

# Theoretical Analysis of Reactions between Phosphylnitrenes and Boranes: The Fate of the Adducts

Minh Tho Nguyen,\* Annik Van Keer, and Luc G. Vanquickenborne

Department of Chemistry, University of Leuven, Celestijnenlaan 200F, B-3001-Leuven, Belgium

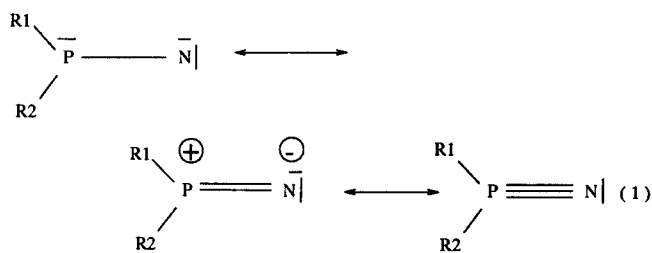
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Ab initio molecular orbital calculations have been carried out to determine the minimum-energy pathways and thereby to probe the mechanism of reactions between phosphylnitrenes ( $R^1R^2P\equiv N$ ,  $R^1, R^2 = H, F$ ) and boranes ( $H_2XB$ ,  $X = H, F, CH_3$ , and  $C_2H_5$ ). Geometries have been determined using the MP2/6-31G(d,p) model, while relative energies have been estimated using, depending on the size of the system, the quadratic configuration interaction model (QCISD and QCISD(T)) with various basis sets including 6-31G(d,p), 6-311G(d,p), and 6-311++G(d,p). The stability of the primary complex adduct is strongly dependent on the substituents of the boranes. When the borane bears a H atom, the primary adduct is not at all stable and readily collapses to an amine isomer via a H-shift from B to N. This shift becomes more difficult if the substituent is F or  $CH_3$ . In the F case, a phosphorane isomer, owing to the strength of the P–F bond, turns out to be favored. When non-hydrogen boranes ( $BF_3$  and  $B(CH_3)_3$  for example) could be used, the primary adducts could be stabilized and even exist as discrete intermediates. F substituents on the nitrene show no significant qualitative effect. In the  $H_2PN + H_2BC_2H_5$  reaction, a retro-ene reaction of the adduct directly gives rise to an amine product via a five-membered transition structure. In the reverse reaction of a HX molecule plus an iminoborane ( $RB\equiv N-PR^1R^2$ ), both 1,2-addition to B and N and 1,3-addition to B and P reactions are possible.

## Introduction

Since the first observation reported a decade ago<sup>1</sup> that phosphylnitrenes (**I**) ( $R^1R^2PN$ , phosphinonitrenes) could be generated as discrete intermediates following thermolysis or photolysis of phosphylnitrides (**II**), these compounds have emerged as potential building blocks in synthetic organophosphorus chemistry.<sup>2</sup> Thus a Curtius-type rearrangement either from **I** or **II** giving iminophosphanes (**III**) has not taken place, but in the presence of trapping agents (AX), different 1,2-adducts (**IV**) have been identified. In some cases, formation of polyphosphazenes (**V**) has also been observed (Scheme 1).

Depending on the nature of the substituents, molecule **I** can be regarded as either a  $\lambda^3$ -phosphylnitrene or a  $\lambda^5$ -phosphonitrile (eq 1).<sup>3</sup> Such a diversity of electronic structures could

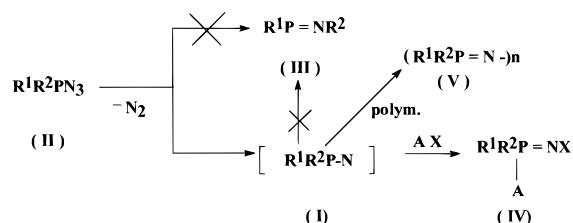


lead to a variety of contrasting chemical behaviors. Although

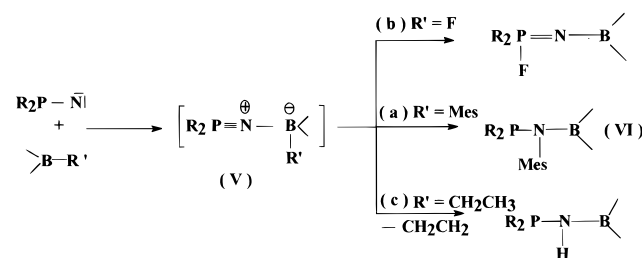
<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, June 1, 1996.

