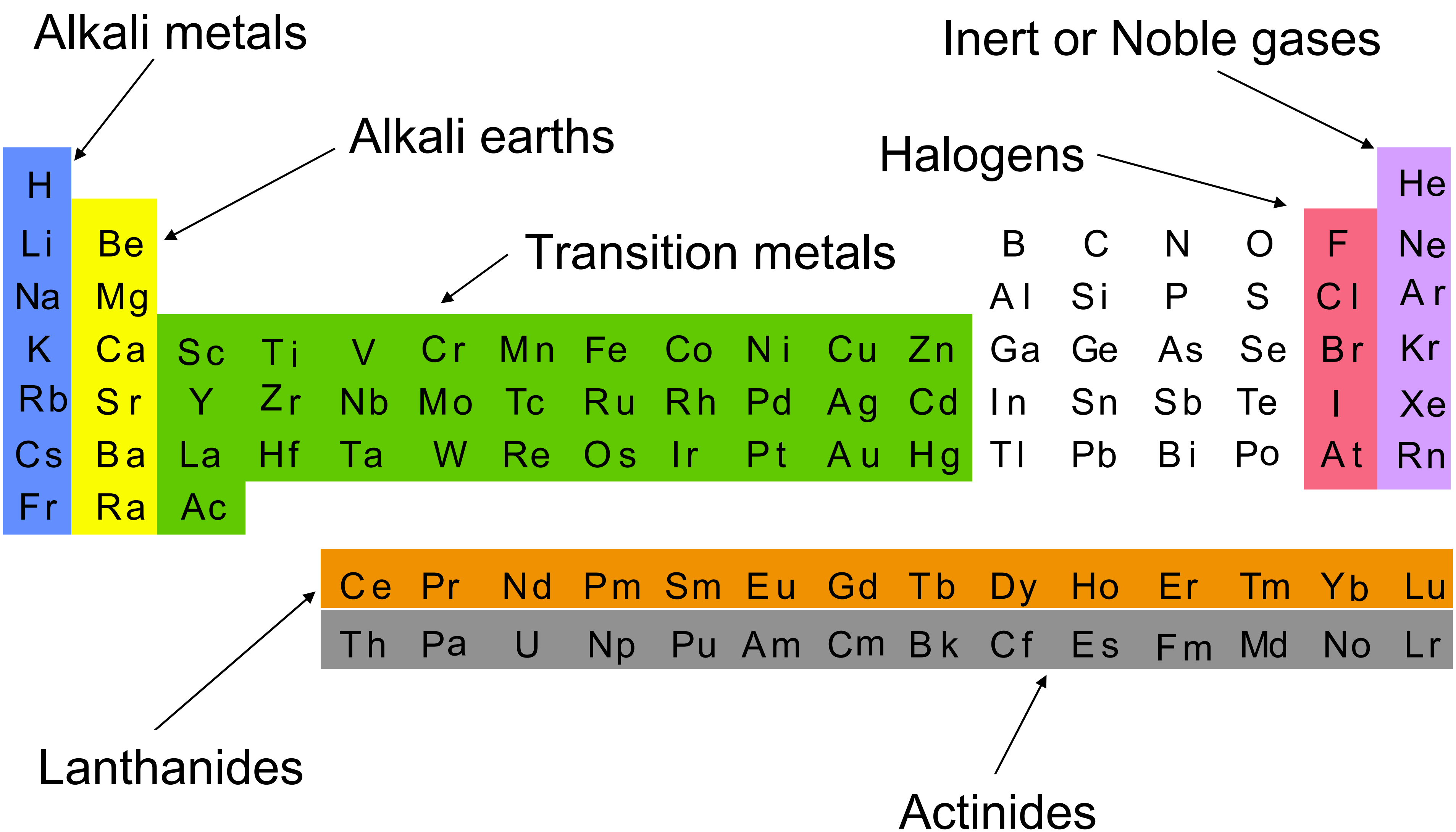
The 18 Electron Rule

References: Gray: chapter 5
OGN: chapter 18

Element Groups



The Chemists

Geoffrey Wilkinson

E. O. Fischer

Nobel Prize, chemistry, 1973

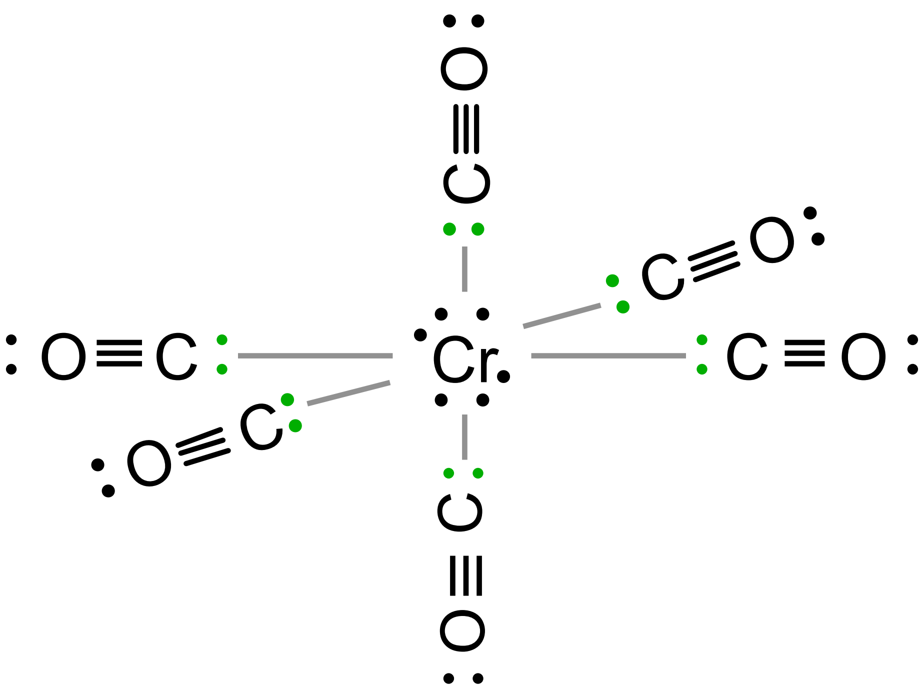
"For their pioneering work, performed independently, on the chemistry of the organometallic, so called sandwich compounds"

18 e⁻ Rule for Transition Elements

- Remember the dot structure for CO?

- Consider Cr, a transition element:
  Chromium: [Ar] $(4s)^2$ $(3d)^4$ → 6 valence e^-

- Like most transition elements, Cr needs 18 e^- in its shell.



12 e^- from CO's + 6 e^- from Cr
= 18 total e^-; formula is $Cr(CO)_6$

Dot structures can predict molecules; if we are given an exception, we can explain its existence, and figure out some of its chemical properties.

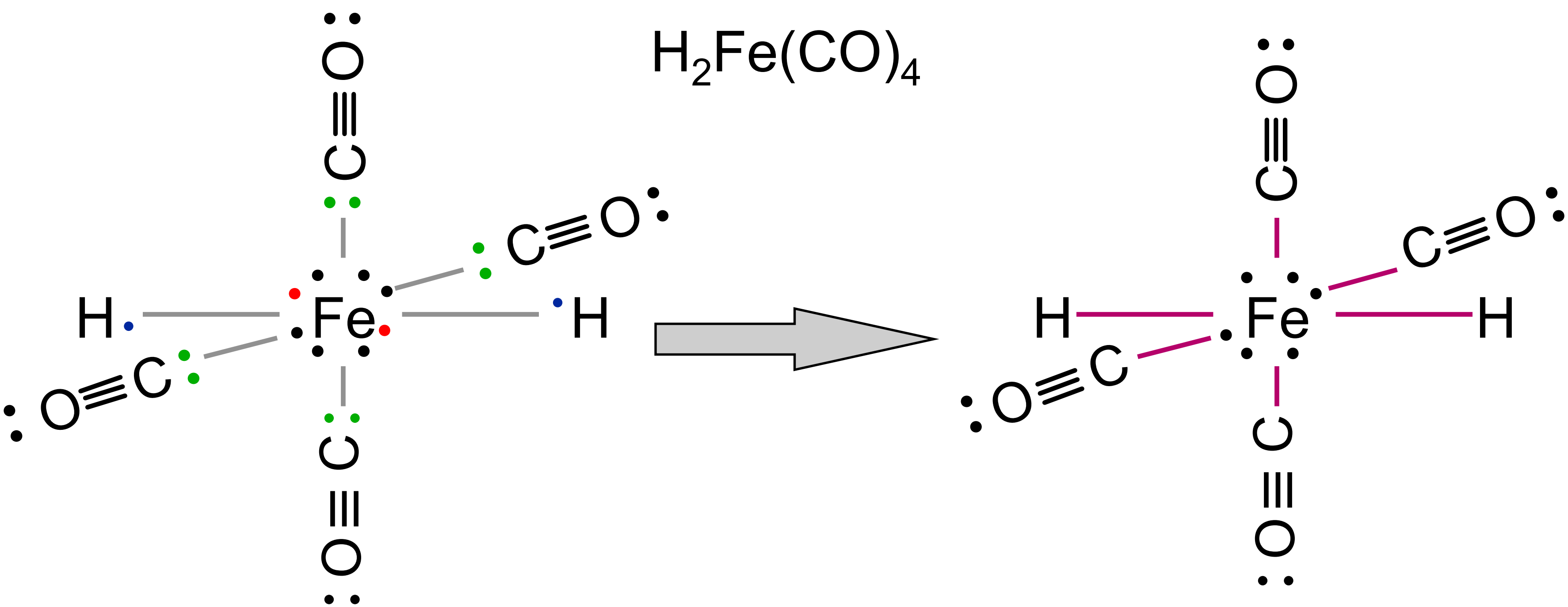
Using the 18 e^- rule

- Given that $H_2Fe(CO)_x$ exists, what does x equal?

