

Case 4: Quantifying Bonding in TM Compounds

Motivation

In organometallic chemistry one of the first types of bonding that we are alerted to is transition metal-carbonyl (TM-CO) bonding. This is described using the Dewar-Chatt-Duncanson model of synergistic CO \rightarrow metal σ -donation and metal \rightarrow CO π -backbonding, **Figure 1**. This model is well established and many ligands have their σ -donor/ π -acceptor abilities classified according to their effect on the vibrational spectrum of a CO ligand in the trans position. As π -backbonding increases in the M-L bond the amount of metal-CO π -backbonding decreases, weakening the M-CO bond and strengthening the CO bond, leading to a rise in the CO stretching frequency. Experimental evidence has also suggested that strong σ -donor ligands prefer axial coordination sites while strong π -acceptor ligands prefer equatorial sites.

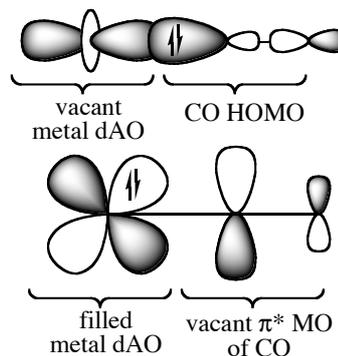


Figure 1 σ -donation and π^* -backdonation

In this paper a number of $\text{Fe}(\text{CO})_4\text{L}$ complexes are examined looking at the σ -donor, π -acceptor properties, and the site preference of the ligands, **Figure 2**. The ligands examined in the paper include, CO, CS, N_2 , NO^+ , CN^- , NC^- , $\eta^2\text{-C}_2\text{H}_4$, $\eta^2\text{-C}_2\text{H}_2$, CCH_2 , CH_2 , CF_2 , NH_3 , NF_3 , PH_3 , PF_3 and $\eta^2\text{-H}_2$. We will use this paper as an example where bond dissociation energies, and the CDA (charge decomposition analysis) have given insight into a type of bonding that you are already familiar with.

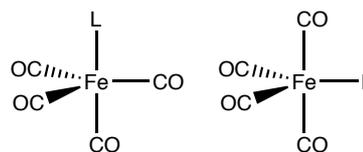


Figure 2 Axial vs. equatorial coordination in $\text{Fe}(\text{CO})_5\text{L}$ complexes

Computational Details

- ◆ DFT \Rightarrow which functional?
Becke3 exchange & LYP correlation \Rightarrow B3LYP
- ◆ Fe
Uses small core PP (non-relativistic!), (411/2111/41) split valence basis set
- ◆ All other atoms 6-31G(d) Pople basis set
- ◆ Geometries
optimised, *but* used symmetry constraints, frequency to check the minimum
- ◆ Energies
single point at higher level of theory CCSD(T)
- ◆ Program packages:
Gaussian, Aces II, MolPro
- ◆ Population Analysis: CDA, NBO

Computational Details

Geometry optimizations and energy calculations were performed using Becke's three-parameter hybrid-functional in combination with the exchange correlation functional according to Lee, Yang and Parr (B3LYP) [24]. A non-relativistic small-core effective core potential and a (441/2111/41) split-valence basis set were used for Fe [25 a] and an all-electron 6-31G(d) basis set was chosen for first- and second-row elements [25 b-d]. This combination of basis sets is further denoted as basis set II [26]. All stationary points found on the potential energy surface were further characterized by numerical frequency analyses. Improved estimates for bond dissociation energies are obtained by single-point energy calculations on the B3LYP/II geometries using coupled-cluster theory with singles and doubles and a non-iterative estimate of triple substitution (CCSD(T)) [27]. All geometry optimizations are performed using individual symmetry constraints (Table 1) for each complex. All calculations used the program packages Gaussian 94/98 [28], ACES II [29] and MOLPRO 96/2000 [30]. Metal-ligand donor-acceptor interactions were examined in terms of charge donation, back donation and repulsive polarization using the program CDA 2.1 [5, 31] and Weinhold's NBO analysis [6] as implemented in Gaussian98 [28 b].

It is worth mentioning the use of symmetry constraints in a geometry optimisation. Symmetry can significantly reduce computation times, because fewer integrals need to be calculated. There are two reasons for this, some integrals will be zero by symmetry arguments, and some will be equivalent by symmetry. The only problem is, the calculation will not break this symmetry "by itself", and you cannot be sure you have the lowest energy structure. (There can be special circumstances where *symmetry breaking* occurs, these are by their very nature very interesting!) Thus to be absolutely sure, the calculation should be carried out with no symmetry, however at very high levels of calculation, this may preclude carrying out the calculation at all.

