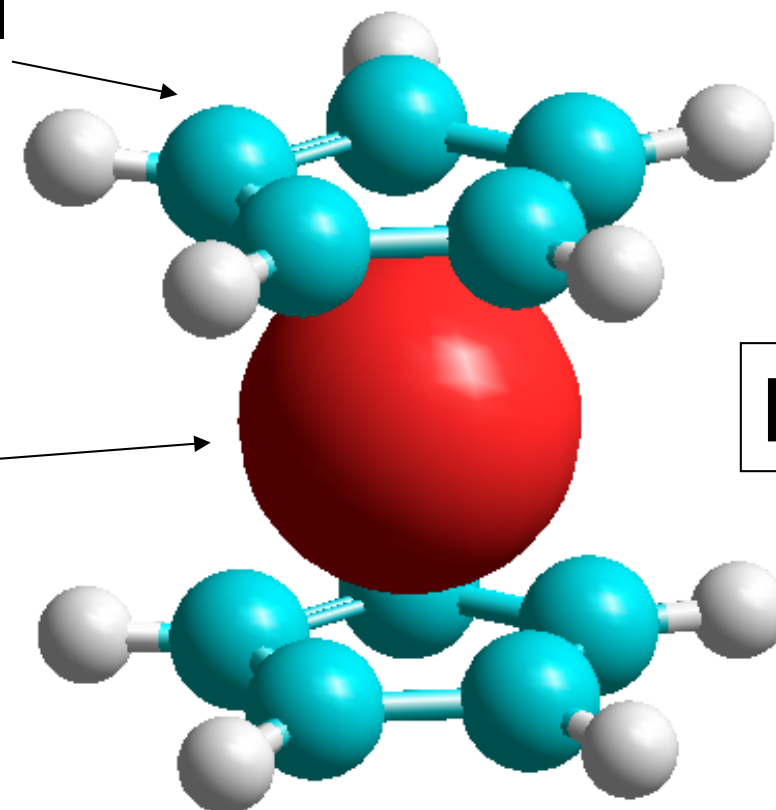


Complexes of π -bonded and aromatic ligands

cyclopentadienyl
anion ligand

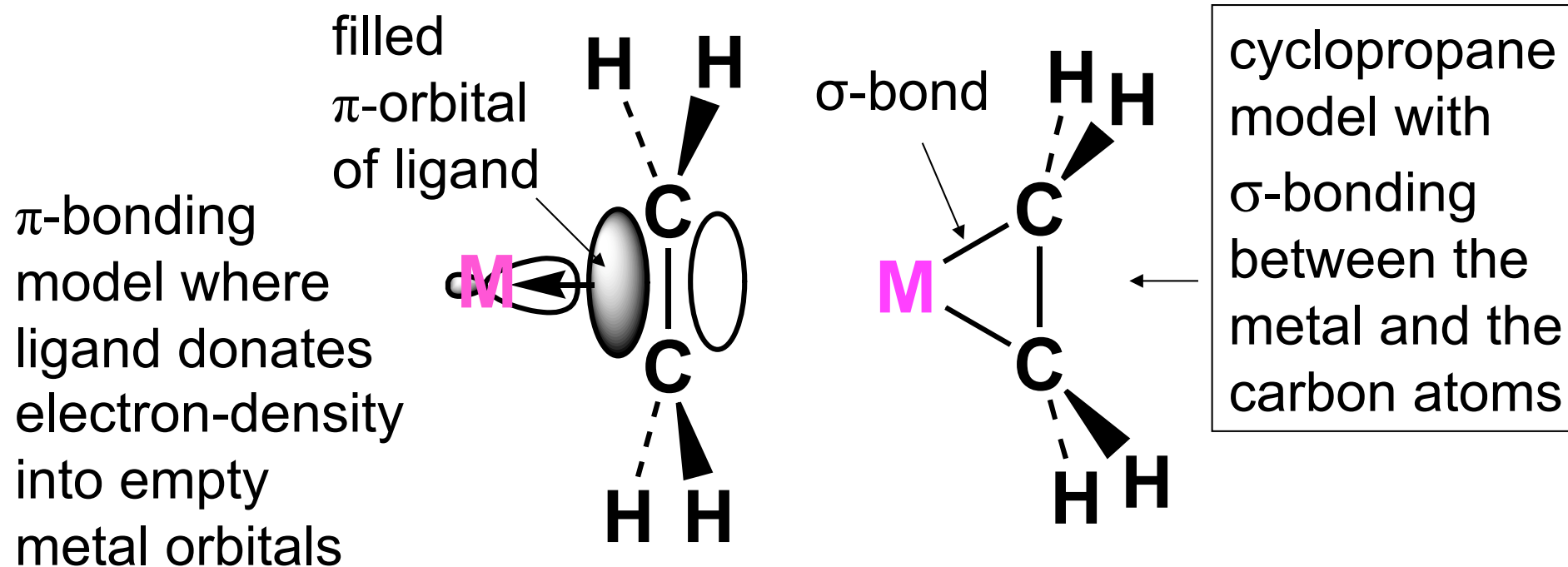
Fe



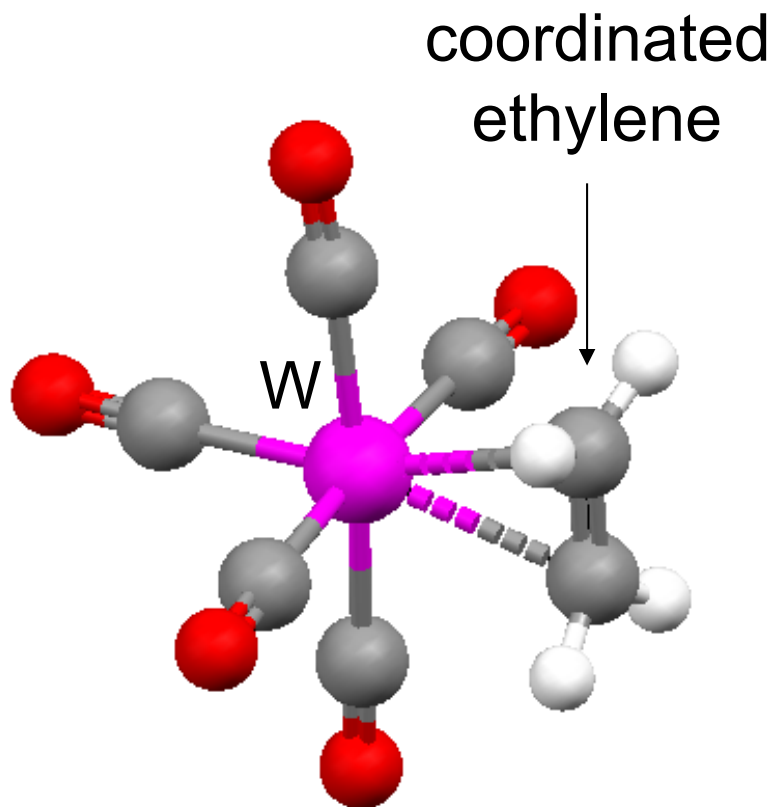
Ferrocene

π -bonded ligands

Ethylene, the simplest alkene, binds to d-block metals in a side-on fashion. It is viewed as either donation of electron density from a π -orbital into the d-orbitals of the metal, or as formation of a cyclopropane type ring with the metal taking the place of one methylene group:



π -bonded ligands and the 18-electron rule



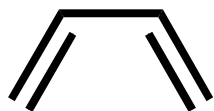
The complex
 $[\text{W}(\text{CO})_5(\text{CH}_2=\text{CH}_2)]$
CCD: REDNUK

Each double bond coordinated to a metal ion contributes a pair of electrons, as is the case for a CO ligand. Thus, in $[\text{W}(\text{CO})_5(\text{CH}_2=\text{CH}_2)]$ at left, the 18-electron rule holds exactly as it would for $[\text{W}(\text{CO})_6]$:

$\text{W}(0)$	=	d^6
5 CO	=	10
1 $\text{CH}_2=\text{CH}_2$	=	2
		18 e

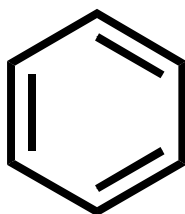
π -bonded ligands and the 18-electron rule

For ligands with more than one double bond, each double bond contributes a pair of electrons for the 18-electron rule. Thus, butadiene, benzene, COD and COT can contribute 4, 6, 4, and 8 electrons respectively, although some of the double bonds may not coordinate, in which case fewer electrons (2 per coordinated double bond) are counted:



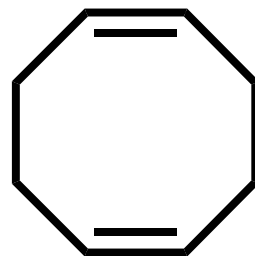
butadiene

4e



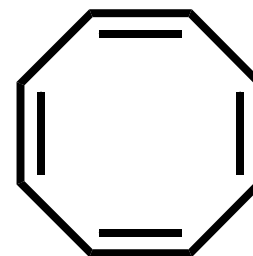
benzene

6e



cyclooctadiene
(COD)

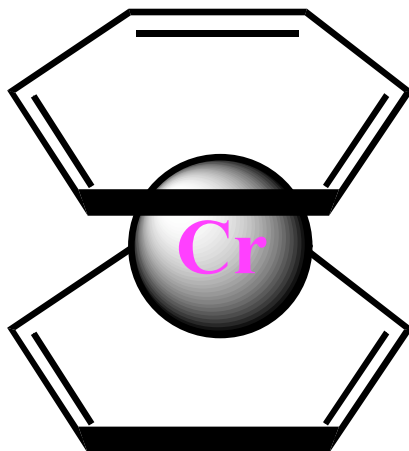
4e



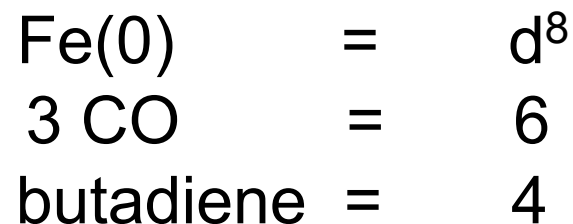
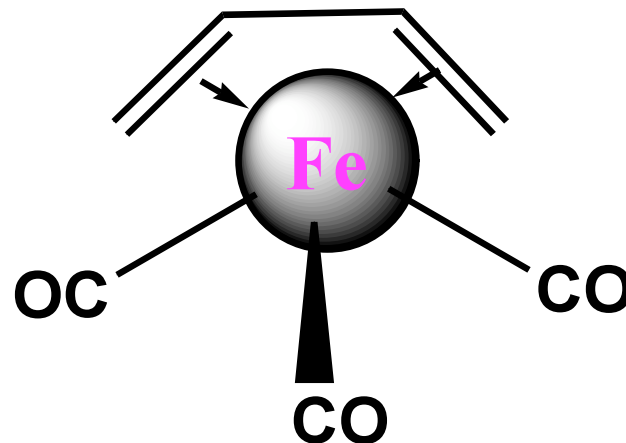
cyclooctatetraene
(COT)