  Iron: [Ar] $(4s)^2$ $(3d)^6$ $\rightarrow$ 8 valence e^-

  Hydrogen: $(1s)^1$ $\rightarrow$ 1 valence e^-

- Fe wants to have 18 e^-, because it's a transition element, but it only has 8. The H's give 2 e^-, but we still need 8 electrons. Since each CO supplies 2 e^-, there must be 4 CO's:



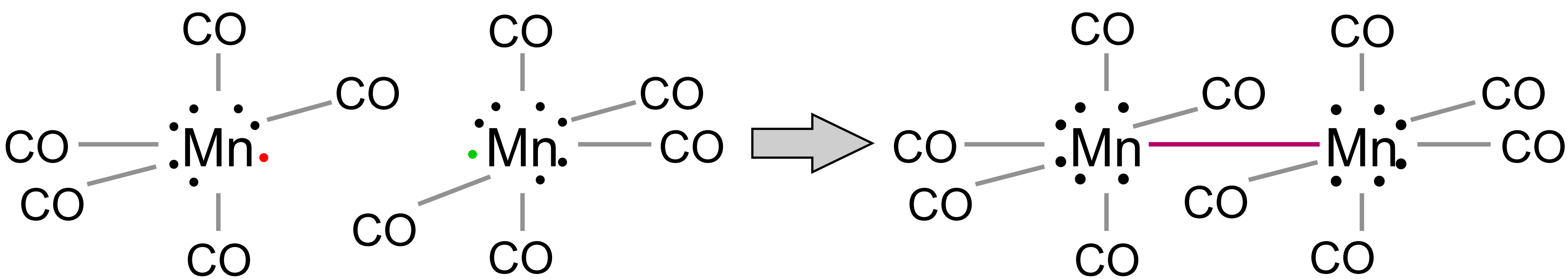
$H_2Fe(CO)_4$

Dimer-Forming Transition Elements

- Given that $Mn(CO)_5$ exists, find its chemical properties:

  Manganese: [Ar] $(4s)^2$ $(3d)^5$ → 7 valence e^-

- 5 CO's provide 10 electrons to Mn, leaving Mn with 17 total e^-; but Mn wants 18 electrons. So, Mn forms a dimer:



$Mn_2(CO)_{10}$

- Halides, like fluorine, also act this way, because they also need only one electron to fill their shell. There are other similarities between transition elements with 7 valence e^- and halides...

Transition Metals That Are Like Halides

- As we have seen, transition elements with 7 valence e^- (like Mn and Re) which are bonded to 2 e^- donors (like CO) form dimers, because they need only one extra e^-.
- Another similarity is reactivity with light:

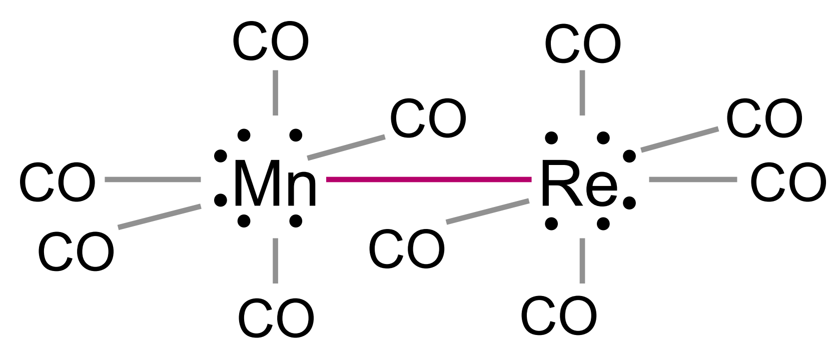
$$Br_2 \xrightarrow{h\nu} 2\ Br$$

$$Mn_2(CO)_{10} \xrightarrow{h\nu} 2\ Mn(CO)_5$$

- Another similarity is a phenomenon called “coupling”:

$$Br + I \longrightarrow Br\text{—}I$$

$$Mn(CO)_5 + Re(CO)_5 \longrightarrow$$

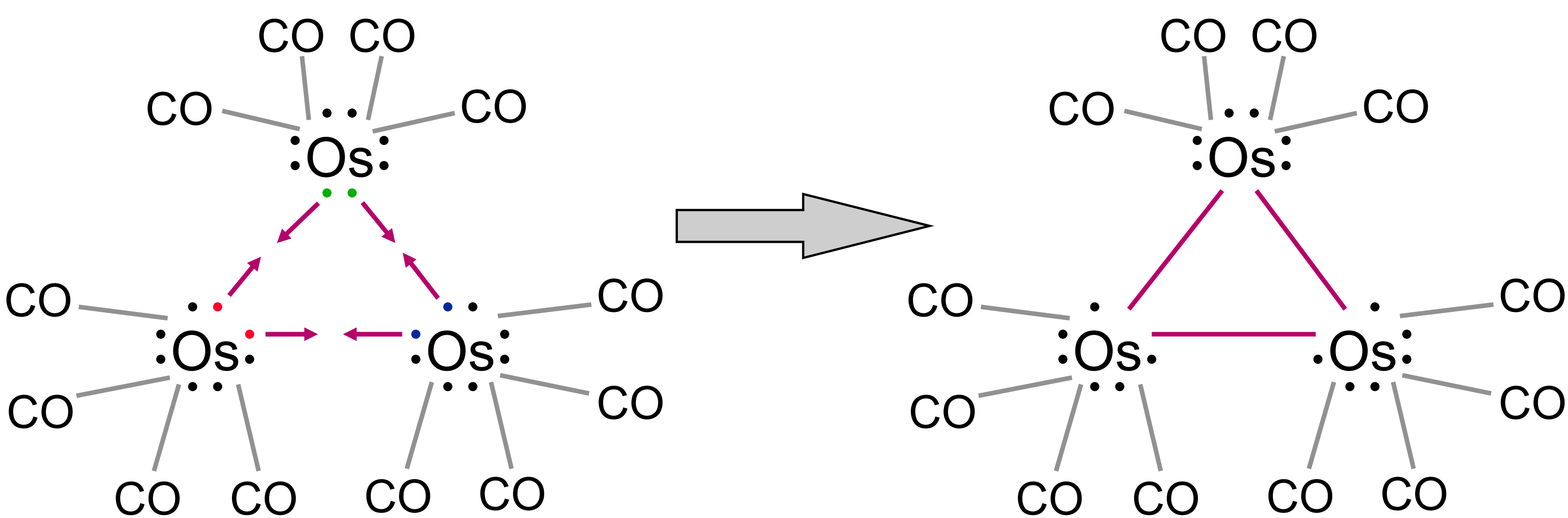


Another Transition Element Structure

- Given that $Os_3(CO)_{12}$ exists, what is its structure?

  Osmium: [Xe] $(6s)^2$ $(5d)^6$ $\rightarrow$ 8 valence e^-

- By symmetry, there must be 4 CO's attached to every Os. That would give us 8 + 4(2) = <u>16 e^-</u> for each Os. But each Os needs 2 more e^- to make 18. So the Os's can form a triangle, with each Os contributing 2 valence e^-'s to the single bonds:

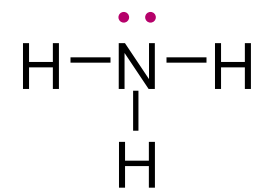


What's the Best Way to Count Things?

- 1 e^- donor: Anything that has one e^- that is not in a bond. Examples:

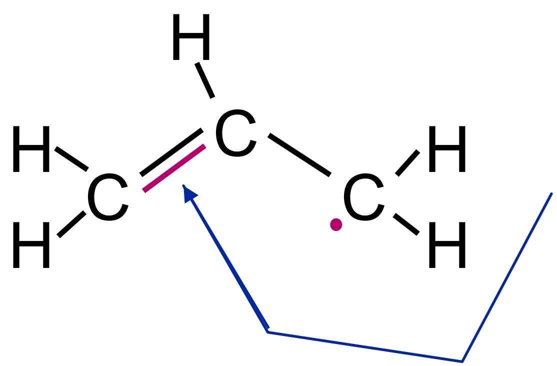
- 2 e^- donor: Anything that has two e^-'s that are not in a bond (called a "lone pair"). Examples:

:CO (the one we have been using)



- 3 e^- donor: Anything having three e^-'s to spare. Example:

The allyl radical:



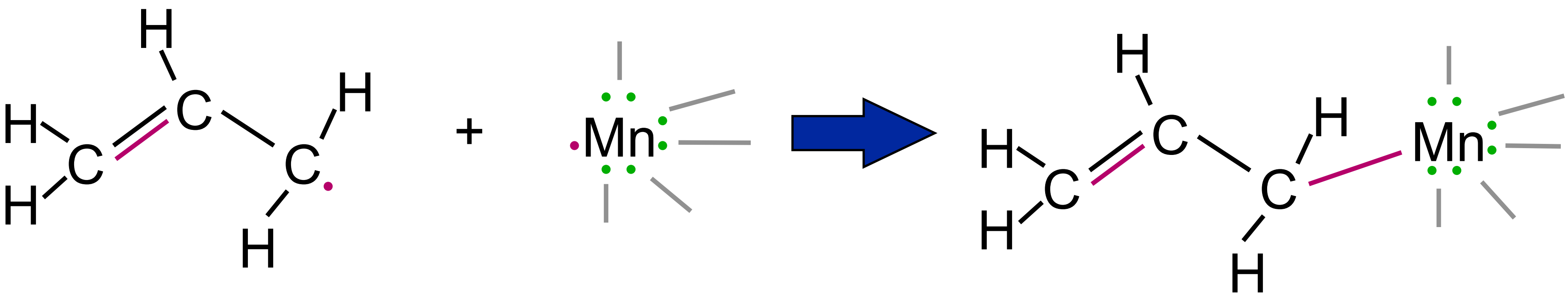
This bond can donate two e^- to a metal; So this radical is either a 1 or a 3 e^- donor

Radical: atom or molecule with an incomplete valence shell, making it very reactive

How Many e^- Do We Want Donated?

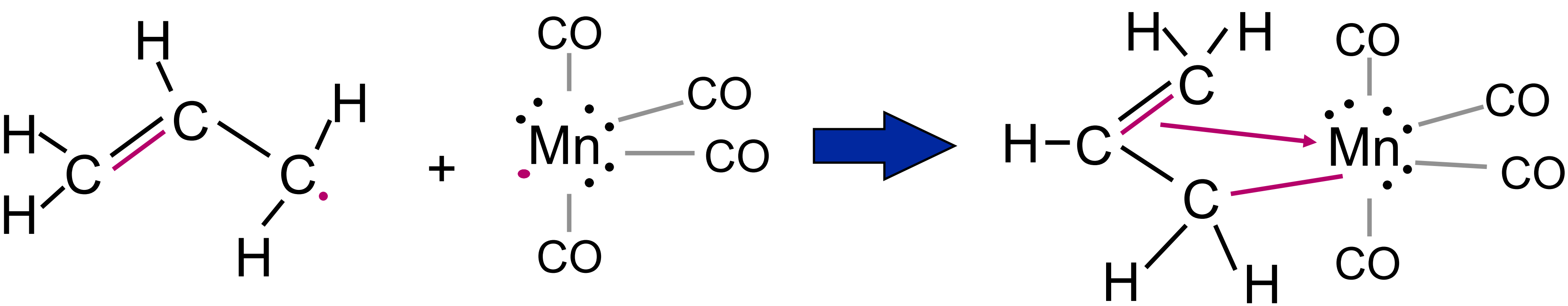
- It depends on the specific case. For example,

allyl—Mn$(CO)_5$ → Mn$(CO)_5$ has 17 e^-, so we want 1 e^- donated

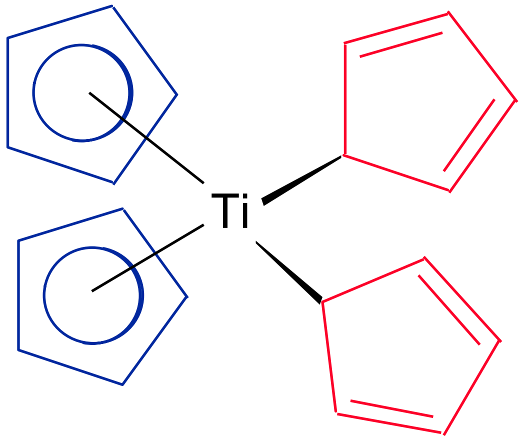


- On the other hand, if we have...

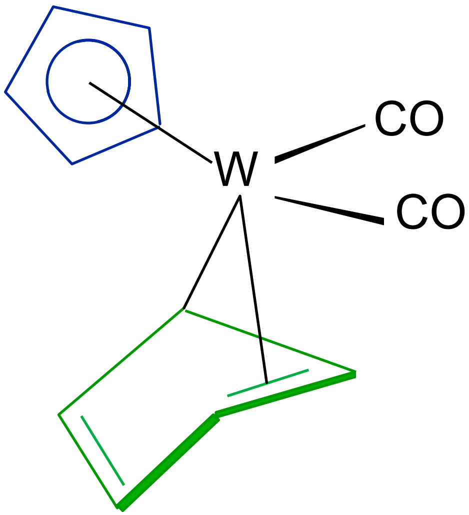
allyl—Mn$(CO)_4$ we now need 3 e^- from the allyl radical



What is η?



