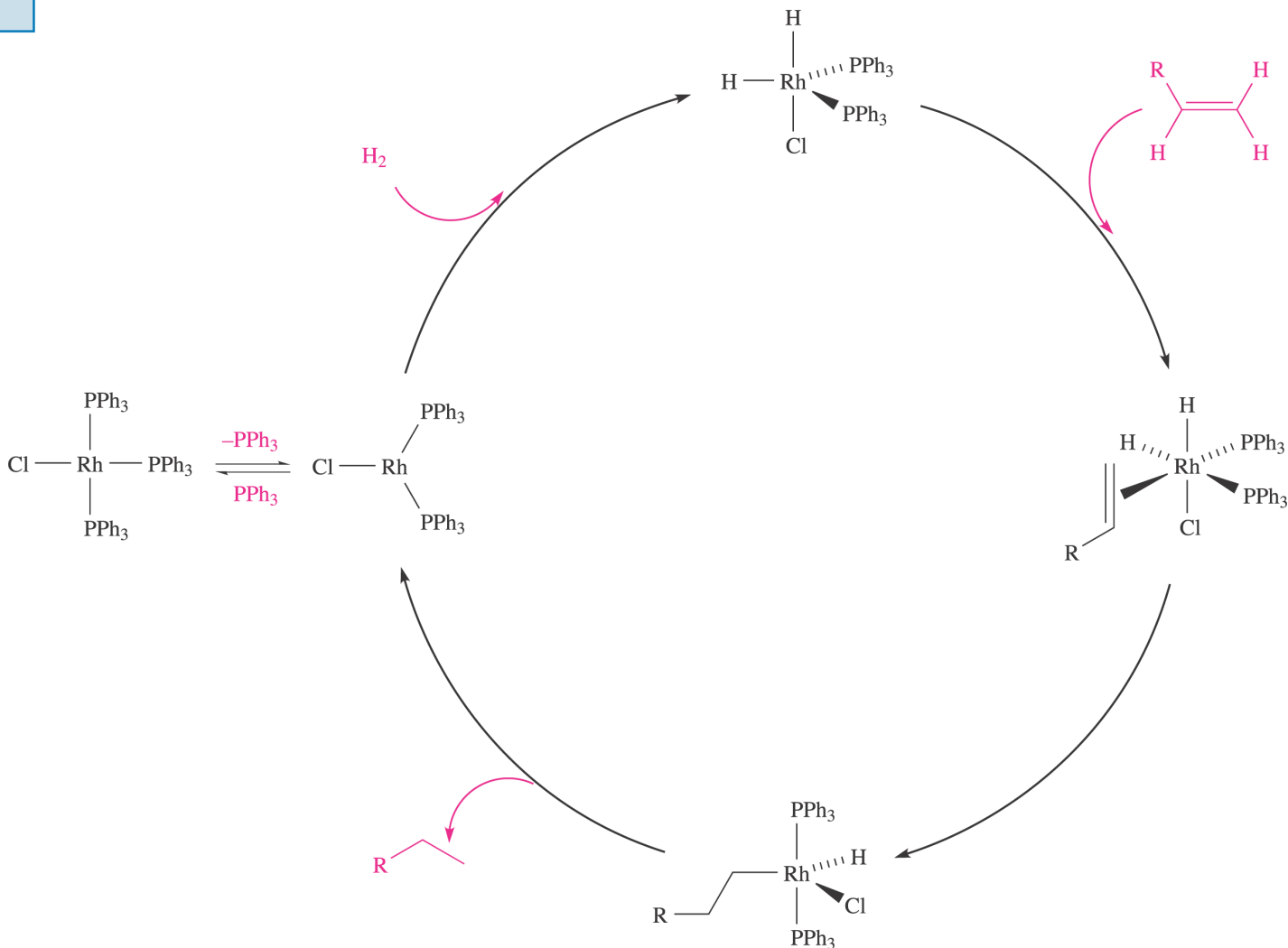
M-to-alkene back-donation
(b)



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Catalisador de Wilkinson (hidrogenação de alcenos)