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- (2) For a review see: Majoral, J. P. *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Georg Thieme Verlag: Stuttgart, Germany, 1990; p 455.
- (3) (a) Nguyen, M. T.; McGinn, M. A.; Hegarty, A. F. *J. Am. Chem. Soc.* **1985**, *107*, 8029. (b) Nguyen, M. T.; Ha, T. K. *Chem. Phys. Lett.* **1989**, *158*, 135. (c) Nguyen, M. T.; Vansweevelt, H.; Ha, T. K.; Vanquickenborne, L. G. *J. Chem. Soc., Chem. Commun.* **1990**, 1425. (d) Nguyen, M. T.; Van Keer, A.; Ha, T. K.; Vanquickenborne, L. G. *THEOCHEM*. **1994**, *130*, 125.

## Scheme 1



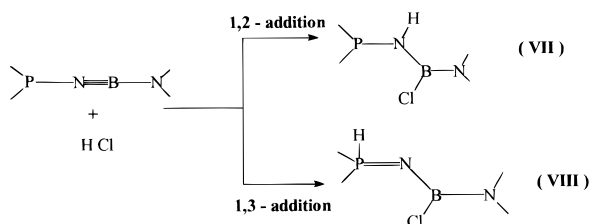
## Scheme 2



compound **IV** is formally the product of a 1,2-addition of an AX reagent to a phosphylnitrene, the mechanism of its formation has not been well established. Recently, Alcaraz and co-workers<sup>4</sup> studied the reactions of **I** with different boranes; their experimental observations are summarized in Scheme 2. These results strongly suggest an initial formation of a nitrene–borane adduct (**V**) which, depending on the migratory aptitude of the substituents on both partners, subsequently undergoes either a 1,2-migration reaction (a), a 1,3-migration reaction (b), or a retro-ene reaction (c) (Scheme 2). Nevertheless, the competition between these reaction modes could not be unveiled from the experimental study. The possible existence of transient nitrene–borane adducts is of particular interest as they represent

- (4) Alcaraz, G.; Baceiredo, A.; Dahan, F.; Bertrand, G. *J. Am. Chem. Soc.* **1994**, *116*, 1225.
- (5) Scriven, E. F. V.; Turnbull, K. *Chem. Rev.* **1988**, *88*, 297.

## Scheme 3



a stabilized complex of a nitrene with a Lewis acid. In fact, while nitrenes usually form primary adducts with Lewis bases<sup>5</sup> of the type  $R-N^--X^+(L)_n$  in which a nucleophile approaches the vacant nitrogen p orbital (e.g., the interaction of a carbon-ylnitrene with a thiophene or phosphine derivatives), their complexation with Lewis acids in which the nitrene plays the role of the nucleophile yielding  $R-N^+-Y^-(L)_n$  is a rather rare phenomenon.

