

Metal-Metal Bonding

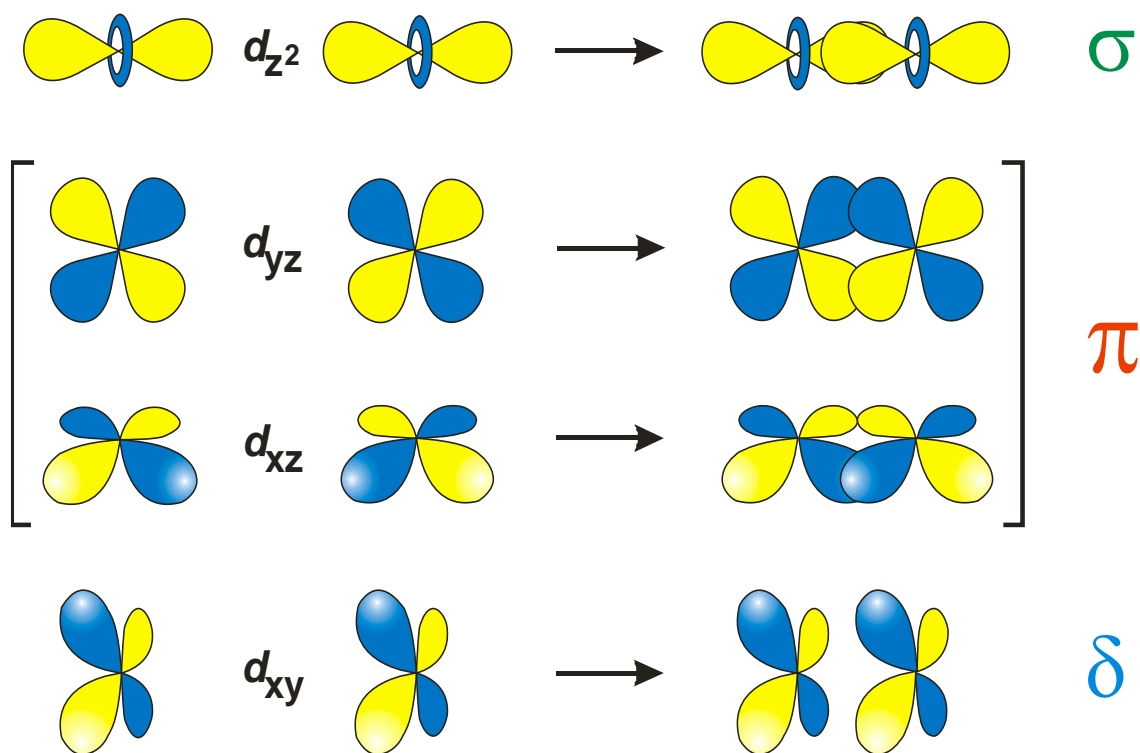
There are three general classes of M-M bonding:

Covalent: Electron precise bonds. M-M bond counts as one e- from each metal center. Most common type of M-M bonding.

Dative: Where one metal uses a filled *d* orbital “lone pair” to coordinate to an empty orbital on a second, more unsaturated metal. Most **dative bonding** situations can also be electron-counted as **covalent bonds**.