$Ti(\eta^1\text{-}C_5H_5)_2(\eta^5\text{-}C_5H_5)_2$

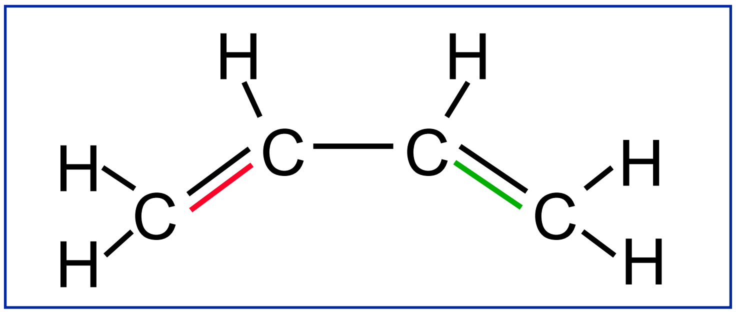


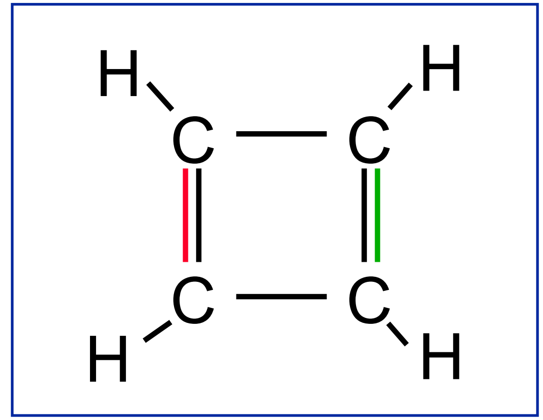
$W(\eta^3\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)(CO)_2$

- **The <u>hapticity</u> η of a molecule is the number of its atoms within bonding distance of the metal atom (from the Greek *haptein*, "to fasten").**
- **The value of η gives us an idea of how many electrons are being donated from the molecule to the metal atom.**

More Electron Donors

- 4 electron donor:



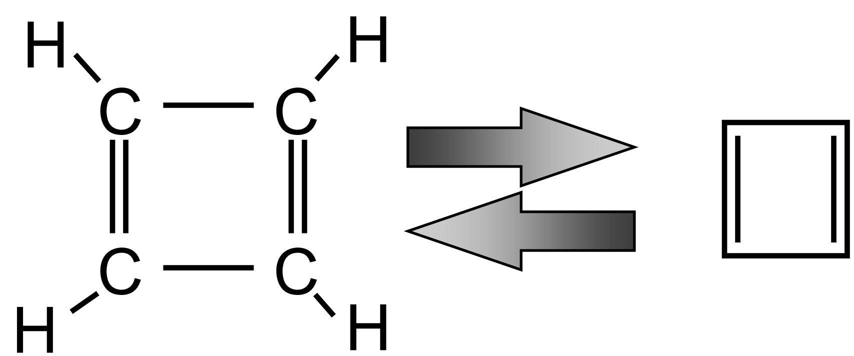


<u>Butadiene</u>: can be used as a 2 or 4 electron donor.

<u>Carbon Structure Shorthand:</u>

In order to make drawing hydrocarbon structures simpler and more compact, repetitive information is left out.

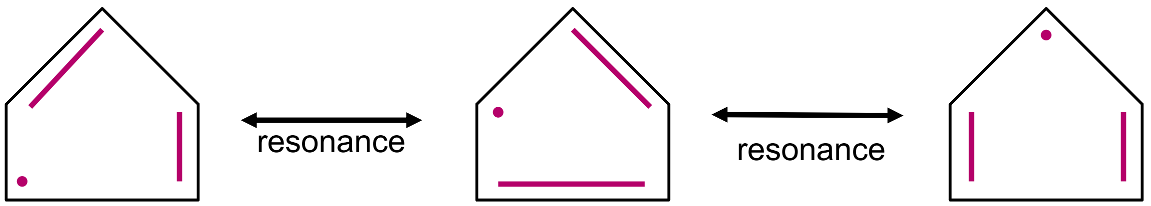
•C is implied at any corner
•H are added to each C as necessary to satisfy the 8 e^- rule.