8e

π -bonded ligands and the 18-electron rule

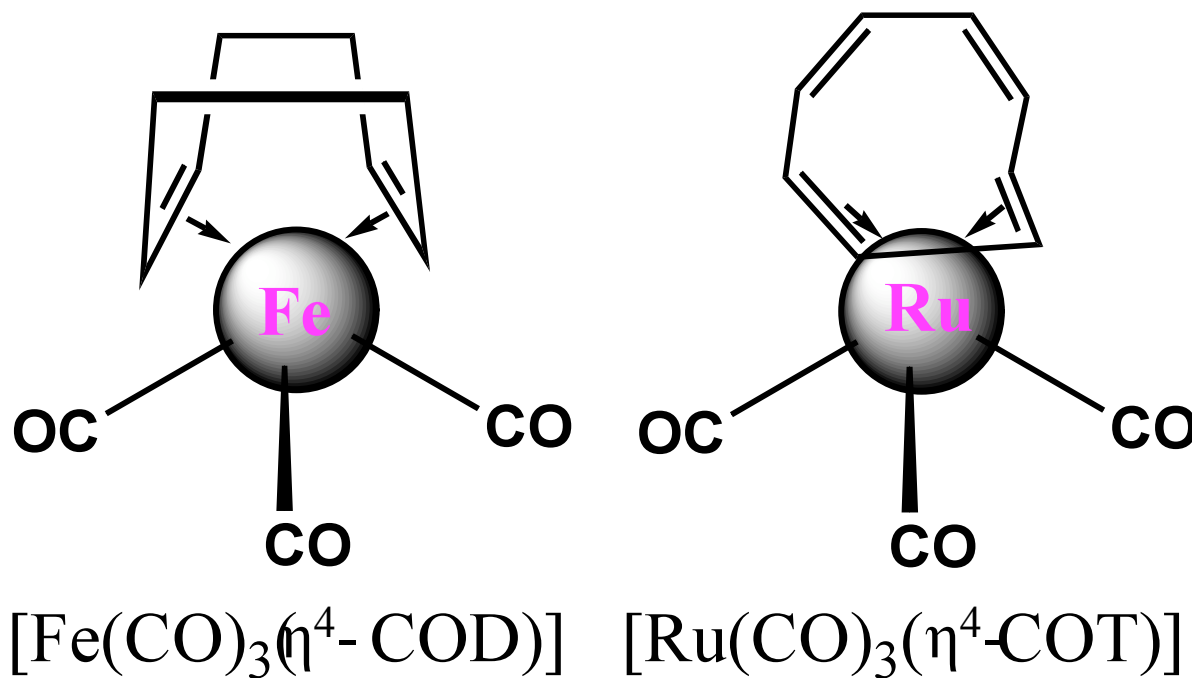


18 e



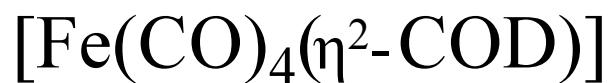
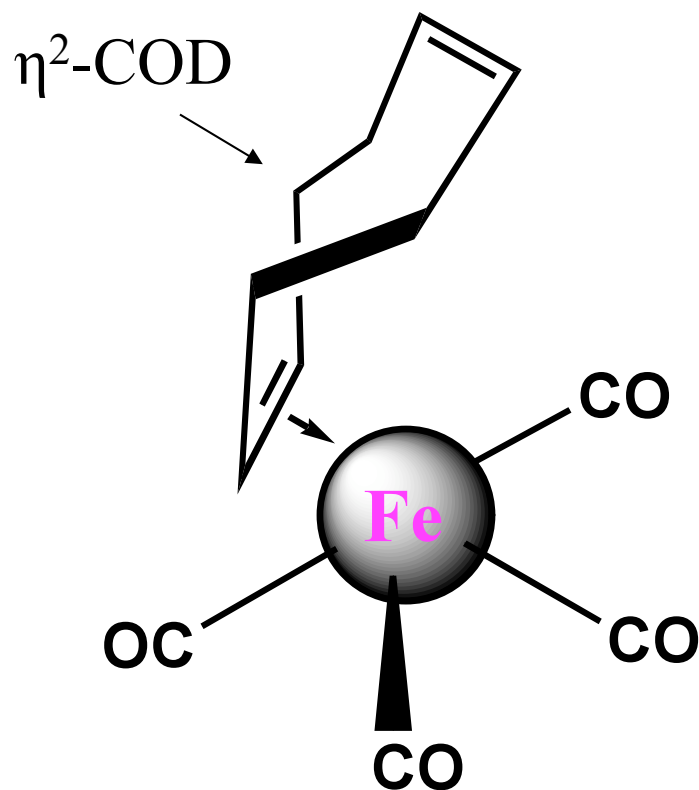
18 e

π -bonded ligands and hapticity



Hapticity is the number of carbon atoms from the ligand that are directly bonded to the metal, denoted by the Greek letter η (eta). Thus, COT above is using only two of its four double bonds, and so is η^4 .

π -bonded ligands, the 18-electron rule, and hapticity

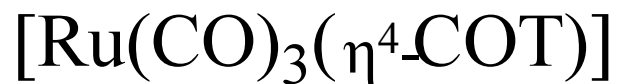
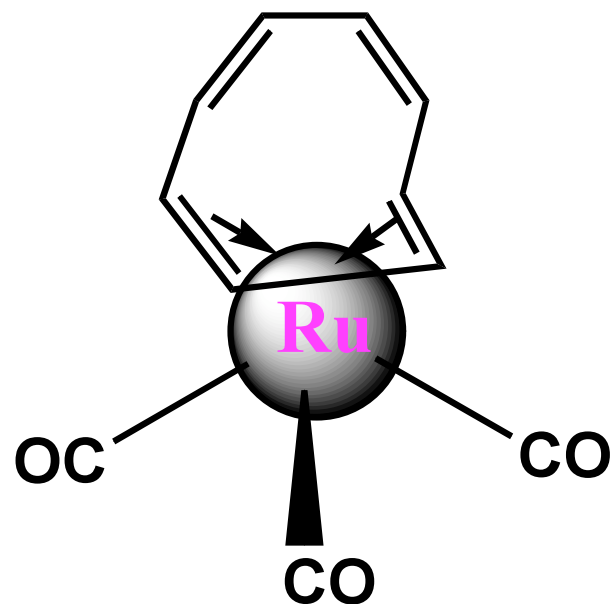


One can predict the probable hapticity of the alkene ligand from the 18-electron rule. Thus, with $[\text{Fe}(\text{CO})_4(\eta^2\text{-COD})]$, the 18-electron rule indicates only one double bond should be bound to the Fe:

Fe(0):	d^8
4 CO:	8e
one double bond from $\eta^2\text{-COD}$:	2e

18e

π -bonded ligands, the 18-electron rule, and hapticity



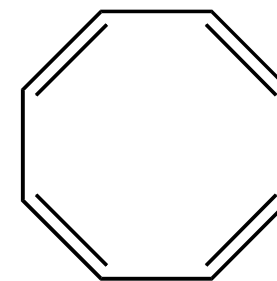
One can predict the probable hapticity of the COT in $[\text{Ru}(\text{CO})_3(\eta^4\text{-COT})]$. The 18-electron rule indicates only two double bonds should be bound to the Ru:

Ru(0):	d^8
3 CO:	6e
two double bonds from $\eta^4\text{-COT}$:	4e

18e

EXAMPLE: π -bonded ligands and the 18-electron rule

What is the hapticity of COT (cyclooctatetraene) in $[\text{Cr}(\text{CO})_3(\text{COT})]$?

