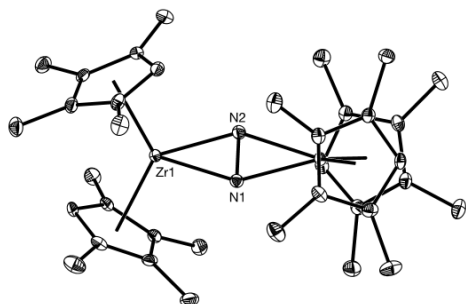
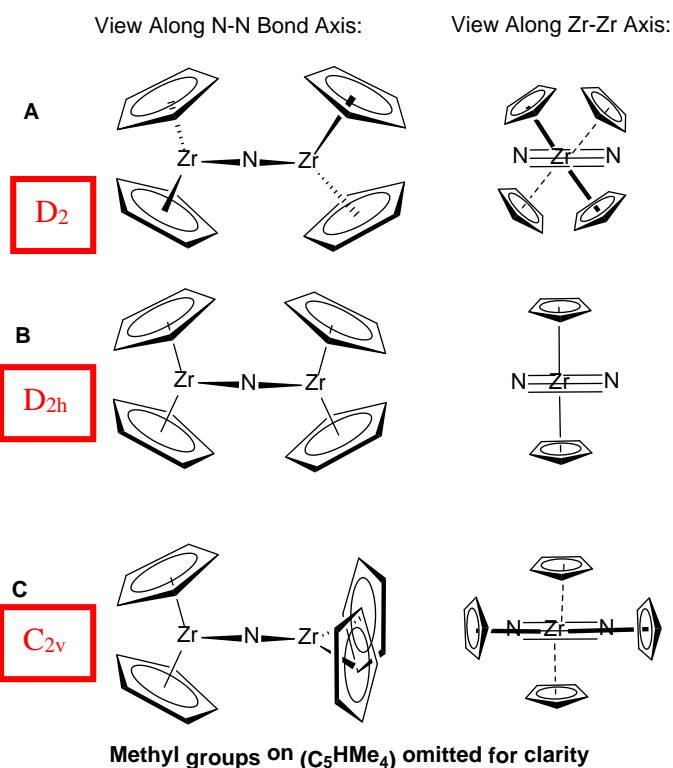


Problem 1 (4 points)

In 2004, a bimetallic Zr compound exhibiting side-on N_2 binding was reported by Chirik and coworkers (*Nature*, **2004**, 427, pp. 527-530). The crystal structure of this compound was obtained, and the ORTEP view is shown below.



Depending on the relative orientations of the dinitrogen ligand and the two $(Me_4HC_6)_2Zr$ units that it bridges, several different point groups could be imagined for this molecule. Three examples are shown in the figure to the right (A, B, and C—Example A corresponds to the structure reported by the Chirik group).

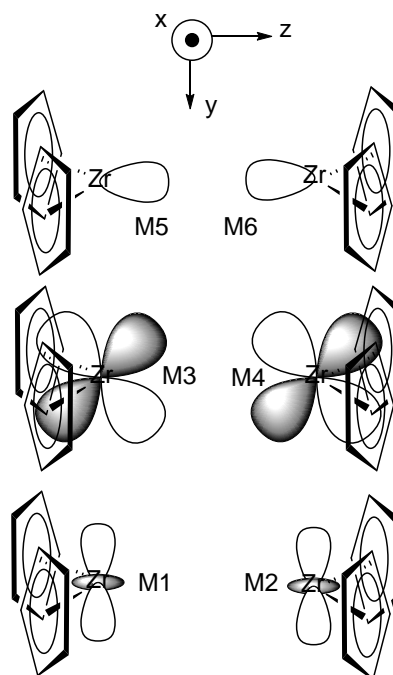


Part A.