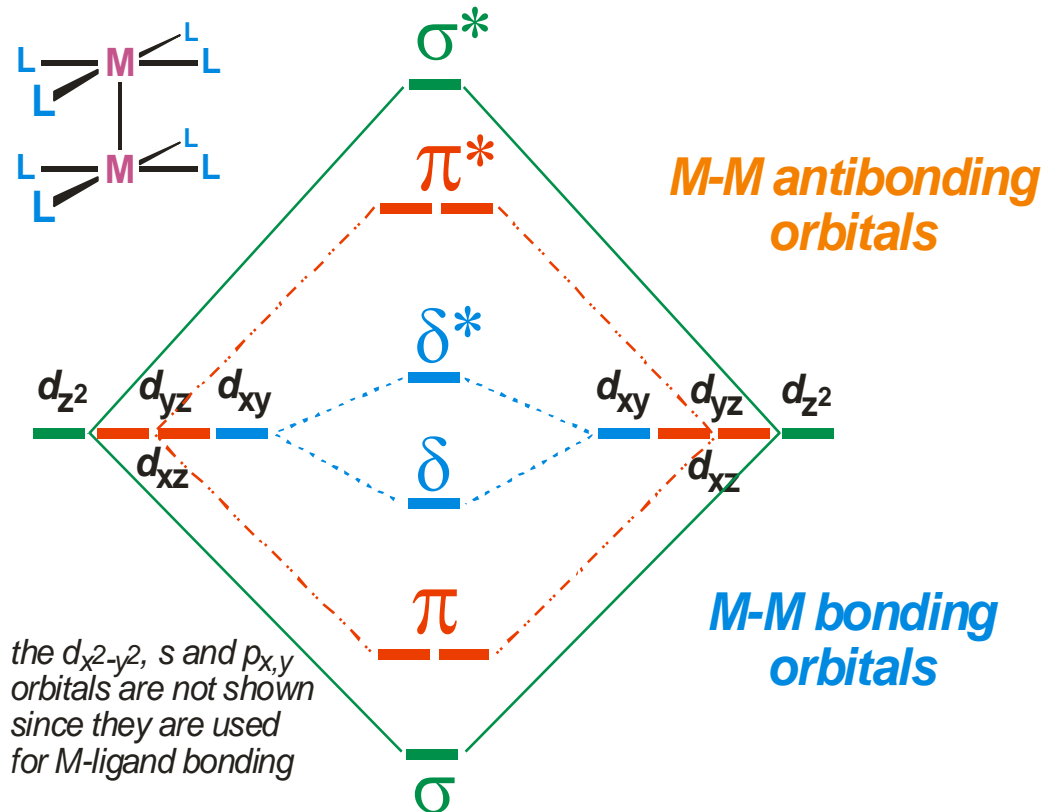
Symmetry: Weak metal-metal interactions caused by molecular orbital symmetry interactions of filled & empty M-M bonding and/or antibonding orbitals. Typically seen for d^8 metals. Not at all common.

Overlap of *d* orbitals to make different types of **covalent** M-M bonding interactions (strongest to weakest):



the $d_{x^2-y^2}$ orbitals (not shown) are used for M-L bonding

A qualitative MO diagram for the interaction of two square planar metal centers showing the M-M bond forming interactions:



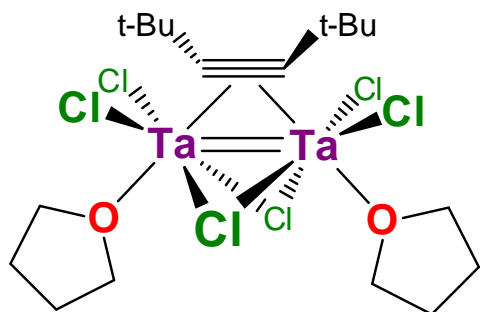
As one fills the lower energy M-M bonding orbitals, one makes one M-M bond for each pair of electrons added (one per metal). But once you add more than 8 e⁻ the antibonding orbitals begin to fill and this starts canceling out M-M bonds.

Electron Count	Resulting M-M Bond
d ¹ - d ¹	Single bond
d ² - d ²	Double bond
d ³ - d ³	Triple bond
d ⁴ - d ⁴	Quadruple bond → optimum
d ⁵ - d ⁵	Triple bond
d ⁶ - d ⁶	Double bond (<i>M-L bonding usually dominates</i>)
d ⁷ - d ⁷	Single bond
d ⁸ - d ⁸	No bond (<i>symmetry interaction</i>)

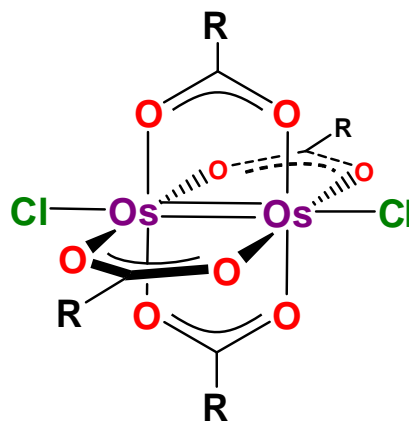
Note that the table on the previous page specifically refers to two square-planar metals interacting as shown in the MO diagram. Metal centers with other geometries can often adopt M-M bond orders different from that shown in the table. Electron-counting can often provide some guidance on this. **Although, if you don't have any d electrons, you generally can't have any M-M bonding.** Nor can you have a higher M-M bond order than the # of d electrons being shared between the metal centers. For example, two d^2 metals could only form a maximum of a M=M double bond.

