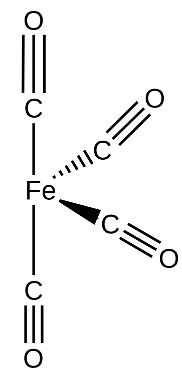
Created by Burke Scott Williams (swilliams@jsd.claremont.edu) and posted on VIPEr on 01/10/2009. This work is licensed under the Creative Commons Attribution Non-commercial Share Alike License in 2009. To view a copy of this license visit http://creativecommons.org/about/license/

An 18 Electron Guideline Worksheet

Use what you learned in the primmer and the hints below to count electrons by both the Closed Shell (CS) and Neutral Ligand (NL) Methods.

1. First let's figure out how to deal with charged complexes. Remember that each of the complexes, unless specified otherwise, is an 18 e^- species.

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

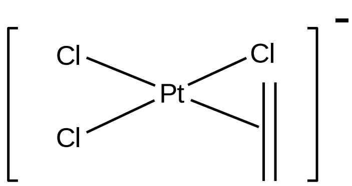


	L or X	**e^- (CS)**	**e^- (NL)**
Fe	n/a		
CO (x4, remember!)			
2^- charge	n/a		
TOTAL	n/a	**18**	**18**

Explain below in one sentence each (a) how we deal with overall charges on the complex in the two methods and (b) how this can be rationalized.

2. Now let's look at a complex which is unusual in two ways. Zeise's Salt (first synthesized in 1825!) is a *square planar* complex. Square planar complexes are almost invariably d^8, 16 e^- species. You'll learn why this is later. The second interesting feature is that it's a π-complex (remember the Dewar-Chatt-Duncanson model?)

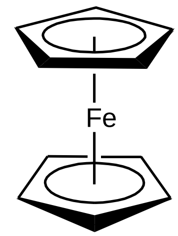
$[Pt(C_2H_4)Cl_3]^-$



	L or X	**e^- (CS)**	**e^- (NL)**
Pt	n/a		
C_2H_4			
Cl			
1^- charge	n/a		
TOTAL	n/a	**16**	**16**

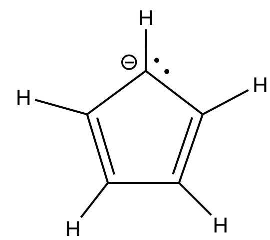
Created by Burke Scott Williams (swilliams@jsd.claremont.edu) and posted on VIPEr on 01/10/2009. This work is licensed under the Creative Commons Attribution Non-commercial Share Alike License in 2009. To view a copy of this license visit http://creativecommons.org/about/license/

3. The first organometallic compound most students encounter is ferrocene. Each of the rings of the "sandwich" is a cyclopentadienide anion (Cp^-, $C_5H_5^-$) . This *is* an 18 e^- compound.



$FeCp_2$

	L or X	e^- (CS)	e^- (NL)
Fe	n/a		
Cp	Leave Blank		
TOTAL	n/a	**18**	**18**

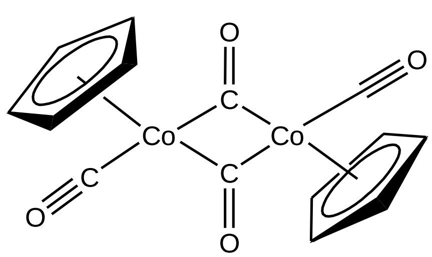


Obviously, we can't class Cp^- as "X" or "L" given your above answer. Cp^- is a *composite* ligand. It is possible for a ligand to act as an "L_2" ligand (ethylene diamine, en, $H_2NCH_2CH_2NH_2$, is a good example), or an XL ligand (such as acetate, which can coordinate through both the anionic oxygen (X) and the neutral oxygen (L) at the same time). Many other such L_mX_n ligands are possible. Given your electron counts above, give a classification to Cp^- and justify your choice on the basis of the Cp^- structure at right.

Nota Bene: All n-membered all-sp^2 rings of this type donate n electrons in the neutral ligand method or either n (even values of n) or n+1 (odd values of n) for the closed shell method.

4. Now let's try a dimeric species. Obviously, when you have two metals, *each* of the metals should go to 18. You can either count to 36 for the metals together, or, as we'll do it here, divide the molecule in half, trying to share any bridging ligands equally. Note that "μ" indicates a ligand bridging two metals.