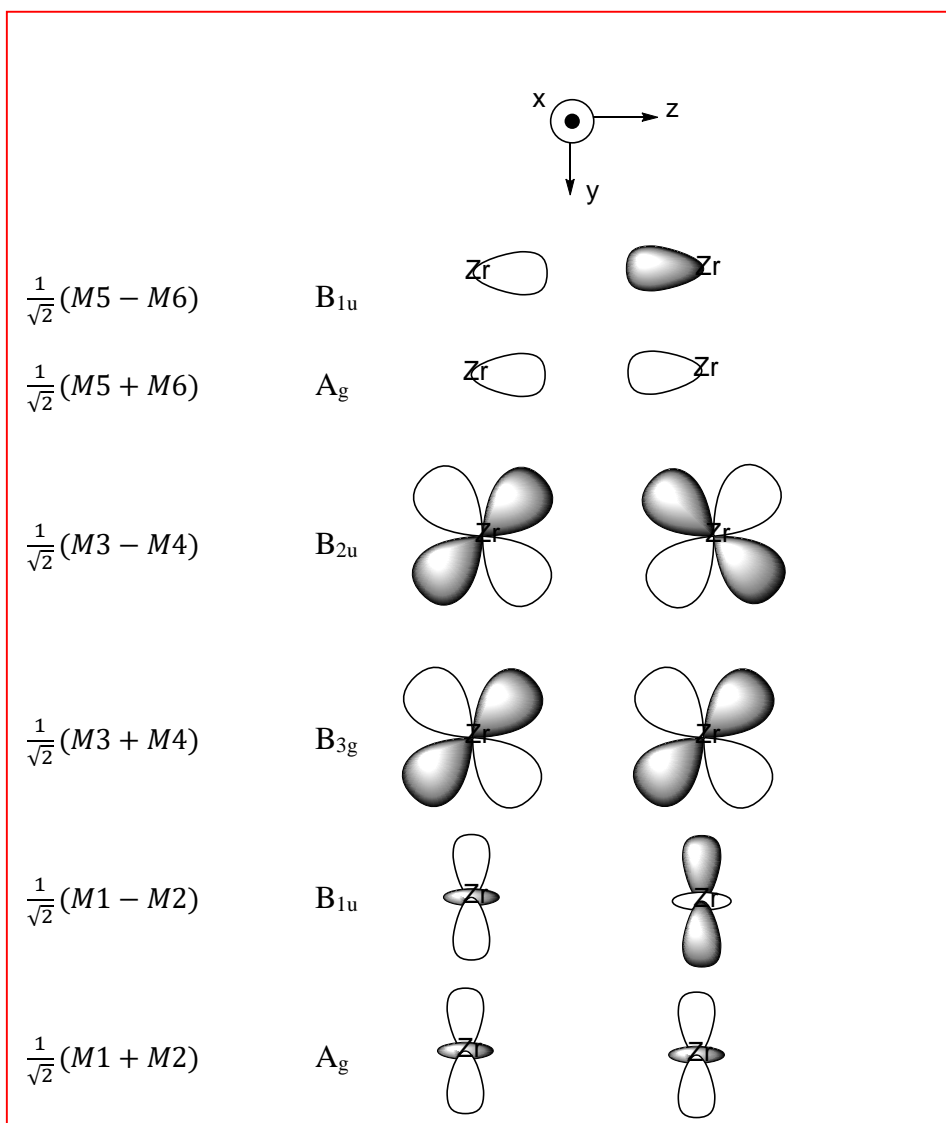
1. Determine the point group of these three structures (A, B, and C), ignoring the methyl groups on the Cp rings.

2. Using structure B, and the point group to which it belongs, derive SALCs for the frontier metal orbitals found in the metallocene wedge. Use the approximation that these are bent Cp_2Zr fragments, and for your basis set, consider only the three d-orbitals we have described in class, shown to the right, for a total of 6 SALCs. Use the indicated labels (M1-M6) in your derivation of the SALCS using the projection operator. Indicate the Mulliken symbols of each SALC, and write out the normalized wavefunction corresponding to each SALC.