Some Covalent Multiple Bonded Examples:

Double Bonds



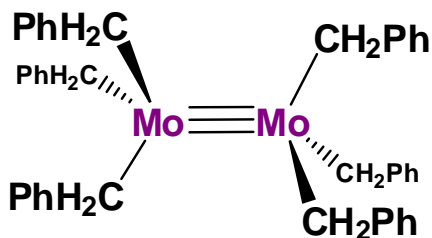
$$Ta-Ta = 2.68 \text{ \AA}$$



$$Os-Os = 2.30 \text{ \AA}$$

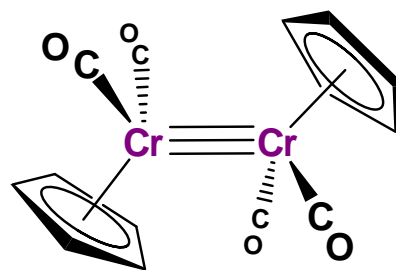
Triple Bonds

Chisholm d^3-d^3 Triple Bonds



$$Mo-Mo = 2.17 \text{ \AA}$$

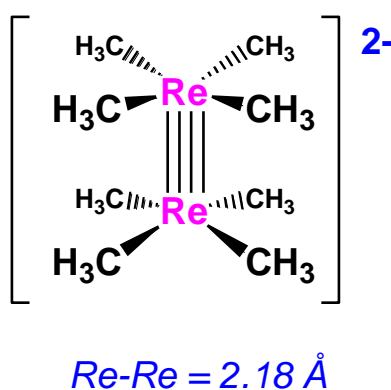
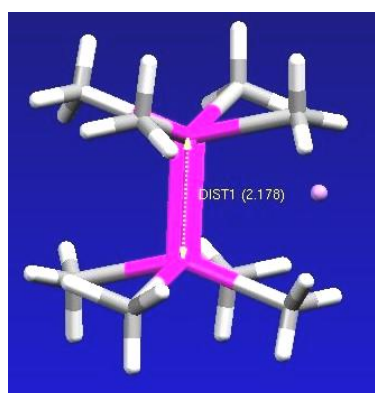
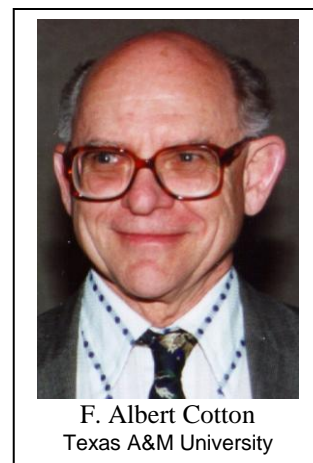
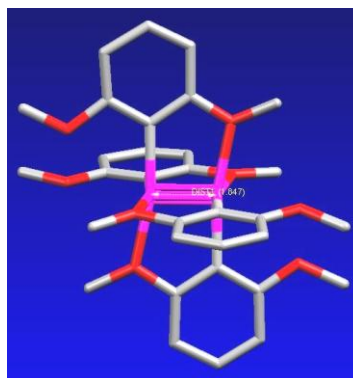
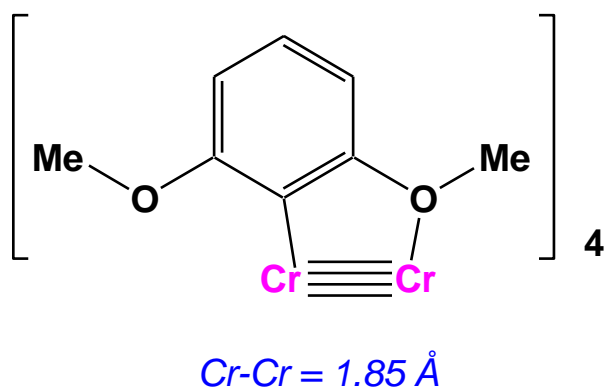
d^5-d^5 Triple Bond



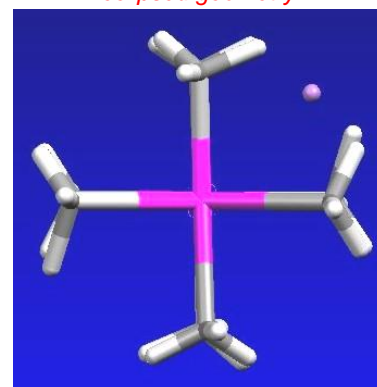
$$Cr-Cr = 2.27 \text{ \AA}$$

Quadruple Bonds (Cotton)

d^4-d^4 electronic configurations often lead to the formation of quadruple M-M bonds. Prof. F. Albert Cotton at Texas A&M is famous for his discovery and extensive studies of M-M quadruple bonds (and other M-M bonded systems).



