Investigation of reactions driven by weak donor-acceptor interactions

PhD Theses

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1. Introduction

By the help of the computational chemistry the mechanism of rapid reactions and the geometry of the intermediates and transition states can be easily investigated, the interactions determining the stability of the system can be identified.

Chemical bonds can be divided into two groups: strong chemical bonds and weak (intermolecular) bonds. The energy difference between this two type of bond groups is usually two order of magnitude (50-200 kcal/mol vs. <10 kcal/mol).

Weak intermolecular bonds often play an important role in the structure of the molecules or in the reaction mechanism. Neglecting the intermolecular forces can cause significant error in the computational results.

The arbitrary categorization of the bonds can be overwritten in special cases. Weak donor-acceptor interactions and strong hydrogen bonds are two such examples.

During a reaction strong chemical bonds are forming and breaking between the participating atoms, however the mechanism of the reaction can also be affected by the number and strength of the forming intermolecular forces.

In my PhD thesis I would present the role of such weak donor-acceptor interactions in different reactions. I investigated hydrogen activation reactions of diphosphineboranes, in which the intermolecular interactions have significant role both in the intermediate and the product. Furthermore I explored the mechanism of hydrosilylation reaction in which I also found that the weak interactions have large influence on the reaction. Finally at the end of my PhD thesis I would present an unusual benzazaphosphole transition-metal complex in which weak interactions stabilize the system.

2. Used computational methods

Choosing a proper DFT method with a proper basis set which can describe the given problem is essential. Results of the DFT calculations were compared with experimental results or with the results MP2 and CCSD(T) calculations in each cases.

Stabilizing interactions were investigated with two different analysis methods. By the help of AIM analysis the topology of the electron density of the molecules thus the bonding structure can be described. The magnitude of the stabilizing interaction can be calculated by NBO analysis.
3. Results

3.1 Hydrogen activations with non–metals

In several hydrogen activation reactions transition metals catalysis is applied. Two different mechanistic pathways can be distinguished during dihydrogen activation with transition metals. These two mechanisms differ by the presence or the absence of an assisting base in the system, however in both cases the first step is assumed to be the formation of an η²-H₂ complex, also known as σ complex. The stability of this complex molecule arises from the superposition of two bonding interactions: 1) donation of the σ bond of dihydrogen to an empty d orbital of the metal, and 2) back-donation from a d-type occupied orbital of the metal to the σ*(H-H) orbital. The stability of the η²-H₂ complex depends on the balance between these two interactions.

Unfortunately the usage of transition metal complexes is not possible in all cases because of financial and environmental concerns. Recently, the feasibility of dihydrogen activation with non-metals has stimulated intense research, and major breakthroughs have been reported with main-group compounds. This kind of activation is difficult to achieve because in the main-group elements the absence of the empty orbital hinder the interaction between the σ bond of dihydrogen and the molecule.

With a para-phosphine-borane – (C₆H₂Me₃)₂P(C₆F₄)B(C₆F₅)₂ – Stephan and co-workers activated dihydrogen reversibly under mild conditions, thereby opening new avenues in metal-free catalytic hydrogenation. Several theoretical works dealt with the understanding of this reaction. Frustrated Lewis pairs are Lewis acid-base pairs in which the dative bond can not form because of the bulky groups on the acid and the base. However the weak interactions between acid and base cause a reactive center where the dihydrogen can be easily polarized resulting a zwiterionic structure.

Dihydrogen activation with Frustrated Lewis pairs

According to the theoretical works of the dihydrogen activation reactions the FLPs activate H–H bond in a different way compared to the transition metals. The most important difference is the absence of the η²-H₂ complex from the reaction.

In 2007, Buorissou and co-workers synthesized orto substituted phosphine-boranes. In this orto-phosphine-boranes there are two or three Lewis bases beside one
Lewis acid and these boranes can be used for complexation of transition metals, however the ability of these molecules for dihydrogen activation was not investigated. During my PhD work I studied the dihydrogen activation reaction of the above mentioned orto-phosphine-boranes.