Zr_2 Frontier MOs (N-N bond along y-axis)

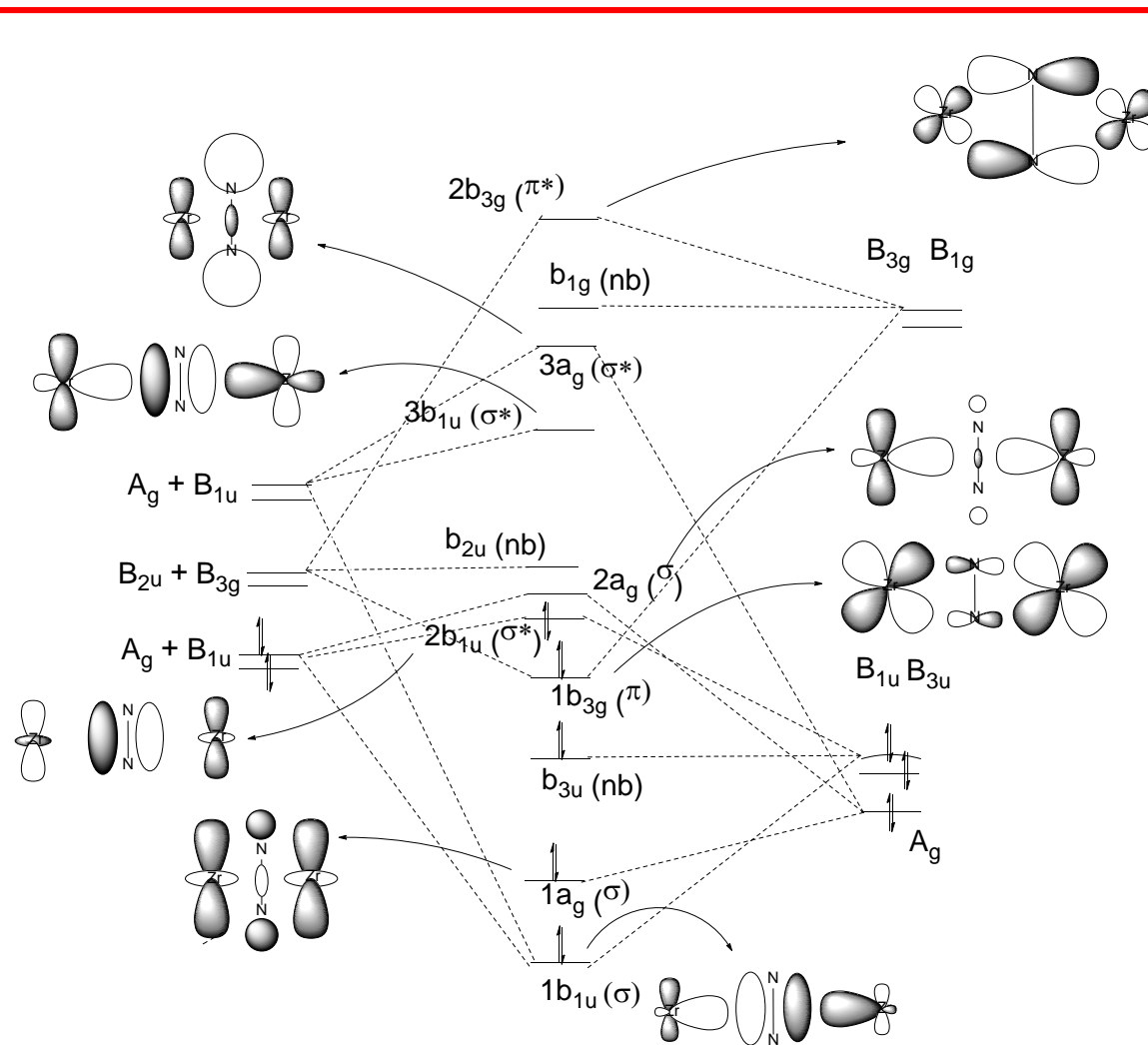


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3. Indicate the Mulliken symbols of the five frontier MOs of dinitrogen (HOMO-1, HOMO, LUMO). Derive the qualitative MO diagram corresponding to the interaction between the 6 Zr_2 SALCs and the frontier orbitals of N_2 . This should be done using structure B from part 1. Indicate the Mulliken symbols for each MO. Sketch each of the resulting MOs, indicate the axial symmetry of each MO with respect to axis defined by the two Zr atoms, and whether each MO is bonding, non-bonding, or anti-bonding with respect to the Zr- N_2 interaction. Populate the diagram with electrons. Indicate the orbital(s) responsible for the elongation of the N-N distance.



