

Some important points on “backbonding”

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In Classical sense, Back bonding can be best described As:

“dative π -bonding” btw orbitals (any two p or d orbitals or a mixture of both) of appropriate energies (& obviously parallel).

[Here, by Appropriate energies, we mean to infer that Orbitals involved are of proper symmetry, shape & size]

- Back-bonding can also be visualised as type of resonance
- **This type of bonding is possible between atoms in a compound in which one atom has lone pair of electron and the other has vacant orbital placed adjacent to each other.**
- Consequently, the Bonding acquires partial double bond Character.(Back bonding results in a decrease in bond length and increase in bond order.)
- Generally, Back bonding increases stability. It does affect properties of molecules, like hybridisation & Dipole moment.

In Π back bonding, the electrons move from an atomic orbital on one atom to a π^* anti-bonding orbital on another atom or ligand.

Such type of bonding is common in organometallic chemistry of transition metals which have multi-atomic ligands such as carbon monoxide, ethylene or the nitrosonium cation e.g, $\text{Ni}(\text{CO})_4$ and Zeise's salt, $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$

The electrons from the metal are used to bond to the ligand in order to release the metal from excess negative charge.

This type of bonding is mostly observed in CO ligands which is a sigma donor as well as pi- acceptor. [The typical **example** given for synergy in chemistry is the synergic **bonding** seen in transition metal carbonyl complexes.]

1. **CO has much less dipole moment (0.11D)** than expected due to back-donation from LONE PAIR ORBITAL OF Oxygen into vacant orbital of carbon. (similar behavior from nitric acid, NO)
 2. **Me₃NO has greater dipole moment than Me₃PO** as there is **2pπ—3dπ** back donation from Oxygen into vacant d-orbitals of phosphorus (just like in CO)
 3. Me₃N has sp³ hybridisation & pyramidal shape at N, but in (SiH₃)₃N again there is **2pπ—3dπ** back bonding btw LONE PAIR ORBITAL OF NITROGEN into vacant orbital of SILICON. HENCE **TRISILYL AMINE IS sp², PLANAR & is LESS BASIC THAN TRIMETHYL AMINE.**
 4. **Me₃C-OH is less acidic than Me₃Si-OH** due to stabilisation of negative charge in Me₃Si-O⁻ ion by **2pπ—3dπ back bonding**
 5. **Me₂O forms adduct with BF₃ but (SiH₃)₂O do not react with BF₃** due to weakening of basic character of Disilyl ether by back bonding.
 6. BF₃ < BCl₃ < BBr₃ < BI₃ is order of lewis acidic character due to stronger **2pπ-2pπ back bonding in BF₃ (LONE PAIR ORBITAL OF Fluorine into vacant orbital of boron) and gradually back bonding becomes weakest in BI₃ (2pπ—5pπ) hence BF₃ has stronger partial double bond character and consequently behaves as less electron deficient.**
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1. **BH₃ does not exist**(it exist only as dimer or higher boranes) but BX₃ exist, (X=halogen). It can be attributed to absence of possibility of back bonding in BH₃.
 2. **BF₃ is only partially hydrolysed** into [BF₃(OH)]⁻ whereas BCl₃ & BBr₃ are completely hydrolysed into B(OH)₃ or H₃BO₃ and HCl/HBr
 3. **B-F bond length increases when BF₃(130 pm) reacts with F⁻ to form (BF₄)⁻ [143 pm].** Its due to absence of Back-bonding in (BF₄)⁻ hence B-F bond has completely single bond character.
 4. **Si-O and P-O bonds are much stronger than expected to partial double character** owing to possibility of back-bonding.
 5. BOND angle of NF₃(102 degree) is lesser than in NH₃ (107) as per VSEPR theory which suggests that in case of less electronegative terminal atoms like H, Bond pairs would be closer to more electronegative central atom, N and hence bonds open up due to repulsion b/w bond pairs electron density in vicinity. **BUT bond angle of PF₃ (100) is greater than PH₃, its due to possibility of back**

bonding in PF₃ B/W LONE PAIR OF FLUORINE & VACANT d-orbital of phosphorous ($2p\pi—3d\pi$) henceforth *P-F bond acquires partial double character and we know well that multiple bonds causes more repulsion so bond angle is greater.*

6. SiCl₄ has abnormally low boiling point than CCl₄,

1. **Bonding in Metal Carbonyls:** The carbon atom in carbon monoxide has a lone pair of electrons that can be used to form a sigma bond with a metal. Because carbon monoxide has low-lying orbitals, it can accept electrons **back** from the metal and further strengthen the bonding between the metal and the carbon monoxide ligand. This process of “accepting electrons **back** from the metal” is termed backbonding. HERE, its important to understand that as Metal is more negatively charged; then M-C Back-bonding is stronger & C-O bond would have been weaker than in CO.
2. Due to possibility of Back-bonding with metal (similar to carbonyl complexes), **Ph₃P or R₃P or PF₃ behave as strong ligand in complexes.**
3. NOTE- $3p\pi—3p\pi$ Back bonding in AlCl₃ is not as effective hence it easily forms dimer in vapor phase or non-polar solvent.