Using another approach, Nöth and co-workers<sup>6</sup> recently showed that analogues of products **VI** (Scheme 2) can also be obtained by addition of hydrogen compounds to (phosphanylimino)boranes (Scheme 3). The latter has been observed to react with HCl, producing a mixture of both products **VII** and **VIII**. On heating or on standing at ambient temperature, the hydrogen atom on N in **VII** actually migrates to P, yielding **VIII**. Such behavior was not observed by Alcaraz et al.<sup>4</sup> (Scheme 2, reaction c). The goal of this investigation is to examine quantitatively the reaction mechanism of the nitrene-borane additions, in particular the various transformations of the primary adducts. We carried out ab initio molecular orbital calculations on several simple model systems, including  $H_2PN + BH_3$ ,  $F_2PN + BH_3$ ,  $H_2PN + BH_2F$ ,  $H_2PN + BH_2CH_3$  and  $H_2PN + BH_2C_2H_5$ . Combination of the results for these systems allows us to determine the migratory aptitude of H, F, and  $CH_3$  substituents as well as to identify the retro-ene fragmentation. As the (difluorophosphanyl)nitrene  $F_2PN$  has been shown to be a remarkably stable species,<sup>3</sup> it is also of interest to emphasize its behavior in this reaction.

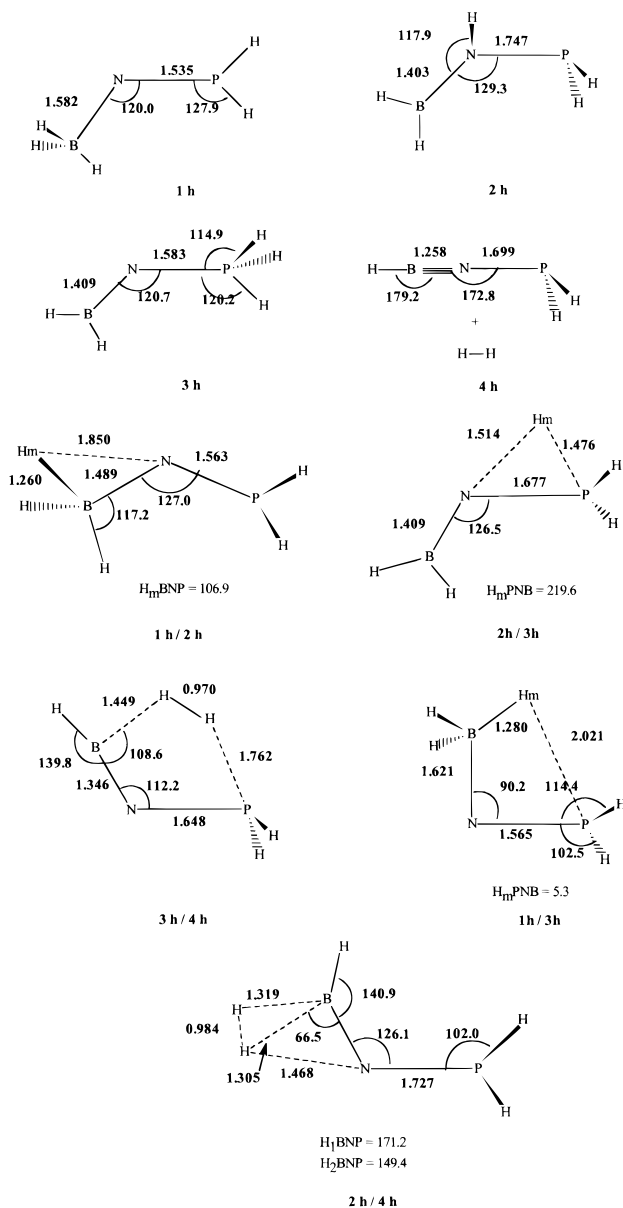
## Computational Details

All ab initio molecular orbital calculations were performed using a local version of the Gaussian 92 set of programs.<sup>7</sup> Reactants, transition structures, and products were fully optimized at both Hartree-Fock (HF) and second-order Møller-Plesset perturbation theory (MP2) levels with the dp-polarized 6-31G(d,p) basis set. All stationary points were characterized by harmonic vibrational analysis using HF wave functions, and the identity of each transition structure was determined by intrinsic reaction coordinate (IRC) calculations which show unambiguously both connecting equilibrium structures. Subsequently, single-point energy calculations using the MP2/6-31G(d,p) geometries and the quadratic configuration interaction methods (QCISD and QCISD(T)) were performed, also with the larger 6-311G(d,p) and 6-311++G(d,p) basis sets. The higher level energy calculations for each system were chosen according to its size. The zero-point vibrational (ZPE) energies were obtained from HF/6-31G(d,p) harmonic wavenumbers and scaled by 0.9 to account for the systematic overestimation. Throughout this paper bond lengths are given in angstroms, bond angles in degrees, total energy in hartrees, and zero-point and relative energies, unless otherwise noted, in kilocalories per mole.