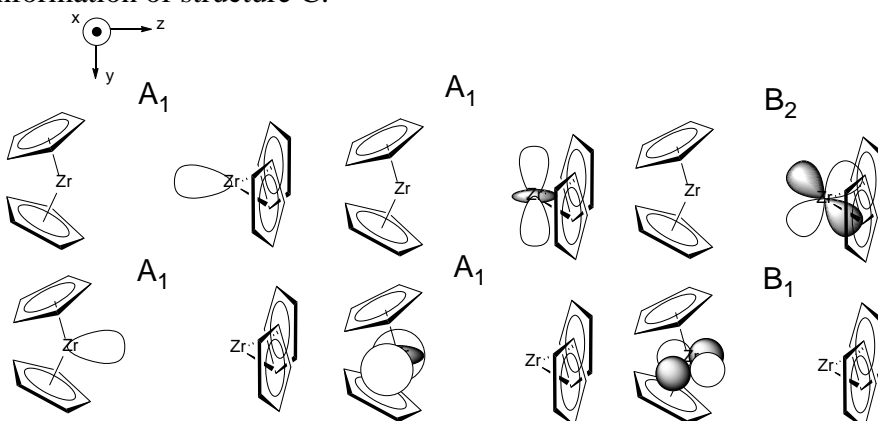
The MOs $1a_g$ and $1b_{3g}$ correspond to donation from N_2 σ -bonding orbital, and M backbonding into N_2 π anti-bonding orbital, respectively. Both of these interactions increase the N-N distance.

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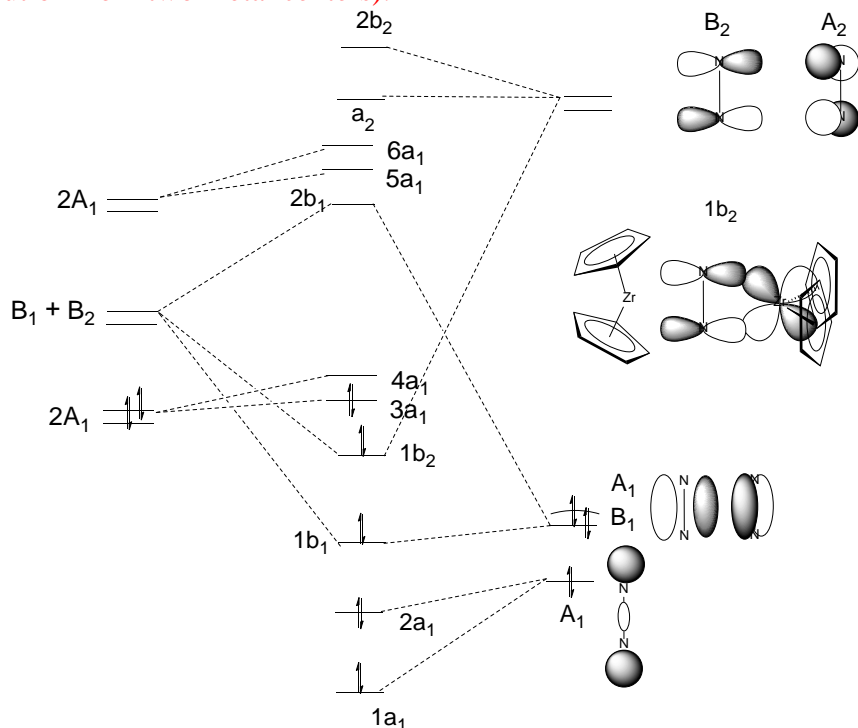
4. Provide an explanation for why the isolated compound (from the *Nature* paper) does not exhibit the conformation of structure B.

Steric constraints might prevent the $\text{Me}_4\text{C}_5\text{H}$ ligands from becoming eclipsed in the idealized D_{2h} geometry.

5. By inspection, generate SALCs for the frontier orbitals of the two metallocene fragments in the point group of structure C. Derive an MO diagram for the interaction with N_2 and draw the MOs responsible for elongation of the N-N distance. Indicate whether you expect B or C to exhibit the longer N-N distance. Provide an explanation for why the isolated compound does not exhibit the conformation of structure C.