Reference:

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

Analysis

A rather extensive set of calculations has been carried out to find the geometry and energy of the axial and equatorial structural isomers for each of the ligands mentioned above. Frequency analysis were carried out, and the carbonyl stretching frequencies calculated. As each complex has been treated at exactly the same level of theory and with the same basis sets the results are fully comparable. The L=CO compound Fe(CO)₆ is taken as the "reference" compound. Rather than examining all the results in detail, I have chosen to focus on two sub series of related compounds, looking at (a) σ -donor π -acceptor properties of ligands and (b) the axial/equatorial positioning of ligands.

complex	σ -donation	π -acceptance	repulsion	residue	R _e (Å)	D _e (kcal mol ⁻¹)
Fe(CO) ₄ CN ⁻ _(eq)	0.62	0.08	-0.26	-0.03	1.695	89.9
Fe(CO) ₄ CO _(eq)	0.47	0.29	-0.31	0.01	1.805	47.9
Fe(CO) ₄ NO ⁺ _(eq)	0.19	0.42	-0.31	0.03	1.959	107.4

Table 1 Data from the CDA analysis for equatorial CN⁻, CO and NO⁺ ligands

Traditionally, NO⁺ is considered one of the strongest π -acceptors while CN⁻ one of the poorest π -acceptors (and strongest σ -donors). The carbonyl is our reference, somewhere on the stronger side of π -acceptors. The CDA analysis (remember) divides electron density into that (a) donated from L to TM (b) that donated from TM to L and (c) reorganisation due to electron-electron repulsion in the bonding region. The usefulness of the CDA analysis is tested by the size of the residue quantity which should be close to zero.

Looking at the results shown in Table 1 we can see that the CDA results certainly support this empirically based classification, CN⁻ has essentially no π -acceptor character (0.08) while NO⁺ is substantially stronger (0.42). It is also clear that π -acceptance and σ -donation work in opposite directions, CN⁻ is a very strong σ -donor while NO⁺ is a very weak σ -donor. All of the ligands exhibit a significant M-L repulsion, and almost no residue.

The CDA analysis is often paired with an estimate of bond strength determined by bond dissociation energies. In this paper these have been calculated at the CCSD(T) level, ie at a high level, and in this case the $\Delta E = [E(\text{Fe}(\text{CO})_4) + E(\text{L})] - E(\text{M}(\text{CO})_4\text{L})$. Two values are given in the paper, the value determined from the energy alone (D_e),

and a second value (D_0) which includes the zero-point-energy (ZPE). Normally this term is very small and so ignored. The zero point energy, is the energy inherent in a molecule at absolute zero due to its vibrational motions, it can be calculated by summing over the first harmonic for all the harmonic vibrational modes in the molecule (ie those calculated in the frequency analysis). The best calculations include these terms because they are important if you want very accurate energies, they can also be very important if you have two isomers or structures of almost identical stability, the ZPE can be enough to reverse the order of stability! We see that NO^+ forms the strongest bond while CO the weakest bond, this shows that σ -donation alone can form a very strong bond, and that high bond strength should not necessarily be associated with significant π -backbonding.

The trend in bond lengths (Fe-L) follows that of π -acceptance by the ligand. That is, the longest bond occurs for the ligand with the greatest amount of π -back-donation. If we had assumed a constant amount of σ -donation, this would come as a surprise, as the largest amount of π -back-donation should indicate the highest bond order (as more electrons are involved in bonding), and thus the strongest bond. In fact, NO^+ does form the strongest (and longest!) Fe-L bond.

However, bond stability does not follow the expected trend, of increasing bond strength as the amount of π -back-donation increases (indicating an increase in bond order), this is because, as the amount of π -back-donation increases, the amount of σ -donation decreases. The resultant bond strength does not reflect our intuitive picture, and there appears to be no simple relationship.

complex	σ -donation	π - acceptance	repulsion	residue	R_e (Å)	D_e (kcal mol ⁻¹)
$\text{Fe}(\text{CO})_4\text{CO}_{(\text{eq})}$	0.47	0.29	-0.31	0.01	1.805	47.9
$\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4_{(\text{eq})}$	0.44	0.27	-0.38	-0.02	2.145	42.2
$\text{Fe}(\text{CO})_4\text{C}_2\text{H}_2_{(\text{eq})}$	0.51	0.30	-0.41	0.00	2.097	39.5

Table 2 Data from the CDA analysis for CO, ethylene and acetylene ligands

Two ligands for which it is more difficult to evaluate the σ -donor π -acceptor nature are η_2 bound ethylene and acetylene, this is because both of the p-orbitals that contribute to the ligand π -bond also contribute to the TM-L bonding. So how do ethylene and acetylene compare to CO? It is clear from the table that they both resemble the carbonyl ligand quite closely, σ -donation dominates over π -acceptance, and electron-electron repulsion is quite strong. The bond strengths are similar.