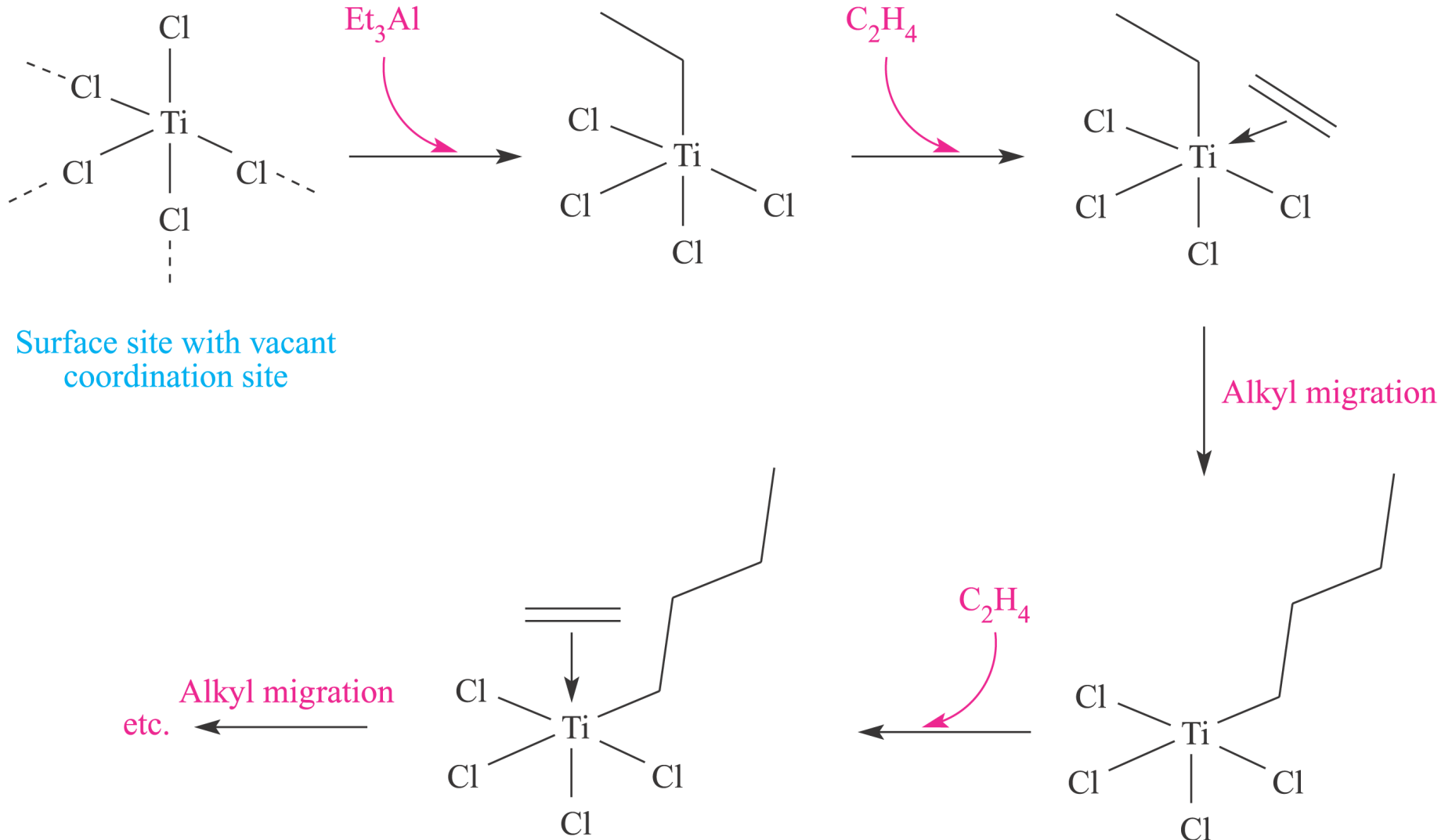
27.7





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Catalisador de Ziegler – Natta (polimerização do etileno)





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Catalisador de Ziegler – Natta (polimerização do etileno)