Reaction profile for the activation of dihydrogen by the orto-diphosphine-borane is shown below.

Two different reaction paths are possible depending on the structure of the starting molecules. In case of the reaction path having lower barrier an intermediate is forming and this intermediate has a very similar structure to the structure of the \( \eta^2-H_2 \) transition metal complex.

From the results of the AIM and NBO analysis it can be concluded that both phosphine group interact with the \( \sigma^* \) orbital of the dihydrogen molecule and the bonding orbital of the \( H_2 \) donates electron to the empty orbital of the boron. Thus the \( \eta^2-H_2 \) complex intermediate is stabilized by similar donating-back donating interactions like in the transition metal complex intermediate.

I investigated the effect of different substituents on the stabilization of the \( \eta^2-H_2 \) complex intermediate. The result of the calculations shows that bulky substituents on phosphine groups and silyl groups on the boron atom can decrease further the relative energy of the complex intermediate.

The structure of the complex changes in case of the silyl groups on the boron atom. The position of the H–H bond is parallel to the B–Si bond which means that the phosphine groups can not donate electron to the \( \sigma^* \) H–H orbital. NBO analysis shows significant interactions between B–Si bond and the dihydrogen and that the interaction between the phosphines and the dihydrogen is negligible.

Based on this the question arises whether the \( \eta^2-H_2/BR_3 \) complexes can be stabilized. Until now according to the literature the BH\(_5\) molecule is the only stable \( \eta^2-H_2/BR_3 \) complex which can be prepared in krypton matrix\(^{iv} \). I investigated the effect of different
R substituents in the following reaction: \( H_2 + BH_2R = \eta^2-H_2/BH_2R \). It is proven by simulations that the silyl groups (SiH\(_3\), SiF\(_3\)) can stabilize the resulting complexes compared to the BH\(_5\) molecule. This stabilization can increase if all of the hydrogens are replaced by silyl groups, however in these cases (BH(SiH\(_3\))\(_2\), B(SiH\(_3\))\(_3\)) instead of an \( \eta^2-H_2 \) complex a pentacoordinated boron form. The structure of this pentacoordinated boron adduct is a distorted trigonal bipyramid. In the literature there is only a few example for neutral pentacoordinated boron compound.

![Diagram of a pentacoordinated boron adduct](image)

**Disubstituted pentavalent boron (BH(SiH\(_3\))\(_2\)) molecule** (\( \omega B97XD/aug-cc-pVTZ \))

### 3.2 Reaction of hydrosilanes with alcohols

There are three ways to activate the Si–H bond. One often used method is the transition metal activation. The second possibility is the coordination of a group to the silicon atom resulting a pentacoordinated silicon in which the Si–H bond is elongated. Finally the third option is the usage of a strong Lewis acid for an activation where the Lewis acid B(C\(_6\)F\(_5\))\(_3\) can interact with the hydride in the Si–H bond thus the hydrogen moves away from the silicon. The activated Si–H bond can easily react with alcohols or amines. In 2007, the synthesis of *ortho-*[(dimesitylboryl)phenyl]-methoxydimethylsilane was reported by Kawachi *et al.* \(^v\). The dehydrogenative condensation of *ortho-*[(dimesitylboryl)phenyl]-dimethylhydrosilane with methanol can take place very fast without any catalyst.

\[
\begin{array}{ccc}
\text{SiMe}_2\text{H} & + & \text{ROH} \\
\text{BMe}_{\text{s}_2} & \rightarrow & \text{SiMe}_2\text{OR} \\
\text{BMe}_{\text{s}_2} & + & \text{H}_2
\end{array}
\]

**Reaction of *ortho-*[(dimesitylboryl)phenyl]-dimethylhydrosilane with alcohols**

During my PhD study I investigated the above mentioned reaction mechanism in detail by the help of computational chemistry. Furthermore I checked the effect of different substituents on the reaction mechanism.
Reaction mechanism of orto-[(dimesitylboryl)phenyl]-dimethylhydrosilane with alcohols (MPW1K/6-31+g*/SCS-RI-MP2/def2-TZVPP, energies in kcal/mol)

