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Acid Mediated Phosphine−Borane Decomplexation: A Model for Characterizing Short-Lived Intermediates with Experimental and *ab Initio* NMR Data

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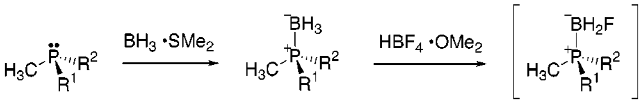
Introduction

Phosphine−borane reagents are used in synthesis where the borane moiety serves as a protecting group for the phosphine, or as an activating group for positions elsewhere in the molecule.[1] These compounds are intriguing, particularly with respect to the unique reactivity that takes place at the boron position. In fact, current interest in boron-functionalized phosphine−boranes[2] provides further impetus for establishing a more detailed understanding of the mechanisms governing this type of chemistry.

Phosphine−boranes are generally synthesized either by the direct complexation of a phosphine with borane (solution in methyl sulfide or tetrahydrofuran, $BH_3{\cdot}SMe_2$, or $BH_3{\cdot}THF$, respectively) or by reduction of a chlorophosphine or phosphine oxide in the presence of a borane source (e.g., $NaBH_4$).[3] Conversely, BH_3 can be effectively removed from the phosphine by treatment of the adduct with an acid ($HBF_4{\cdot}OMe_2$, CF_3SO_4H, CH_3SO_4H) or with a secondary or tertiary amine.[3,4] Although the mechanistic details of acid mediated decomplexation are not clear, evolution of hydrogen is observed and the borane moiety is presumed to undergo nucleophilic substitution (Figure 1).[4d,5]



1 **2** **3**

a: $R^1 = R^2 = CH_3$ **b**: $R^1 = CH_3, R^2 = Ph$ **c**: $R^1 = R^2 = Ph$

Figure 1. Generalized scheme for phosphine−borane reactions considered in this study.

In the reaction of methyldiphenylphosphine−borane (**2c**) with tetrafluoroboric acid ($HBF_4{\cdot}OMe_2$), an intermediary phosphine−fluoroborane compound (**3c**) has been hypothesized on the basis of proton (^1H) and phosphorus (^{31}P) nuclear magnetic resonance (NMR) data.[4d] In a related study, Imamoto characterized alkylsulfonate derivatives of phosphine−boranes, produced by the reaction of phosphine−borane with alkylsulfonic acid.[5] The proposed structures of these compounds are also consistent with substitution at boron.

The following study is intended as a model to demonstrate that relatively new *ab initio* techniques for estimating chemical shielding can effectively augment experimental methods for characterization of short-lived reaction intermediates. Herein, we present proton (^1H) and carbon (^{13}C) NMR chemical shift values for a series of tetrafluoroboric acid mediated phosphine−borane decomplexation reactions (Figure 1). We have performed these comparisons to elucidate intermediate phosphine−fluoroborane structures and to test certain theoretical approaches as applied to this class of compounds.

Experimental and Computational Methods

Experimental Methods. All reactions were performed in flame-dried 5 mm NMR tubes fitted with rubber septa, under an atmosphere of dry argon. Air- and moisture-sensitive reagents were transferred via syringe. Commercial reagents and solvents were used as received. All phosphine−borane complexes (**2a**−**c**) were prepared according to established procedures by complexation of the corresponding commercial phosphines (**1a**−**c**) with borane methyl sulfide ($BH_3{\cdot}SMe_2$). Phosphine−fluoroborane intermediates **3a**−**c** were observed by ^1H and ^{13}C NMR spectroscopy upon treatment of the corresponding phosphine−borane with tetrafluoroboric acid (1 equiv) in $CDCl_3$. ^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively. Proton chemical shifts are reported as δ values in parts per million (ppm) downfield from tetramethylsilane (TMS) and are referenced to residual protons in the NMR solvent ($CHCl_3$: δ 7.24). Carbon chemical shifts are reported as δ values in ppm downfield from TMS and are referenced to the ^{13}C in the solvent ($CDCl_3$: δ 77.0).

Computational Methods. To help characterize the proposed phosphine−fluoroborane complex and thus gain insight into the decomplexation mechanism, we have carried out the following series of calculations using the GAUSSIAN 98 program.[6] As a starting point, we note that Cheeseman and co-workers[7] found that the B3LYP/6-311+G(2d,p)//B3LYP/6-31G* combined approach for calculating ^{13}C chemical shifts (δ) in a representative group of molecules gave good quantitative results when compared to experiment (root mean square (rms) error of 4.2 ppm and a maximum error of −8.4 ppm). Here, B3LYP is an efficient density functional prescription[8] for taking into account electron exchange and correlation effects. For the sake of comparison, it is worth noting that the corresponding Hartree−Fock (HF) ^{13}C δ values reported in ref 7 are in poorer agreement with experiment for the same set of molecules (rms error was 11.1 ppm and a maximum error of 27.7 ppm).

