Lewis Acid-Base Theory: Synthesis of Ammonia Borane and Gas Manipulation
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Overview

Acid-Base Theories

One of the goals of chemistry is to use models that account for trends and provide insights into the properties of reactants that contribute to reactivity. Substances have been classified as acids and bases since the time of the ancient Greeks, but the definition of acids and bases has been modified and expanded over the years.[1]

The ancient Greeks would characterize substances by taste, and defined acids as those that were sour-tasting, such as lemon juice and vinegar. The term "acid" is derived from the Latin term for "sour-tasting." Bases were characterized by their ability to counteract or neutralize acids. The first bases characterized were those of ashes from a fire, which were mixed with fats to make soap. In fact, the term "alkaline" is derived from the Arabic word for "roasting." It has thus been known since ancient times that acids and bases can be combined to give a salt and water.

The first widely-used description of an acid is that of the Swedish chemist, Svante Arrhenius, who in 1894 defined acids as substances which dissociate in water to give hydronium ions, and bases as substances which dissociate in water to give hydroxide ions. This definition is thus limited to aqueous acids and necessitates that an acid contribute a proton.[2] For example, in water HCl is an acid, as it dissociates to give the hydronium ion $(H_3O)^+$ and the chloride ion. Boron trichloride would not be considered an acid, as in water it hydrolyzes to give $B(OH)_3$ and 3 HCl; the product HCl though is an Arrhenius acid.

In 1923 the Danish Johannes Nicolaus Brønsted and the English Martin Lowry independently defined acids and bases on their ability to donate and accept hydrogen ions, or protons. Thus came the concept of acid-base conjugate pairs, and the expansion of the definition of acids and bases in solvents other than water. For example, ammonium is an acid, as it can donate a proton and generate ammonia. Ammonia can accept a proton, to give ammonium. Thus, ammonia is the conjugate base of ammonium. This acid-base reaction can occur in water, ammonia, or other solvents.

This video deals with the acid-base definition of the American chemist, Gilbert N. Lewis, who also defined acids and bases in 1923. (This is the same Lewis from Lewis-dot structures in General Chemistry.) His approach focuses not on the ability of acids and bases to donate and accept protons, but rather on their ability to accept and donate electron pairs, respectively. This encompasses the Brønsted-Lowry definition, as H^+ accepts an electron pair from a Brønsted base during protonation. However, it greatly expands the definition of an acid, now encompassing metal ions and main-group compounds. Here, we compare the ^{31}P NMR of the Lewis acid-base adduct $Ph_3P–BH_3$ to free triphenylphosphine.

Principles

### *Bonding in ~~Ammonia~~ Triphenylphosphineboranes: Lewis Description*

Let's consider the bonding between triphenylphosphine and borane. We will first consider what both molecules look like before they form a *Lewis adduct*.

Recall Lewis dot structures, and valence shell electron-pair repulsion (VSEPR) theory from general chemistry. The Lewis dot structure of triphenylphosphine is shown in **Figure 1**. There are three covalent bonds between the phosphorous atom and one of the carbon atoms in each of the three phenyl rings. Two electrons (a lone-pair) reside on the phosphorous atom to complete the octet. The phosphorous center is sp^3 hybridized and has a tetrahedral geometry, with the lone-pair of electrons residing in an sp^3 orbital. Triphenylphosphine has a lone-pair that can be donated to another molecule and is therefore classified as a *Lewis base*.

The Lewis dot structure of borane is shown in **Figure 2**. There are three covalent bonds between the boron atom and the hydrogen atoms. In this case, the boron center only has six valence electrons and therefore does not follow the 8 e^- rule. Borane is thus planar and sp^2 hybridized, with the sp^2 orbitals forming bonds to the hydrogen atoms and the lone p orbital being empty. Borane is thus a *Lewis acid*.

Since the phosphorous in triphenylphosphine has a filled orbital and the boron of borane has an empty orbital, an *Lewis acid-base adduct* can form, with the triphenylphosphine donating its two electrons to boron. Upon adduct formation, the boron center becomes sp^3 hybridized (**Equation 1**).