## Results and Discussion

The potential energy surface of each of the systems considered will be described in a separate section; whenever possible, a

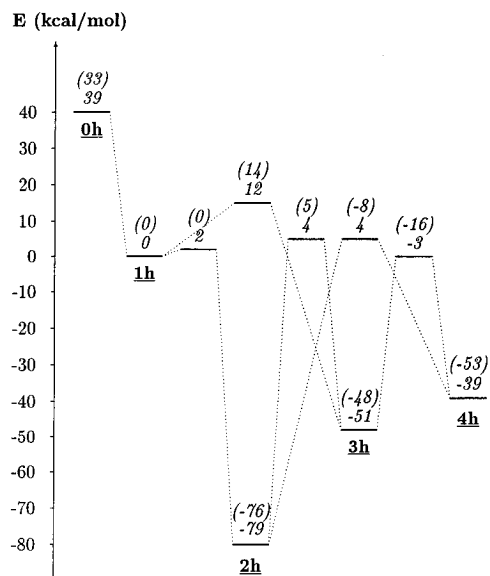
- (6) Nöth, H.; Stolpmann, H.; Thomann, M. *Chem. Ber.* **1994**, *127*, 81.  
 (7) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *GAUSSIAN 92*; Gaussian Inc.: Pittsburgh, PA, 1992.



**Figure 1.** Selected MP2/6-31G(d,p) geometries of the points on the  $H_2PN + BH_3$  reaction pathways.

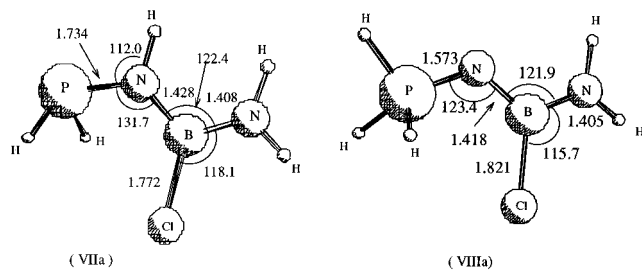
comparison with available experimental findings will be made. For the sake of simplicity in the presentation of data, only a selection of important geometrical parameters are displayed; the energetic results are given in the form of potential energy profiles. To facilitate comparison, we employ the same notation for the stationary points on the reaction routes. Thus, **0** designates the reactant partners (a borane plus a phosphanylnitrene), **1** the primary adduct of the type **V**, **2** the rearranged amine of the type **VI** or **VIa** resulting from a 1,2-shift of a substituent from B to N, **3** another rearranged iminophosphorane of the type **VIb** formally resulting from a 1,3-shift from B to P (Scheme 2), **4** the  $-B=N-P<$  product resulting from a HX elimination of **3**, and finally **5** the product of a retro-ene reaction. In addition, the letter **h** stands for the unsubstituted  $H_2PN + BH_3$  system, **f** for  $H_2PN + BH_2F$  (fluorine on borane), **m** for  $H_2PN + BH_2CH_3$  (methyl on borane), **e** for  $H_2PN + BH_2C_2H_5$  (ethyl on borane), and finally **F** for  $F_2PN + BH_3$  (fluorine on nitrene). **X/Y** indicates a transition structure (TS) linking both equilibrium structures **X** and **Y**.