$[CoCp(CO)(\mu\text{-}CO)]_2$

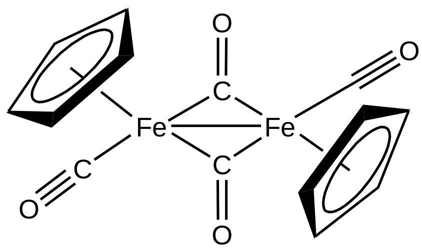


	L or X	e^- (CS)	e^- (NL)
Co	n/a		
Cp			
CO			
μ-CO			
TOTAL	n/a	**18**	**18**

Created by Burke Scott Williams (swilliams@jsd.claremont.edu) and posted on VIPEr on 01/10/2009. This work is licensed under the Creative Commons Attribution Non-commercial Share Alike License in 2009. To view a copy of this license visit http://creativecommons.org/about/license/

5. One kind of bonding we have yet to deal with is metal-metal bonding. Let's try a couple of metal-metal bonded complexes that are each 18 *e*⁻.

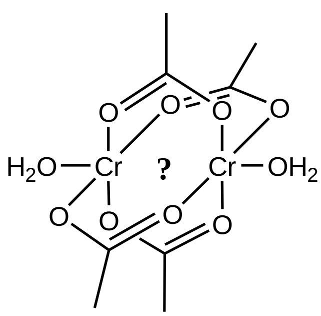
[FeCp(CO)(μ-CO)]$_2$



	L or X	*e*⁻ (CS)	*e*⁻ (NL)
Fe	n/a		
Cp			
CO			
μ-CO			
Fe-Fe bond			
TOTAL	n/a	**18**	**18**

6. We can also use the 18 electron guideline to predict the *bond order* (number of bonds) between two metals in a dimer. For this one *forget everything you know* about what kind of bonding is possible between two atoms (yes, this is a real molecule).

[Cr(OH$_2$)(μ-OAc)$_2$]$_2$



	L or X	*e*⁻ (CS)	*e*⁻ (NL)
Cr	n/a		
H$_2$O			
μ-OAc* (anion)			
μ-OAc* (neutral)			
Cr-Cr bond			
TOTAL	n/a	**18**	**18**

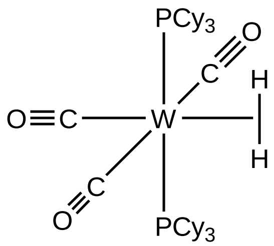
* Note that there are "two ends" to each acetate (see text of #3). Make sure each Cr gets an equal share!

In case this mode of bonding is new to you, it involves σ, π, and δ-bonding!

Created by Burke Scott Williams (swilliams@jsd.claremont.edu) and posted on VIPEr on 01/10/2009. This work is licensed under the Creative Commons Attribution Non-commercial Share Alike License in 2009. To view a copy of this license visit http://creativecommons.org/about/license/

7. We dealt with π-complexes back in #2, now let's do a σ-complex. It's pretty similar. In this case, the metal is bound to the σ-bond of dihydrogen.

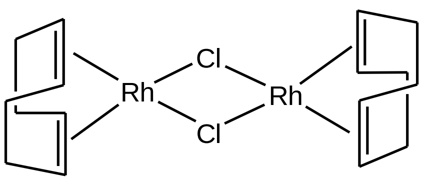
trans-mer-
$W(CO)_3(PCy_3)_2(H_2)$



	L or X	e^- (CS)	e^- (NL)
W	n/a		
PCy_3			
CO			
H_2			
TOTAL	n/a	**18**	**18**

8. Now let's do a bridging halide.

$[Rh(COD)Cl]_2$



	L or X	e^- (CS)	e^- (NL)
Rh	n/a		
COD			
μ-Cl (mode 1)			
μ-Cl (mode 2)			
TOTAL (sq. pl.)	n/a	**16**	**16**

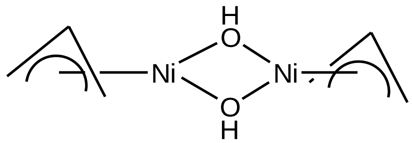
Hint: See OAc in #6 for the "two kinds" of bonding here

Provide a brief explanation for why chlorine is able to bond in both modes here:

Created by Burke Scott Williams (swilliams@jsd.claremont.edu) and posted on VIPEr on 01/10/2009. This work is licensed under the Creative Commons Attribution Non-commercial Share Alike License in 2009. To view a copy of this license visit http://creativecommons.org/about/license/

9. A final common ligand is allyl, $C_3H_3^-$. Figure out the totals for yourself (I suggest counting the metals together, and think about whether you'd expect these to be 16 e^- or 18 e^- metals)!

[Ni(allyl)(μ-OH)]$_2$



	L or X	***e*⁻ (CS)**	***e*⁻ (NL)**
Ni	n/a		
μ-OH			
C_3H_3			
TOTAL	n/a		

There are two ligand types that we have not dealt with here. One of them is metal-ligand multiple bonded ligands (carbenes, carbynes, imides, nitrides, and oxides), and the other is nitrosyl ligands (NO). Different chemists and different textbooks treat them slightly differently, and we have concentrated here on the "core cases" for which the electron counting is straightforward and (relatively) non-controversial.