(1)
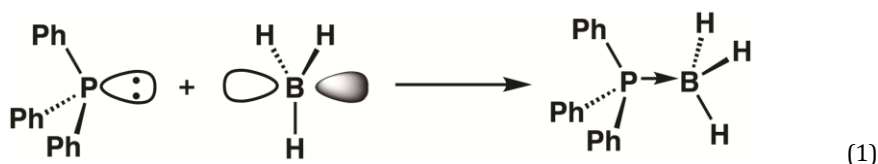
Equation 1 above demonstrates the idea of Lewis acidity, with Lewis acids accepting lone-pairs of electrons, and Lewis bases donating pairs of electrons. Sometimes, Lewis acids are referred to as electrophiles, and Lewis bases as nucleophiles. Bonds between Lewis acids and bases are often called coordinate covalent or dative bonds, and sometimes are designated with arrows as opposed to lines.

Procedure

1. Setup of the Schlenk Line for the synthesis of the borane triphenylphosphine complex (for a more detailed procedure, please review the "Schlenk Lines Transfer of Solvent" video in the *Essentials of Organic Chemistry* series). Schlenk line safety should be reviewed prior to conducting this experiment. Glassware should be inspected for star cracks before using. Care should be taken to ensure that O_2 is not condensed in the Schlenk line trap if using liquid N_2. At liquid N_2 temperature, O_2 condenses and is

explosive in the presence of organic solvents. If it is suspected that O_2 has been condensed or a blue liquid is observed in the cold trap, *leave the trap cold under dynamic vacuum. Do **NOT** remove the liquid N_2 trap or turn off the vacuum pump.* Over time the liquid O_2 will evaporate into the pump—it is only safe to remove the liquid N_2 trap once all of the O_2 has evaporated.

1.1. Close the pressure release valve.

1.2. Turn on the N_2 gas and the vacuum pump.

1.3. As the Schlenk line vacuum reaches its minimum pressure, prepare the cold trap with either liquid N_2 or dry ice/acetone.

1.4. Assemble the cold trap.

2. Synthesis of borane triphenylphosphine complex.[3]
   2.1. Add 5.3 g (20.3 mmol) of triphenylphosphine to a 250 mL Schlenk flask A and prepare the Schlenk flask for the cannula transfer of solvent.
   2.2. Add 20 mL of dry/degassed THF to the Schlenk flask A *via* cannula transfer. Stir the solution to dissolve the triphenylphosphine.
   2.3. Prepare a second Schlenk flask (B) containing 1.15 g (30.5 mmol) $NaBH_4$ for cannula transfer.
   2.4. Cool both Schlenk flask A and B in an ice bath.
   2.5. Cannula transfer the contents of Schlenk flask A into Schlenk flask B.
   2.6. With positive N_2 pressure, replace the rubber septum on Schlenk flask B with an addition funnel fitted with a rubber septum.
   2.7. To the addition funnel, add 8 mL of dry/degassed THF by cannula transfer.
   2.8. With positive N_2 pressure, remove the septum from the top of the dropping funnel and add 2 mL of glacial acetic acid to the addition funnel.
   2.9. Keeping Schlenk flask B in an ice bath, add the THF/glacial acetic acid dropwise over 30 minutes. During the addition, frothing might occur. Make sure that the reaction is stirring vigorously to minimize this.
   2.10. After the addition, allow the reaction to warm to room temperature and stir for an additional hour.
   2.11. Remove the dropping funnel and slowly add 20 mL of water.
   2.12. Prepare a solution of 2 mL glacial acetic acid in 25 mL of water. Slowly add this mixture to the reaction.
   2.13. If crystals do not spontaneously form, cool the reaction in an ice bath to yeah I promote crystallization.
   2.14. Filter the product by suction through a fritted funnel. Wash the resulting solid with 20 mL of water 3 times.
   2.15. Allow the product to dry in the hood before preparing the sample for NMR analysis.
3. ^{31}P NMR analysis of borane triphenylphosphine complex
   3.1. Prepare a NMR sample of triphenylphosphine and of borane triphenylphosphine complex in $CDCl_3$.

3.2. Collect a ^{31}P NMR of each sample (referenced to phosphoric acid) and observe how the phosphorous signal of triphenylphosphine shifts upon coordination to borane.

Representative Results

P-31 NMRs will be provided on the day of filming.

The ^{31}P NMR signal of the borane triphenylphosphine complex is downfield relative to free triphenylphosphine. This is consistent with removal of electron density from the phosphorous center, which is deshielded upon adduct formation.

Summary

The borane triphenylphosphine complex is an example of a Lewis-adduct, whereby a Lewis base donates electrons to a Lewis acid. Though BH_3 and PPh_3 would not necessarily be considered an acid and base (respectively) using other acid-base theories, Lewis acid-base theory predicts (correctly) that the molecules form a stable adduct.