**The  $H_2PN + BH_3$  System.** The relevant selected geometrical parameters and calculated energy profiles are displayed in Figures 1 and 2, respectively. The adduct **1h** exhibits a B-N



**Figure 2.** Schematic energy profiles for the  $\text{H}_2\text{PN} + \text{BH}_3$  reaction. Relative energies were obtained from MP2/6-31G(d,p) + ZPE calculations. In parentheses are given QCISD(T)/6-311++G(d,p) + ZPE values.

distance of 1.582 Å, which is, as expected, much longer than that of 1.4 Å in both isomers **2h** and **3h**, indicating the complex character of **1h**. The P–N bond in **3h** has a rather double-bond character. It should be stressed that the energies of all equilibrium and transition structures are lower than that of the reactants **0h**. The amine **2h**, where all heavy atoms have a classical valence structure, turns out to be the most stable isomer. The energy ordering between the iminophosphane **3h** and the fragment products **4h** is not well represented by MP2 energies.  $\text{HB}\equiv\text{N}-\text{PH}_2$  has an almost linear cumulene geometry, and the energy of such a structure is apparently not well accounted for by second-order perturbation calculations. At the more advanced QCISD(T)/6-311++G(d,p) level, the product **4h** is slightly more favored than **3h**. As seen in Figure 2, the primary complex **1h** is not a stable equilibrium structure; it collapses rapidly and preferentially to the amine **2h** by a hydrogen shift from B to N. **2h** can be decomposed, giving **4h** either by a direct 1,2-elimination of  $\text{H}_2$  or by a two-step route involving an initial generation of **3h** by a 1,2-H shift. The activation barriers of these processes are all substantial and similar to each other. In this case, owing to the higher thermodynamic stability of **2h**, it is likely that this amine derivative will be formed as the major product. As shown in Scheme 2 (reaction c), a secondary amine could effectively be generated by another route and no other isomers have been found. It is worth noting that the conversion  $\mathbf{3h} \rightarrow \mathbf{4h}$  formally implies an unusual 1,3-elimination of  $\text{H}_2$ . Considering now the reverse reaction, namely the addition of a hydrogen compound to a (phosphanylimino)-borane (cf. Scheme 3), the calculated results indicate that the 1,2-addition of a HX molecule to the  $-\text{B}\equiv\text{N}-$  bond and the 1,3-addition of the same molecule to the P and B centers are actually feasible and competitive. This is in agreement with the experimental work of Nöth et al.,<sup>6</sup> where both adducts **VII** and **VIII** have been isolated. Nevertheless, the energy ordering between **VII** and **VIII** as suggested by the experimental study is not in line with our results on simpler systems (Figure 2). To estimate a possible effect of the substituents, we calculated the energy difference between **VIIa** and **VIIIa**. At the MP2/6-31G(d,p) + ZPE level based on the MP2-optimized geometries, **VIIa** remains more stable than **VIIIa** by 22 kcal/mol. We also calculated **VIIIb**, in which the migrating proton, as occurred



in the experimental case, has a cis conformation with respect to the chlorine atom. Still, the conformer **VIIa** remains 22 kcal/mol more stable. Nöth et al. explained the stability of **VIIIa** by an additional resonance form in which the  $\text{NH}_2$  lone pair conjugates with the boron empty p orbital, resulting in a  $\text{N}=\text{B}$  double bond. In the present case, the corresponding geometrical parameters in both structures **VIIa** and **VIIIa** do not differ much from each other (they are both ca. 1.4 Å) and consequently the contribution of the extra resonance form, if any, is expected to be similar in both isomers.

