Tutorial Questions

- N_2 can interact either side-on or end-on, however end on coordination is almost exclusively found, rationalise why N_2 prefers to coordinate end-on

- Explain using MO theory and appropriate diagrams why M-CO bonds are stronger than M-N_2 bonds in similar TM complexes, for example $IrCl(CO)(PPh_3)_2$ and $IrCl(N_2)(PPh_3)_2$.

Tutorial Answers

- N_2 can interact either side-on or end-on, however end on coordination is almost exclusively found, rationalise why N_2 prefers to coordinate end-on
    - the MOs for side-on coordinated N_2 are similar to those of ethyne
    - the MOs for end-on coordinated N_2 are similar to those of CO
    - orbitals are π-donor and acceptor are dependent on the relative energy level of the FOs
    - for example the π*-FOs on N_2 are high in energy and empty therefore they are acceptor FOs
    - when bound side on N_2 the σ-donor and π-acceptor overlap is not very good
    - however end on coordination allows for strong σ-donor and strong π-donor interactions

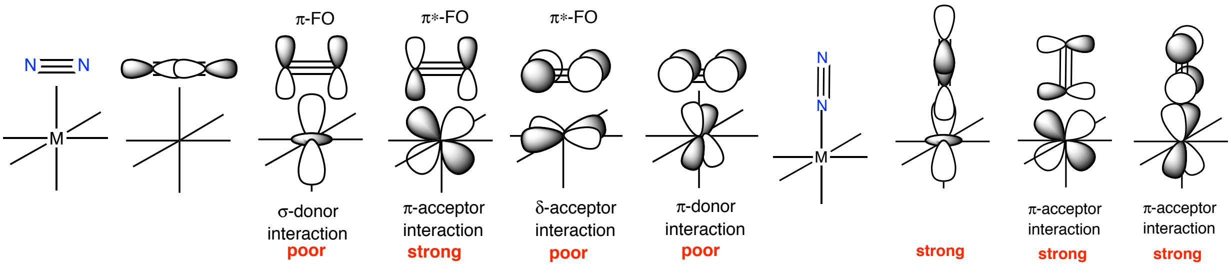


Figure 1 side-on and end-on bonding modes for N_2

- some points to note
    - the π-FO on N_2 are too low in energy and do not interact (well) with the metal

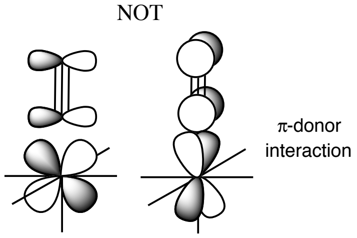


Figure 2 FOs that do not interact

- encourage the students to look for bonding "patterns" for example, alkenes and alkynes have FO patterns similar to N_2, however they cannot bind end-on due to the presence of H-atoms

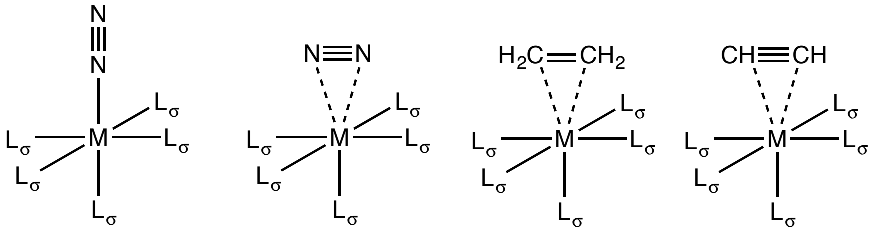
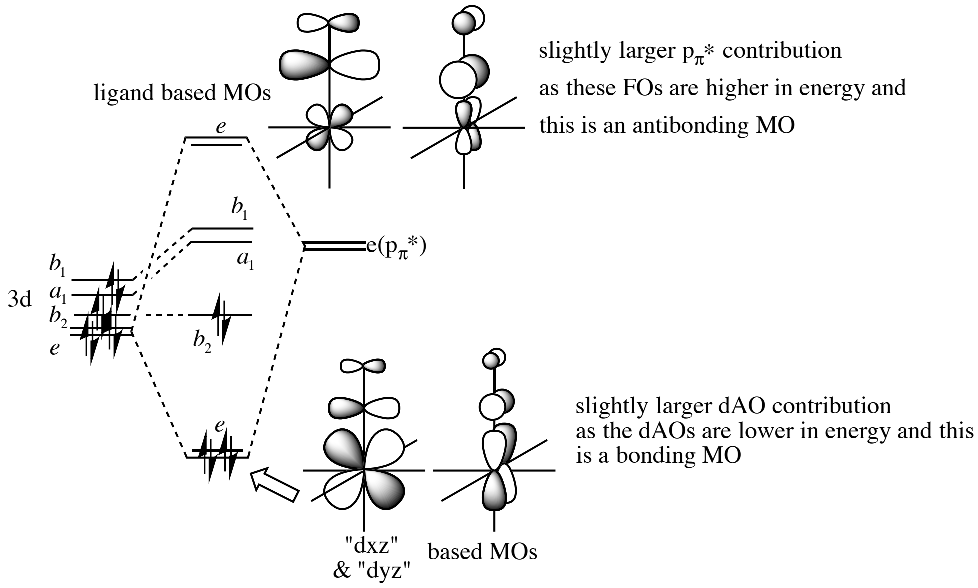