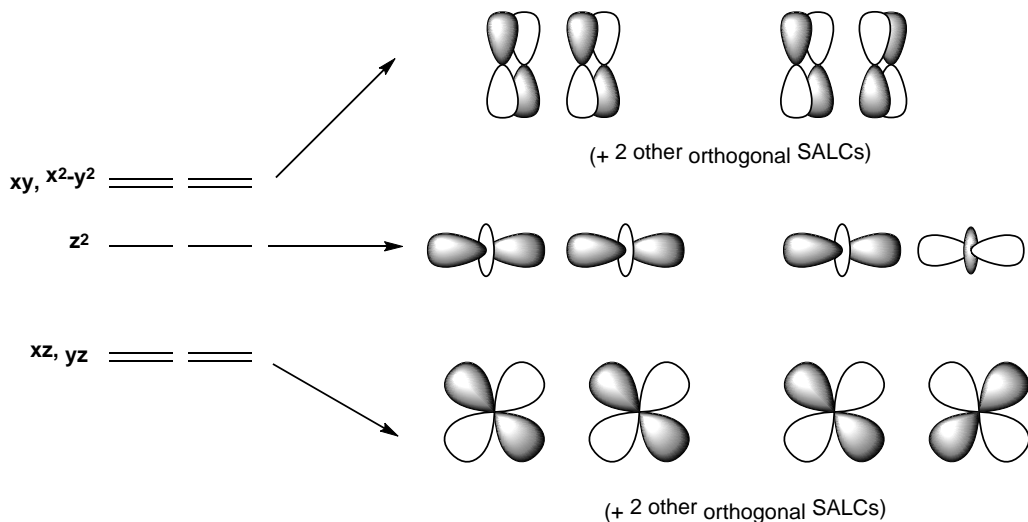


The M-L π back-bonding orbital only has a contribution from one metal center (in D_{3h} structure, there is contribution from two metal centers).