**The  $\text{F}_2\text{PN} + \text{BH}_3$  System.** The calculated results are recorded in Figures 3 and 4. Due to the larger size of the system, only single-point energy calculations at the QCISD/6-311G(d,p) level were carried out. A few significant informations can be noted:

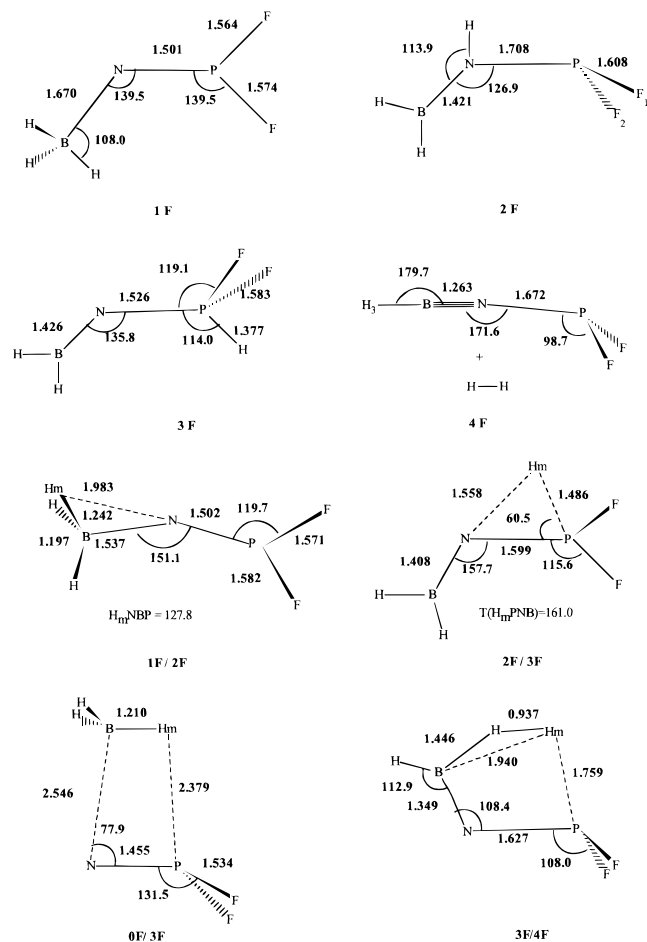
(a) Relative to the unsubstituted system, the rearranged adducts **2F** and **3F** and the product **4F** are markedly stabilized with respect to the reactants, but the amine derivative **2F** clearly remains the most stable isomer. Again, the primary adduct **1F** is not a stable equilibrium structure. The molecular supersystem tends to collapse directly to **2F** by a hydrogen transfer.

(b) From the reactants **0F**, the formation of the phosphorane **3F** is also feasible by a formal 1,2-addition of  $\text{H}_2\text{B}-\text{H}$  to the triple  $\text{P}\equiv\text{N}$  bond; this route is however inhibited by a small energy barrier of a few kcal/mol. This suggests that if the phosphanylnitrene could be strongly stabilized and the 1:1 complex could be destabilized, the 1,2-addition mode would then become possible.

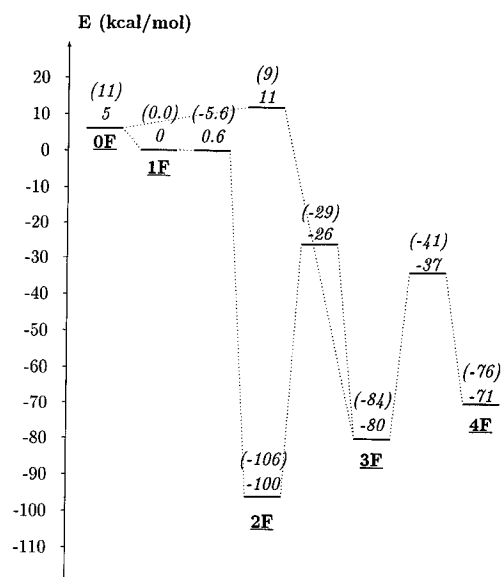
(c) A fragmentation  $\mathbf{2F} \rightarrow \mathbf{4F}$  by a direct 1,2-elimination of  $\text{H}_2$  no longer exists; this can only be done by a two-step route through **3F** in which the initial  $\mathbf{2F} \rightarrow \mathbf{3F}$  conversion is more energy demanding than the  $\mathbf{3F} \rightarrow \mathbf{4F}$  fragmentation.