Figure 3 look for similarities in bonding FOs

- Explain using MO theory and appropriate diagrams why M-CO bonds are stronger than M-N_2 bonds in similar TM complexes, for example $IrCl(CO)(PPh_3)_2$ and $IrCl(N_2)(PPh_3)_2$.
  - consider first the metal dAO part of the TM-MO diagram, shown below for CO

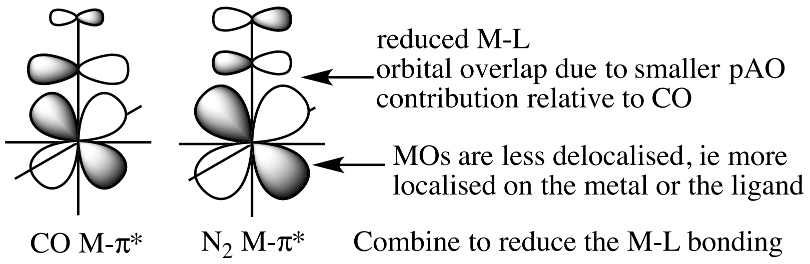


slightly larger p_π* contribution as these FOs are higher in energy and this is an antibonding MO

slightly larger dAO contribution as the dAOs are lower in energy and this is a bonding MO

Figure 4 relevant TM-dAO and ligand FOs

- compare and contrast the important occupied MOs for CO and N_2



reduced M-L orbital overlap due to smaller pAO contribution relative to CO

MOs are less delocalised, ie more localised on the metal or the ligand

Combine to reduce the M-L bonding

Figure 5 relevant TM-dAO and ligand FOs

- in the π* FO of CO, the C makes a larger pAO contribution to the FO, this means there is a much larger orbital to overlap with the metal dAO, increasing the splitting energy of the MOs
- in contrast the π* MO of N_2 has two equal contributions from each N, reducing the overlap of the "front" N pAO with the metal dAO, decreasing the splitting energy of the MOs
- the π* MOs of N_2 lie higher in energy than those of CO. (The combination of degenerate pAOs for N_2 means a larger splitting energy for the π and π* FOs) The higher energy of the N_2 FOs means reduced delocalisation (ie more uneven orbital coefficients) for the MO. Thus the metal dAO interacts less with the π* FOs.

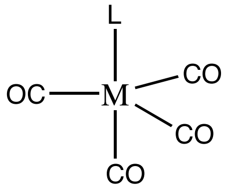


Figure 6 $ML(CO)_4$ complex, L=CO,N_2

complex	σ-donation	**π-acceptance**
$Fe(CO)_4CO$	0.51	**0.28**
$Fe(CO)_4N_2$	0.28	**0.14**

Table 1 Data from the CDA analysis[1]

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[1] Y. Chen, M Hartmann and G. Frenking, *Z. Anorg. Allg. Chem.*, **2001**, Vol 627, p985