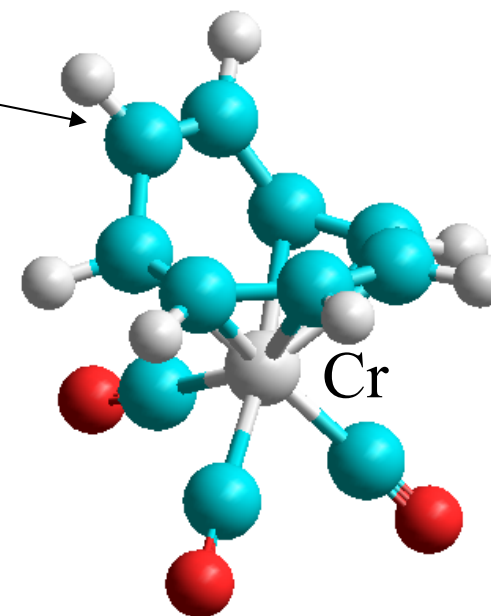
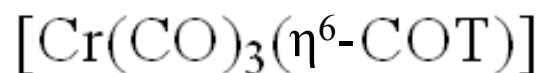
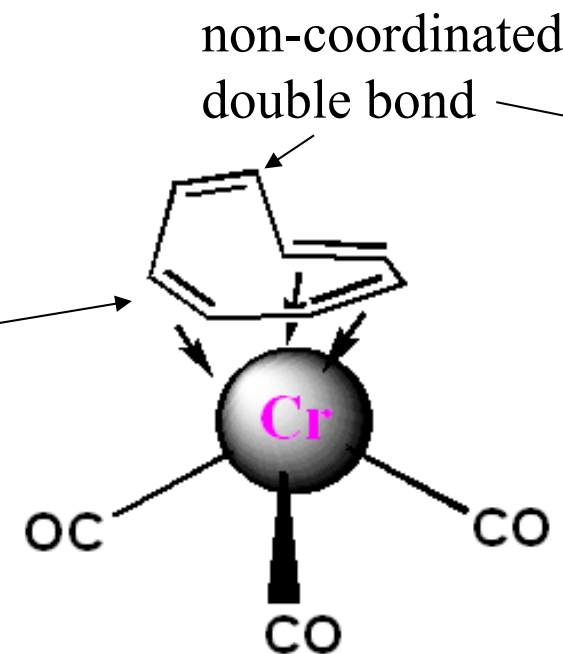


COT

The way to approach this from the 18-electron rule:

Cr(0):	d^6
3 CO:	6
3 double bonds:	6
	18 e

Answer: the hapticity is η^6

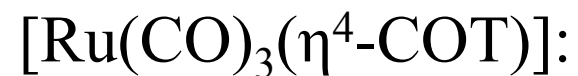
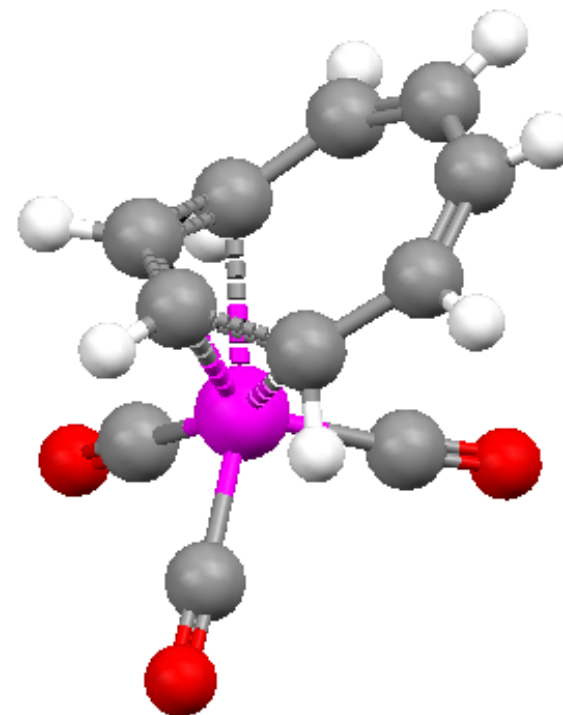


actual structure

EXAMPLE: patterns of π -bonded ligands and the 18-electron rule

Group 8, Fe(0), Ru(0), and Os(0) are d^8 metals and all form $[M(CO)_5]$ complexes. Thus, if we have $[M(CO)_3L]$, there must be two double bonds (= 2 CO) from any polyalkene ligand such as COD or COT to satisfy the eighteen electron rule, e.g. for $[Ru(CO)_3(COT)]$:

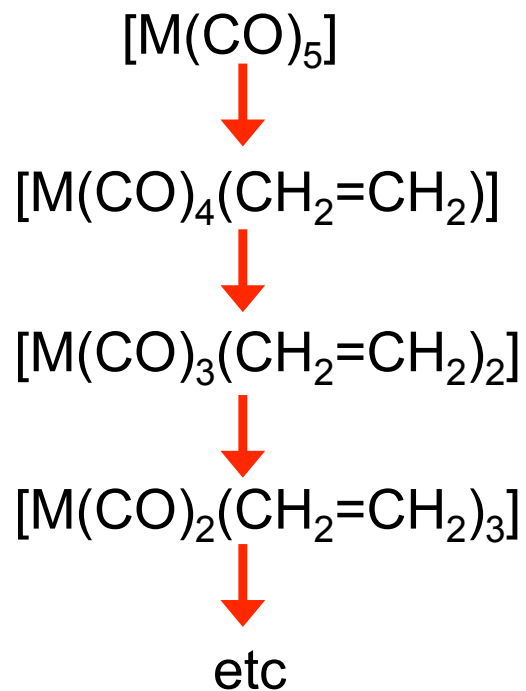
Os(0):	d^8
3 CO:	6e
η^4 -COT:	4e
	18e



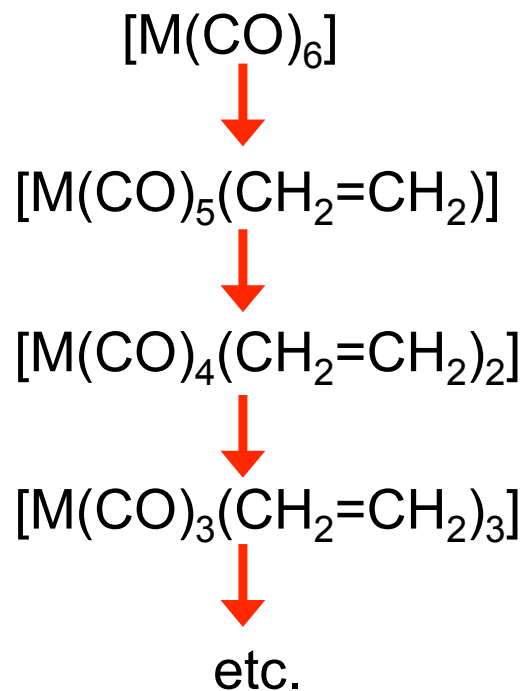
(‘piano-stool’ complex)