In the orto-[(dimesitylboryl)phenyl]-dimethylhydrosilane molecule there are two Lewis acid parts, thus the nucleophilic oxygen atom (Lewis base) from the methanol can react at two sites of the molecule. One of the possible sites is the boron atom and the other is the silyl group which can rotate and have three different positions. Based on this, four possible reaction paths can be found on the potential energy hypersurface.

In the transition states and the intermediate of these four different reaction paths the number and strength of the stabilizing interactions differ. In cases of Ia and Ib there are no stabilizing interactions the in transition states. In the transition state of the Ic reaction path the hydrogen of the silyl group points toward the boron center, thus a stabilizing interaction can be formed between the Lewis acid boron atom and the hydride. In case of Id a stepwise reaction path is obtained where further weak interaction stabilize the system. The above mentioned interaction between the hydride and the boron atom can be found in the transition states and in the intermediate during Id reaction, furthermore during the reaction the partial positive hydrogen of the methanol is located close to the π-system of the phenyl ring and stabilize further the system.

Possible nucleofilic attack of the methanol on the silyl group of the orto-
[(dimesitylboryl)phenyl]-dimethylhydroxilane (MPW1K/6-31+g*)

The acidity of the boron center can have a significant influence on the kinetics of the reaction, thus I investigated effect of other Lewis acids – stronger acids than the dimesitylboryl group. The Lewis acidity can be increased by the changing of the mesityl substituents to pentaflourphenyl groups or the changing of the boron center to aluminum atom. The relative energy of the transition stats are decreased significantly in both cases. The decrease is smaller in case of the less Lewis acidic aluminum derivative. It is worth noting that this significant decrease of energy is not caused only by the Lewis acidity center atom but also caused by the forming interactions between the fluorine and the hydrogen. The relative energy of the products also decrease in both cases (aluminum atom and pentaflourphenyl substituents on boron) because the steric crowding is smaller than in case of dimesithylboryl group.

3.3 Unusual coordination of 1,3-benzazaphosphole to transition metals

In 2008, Heinicke and co-workers synthetized 1-neopentyl-1,3-benzazaphosphole in a good yield within a new type of reactionvi, and in 2013 they prepared the substituted 1-H-1,3-benzazaphosphole derivativevii. The X-Ray structures of the 1-neopentyl-1,3-benzazaphosphole complex with AgCl and the 1-H-1,3-benzazaphosphole complex with HgCl2viii were recorded.

complex of 1,3-benzazaphosphole with AgCl

complex of 1,3-benzazaphosphole with HgCl2

Complexes of 1,3-benzazaphosphole with AgCl and HgCl2

The investigation of these two crystal structure shows that P–Ag bonds do not lie within the extended ligand ring plane, but are tilted away by 32.4 and 12.7° in case of the silver complex. The HgCl2 complex coordinates mercury almost perpendicular to the benzazaphosphole ring plane instead of the expected planar orientation (the phosphorous atom has a lone pair in the plane of the ring). The aim of my work was to understand the structures of these two 1,3-benzazaphosphole complexes and explore the bonding structure.

NBO analyses were done to investigate the interactions inside the complexes.
Based on these calculations beside the expected LP(P)→LP*(Ag)\(^1\) interaction another interaction is found. This new interaction forms between the P=C bond of the 32.4° tilted ligand and the empty d-type orbital of the silver. The energy of this interaction is tenth of the energy of the LP(P)→LP*(Ag) interaction. The participations of the π electrons in the dative bond is more significant in case of the mercury complex. This is shown by the almost perpendicular arrangement of the ligand, the elongation of the C=P bond distance in the complex in comparison with the distance in the ligand and the calculated energy of the stabilizing interaction from the NBO analysis. The relative strength of donation of the π electrons can be increased if the s character in the lone pair of the σ²P atom is significantly increased (66%) in comparison with σ³P atom (49%) thus the lone pair of the phosphorus can participate less in the making of the dative bond.