Applications

Small Molecule Activation

While transition metal ions have historically been regarded as Lewis acids, the notion that they can serve as Lewis bases is being advanced. For example, Jonas Peters and co-workers at Caltech have shown that metal-borane complexes, whereby the metal donates electrons to the Lewis acidic borane (a Z-type ligand) can give rise to novel reactivity. A nickel borane species was shown to reversibly add H_2, heterolytically cleaving the H-H bond.[4] The H_2-added species is a catalyst for hydrogenations of olefins. The group also reported that iron-borane complexes can catalytically reduce nitrogen to ammonia.[5] This was the first example of an iron-based homogeneous catalyst for this challenging yet critical reaction.

Frustrated Lewis Pairs

Another current area of research is that of "Frustrated Lewis Pairs," or FLPs. These are Lewis acid-base "adducts" that due to steric reasons, cannot form a dative bond (**Figure 3**).[6] Douglas Stephan and co-workers from the University of Toronto pondered what reactivity such adducts would have, particularly with the idea of using them for small molecule activation and catalysis. Thinking about transition metal complexes, which can both accept and donate electron density from and to substrates, they hypothesized that the donor/acceptor properties of what they termed "Frustrated Lewis Pairs" might have with regards to reactivity.

In 2006, Stephan and co-workers reported in *Science* that the zwitterionic $(C_6H_2Me_3)_2PH(C_6F_4)BH(C_6F_5)_2$ reversibly loses H_2 to give $(C_6H_2Me_3)_2P(C_6F_4)B(C_6F_5)_2$.[7] This was the first example of reversible H_2 activation with main group elements, and others followed (**Figure 4**). This study paved the way for the development of FLP research. Since then FLPs have been developed that are competent hydrogenation catalysts, and can

activate a variety of small molecules including CO_2. This is an active and exciting new area of research.

Legend

Figure 1. Lewis dot structure of triphenylphosphine

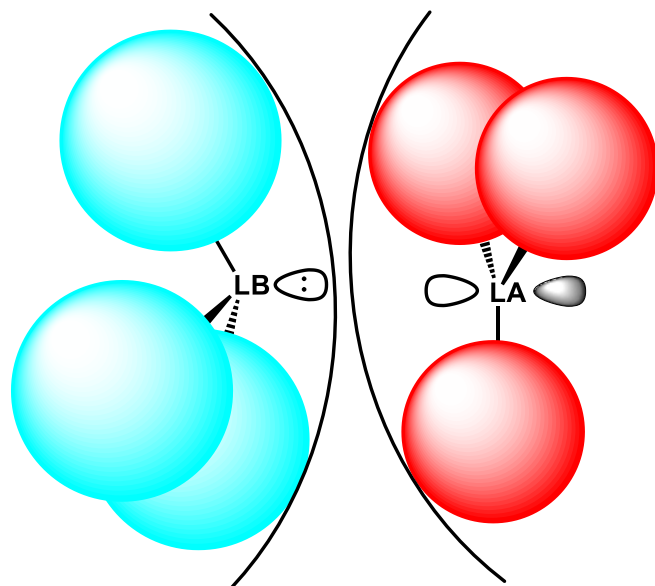**Figure 2. Lewis dot structure of borane**

Figure 3. Concept of FLPs, whereby a Lewis base (LB) and a Lewis acid (LA) cannot form an adduct due to sterics. Reprinted with permission from reference 5. Copyright 2015 American Chemical Society.
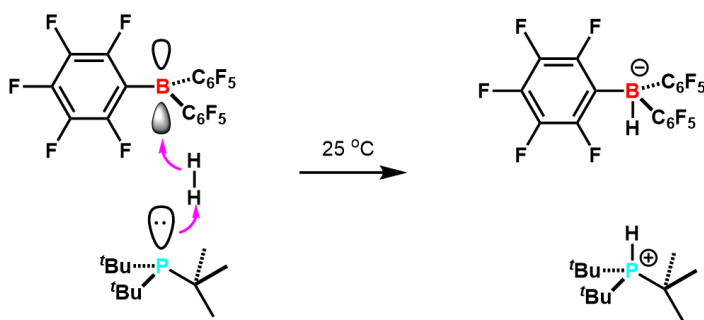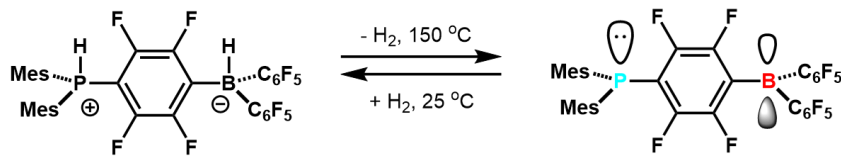
Figure 4. Early examples of reactivity of FLPs with H₂. Adapted from reference 5.