Karl Ziegler



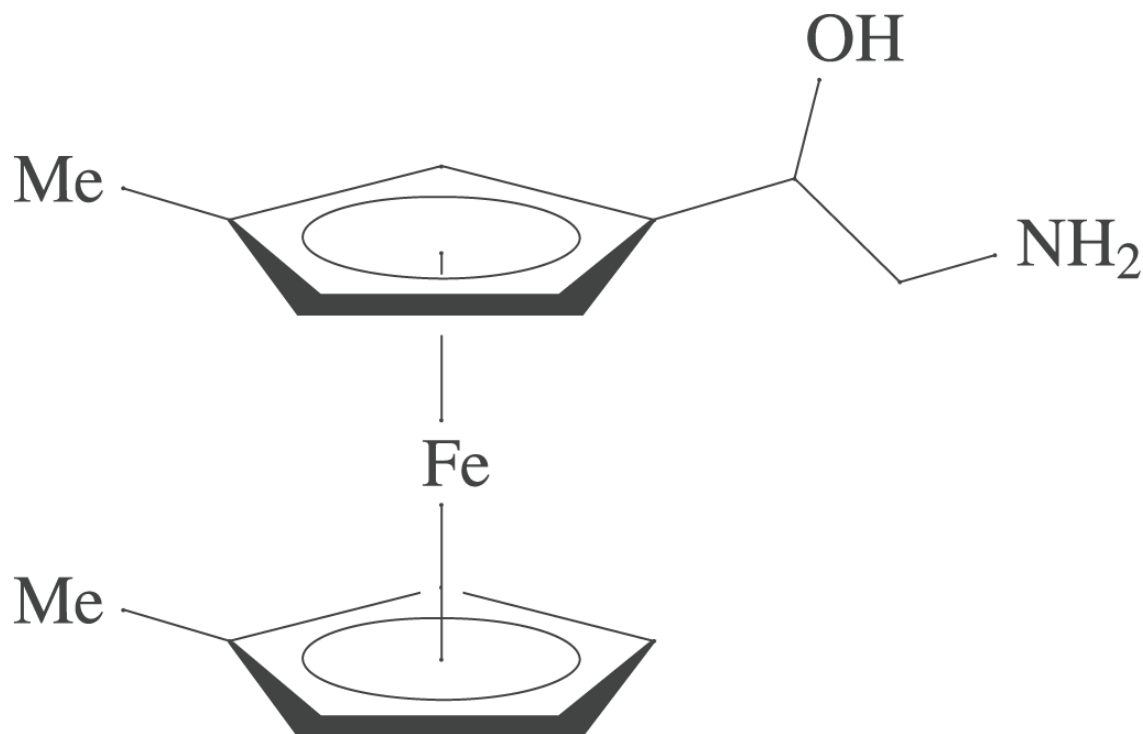
Giulio Natta

The **Nobel Prize** in Chemistry **1963** was awarded jointly to Karl Ziegler and Giulio Natta *"for their discoveries in the field of the chemistry and technology of high polymers"*



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Ligantes orgânicos com ligação π