However, if one were to use the preference of a ligand for binding to the equatorial site over axial to indicate π -acceptance ability, then the significantly more stable equatorial isomers of both ethylene (-8.6 kcal mol⁻¹) and acetylene (-10.6 kcal mol⁻¹) would lead you to believe they were much better π -acceptors than they

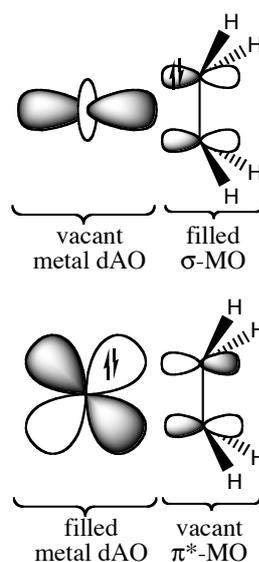


Figure 3 σ -donation and π^* -backdonation for ethylene

actually are!

Case 5: Backbonding in TM-Silyl compounds: Si dAOs or σ^* -FMOs

Motivation

There is an on going debate about the nature of TM-Si or TM-P bonds. Do the low lying but empty dAOs on the Si or P participate in backbonding, by accepting electron density from filled dAOs on the TM, analogous to $M \rightarrow \pi^*$ backbonding in TM-CO compounds? Or is the backbonding into a SiR_3 , or PR_3 σ^* fragment MO? While these are the more popular alternatives, there are other hypothesis that invoke increasing ionic character in the bonds, or increasing σ -inductive effects alone. Once you begin to examine TM, or indeed any type of bonding in detail, you soon come to realise that "bonding" is significantly more complicated than the simple working models or "cartoons" that we are familiar with imply.

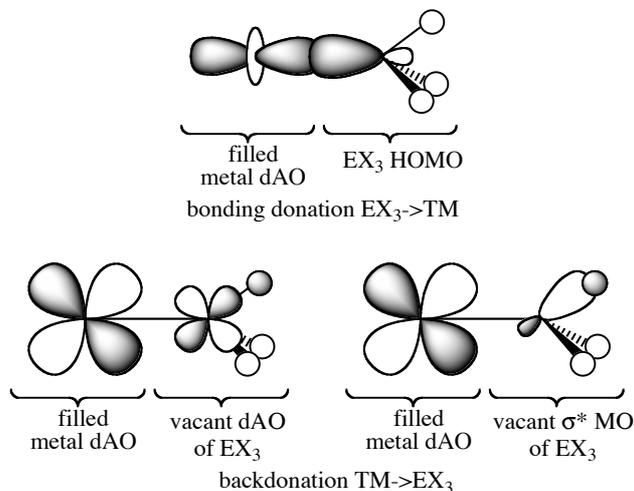


Figure 4 Os-Si (a) σ -bonding (b) backbonding

In this paper a series of five-coordinate Os-Silyl compounds of the type $Os(SiR_3)Cl(CO)(PPh_3)_2$ has been synthesised with increasingly electronegative substituents on the silyl group (SiR_3) where $R = F, Cl, OH,$ and Me . While these compounds were physically characterised, I am primarily interested in the theoretical calculations on a parallel series of model complexes (where the PPh_3 ligands were replaced with PH_3 ligands), and in the investigation of Os-Si bonding. The structures are square pyramidal with the silyl group taking the apical position. The structure can, however also be considered locally octahedral with a vacant site. Below are pictured two views of the structure, one showing the basal Cl ligand bent away from the plane via an interaction with one of the silyl Cl substituents. The second showing a view down the Si-Os bond.

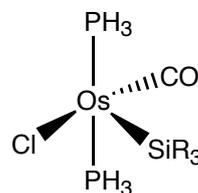


Figure 5 $Os(SiR_3)Cl(CO)(PH_3)_2$

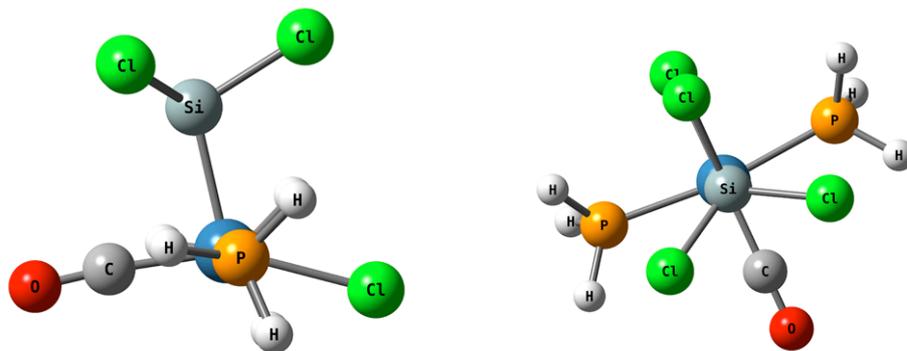


Figure 6 Views of optimised structure of $Os(SiCl_3)Cl(CO)(PH_3)_2$

Reference:

K Hübler, P. Hunt, S. Maddock, C. Rickard, W Roper, D. Salter, P. Schwerdtfeger, and L. Wright, *Organometallics*, 1997, Vol 16, p5076

Although this paper is quite old, this debate has not moved significantly forward in the intervening years. Older text books still adhere to the dAO hypothesis and newer text books mention the σ^* -backbonding orbitals. The dAO \rightarrow σ^* backbonding hypothesis finds current favour in the literature. For example a recent paper, 2004, discusses this effect for a series of Ru-silyl complexes, $\text{Cp}(\text{PR}_3)\text{RuSiX}_3$, using $\text{SiX}_3=\text{SiCl}_3$, SiMeCl_2 , and SiPhCl_2 .[§]

Computational Details

We have been over the computational details of several papers now, so this time I will leave it up to you to read and digest these details, and we will go right onto the interesting stuff! The calculations were carried out at the BLYP level with valence double-zeta type basis sets.

Analysis

A decrease in the CO stretching frequency ($\text{OH} < \text{Cl} < \text{F}$) is seen for this series of compounds, **Table 3**, and this behaviour is normally associated with a decrease in the amount of electron density available for back-bonding on the metal (a reduction in the amount of back-bonding from

the M into the π^* -CO orbitals, strengthens the CO bond). However, this could be due to a simple lack of electron density due to inductive σ -withdrawing effects (for example due to the high electronegativity of the ligand). The crystal structures (and optimised geometries) of the $\text{Os}(\text{SiR}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ compounds show that the Os-Si bond becomes shorter as the substituents become more electronegative ($\text{F} < \text{Cl} < \text{OH} < \text{Me}$). The Os-SiF₃ bond distance is very short (2.254Å) significantly shorter than the Os-Si single bond distance computed from the sum of the covalent radii (2.50 Å). This indicates that there is some multiple bonding character to the Os-Si bond, at least in the SiF₃ compound.

As the Os-Si bond gets shorter the Si-R bonds get longer. Not all the silyl substituents are identical, considering the SiF₃ structure, one Si-F bond is slightly longer than the other two (1.595 vs. 1.567 Å), and longer than the Si-F bond in HSiF₃ (1.561Å). This indicates that the pseudo C_{3v} symmetry of the SiF₃ ligand is broken, and that the C_s symmetry of the molecule dominates. The differentiated F atom lies eclipsed with the single Cl ligand, and trans to the CO ligand. These bond distances suggest that Os-Si backbonding occurs, however, the specific nature of the back-bonding is unclear. It may be that one Si-F σ^* orbital is more heavily involved in accepting electron density than the other two.

R	CO stretch (cm ⁻¹)	Os-Si bond length (Å)	group electronegativity
F	1946	2.254	3.47
Cl	1944	2.273	3.10
OH	1919	2.319	2.76
Me	-	2.374	2.30

Table 3 Changes in CO stretching frequencies, Os-Si bond lengths and group electronegativities on substitution of R in SiR₃

[§] S. Freeman, J. Petersen and F. Lemke, *Organometallics*, 2004, Vol 23, p1153
P. Hunt, March 2006

R	NBO population			
	3s(Si)	3p(Si)	3d(Si)	q(Si)
F	0.73	1.11	0.07	2.08
Cl	1.04	1.81	0.16	1.88

A NBO (Natural Bond Orbital) analysis was carried out on the compounds, **Table 4**. Quite surprisingly the charge on the Si atom varies in a non-systematic way with the decreasing electronegativity of the substituent groups. This indicates that the bonding is highly sensitive to various stabilising and destabilising influences. For example, Cl is of a similar size to Si, and lies in the same row, hence the orbitals of Si and Cl are expected to overlap better than those of the other substituents, this is reflected in the smaller positive charge on the Si atom for the SiCl_3 compound. The Si atom with F and OH substituents donates essentially twice as much to the Os center. The charge on Si of SiMe_3 lies midway between these two extremes. σ -inductive donation and σ^* -acceptance cannot be easily separated as both are represented by the 3s population on Si. SiOH_3 has the smallest 3s population, and so is the most likely to contribute to σ -inductive donation and the least likely to undertake σ^* -acceptance, conversely the Si 3s population is greatest for SiCl_3 and so is the least likely to donate σ -inductively, but the most likely to participate in σ^* -acceptance. The 3d Si AO population is minimal for all the compounds examined.