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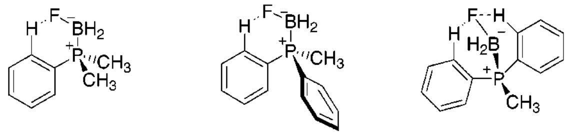
Table 1. Selected B3LYP/6-31G* Optimized Bond Lengths (Å)[a]

bond	**1c**	**2c**	**3b**	**3c** (**5**)	**3c** (**6**)
B−P	NA	1.942	2.022	2.032	2.025
H_3C−P	1.867	1.840	1.841	1.840	1.836
Ph1−P	1.858	1.834	1.829	1.835	1.833
Ph2−P	1.852	1.838	NA	1.826	1.833
B−F	NA	NA	1.414	1.417	1.420
BH_2F- - -HPh1	NA	NA	2.297	2.270	2.321
BH_2F- - -HPh2	NA	NA	NA	4.376	2.316

[a] For atom designations see structures **1c**, **2c**, and **3b** in Figure 1 and structures **4**, **5**, and **6** in Figure 2.



4 **5** **6**

Figure 2. B3LYP/6-31G*-optimized structures (**4**−**6**) illustrating the weak F- - -H intramolecular interaction.

Also in the above notation, the B3LYP/6-31G* indicates the method and basis used in the geometry optimization while the B3LYP/6-311+G(2d,p) denotes the level of theory and basis set used to find the chemical shielding (σ) at this fixed geometry. Since all results reported here are obtained using B3LYP/6-31G* geometries, we will drop the latter portion of this designation in any further discussion.

Results and Discussion

Selected optimized bond lengths of **3b** and the series **1c**, **2c**, and **3c** are given in Table 1. Note that we have estimated and reported the chemical shift values of the CH_3 group common to all the molecules. In general, the C−P bonds shorten by a few hundredths of an angstrom upon addition of the BH_3 group. Subsequent substitution of F for H causes a lengthening of the B−P bond by about a tenth of an angstrom, making the BH_2F a better leaving group. The optimized geometry of **3b** illustrated as **4** in Figure 2 indicates the presence of an intramolecular F atom interaction with a phenyl hydrogen at a distance of 2.297 Å, as reported in Table 1. This apparent Coulombic attraction is also found in **3c** and has led to two low energy structures for this molecule (**5** and **6**, Figure 2). Structure **5** depicts a single F- - -H interaction at 2.270 Å and is 0.001 au higher in energy than **6**, which contains two F- - -H interactions, both at around 2.32 Å. As will be shown below, these two different structures lead to ^{13}C chemical shifts that are over 5 ppm apart.

Table 2. Absolute ^{13}C and ^{1}H Isotropic Shielding Constants (σ) for the a Series of Molecules and Tetramethylsilane (TMS) Using Balanced (Bal) and Locally Dense (LD) Basis Sets[a]

	Hartree−Fock			B3LYP		
compd	Bal	LD	Bal−LD	Bal	LD	Bal−LD
^{13}C						
1a	175.7	175.2	0.5	162.7	162.5	0.2
2a	179.8	179.3	0.5	166.6	166.6	0.0
3a	184.0	184.4	−0.4	173.0	173.0	0.0
TMS	188.8	188.4	0.4	177.6	177.6	0.0
^{1}H						
1a	31.2	31.3	−0.1	30.9	30.9	0.0
2a	31.0	31.2	−0.2	30.7	30.8	−0.1
3a	30.9	31.3	−0.4	30.8	31.0	−0.2
TMS	31.8	32.0	−0.2	31.5	31.7	−0.2

[a] The LD calculations use a 6-311+G(2d,p) balanced (Bal) basis set on $Si(CH_3)$ in TMS and on $P(CH_3)$ in the **a** series along with a 3-21G basis set on all other atoms. All geometries were found at the B3LYP/6-31G* level.

To explore the possibility of reducing computational cost while at the same time obtaining good chemical shielding estimates for the larger systems, we present the results from a locally dense[9] basis study on the series **1a**−**3a**. Here, the locally dense set (LD) denotes a 6-311+G(2d,p) basis on the $P(CH_3)$ group (and for the $Si(CH_3)$ group of TMS) along with a 3-21G basis on all other atoms. The balanced set (Bal) describes all atoms with the 6-311+G(2d,p) basis set.

Table 2 gives the results showing that for ^{13}C and ^{1}H the HF level of theory along with the LD basis produced σ values within ±0.5 ppm of the corresponding Bal results.