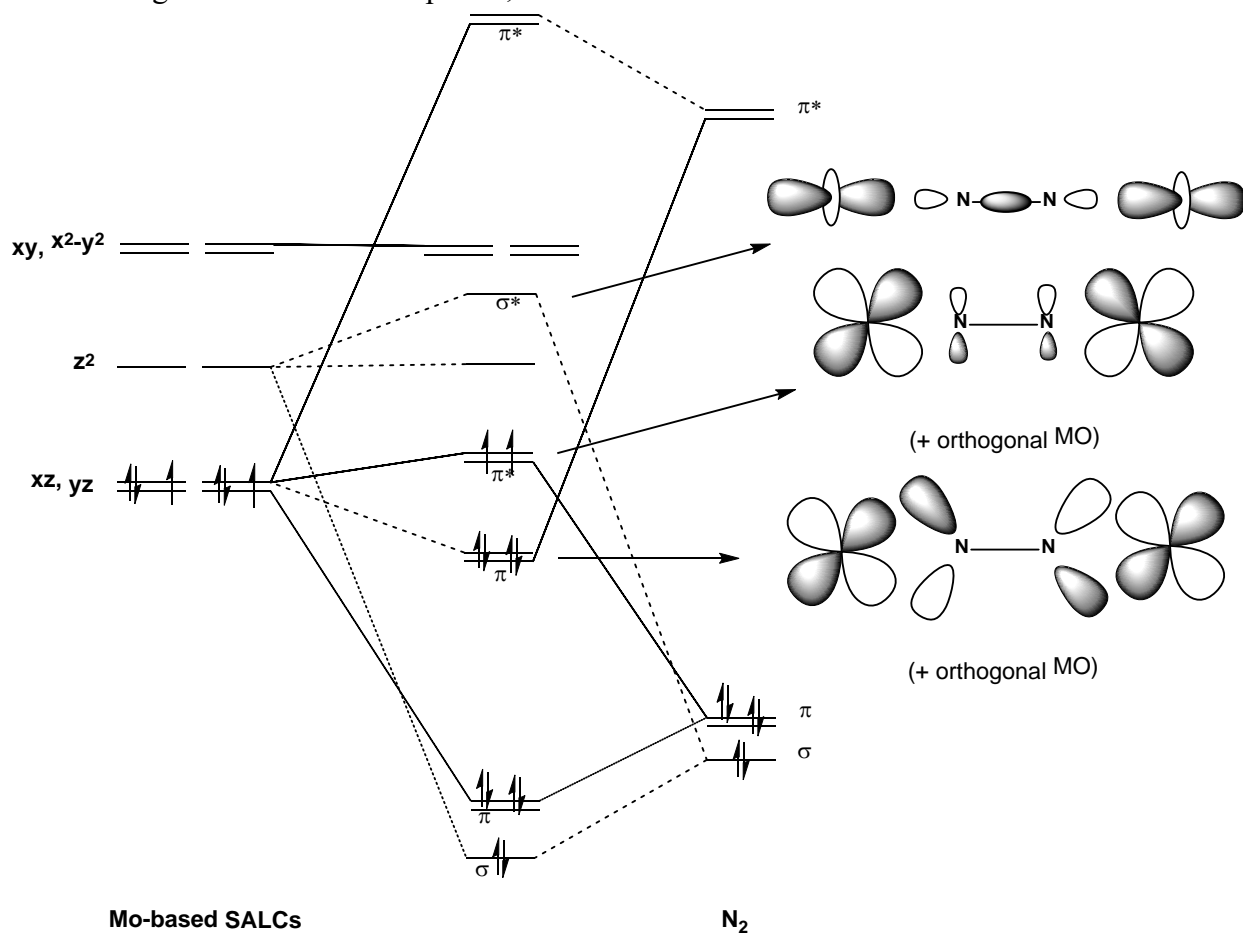


Problem 2

1. Metal based SALCs and their sketches



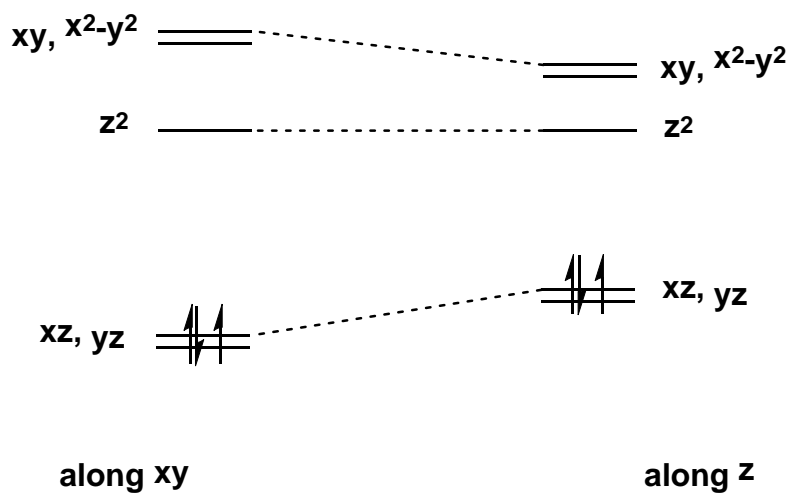
2. MO diagram of the dimeric species, and the Mo–N₂–Mo interactions.



The dimeric species is expected to be paramagnetic, with $S = 1$.

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3. Lone pairs directed in the z axis. Metal valence electron count stays the same.