EXAMPLE: patterns of π -bonded ligands and the 18-electron rule

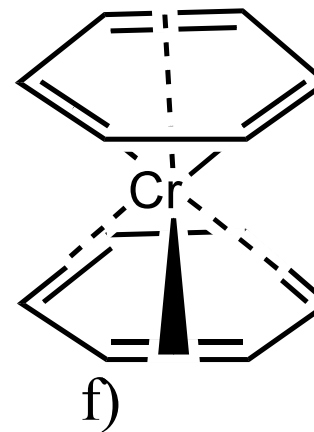
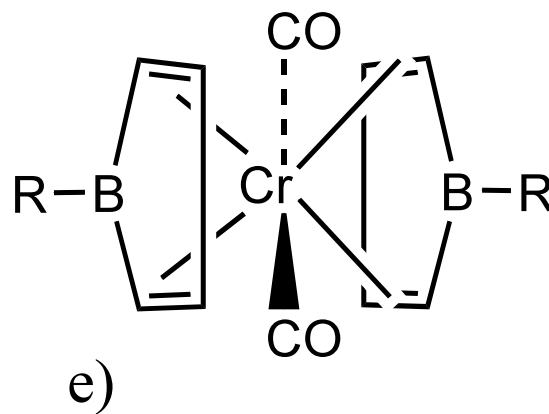
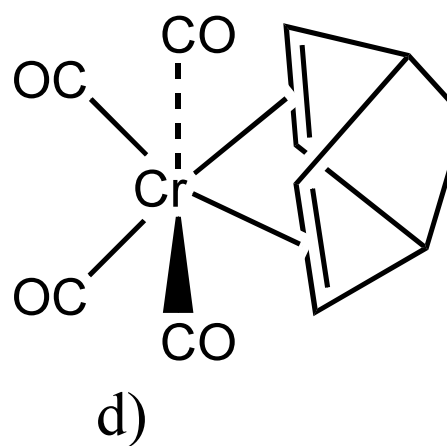
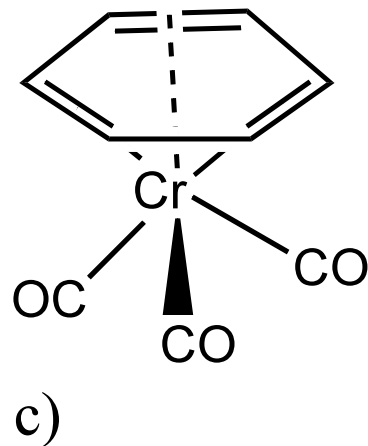
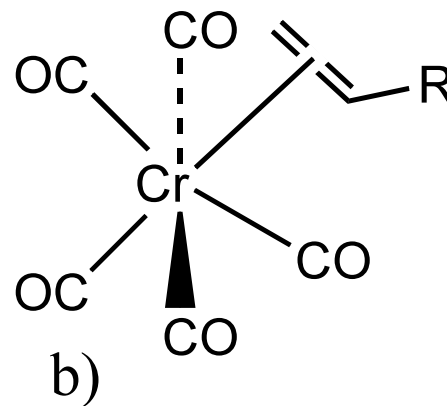
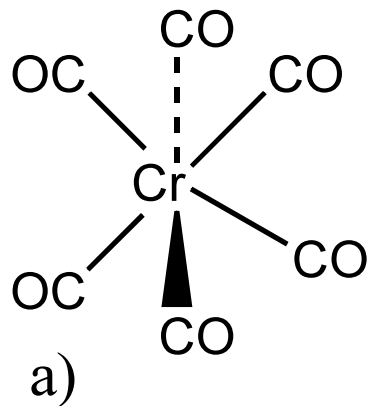
Group 8
Fe(0), Ru(0), Os(0)



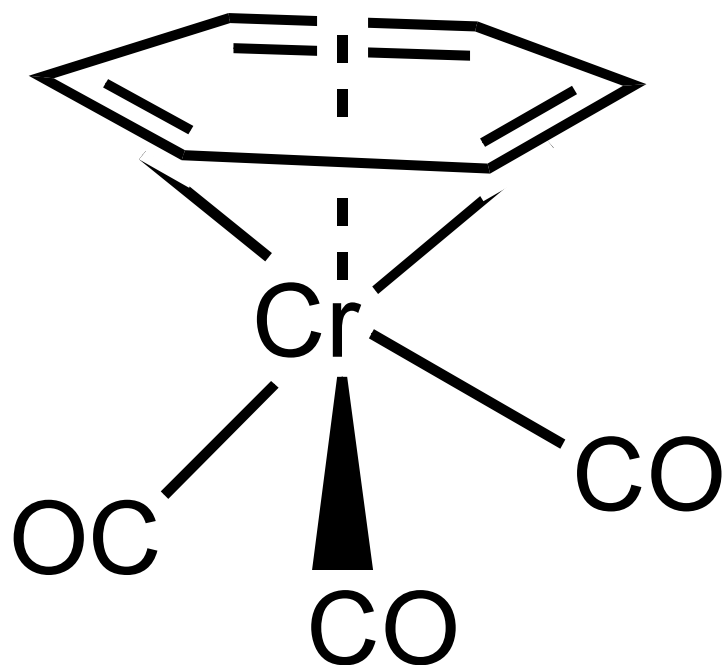
Group 6
Cr(0), Mo(0), W(0)



A series of Cr(0) complexes with sequential replacement of the CO groups on the Cr(0) with coordinated alkene groups. The series runs all the way from $[\text{Cr}(\text{CO})_6]$ (a) to $[\text{Cr}(\text{benzene})_2]$ (f). A complex with five double bonds and one CO is not known.



'Piano-stool compounds'



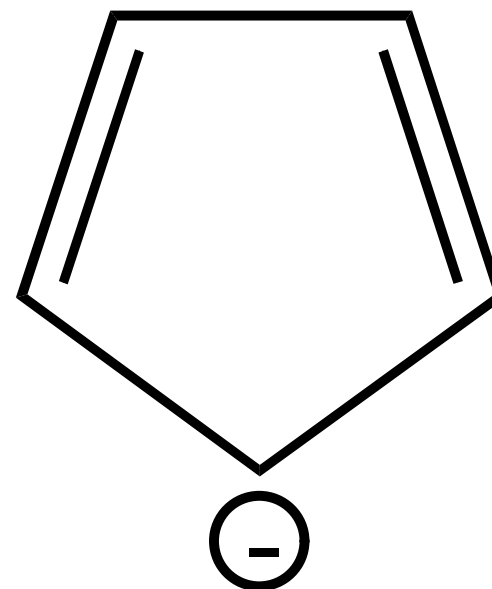
Compounds that contain e.g. one aromatic ring ligand and three carbonyls are referred to as 'piano-stool' compounds. The complex at left obeys the 18-electron rule as:

Cr(0):	d^6
3 CO:	6e
1 benzene:	6e

18e

Ferrocene: the cyclopentadienyl anion ligand

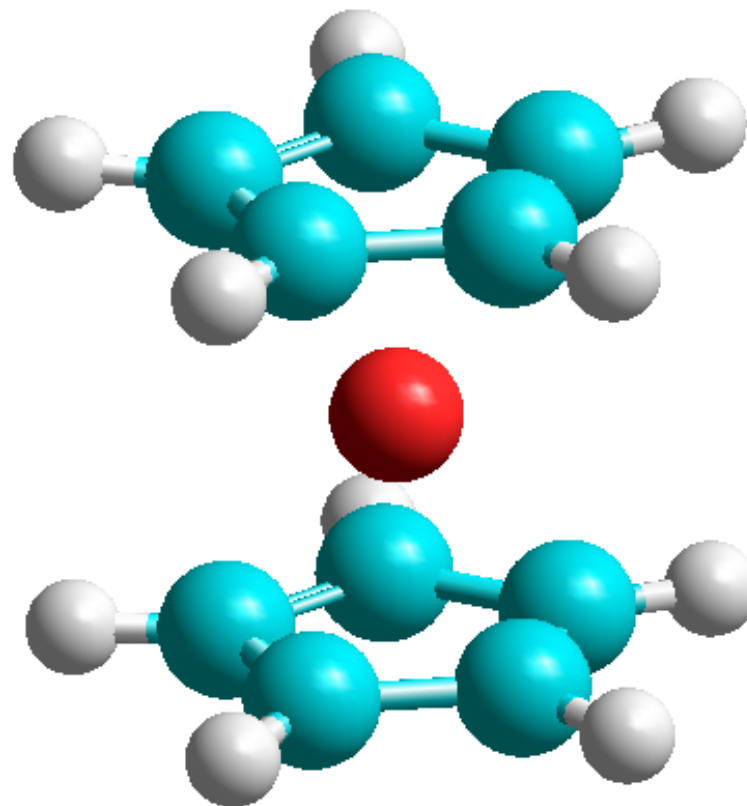
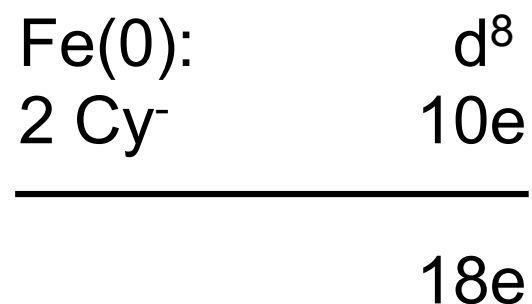
Ferrocene contains the cyclopentadienyl anion ligand, (Cy^-) which contributes five electrons for the 18-electron rule, which is to be expected from the presence of two double bonds (4 electrons) and a negative charge (1 electron). The anion is stable because it is aromatic, which requires $4n + 2$ electrons in the π -system. Cy^- has 5 electrons in the π -system from the five sp^2 hybridized C-atoms, plus one from the negative charge, giving six electrons in the π -system.



Cyclopentadienyl
anion (Cy^-)

Ferrocene: the cyclopentadienyl ligand

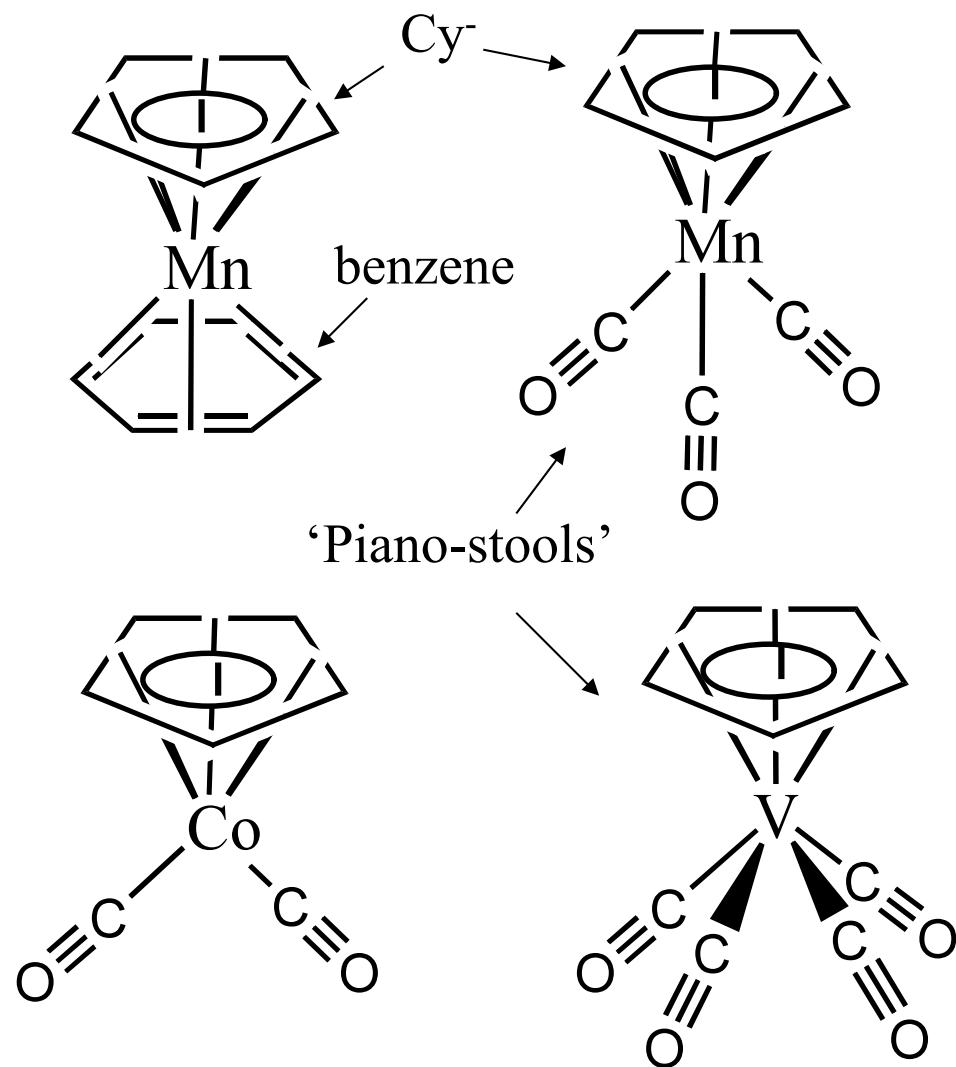
Ferrocene is a remarkable molecule. It can be sublimed without decomposition at 500 °C. The 18-electron rule works for ferrocene as follows:



Ferrocene
= 'sandwich compound'

The cyclopentadienyl ligand and metals with odd numbers of d-electrons:

The fact that Cy^- contributes 5 electrons to the 18-electron rule means that metals with odd numbers of d-electrons such as V, Mn and Co can more easily form neutral complexes with CO's or other neutral ligands such as benzene present. Check the complexes at right for the 18-electron rule.