Another way of estimating the amount of backdonation in the Os-Si bond is to look at the MO components. The oxidation state is formally osmium(IV) and can be derived starting from the d^8 Os, losing 1e each to CO and Cl, the remaining ligands being classed as formally neutral, thus leaving 6e or three lone pairs on the Os center. The three highest energy occupied MOs in this complex are thus Os dAO lone pairs. The highest energy is a d_{z^2} type orbital which has been rotated so that the lobe points toward the in-plane Cl substituent on the silyl, **Figure 7** and **Figure 8**.

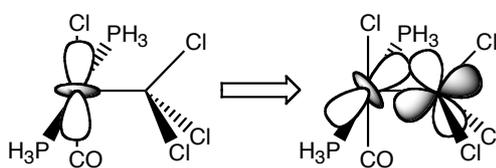


Figure 7 Cartoon of HOMO, indicating rotation of the d_{z^2} orbital

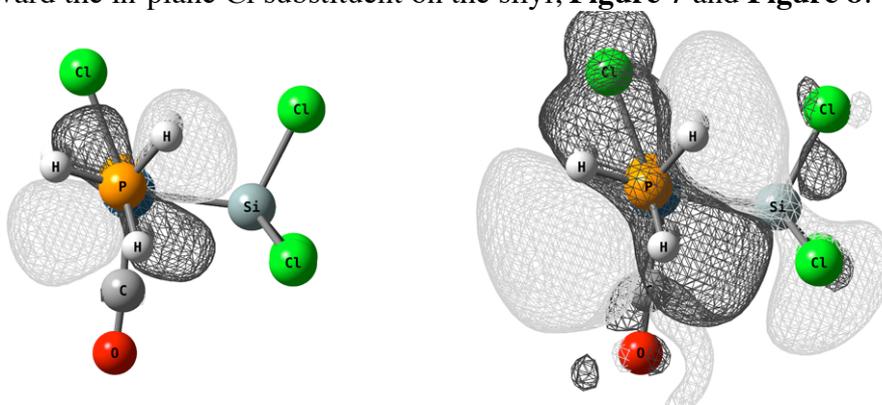


Figure 8 HOMO iso-surfaces at (a) 0.02 (b) 0.002

The next highest energy orbital, the HOMO-1 lies in the plane of the phosphine ligands and CO group, and hence is not able to interact with the silyl group. However it is able to donate electron density into the CO π^* fragment MO, **Figure 9**.

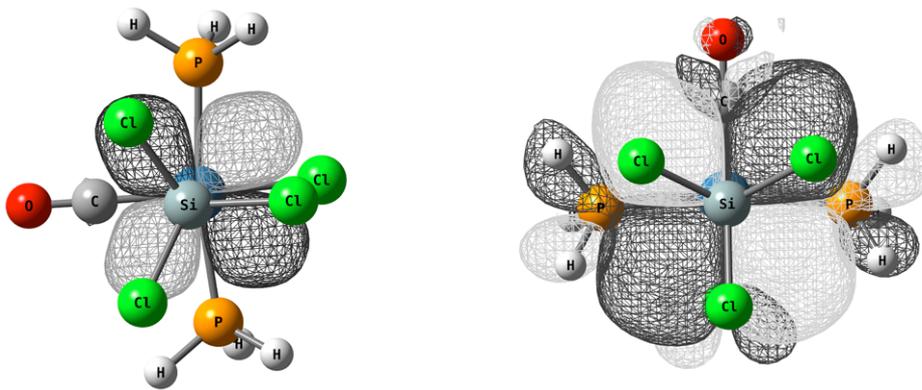


Figure 9 HOMO-1 iso-surfaces at (a) 0.02 (b) 0.002

The HOMO-2, however can interact with the silyl ligand as this is another dAO which lies in the plane of the PH_3 ligands, **Figure 10** and **Figure 11(a)**. The orbital replotted at a lower iso-surface clearly shows interaction with the dAOs of the Si, **Figure**

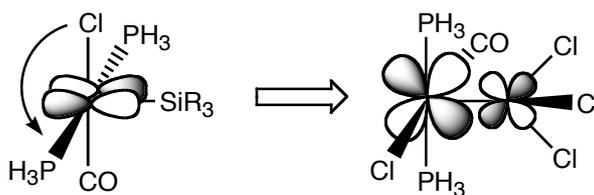


Figure 10 Cartoon of the HOMO-2

11(b). This orbital may look like it interacts with the silyl substituents, but a "side-on" shot shows that this is not so, **Figure 11(c)**.