The Bal-LD difference at the B3LYP level is even smaller at approximately ±0.2 ppm. To spot check these results with respect to the larger systems, we found that the HF value for **2b** gave ^{13}C and ^{1}H chemical shift Bal-LD differences of 1.8 and 0.1 ppm, respectively. It is also worth noting that the latter HF calculation using the balanced basis set required 62 CPU hours compared to 1.5 h for the LD calculation. If the above trends are correct, we might expect the B3LYP differences to be smaller. In any case, the ^{13}C difference is relatively small compared with the accuracy reported in ref 7. We conclude that the LD basis could suffice in predicting trends in chemical shifts that occur with the structural changes proposed in this study.

In fact, the ^{13}C LD estimates given in the top portion of Table 3 show HF and B3LYP δ values that, in general, trend reasonably well with experiment. On the other hand, the LD ^{1}H δ values do not always change in accordance with experiment. The overall approach used to track ^{1}H δ is apparently too insensitive to follow the changes in molecular structure, independent of the choice of basis set.[10] Also, it is understandable that changes in the ^{1}H response are smaller (less than 0.9 ppm for each **a**, **b**, and **c** series) since these atoms are further removed from the point of substitution.

In analyzing the ^{13}C chemical shifts reported at the top of Table 3, we see that the HF and B3LYP rms error when compared with the nine experimental values is 3.1 and 2.9 ppm with maximum error values of −5.0 and

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Table 3. *Ab Initio* and Experimental ^{1}H and ^{13}C Chemical Shift Values (δ) for CH_3[a]

compd	B3LYP	HF	exptl	B3LYP	HF	exptl
	^{1}H			**^{13}C**		
1a	0.8	0.7	1.00	15.1	13.2	16.3
2a	0.9	0.8	1.33	11.0	9.1	12.8
3a	0.7	0.7	1.77	4.6	4.0	∼9[b]
1b	0.9	0.9	1.30	18.4	16.6	14.5
2b	1.1	1.1	1.57	12.1	10.5	13.0
3b	1.0	1.0	2.16	2.3	2.6	5.2
1c	1.3	1.3	1.60	13.2	12.4	12.5
2c	1.4	1.5	1.84	11.3	10.3	11.7
3c (5)	1.5	1.5	2.40	6.5	6.7	4.9
3c (6)	1.3	1.1		0.1	0.9	

[a] Results are found with the LD basis (see text) using the B3LYP/6-31G* optimized geometries. The δ values are reported in ppm relative to TMS. [b] A weak, broad resonance centered at ∼9 ppm was observed following the addition of $HBF_4 \cdot OMe_2$.

−4.8 ppm, respectively. This shows better agreement with experiment than what was found for the selection of molecules reported in ref 7. Furthermore, there is little difference between the HF and B3LYP calculated values. The reason for this could be attributed to the fact that electron correlation is believed to be less important in estimating chemical shielding for chromophores containing single bonds.

The (B3LYP and HF) ^{13}C δ estimates for the two minimum energy structures, **5** and **6**, are below (0.1 and 0.9 ppm) and above (6.5 and 6.7 ppm) the experimental value of 4.9 ppm. One might be tempted to take the average of the two calculated estimates giving 3.8 ppm for HF and 3.3 ppm for the B3LYP value. In this case, the values fall just under the experimental δ; i.e., they are slightly too shielded. In general, we find an overestimation of calculated shielding for all of the boronatophosphine compounds. With or without averaging, the closeness to the experimental value could be taken as further evidence for the existence of the phosphine−fluoroborane intermediate. A more detailed study that may be of interest would be to find the barrier height for interconversion of **5** and **6** as well as how δ is affected during this process.

Conclusion

We have presented evidence that the local density method greatly reduces computational times while providing good B3LYP and HF estimates of ^{1}H and ^{13}C NMR chemical shift values for the compounds reported here. We also find good agreement between the experimental and theoretical ^{13}C NMR values for this series of phosphine−borane compounds. In the case of the short-lived intermediates, this close agreement can be viewed as support for previously proposed phosphine−fluoroborane structures. Furthermore, lengthening of the phosphorus−boron bond upon substitution with fluorine is demonstrated by the *ab initio* optimized geometries. This fact substantiates a mechanistic hypothesis whereby substitution at boron facilitates hydrolysis of the resulting phosphine−fluoroborane intermediate. Lastly, intramolecular Coulombic attractions are believed to be responsible for two different **3c** intermediate structures that are close in energy but give rise to ^{13}C NMR shielding that differ by about 5 ppm.

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Supporting Information Available: Summaries of all B3LYP/6-31G* geometries and energy data. This material is available free of charge via the Internet at http://pubs.acs.org.

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