More Electron Donors

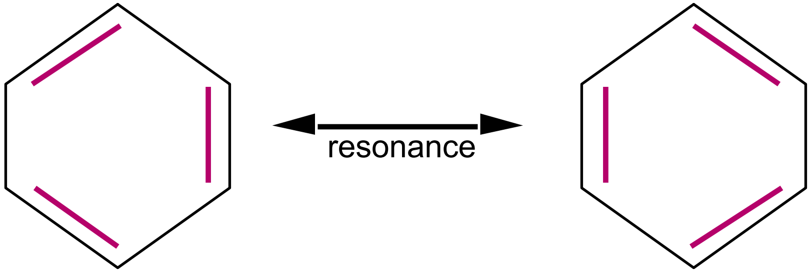
- 5 e⁻: Cyclo-pentadienyl (Cp)

—can be a 1, 3, or 5 e⁻ donor



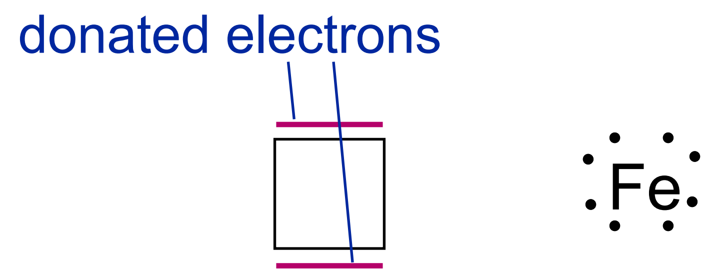
- 6 e⁻ donor: benzene

—can be a 2, 4, or 6 e⁻ donor



Another Transition Element Structure

- Given $(C_4H_4)Fe(CO)_x$ exists, what is the value of x?

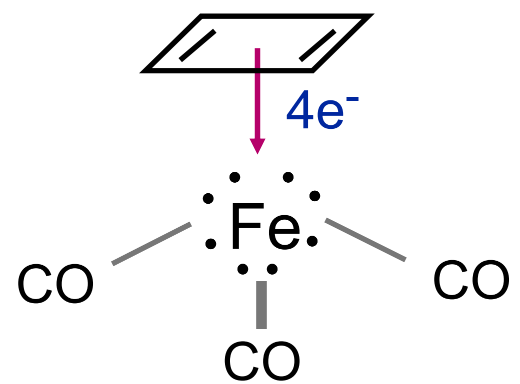


— Fe has eight e^-

— Butadiene (C_4H_4) donates 4 e^-

4 + 8 = 12 e^- so far

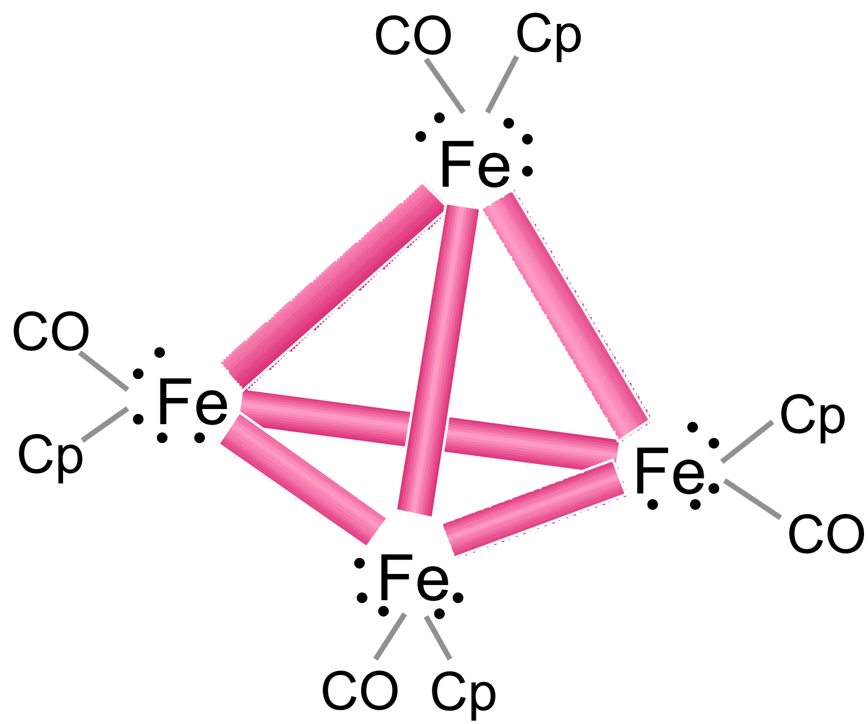
— We need 6 more e^-, so we use <u>three</u> CO's.