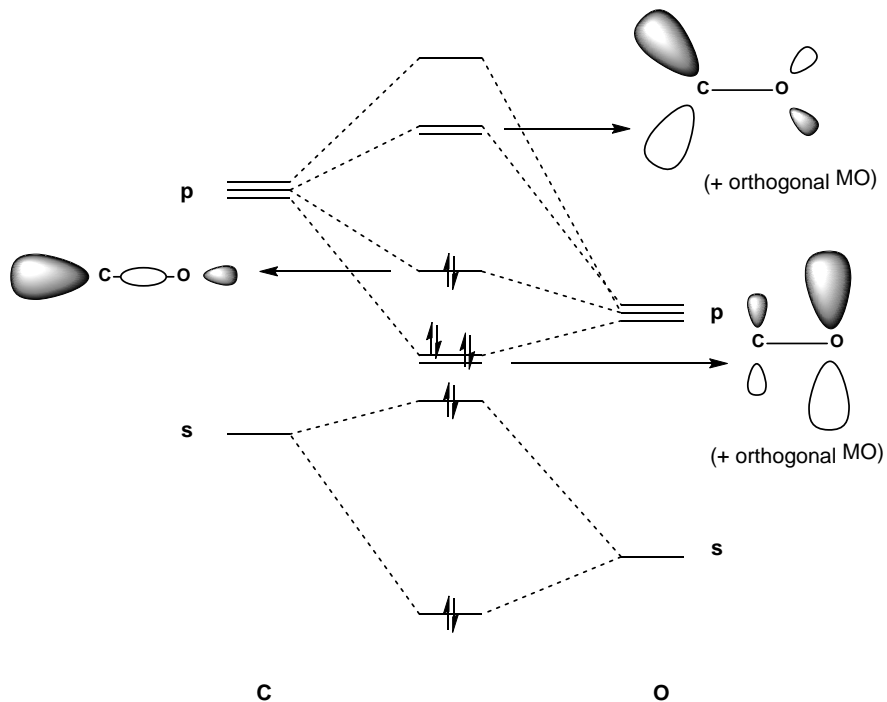


4. Bonding analysis with this new Mo-amide fragment

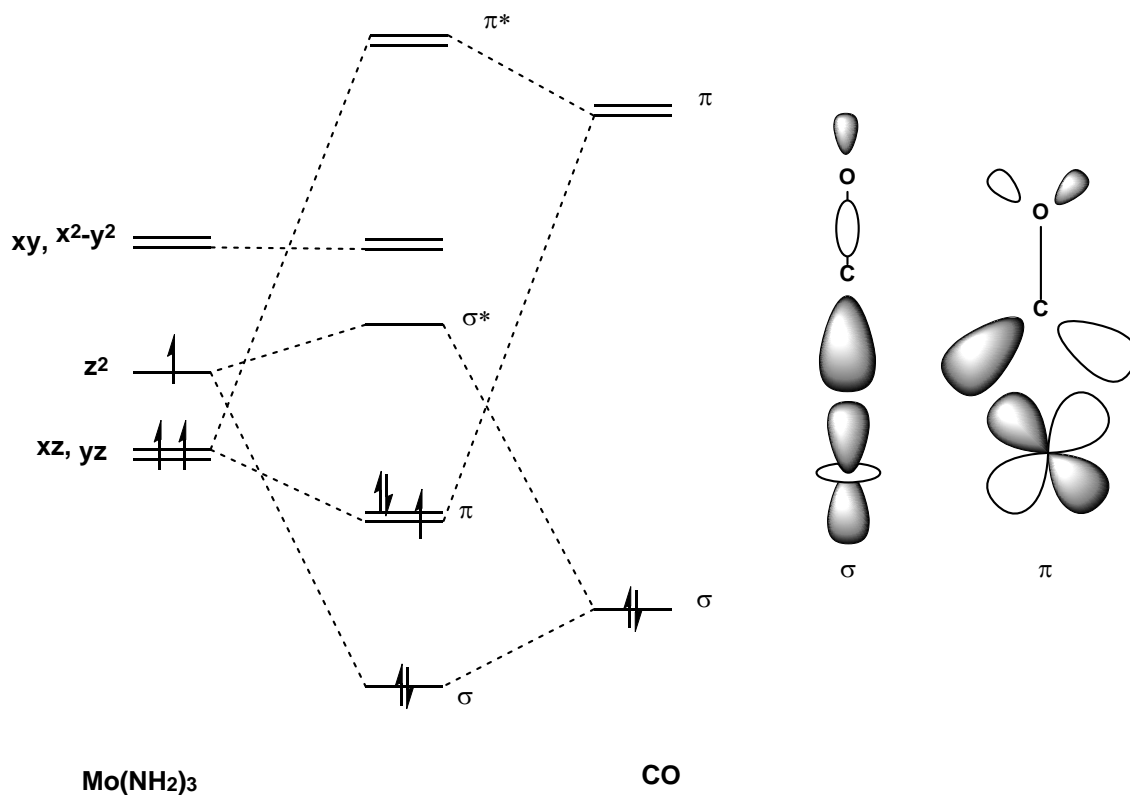
Dinitrogen will be more activated in the latter case, in which the lone pairs are directed in the direction of the z axis. A higher energy xz, yz set will result in a better overlap with the π^* orbitals of N_2 , resulting in a stronger Mo– N_2 –Mo π backbonding interaction. IR or Raman techniques can be used to determine the stretching frequency of the N_2 ligand.