To understand this behavior – the mercury(II) ion interact with the C=P double bond instead of the phosphorous lone pair – I investigated the structures and the interaction energies of the following model complexes.

**Geometry of the ligand L, P – Hg distance (Å), energy of the Kohn-Sham HOMO (eV), energy of the π(C=P) → LP*(Hg) interaction (kcal/mol)**

<table>
<thead>
<tr>
<th>L</th>
<th>L(PMe₃)HgCl₂</th>
<th>P – Hg distance</th>
<th>energy of the L HOMO</th>
<th>NBO interaction π → LP*</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP(CH₂)</td>
<td>3,49</td>
<td>-9,50</td>
<td>8,6</td>
<td></td>
</tr>
<tr>
<td>phosphaethene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>propene</td>
<td>2,99(^2)</td>
<td>-8,93</td>
<td>9,6(^3)</td>
<td></td>
</tr>
<tr>
<td>phosphole</td>
<td>3,28</td>
<td>-8,51</td>
<td>12,3</td>
<td></td>
</tr>
</tbody>
</table>

\(^1\) According to the formalism of the NBO program: between the lone pair (LP) of the phosphorous atom (63% s and 37% p characteristic) and the s orbital (LP*) of the silver.

\(^2\) C – Hg distance

\(^3\) π(C=C) → LP*(Hg)
<table>
<thead>
<tr>
<th>Ligand</th>
<th>E_{\text{HOMO}}</th>
<th>E_{\text{LUMO}}</th>
<th>E_{\text{δ}}</th>
</tr>
</thead>
<tbody>
<tr>
<td>phosphabenzen</td>
<td>2.95</td>
<td>-8.65</td>
<td>21.5</td>
</tr>
<tr>
<td>oxaphosphole</td>
<td>2.87</td>
<td>-7.85</td>
<td>34.6</td>
</tr>
<tr>
<td>tiaphosphole</td>
<td>3.08</td>
<td>-7.70</td>
<td>15.4</td>
</tr>
<tr>
<td>2-aminothene</td>
<td>2.79</td>
<td>-7.46</td>
<td>62.1</td>
</tr>
<tr>
<td>1,3-benzazaphosphole</td>
<td>3.11</td>
<td>-7.40</td>
<td>33.2</td>
</tr>
<tr>
<td>1,3-azaphosphole</td>
<td>2.57</td>
<td>-7.08</td>
<td>149.2</td>
</tr>
</tbody>
</table>

The calculated NBO interaction energy of the $\pi$ donation significantly depends on the HOMO energy of the above mentioned ligands (table). The higher the energy of the HOMO, the stronger the stabilizing $\pi(\text{C}=\text{P}) \rightarrow \text{LP}^*(\text{Hg})$ interaction becomes. The

\[ \text{LP}(\text{P}) \rightarrow \text{LP}^*(\text{Hg}) \]
aromatic systems are exceptions because in these systems the \( \pi \) electrons of the C=P double bond are delocalized. In conclusion the electron rich N–C=P system prefers more the \( \pi \) donation than the lone pair donation from the phosphorus atom.

4. Theses

1) I revealed the possible mechanisms of the hydrogen activation of the di(ortho-phosphinephenyl)phenylborane. In case of the $\textit{cis}$ conformer of the starting material - di(ortho-phosphinephenyl)phenylborane - the energy barrier is the lowest and the reaction is a stepwise reaction. The intermediate of this stepwise reaction is an $\eta^2$-H\(_2\) complex which was unknown in the frustrated Lewis pair (FLP) chemistry however very common in transition metal catalysis.