(d) Overall, the reaction path displayed in Figure 4 can be regarded as similar to that of the unsubstituted system (Figure 2) in the sense that there is, in both cases, a thermodynamic driving force leading to the major formation of an amine derivative **2**. Apparently, substitution on the nitrene does not exert a qualitative modification of the reaction course.

**The  $\text{H}_2\text{PN} + \text{BH}_2\text{CH}_3$  System.** We mainly consider the reaction paths in which the methyl group migrates. A H-migration from  $\text{BH}_2\text{CH}_3$  is of course possible and is expected to have a behavior similar to that in the two previous cases. The purpose here is to establish the migratory aptitude of  $\text{CH}_3$ . The calculated results are summarized in Figures 5 and 6. While the primary adduct **1m** is not stable with respect to a H-migration, its rearrangement to the **2m'** isomer is almost a barrier-free process. **1m** is in contrast quite resistant to the methyl migration. In fact, we were not able to locate the TS **1m/2m** involving a  $\text{CH}_3$ -shift from B to N; the supersystem tends to approach the  $\text{CH}_3 + \text{H}_2\text{BNPH}_2$  dissociation limit. The TS **2m/3m** involving a  $\text{CH}_3$ -migration between N and P has been located and the energy barrier becomes substantial (about 90 kcal/mol). These results are in line with the well-known fact that a 1,2-methyl migration is an extremely difficult process to achieve in electron-rich systems such as radicals and anions.

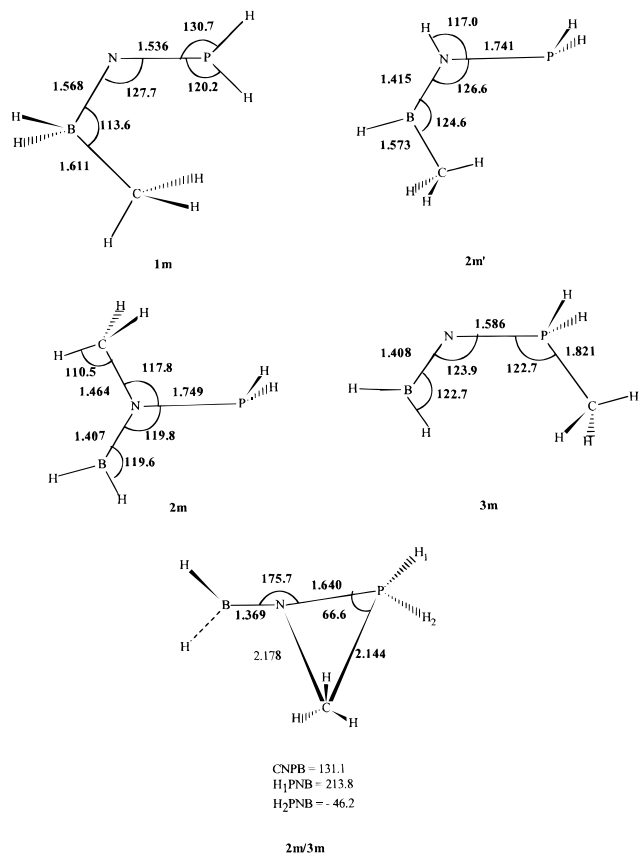


**Figure 3.** Selected MP2/6-31G(d,p) geometries for the points on the  $F_2PN + BH_3$  reaction pathways.

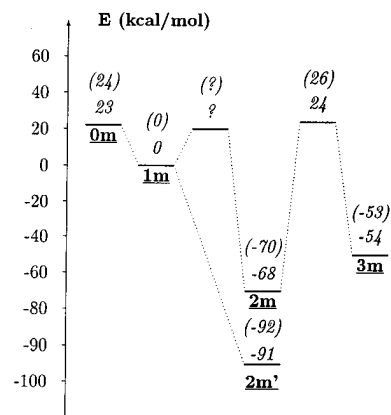


**Figure 4.** Schematic energy profiles for the  $F_2PN + BH_3$  reaction. Relative energies were obtained from MP2/6-31G(d,p) + ZPE calculations. In parentheses are given the QCISD/6-311G(d,p) + ZPE values.

