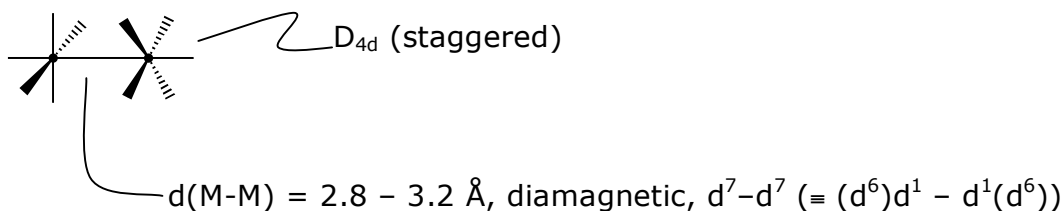


5.04, Principles of Inorganic Chemistry II  
 MIT Department of Chemistry  
**Lecture 22: Metal-Metal Bonding: Single Bonds**

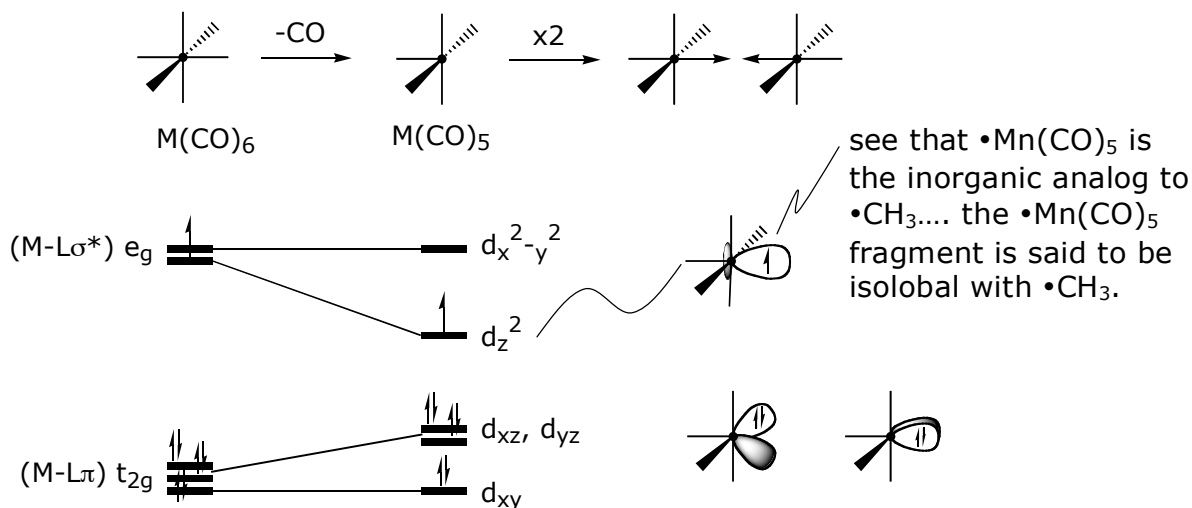
Metal-Metal bonding is common for metals in low oxidation states, and generally increases in strength along the series  $3d \ll 4d < 5d$ . There are limiting forms of metal-metal bonding depending on d-orbital occupation. Usually  $d^1$  and  $d^2$  metals do not form complexes with unsupported (i.e. no bridging ligands) metal-metal bonds. Triple and quadruple metal-metal bonds are formed between  $d^3$  and  $d^4$  metals, respectively. Single metal-metal bonds are formed between  $d^7$  and  $d^9$  metals. Polynuclear clusters can support a wide variety of metal d-electron counts.