Complexes of low-spin d^8 metal ions that do not obey the 18-electron rule.

The Fe group (Fe, Ru, Os) as neutral metals are d^8 metals that obey the 18-electron rule in complexes such as $[\text{Ru}(\text{CO})_5]$ (**TBP**) or $[\text{Fe}(\text{Cy})_2]$ (ferrocene). Low-spin d^8 metal ions of higher charge may not obey the eighteen electron rule. Thus, complexes of $M(\text{I})$ d^8 metal ions such as $\text{Co}(\text{I})$, $\text{Rh}(\text{I})$, and $\text{Ir}(\text{I})$ sometimes obey the 18-electron rule, and sometimes do not. Low spin $M(\text{II})$ d^8 metal ions such as $\text{Ni}(\text{II})$, $\text{Pd}(\text{II})$, and $\text{Pt}(\text{II})$ almost never obey the 18-electron rule. These always form **16-electron complexes**, that are **square planar**. The message here is that $M(0)$ d^8 metal ions obey the 18-electron rule, $M(\text{II})$ d^8 metal ions almost never do, and $M(\text{I})$ d^8 metal ions sometimes do. This is summarized on the next slide.

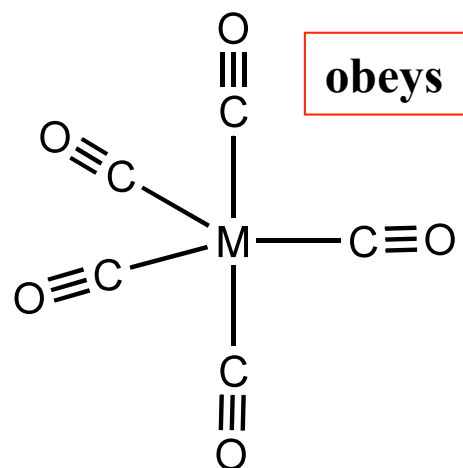
Complexes of low-spin d^8 metal ions.

M(0)

Fe(0), Ru(0), Os(0)

obey the 18-electron rule

Examples:



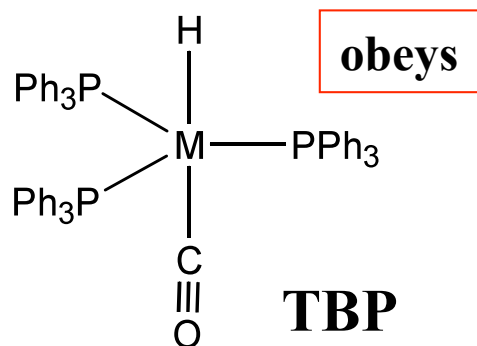
TBP

M = Fe, Ru, Os

M(I)

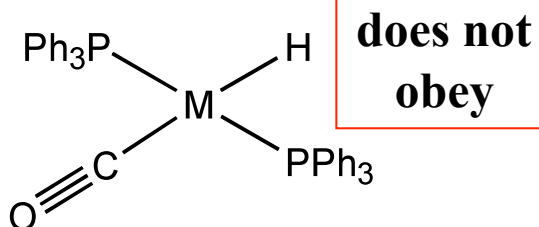
Co(I), Rh(I), Ir(I)

sometimes obey the 18-electron rule



TBP

M = Co, Rh, Ir



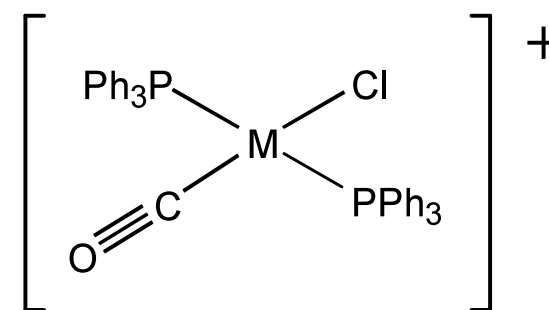
square planar

M(II)

Ni(II), Pd(II), Pt(II)

almost never obey 18-electron rule

does not obey



square planar

M = Ni, Pd, Pt

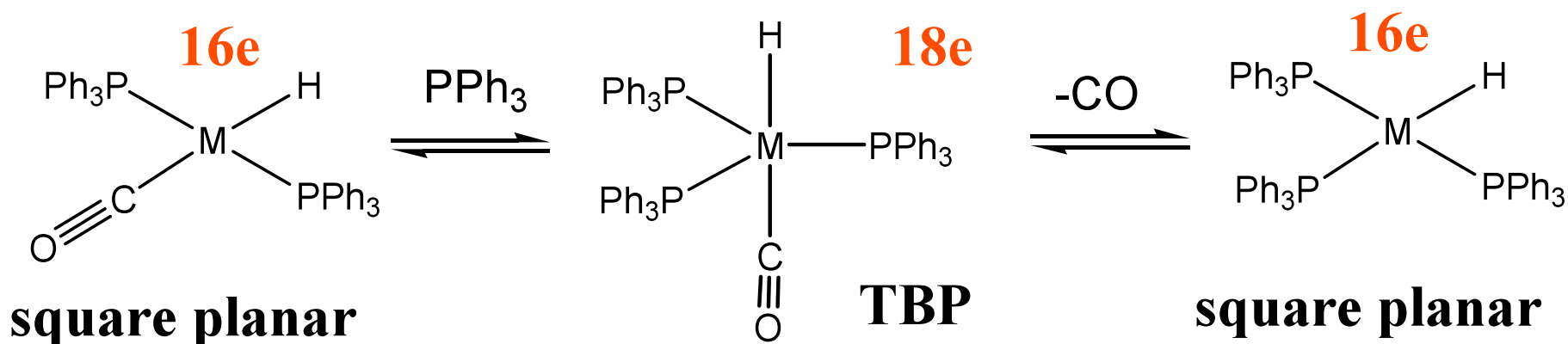
Catalysis by 16-electron organometallics