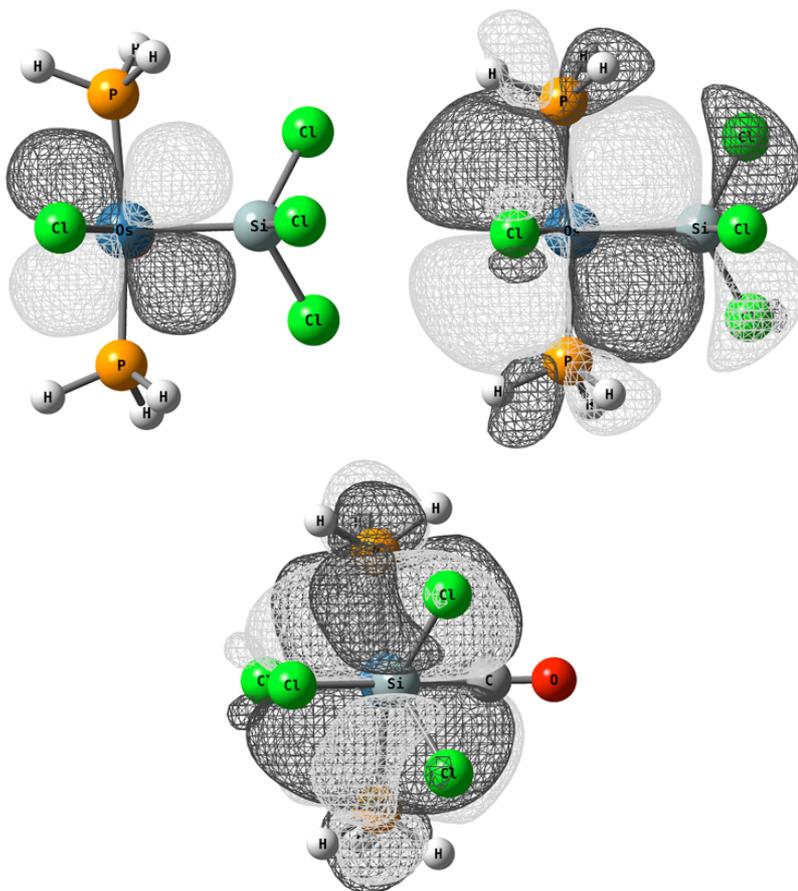


Figure 11 HOMO-2 iso-surfaces at (a) 0.02 (b) 0.002 top view (c) 0.002 looking down Si-Os bond

One way of measuring the dAO population on the Si due to backdonation is to look at the contribution of the Si dAOs to these localised MOs, **Table 5**. In this study a comparison was made with the dAO population on the Si in the free silanes HSiR₃, and this showed no significant change in the amount of dAO population on the Si! This is important, as it means that the dAOs primarily polarize the existing bonding and antibonding MOs on the SiR₃ fragment, and have little to do with the proximity of the TM.

So what can we say add to the TM->Si back-bonding debate, is it the Si dAOs, or is it the Si-R σ^* -FMOs that receive the electron density? I'm afraid its pretty inconclusive, although the orbital pictures certainly make it look like dAO participation is important, the population analysis and lengthening of the Si-F bonds make it look like Si-R σ^* -FMOs are more important. H cannot operate as a back-donation source, so the significant presence of the dAOs in the HSiR₃ calculations is indicative of the dAOs acting only as polarization functions, and not as orbitals available to receive electron density. Of course this is *the key problem*, including the d-polarization functions in order to get a good description of the bonding makes sense when we say the Si wants to partially rehybridize, but it does make it difficult to determine if they are really used.

Case 6: Quantifying Lewis Acidity: a comparison between BCl_3 and BF_3

Motivation

In the first year (at Imperial anyway) the Lewis acidity of various compounds is discussed. Lewis acidity being the ability of a substance to act as an electron pair acceptor. Boron compounds of the type BX_3 (we are taught) are electron deficient, the B atom contributes $3e$ to its valence shell and then each "X" contributes another e , giving a total of $6e$, when really $8e$ are required to reach a full octet. The boron center is electron deficient and hence boron compounds readily accept additional electrons.

Population analysis using a variety of methods all show the same trend, as the electronegativity of the halide increases there is an increasing positive charge on the boron atom. This being the case, where $\text{X}=\text{halide}$ we would expect the acidity of BX_3 compounds to decrease from $\text{BF}_3 > \text{BCl}_3 > \text{BBr}_3$ since, this is the order of their electronegativity, F will withdraw more electron density from the B center making it even more Lewis acidic.