Single Metal-Metal Bonded Complexes

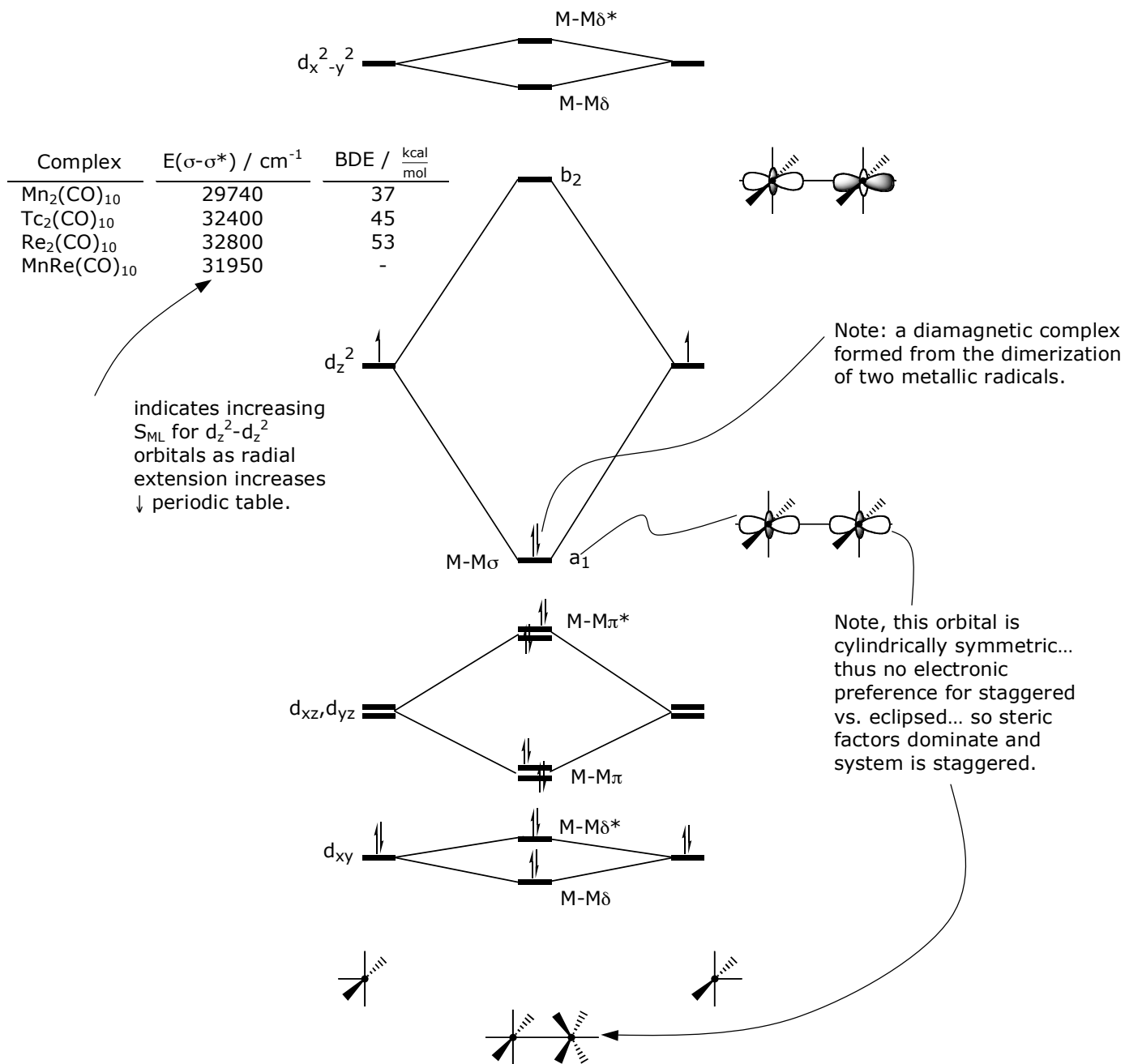
We will consider the paradigmatic single M-M complex,  $M_2(CO)_{10}$  ( $M = Mn(0), Re(0)$ )



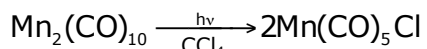
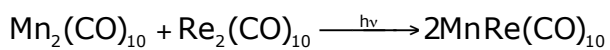
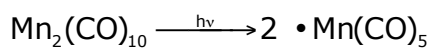
Strategy for group fragment approach... correlate to  $M(CO)_6$  ( $O_h$ ), remove a ligand to give  $M(CO)_5$  ( $C_{4v}$ ), and dimerize:



The energetic stabilization of the  $e^-$  in  $d_{z^2}$  by dimerization is the driving force for metal-metal bond formation:



This MO diagram rationalizes the photochemistry of  $\text{M}_2(\text{CO})_{10}$  complexes. The reactivity out of the excited state is radical...



## Cluster Formation

As mentioned above, odd electron occupancy of the  $e_g$  orbitals ( $O_h$ ) prompts ligand loss in order to stabilize  $d_{2^2}$ . Further stabilization occurs by metal-metal single bond formation. Can take limiting argument to explain cluster formation across the periodic table:

		Group				
		6	7	8	9	10
		Cr(CO) <sub>6</sub> Mo(CO) <sub>6</sub> W(CO) <sub>6</sub>	Mn <sub>2</sub> (CO) <sub>10</sub> Tc <sub>2</sub> (CO) <sub>10</sub> Re <sub>2</sub> (CO) <sub>10</sub>	Fe <sub>3</sub> (CO) <sub>12</sub> Ru <sub>3</sub> (CO) <sub>12</sub> Os <sub>3</sub> (CO) <sub>12</sub>	- Rh <sub>4</sub> (CO) <sub>12</sub> Ir <sub>4</sub> (CO) <sub>12</sub>	Ni(CO) <sub>4</sub> - -
$e_g$	$=$					
$t_{2g}$						
		bury $d^6$ no $e^-$ in $\sigma^*$ stable	bury $d^6$ $1e^-$ in $\sigma^*$ lose 1 CO 1 M-M	bury $d^6$ $2e^-$ in $\sigma^*$ lose 2 CO 2 M-M	bury $d^6$ $3e^-$ in $\sigma^*$ lose 3 CO 3 M-M	filled d-orbitals no electronic stabilization
		maximum stabilization afforded by metal-metal $\sigma$ bond formation				

In each case, the clusters assume an octahedral coordination as a result of burying 6 d electrons in what is formally  $t_{2g}$  orbitals. The system loses the number of CO's that is equivalent to the number of  $e^-$ s in  $M-L\sigma^*$ ... this permits maximum M-M bond formation and thus maximum stabilization.