The ease of ligand substitution of M(I) d^8 metal ions, and their ability to undergo a variety of other reactions such as oxidative addition, discussed later, leads to widespread use of these complexes, almost always square planar 16-electron complexes of Rh(I), as catalysts. One of the most important abilities of these complexes is to take a CO molecule and insert it into an organic molecule, as in:



16-electron complexes of M(I) ions and catalysis

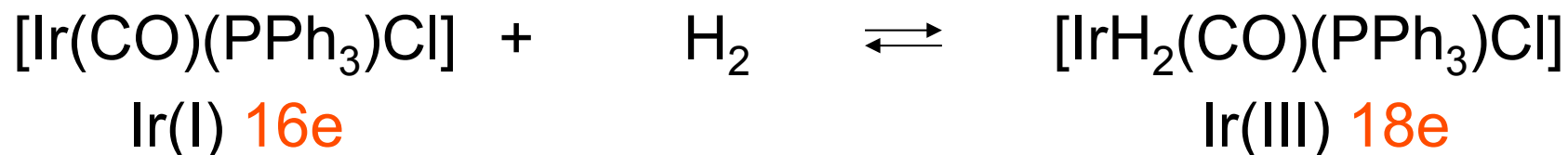
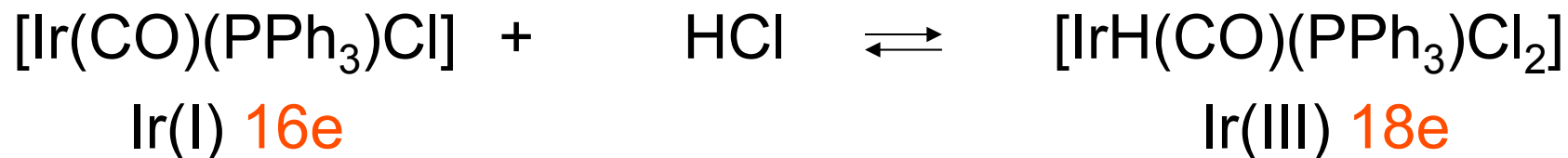
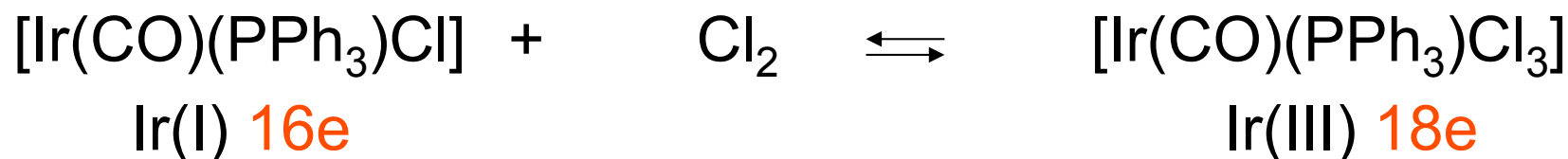
The reactions of 16-electron (16e) complexes are S_N2 (associative), and involve 18-electron (18e) intermediates. They undergo ligand exchange very easily by switching between 16e and 18e forms:



M(0) d^8 metal ions are permanently locked into being 5-coordinate 18e complexes, so cannot easily undergo ligand exchange as can M(I) ions. M(II) d^8 metal ions are locked into being square planar 16e forms, and so do not easily form the 18e intermediate to undergo substitution. Only the M(I) ions can easily switch between 16e and 18e forms, and so very easily undergo ligand exchange. They are thus widely used in catalysis for this reason. Many organometallic catalysts are 16e Rh(I) complexes.

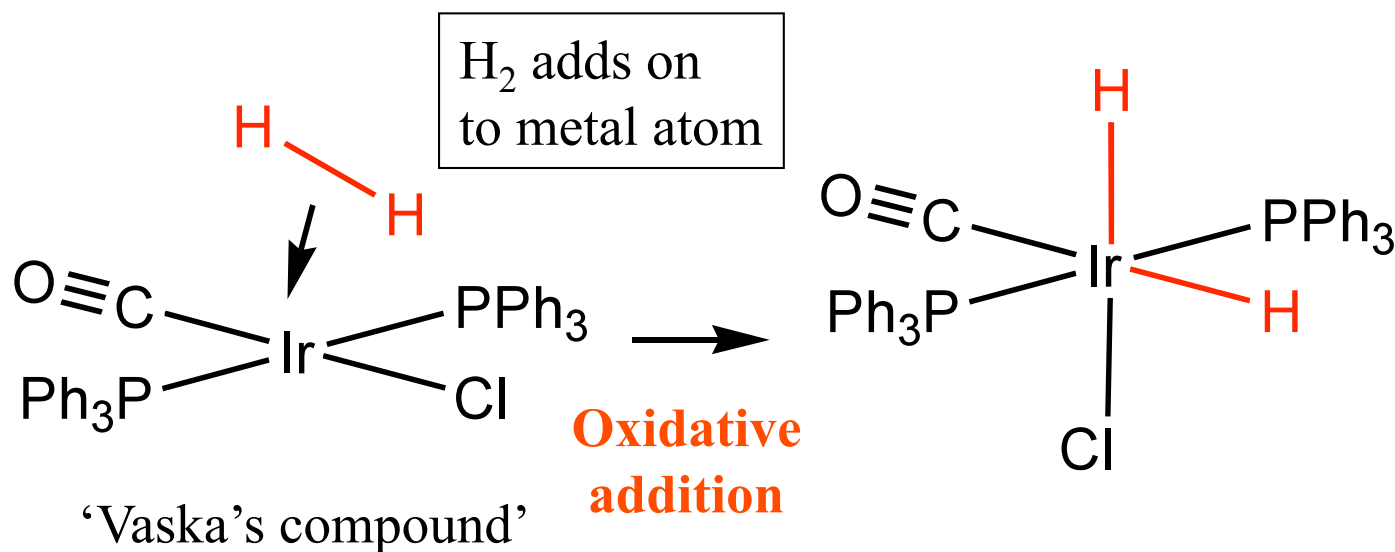
Oxidative addition:

Another important aspect of catalysis is oxidative addition, which the M(I) d^8 ions undergo very easily with a wide variety of oxidants:



Oxidative addition:

In oxidative addition it may seem surprising that something like H_2 can be an 'oxidant'. One should note that what is changing is the formal oxidation state of the iridium from Ir(I) to Ir(III):



Ir(I) because PPh_3 and CO are neutral, so only Cl^- has a formal charge

Ir(III) because PPh_3 and CO are neutral, but both the 2 H^- and Cl^- have formal 1- charges