However, the Lewis acidity of these compounds progresses as $\text{BBr}_3 > \text{BCl}_3 > \text{BF}_3$. The explanation for this reversal of the expected trend is placed on the p-AOs of the halide, these orbitals can form a π -bond, where the lone pairs on the halide back-donate electron density into the empty pAO on the boron atom. The fluorine $2p_\pi$ orbitals overlap best with the boron atom $2p_\pi$ orbitals and hence are donate more electron density to the boron center thus reducing its electron deficiency and Lewis acidity. The chlorine $3p_\pi$ orbitals do not overlap as well and hence are better acids.

However as indicated above the more electronegative the halide the higher the charge on the boron atom, and population analysis methods already include back-donation. Moreover the B-N bond energy for chlorine in $\text{X}_3\text{B-NH}_3$ is stronger than that for fluorine, and it has been shown that the p_π orbitals of Cl overlap better than those of F with the boron $2p_\pi$ orbitals. Thus the p_π orbital overlap hypothesis is negated.

Why is BCl_3 a better Lewis acid than BF_3 ?

In this paper the underlying reasons for the acidity of the boron trihalides are analysed using EPA, the Energy Partitioning Analysis. The introduction of this paper is very informative, it tells us of the many calculations carried out to investigate, and hypotheses developed to explain, the "anomalous" trend in Lewis acidities for BX_3 compounds. You may find it surprising that in 2006 (or at least 2003 given this paper) we are still discussing, and disagreeing about the bonding in molecules as simple as BF_3 !

We have been over the computational details of several papers now, so this time I will leave it up to you to read and digest these details, we will go right onto the interesting

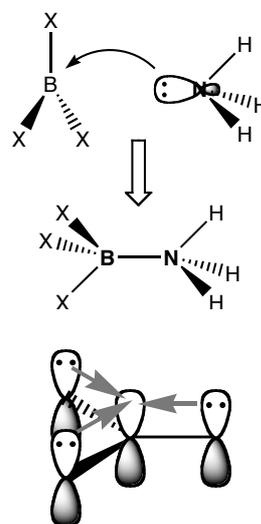


Figure 12 σ -donation and π^* -backdonation

stuff! While a range of basis sets and computational methods have been compared, here we will examine the results at the PW91/QZ4P level.

Reference:

F. Bessac and G. Frenking, *Inorg. Chem.*, 2003, Vol 42, p7990

Analysis

There are two primary energy components to the EPA analysis. The first is ΔE_{deform} the energy required to distort the geometry and electronic structure from the stable gas phase into the configuration found in the final complex, in this paper it is called ΔE_{prep} for energy of preparation. The gas phase boron trihalides are planar with a D_{3h} symmetry, while in the compound the halide ligands are folded back in a local C_{3v} like structure. The second energy component is $\Delta E_{\text{interaction}}$ the energy of interaction of the fragments once they have obtained the distorted geometry. This information is shown in **Table 6**.

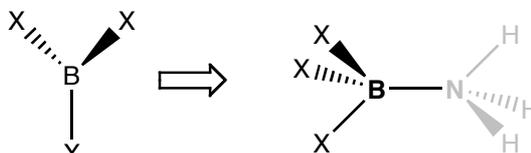


Figure 13: Distortion of geometry

	$\Delta E_{\text{prep}}(\text{BX}_3)$	$\Delta E_{\text{prep}}(\text{NH}_3)$	$\Delta E_{\text{interaction}}$	D_0
Cl	21.9	0.3	45.6	19.4
F	21.8	0.2	42.9	17.6
Δ	0.1	0.1	2.7	1.8

Table 6 Preparation energies, interaction energies, and bond dissociation energies (corrected for zero-point-energy motions) in kcal mol⁻¹

We can see that there is substantial energy associated with deforming the boron compounds from a planar (gas-phase) to a pyramidal (adduct) geometry ≈ 20 kcal mol⁻¹, and very little energy associated with the gas phase to the adduct geometry distortion in NH_3 , ≈ 0 kcal mol⁻¹. The last row of **Table 6**, shows the differences in these energies for the BCl_3 and BF_3 adducts. We can see that despite the size of these contributions they are almost for BCl_3 and BF_3 . The energy of interaction of the distorted fragments is shown in column 3, and there is a significant difference between the halides; BCl_3 interacts more strongly with NH_3 than BF_3 hence the $\text{Cl}_3\text{B} \leftarrow \text{NH}_3$ adduct is intrinsically a stronger Lewis acid than BF_3 . This is confirmed by examining the dissociation energies (D_0) of the two adducts.