Problem 3

1. Full MO diagram of CO with drawings of its frontier orbitals.



2. MO diagram of (CO)Mo(NH₂)₃ with drawings of the Mo–(CO) interactions.



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3. By reducing the complex, the resonance form with the Mo–C triple bond is favored. In MO terms, the added electron populates the Mo–CO π back bonding orbital, strengthening the Mo–C bond and weakening the C–O bond. Formally, the oxidation state assignment would change from Mo(II) to Mo(VI). The d-electron count changes from d^4 to d^0 , and the valence electron count would not change ($16 e^-$).

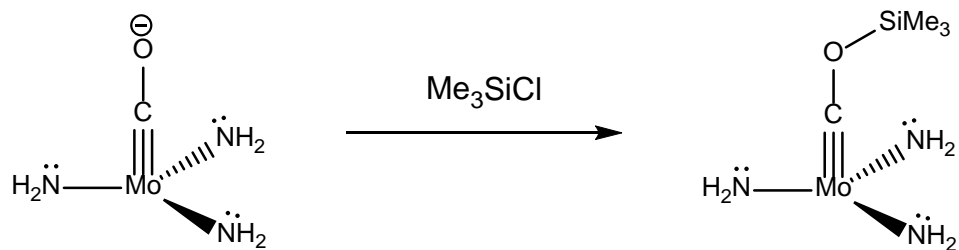
Generally, more reduced metal complexes will display stronger π back bonding. As we move from left to right in a period, the electronegativity of the elements increases. The increase in $\nu(\text{CO})$ corresponds to a reduction in the basicity of the metal and in the strength of π back bonding (see table below). Moving down a group has little effect. Strongly σ or π donating ligands will result in more activated M–CO complexes. Having fewer donor ligands causes a significant reduction of back bonding.

TABLE 2.9 Effects of Changing Metal, Net Charge, and Ligands on π Basicity of Metal, as Measured by $\nu(\text{CO})$ Values (cm^{-1}) of the Highest Frequency Band in IR Spectrum

<i>Changing Metal Across the Periodic Table</i>					
$\text{V}(\text{CO})_6$ 1976	$\text{Cr}(\text{CO})_6$ 2000	$\text{Mn}_2(\text{CO})_{10}$ 2013(av) ^a	$\text{Fe}(\text{CO})_5$ 2023(av) ^a	$\text{Co}_2(\text{CO})_8$ 2044(av) ^b	$\text{Ni}(\text{CO})_4$ 2057
	$\text{Cr}(\text{CO})_4$ 1938 ^c		$\text{Fe}(\text{CO})_4$ 1995 ^c		$\text{Ni}(\text{CO})_4$ 2057
<i>Changing Metal down the Periodic Table</i>					
$[\text{Cr}(\text{CO})_6]$ 2000	$[\text{Mo}(\text{CO})_6]$ 2004		$\text{W}(\text{CO})_6$ 1998		
<i>Changing Net Ionic Charge in an Isoelectronic Series</i>					
$[\text{Ti}(\text{CO})_6]^{2-}$ 1747 ^d	$[\text{V}(\text{CO})_6]^-$ 1860 ^d		$\text{Cr}(\text{CO})_6$ 2000		$[\text{Mn}(\text{CO})_6]^+$ 2090
<i>Replacing π-Acceptor CO Groups by Non-π-Acceptor Amines</i>					
$[\text{Mn}(\text{CO})_6]^+$ 2090	$[(\text{MeNH}_2)\text{Mn}(\text{CO})_5]^+$ 2043(av)		$[(\text{en})\text{Mn}(\text{CO})_4]^+$ 2000(av)		$[(\text{tren})\text{Mn}(\text{CO})_3]^+$ 1960

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4. Reaction with Me_3SiCl .



This reaction is consistent with the Mo(VI) resonance picture. The formal negative charge on oxygen indicates that it will act as a nucleophile, attacking the electrophilic center in trimethylsilyl chloride.

5. Rank CO , $[(\text{CO})\text{Mo}(\text{NH}_2)_3]$, $[(\text{CO})\text{Mo}(\text{NH}_2)_3]^-$, and $[(\text{Me}_3\text{SiOC})\text{Mo}(\text{NH}_2)_3]$