View down Re-Re axis showing eclipsed geometry

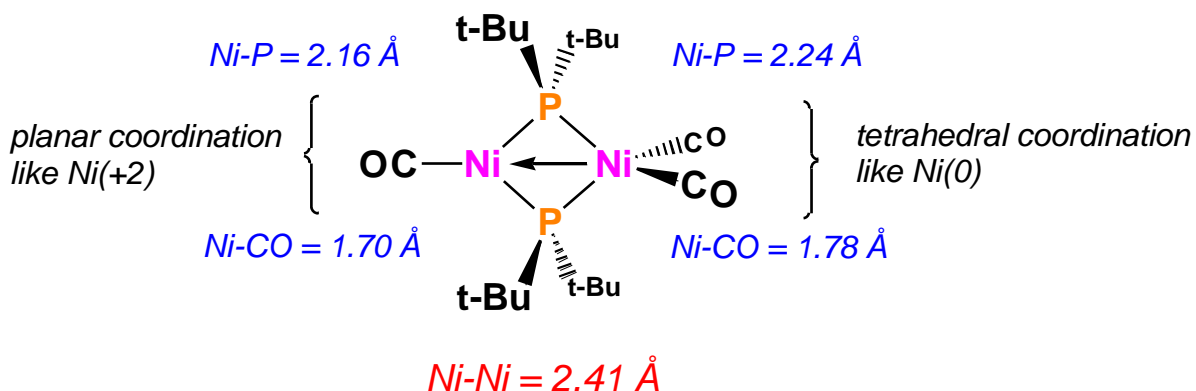


An important orbital feature of quadruple bonds is that they have **eclipsed** D_{4h} -like ligand conformations. This is clearly illustrated above for the non-bridged $[Re_2(CH_3)_8]^{2-}$ complex. There is clear steric repulsion between the methyl groups that could be relieved by rotation to a staggered geometry. But the δ -bond component of the quadruple bond favors an **eclipsed orientation** and imposes a rotational barrier for rotations about the quadruple bond. **Triple bonds** do not have this rotational barrier (free rotation!), thus the $M\equiv M$ triple bonded complexes on the previous page have staggered geometries.

Dative M-M Bonds (unsymmetrical M-M bonded complexes)

When a metal center with at least two *d* electrons and a moderately high electron count (16 or 18e⁻) is adjacent to a metal that is unsaturated and electron-deficient, the more electron-rich metal center can donate a lone pair of *d* electrons to the unsaturated metal to form what is called a dative M-M bond. This is usually indicated by using an arrow (→) instead of a line for a covalent bond.

Consider the following bimetallic nickel complex:



There are two ways of viewing this electronically (see table below) symmetrically dividing the +2 charge on the nickels needed to balance the two anionic phosphide ligands giving you two d⁹ Ni(+1) oxidation state metals, a covalent Ni-Ni bond, and 16 and 18e⁻ metal centers.

Covalent M-M Bonding			
Left Ni		Right Ni	
Ni(+1)	d ⁹	Ni(+1)	d ⁹
[μ-PR ₂] ⁻	2e ⁻	[μ-PR ₂] ⁻	2e ⁻
μ-PR ₂	2e ⁻	μ-PR ₂	2e ⁻
CO	2e ⁻	2CO	4e ⁻
M-M	1e ⁻	M-M	1e ⁻
Total	16e⁻	Total	18e⁻

Dative			
Left Ni		Right Ni	
Ni(+2)	d ⁸	Ni(0)	d ¹⁰
2[μ-PR ₂] ⁻	4e ⁻	2μ-PR ₂	4e ⁻
CO	2e ⁻	2CO	4e ⁻
Ni←Ni(0)	2e ⁻		
Total	16e⁻	Total	18e⁻