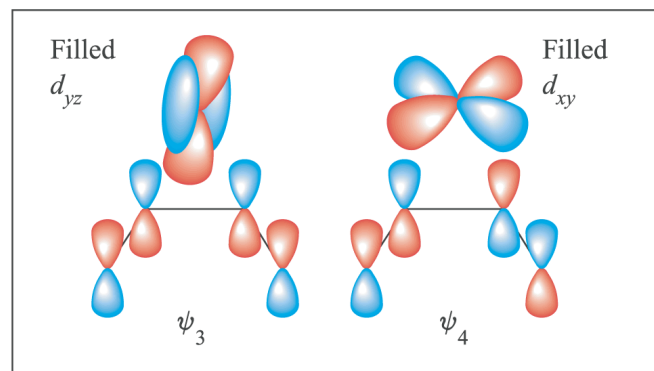
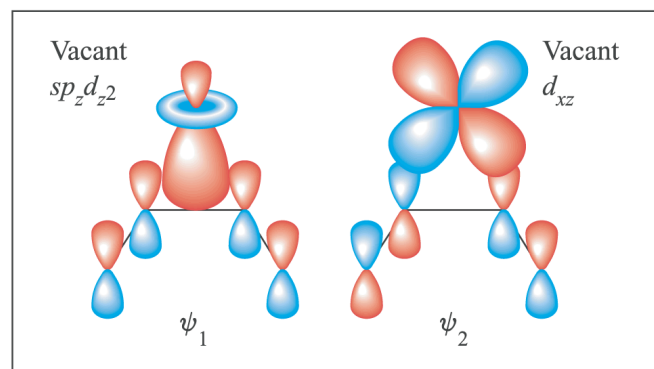
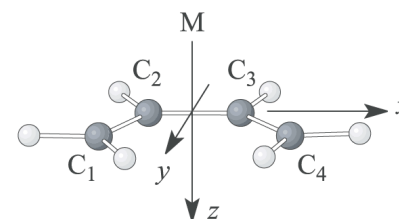
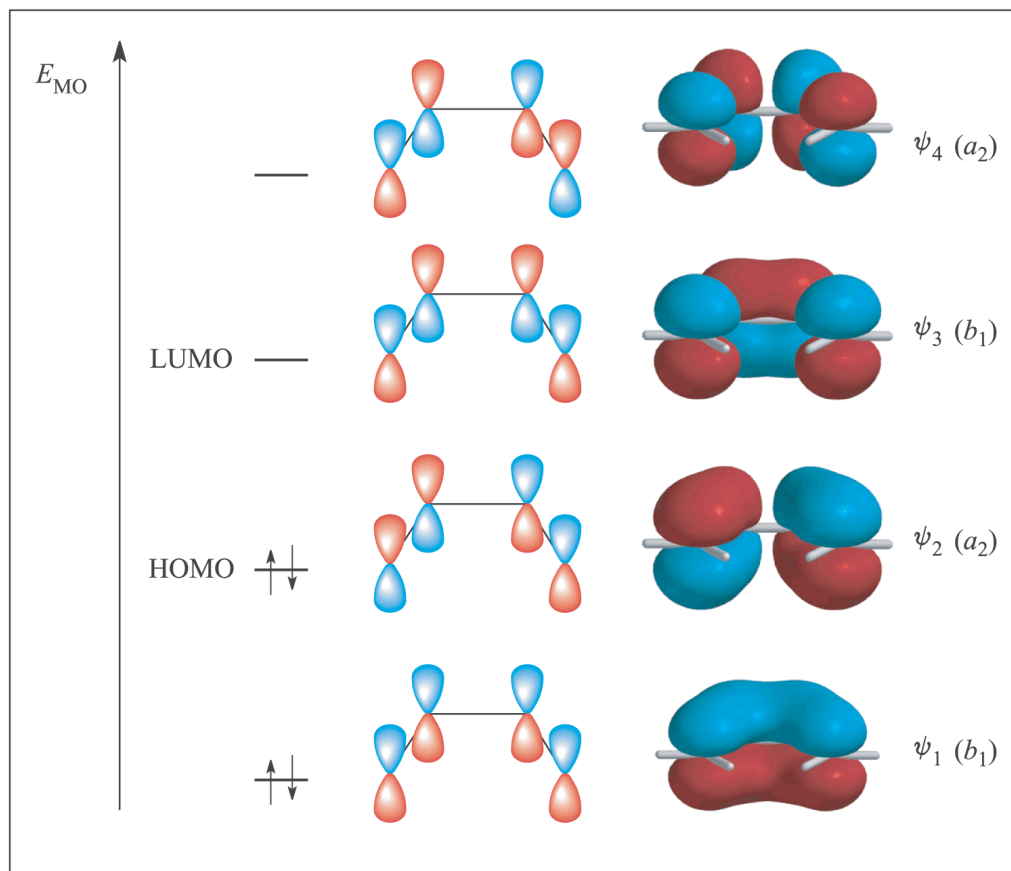


Usado em sistemas para medir glicose do sangue



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MOs para ligantes orgânicos com ligação π