The $\Delta E_{\text{interaction}}$ term can be decomposed into Pauli repulsion, electrostatic attraction (ionic bonding) and orbital interaction (covalent bonding) terms, **Table 7**. The stabilising ionic and covalent attraction terms together dominate the large and destabilising Pauli repulsion term. The difference between the ionic and covalent terms of BCl_3 is only 1.5 kcal mol⁻¹, while for BF_3 it is 14.0 kcal mol⁻¹, this indicates that *relative* to BF_3 it is the enhanced covalent character of the BCl_3 bonding which makes it more stable. This interaction is primarily due to σ -interactions (see last two columns). It is possible that the *additional* π -interactions in BF_3 (only 0.7%!) weaken the covalent interaction!

	ΔE_{Pauli}	$\Delta E_{\text{electrostatic}}$	$\Delta E_{\text{orbital}}$	$\Delta E_{\text{electrostatic}}^-$	$\Delta E_{\text{orbital}}(\sigma)$	$\Delta E_{\text{orbital}}(\pi)$
				$\Delta E_{\text{orbital}}$		
Cl	190.1	-118.6	-117.1	-1.5	90.4%	9.6%
F	125.9	-91.4	-77.4	-14.0	89.7%	10.3%

Table 7 Energy components of interaction energy in kcal mol⁻¹

To further examine this phenomenon the energy of the HOMO and LUMO of the acid and base were examined. The base contributes the HOMO (lone pair) while the relative energy of the LUMO with respect to the HOMO will determine the level of interaction. The HOMO and LUMO with the smallest energy difference between the fragment orbitals will have the greatest interaction, stabilising the bonding orbital into which the lone pair enter, the most, **Figure 14**.

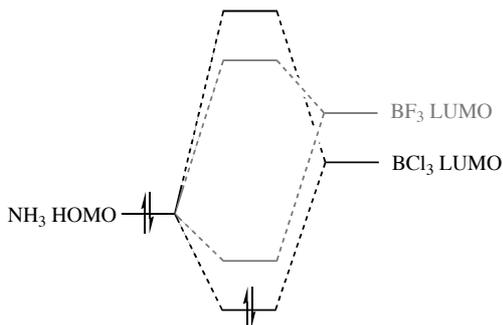


Figure 14 HOMO-LUMO interaction diagram

The LUMO of BCl₃ (-4.302 eV **Figure 15(a)**) was calculated to be deeper in energy than that of BF₃ (-3.625 eV **Figure 15(b)**). This indicates that the interaction of the NH₃ HOMO and BCl₃ LUMO will be greater, ie their covalent interaction will be greater. The HOMO of H₃N->BCl₃ is shown in **Figure 15(c)**, it is related to neither the NH₃ HOMO or the BCl₃ LUMO because their interaction is stabilising and drives the orbital to much deeper energies, the strength of this interaction is evidenced by how deep this bonding MO goes, I found this MO to be the HOMO-5, **Figure 15(d)**. This is a good example of why it is not possible to establish an absolute scale of basicity or acidity, it is the *relative* energy of the HOMO and LUMO orbitals is crucially important.

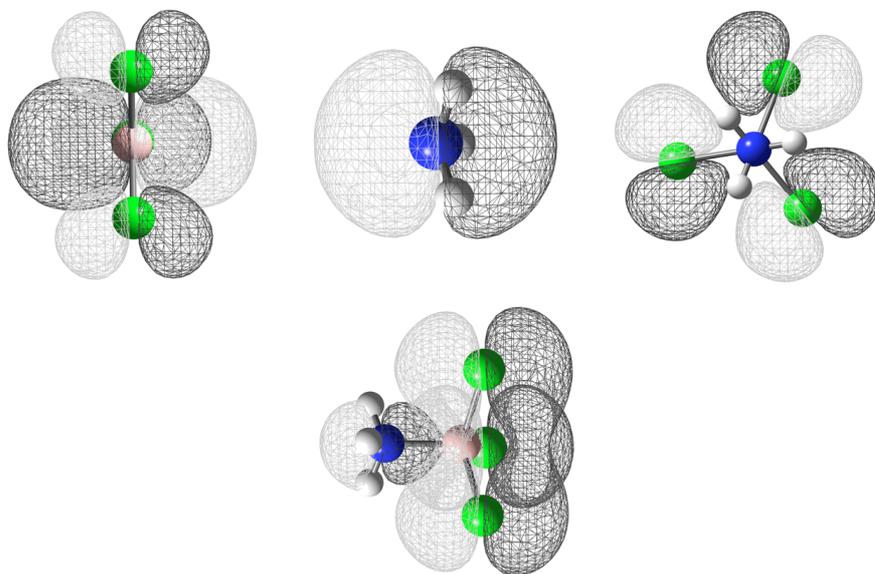


Figure 15 (a) LUMO of BCl₃ and (b) HOMO of NH₃ (c) HOMO of H₃N->BCl₃ (d) HOMO-5 of H₃N->BCl₃