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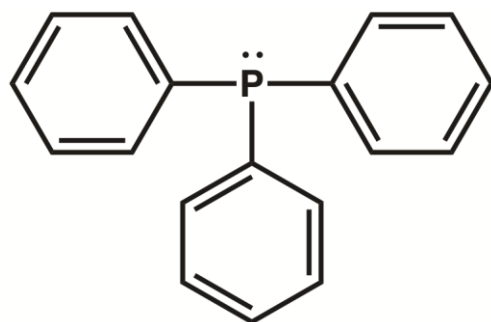7.   G. C. Welch, R. R. S. Juan, J. D. Masuda and D. W. Stephan, *Science*, 2006, **314**, 1124-1126.
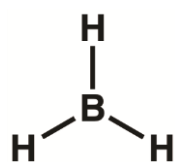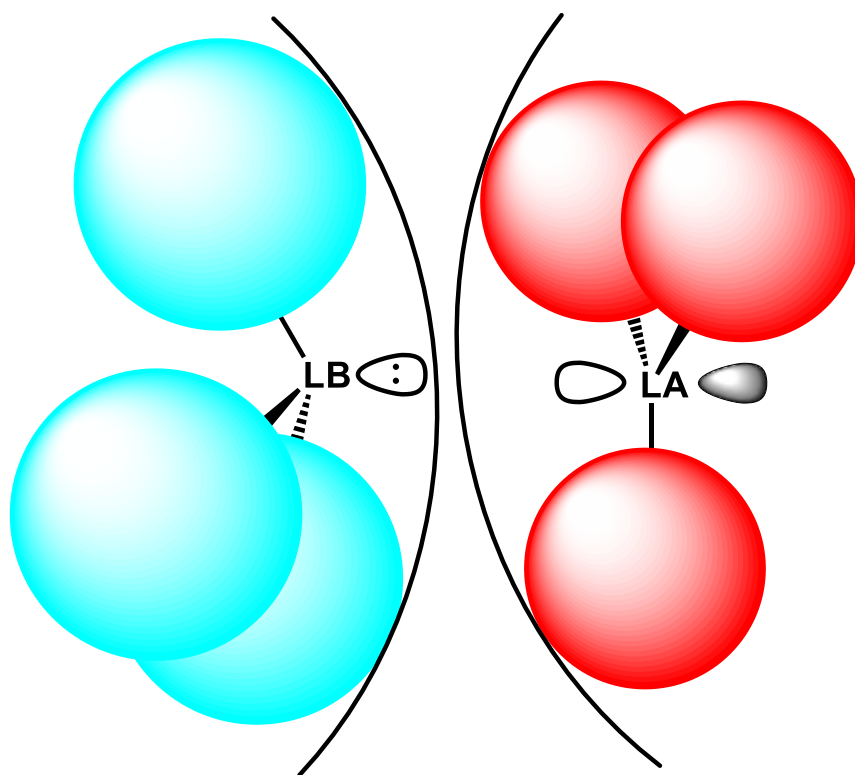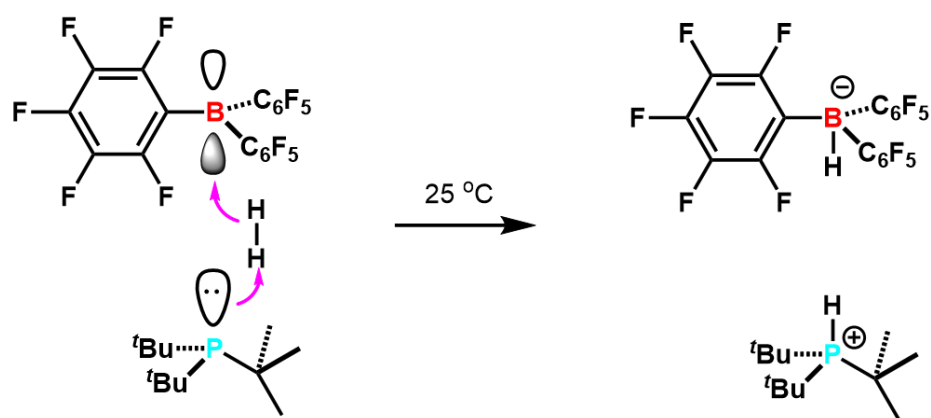
Figure 1.

Figure 2.

Figure 3.

Figure 4.