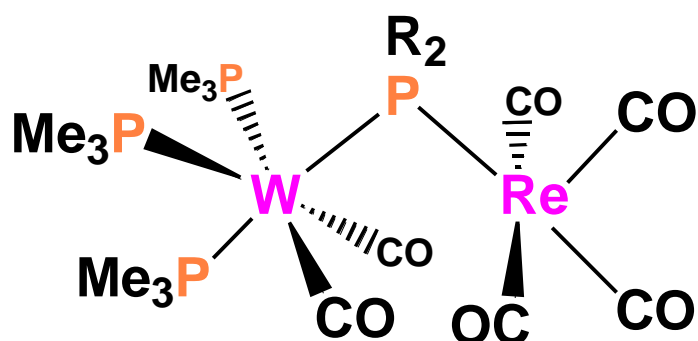
The other method is to note that the one nickel has tetrahedral coordination geometry, just like a d¹⁰ Ni(0) center, while the other nickel has a planar geometry similar to a d⁸ Ni(+2) center. One can “assign” the two negatively charged phosphide ligands with the Ni(+2) center and have them acting as “neutral” 2e⁻ donors to the Ni(0) center. This then gives one an 18e⁻ Ni(0) center

and a three-coordinate $14e^-$ $\text{Ni}(+2)$ center. Let the electron-rich, $18e^-$ d^{10} $\text{Ni}(0)$ center donate one of its lone pairs to the unsaturated $14e^-$ d^8 $\text{Ni}(+2)$ bringing it up to $16e^-$, which is a normal electron-count for a square-planar d^8 $\text{Ni}(+2)$ atom.

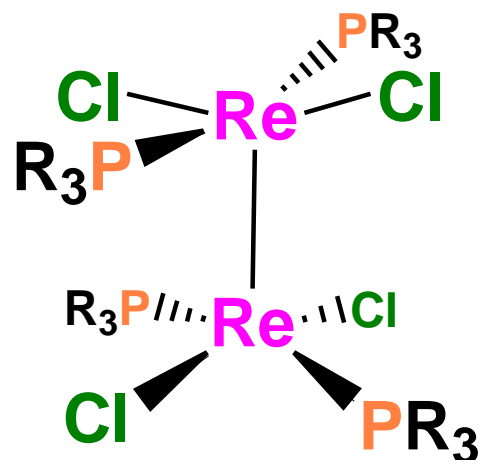
Note that we get the same electron count and some sort of Ni-Ni bond via either method. So you generally don't have to worry about which method you use. Obviously, the covalent method is simpler.

The reason that many consider the dative M-M bond method to be more "accurate" is that if both nickel atoms are classified as $\text{Ni}(+1)$, why don't both have the same geometry? One could explain the differences in geometry & structural features simply because one Ni has an extra CO coordinated and we will have an electronically unsymmetrical complex regardless of the oxidation state assignments.

Problem: Electron-count the following complex using both the covalent and dative M-M bonding methods:



Problem: Electron-count the following complex. What is the order of the Re-Re bond? Why wouldn't it be appropriate to use the dative bond method for this complex?



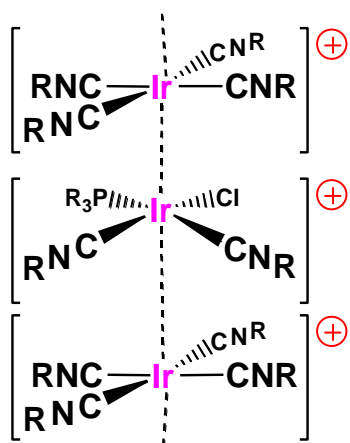
Weak M-M Interactions by Symmetry

Based on the MO diagram at the beginning of this section, d^8-d^8 systems shouldn't have any M-M bonding due to the filling of all the M-M antibonding orbitals, which cancels out the M-M bonding orbitals.

But Harry Gray and others noted that more than a few bi- or polymetallic d^8 complexes do show the presence of weak M-M bonding interactions, both in solution and the solid-state.

For example, the Rh and Ir tetrakis(isocyanide)

complexes, $[M(CNR)_4]^+$, form oligomeric M-M bonded stacks in solution and in the solid-state, in spite of the fact that there should be no covalent M-M bonds.



Gray proposed in 1974 that these persistent, but weak M-M interactions were caused by a molecular orbital symmetry interaction between the filled σ -M-M bonding and σ^* -anti-bonding orbitals with the empty p_z σ and σ^* orbitals. The empty orbitals are pushed up in energy and the filled orbitals down in energy by this symmetry

interaction. This generates a weak M-M bond – strong enough, however, to allow these complexes to form M-M bonds even in solution. This orbital effect is shown in the MO diagram to the right.