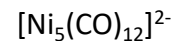
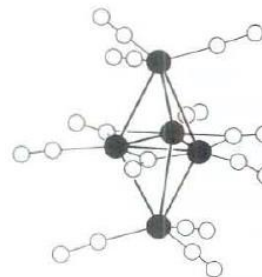
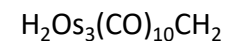
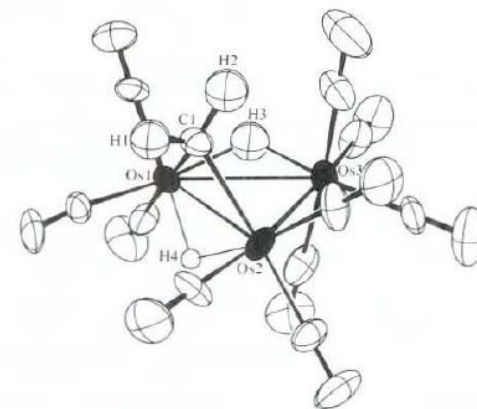
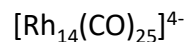
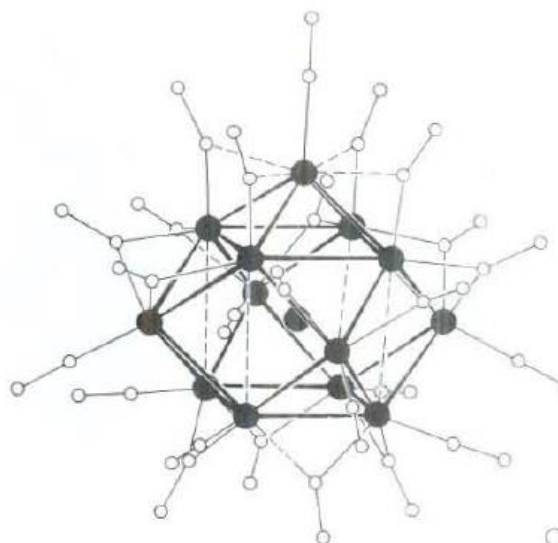
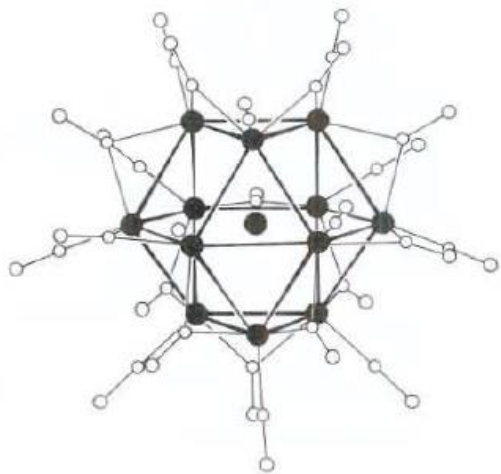
(b)



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Clusters

- São estruturas em forma de poliedros que se mantêm juntos por duas ou mais ligações metal-metal por centro metálico.

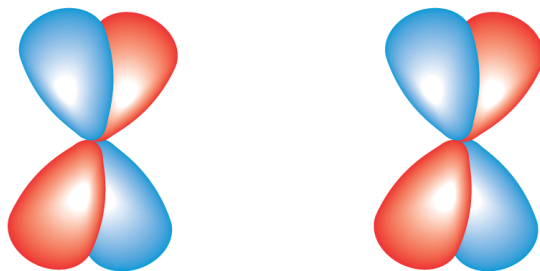




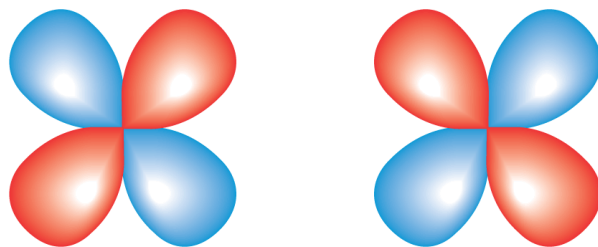
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Ligação entre metais

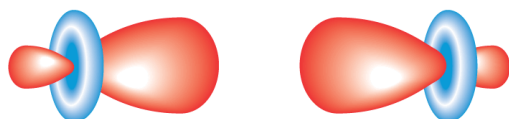
Face-on d_{xy}



Side-on d_{xz} (d_{yz})



End-on $p_z d_{z^2}$



δ

π

σ

Re_2Cl_8