3 CO's donate 6 e^-, making 18 e^- for Fe

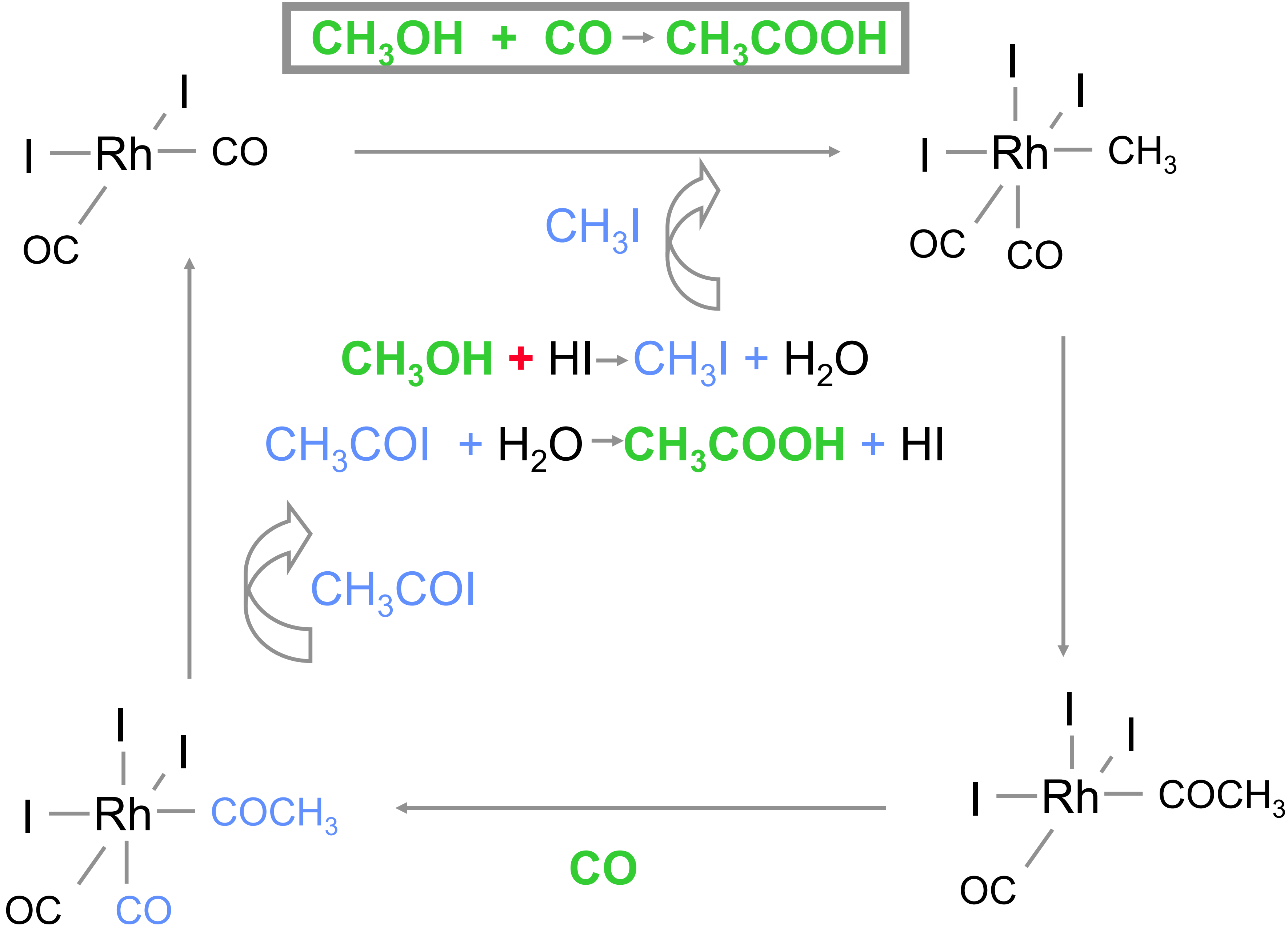
Yet Another Structure

- Can we draw $Fe_4(Cp)_4(CO)_4$?
  - By symmetry, each Fe gets a Cyclo-pentadienyl (Cp) and a CO
  - Cp donates 5 e^-, so now we have 15 e^- for each Fe
  - If we put the Fe's at the corners of a tetrahedron, then each Fe can share a single bond with three other Fe's; we end up with 18 e^- per Fe.



Industrial Homogeneous Catalytic Processes

Reactions/Products	Production/yr 10^3 Metric tons (1990)
Olefin additions	
adiponitrile (for nylon)	420
Olefin polymerizations	12000
Carbonylations	
oxo alcohols	1818
acetic acid/anhydride	1691
Olefin oxidation	
acetaldehyde	273
propylene oxide	815
Alkane and arene oxidations	4800


CH3OH + CO → CH3COOH
CH3I
CH3OH + HI → CH3I + H2O
CH3COI + H2O → CH3COOH + HI
CH3COI
CO
I
Rh
CO
OC
CH3
COCH3

END

The 18 Electron Rule

References: Gray: chapter 5
OGN: chapter 18