2) I showed that, beside the dative bond between the $\sigma$ orbital of the H\(_2\) part and the empty orbital of the boron center in the $\eta^2$-H\(_2\)/di(ortho-phosphinephenyl)phenylborane complex, there is further stabilization which stems from the interactions between the lone pairs of the nearby phosphine groups to the $\sigma^*$ orbital of the H\(_2\). This intermediate on the reaction path can be stabilized further if the phenyl groups on the borane atom are substituted with trimethylsilyl groups.

3) I showed that B(TMS)$_3$ molecule forms a strong adduct with dihydrogen, however structure of the adduct is not $\eta^2$-H\(_2\) complex but a pentacoordinated boron with distorted trigonal bipyramid structure.

4) I revealed the reaction mechanism of \textit{ortho}-(dimesitylboryl)phenyl]-dimethylhydrosilane with alcohols. I found four different reaction paths on the potential energy hypersurface depending on the rotation of the \textit{ortho} positioned silyl group. The reaction which has the smallest barrier is a stepwise reaction.

5) I showed that weak interactions stabilize the intermediate and the corresponding transition states in this stepwise reaction. The barrier height of the \textit{ortho}-(dimesitylboryl)phenyl]-dimethylhydrosilane hydrosilanisation reaction decreases further in the cases of perfluorophenyl and aluminum derivatives.

6) I found that the electron rich N–C=P moiety in the 1,3-bensazaphosphole transition metal complex derivatives prefers the $\pi$ donation to the phosphorous lone pair donation.

5. Publications

Publications pertinent of the theses:

2) Ghalib M., Könczöl L., Nyulászi L., Jones P. G., Palm G. J., Heinicke J. W., Impact of high $\pi$-density on the coordination properties of $\pi$-excess aromatic neutral $\sigma^3P$ ligands - P($\pi$)-donor bonds to Ag$^+$ and HgCl$_2$, DALTON TRANS 43: (1)51-54 (2014), IF: 4.197


4) Könczöl L., Makkos E., Bourissou D., Szieberth D., Computational evidence for a new type of $\eta^2$-H$_2$ complex: when main group elements act in concert to emulate transition metals, ANGEW CHEM INT EDIT 51: (38)9521-9524 (2012), IF: 13.734

Further publications:


8) Heinicke J. W., Ghalib M., Schulzke C., Jones P. G., Könczöl L., Nyulászi L., PHOSPHORUS SULFUR 190: (5-6)806-815 (2015) IF: 0.561


12) Hollóczki O., Kelemen Zs., Könczöl L., Szieberth D., Nyulászi L., Stark A., Kirchner B., CHEMISTRY 14: (2)315-320 (2013), IF: 3.349


Presentations:

a) Könczöl L.
Borán komplexek kvantumkémiai vizsgálata, előadás (magyar)
Szervetlen és Fémorganikus Kémiai Munkabizottság, Budapest, 2013

b) Könczöl L.
Egy érdekes $\eta^2 - H_2$ difoszfinoborán komplex, előadás (magyar)
Szervetlen és Fémorganikus Kémiai Munkabizottság, Szedres, 2012

c) Könczöl L., Benkő Z., Makkos E., Sólyom Zs., Szieberth D., Nyulászi L.
Lewis sav-bázis párokkal történő reverzibilis komplexképzés, előadás (magyar)
Szervetlen és Fémorganikus Kémiai Munkabizottság, Demjén, 2011

d) L. Könczöl, Z. Benkő, E. Makkos, Z. Sólyom, D. Szieberth, L. Nyulaszi
Reversible complexation with Lewis acid-base pairs, előadás (angol)
8th European Workshop on Phosphorus Chemistry, Münster, 2011

e) L. Könczöl, Z. Benkő, W.-W. du Mont, D. Szieberth, L. Nyulaszi
Delocalization in Hetero Penta-1,4-Dienes, előadás (angol)
6th European Workshop on Phosphorus Chemistry, Firenze, 2009

f) Könczöl L., Nyulászi L.
Alumínium-oxigén modell-klaszterek számítása, előadás (magyar)
KeMoMo-QSAR, Szeged, 2008


6. References