However, 1,2-methyl migration becomes much easier for electron-poor systems such as carbocations. Hence, in this view, it seems logical that we observed a transition structure for methyl migration from N to P and not from B to N. Note also that the amine **2m** remains more stable than the phosphorane **3m**. Overall, the present results confirm that a methyl group strongly resists migration among the B, N, and P centers and thereby



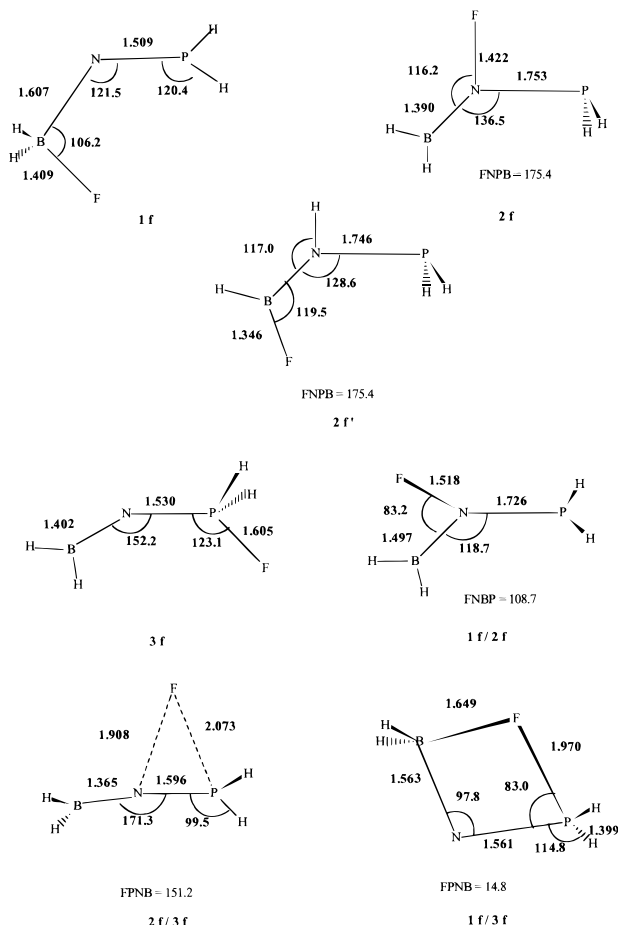
**Figure 5.** Selected MP2/6-31G(d,p) geometries for the points on the  $H_2PN + BH_2CH_3$  reaction pathways.



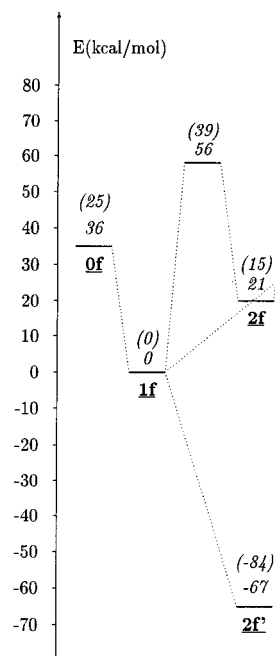
**Figure 6.** Schematic energy profiles for the  $H_2PN + BH_2CH_3$  reaction. Relative energies were obtained from MP2/6-31G(d,p) + ZPE calculations. In parentheses are given the QCISD/6-31G(d,p) + ZPE values.

suggest that a reaction involving, for example, trimethylborane,  $(CH_3)_3B$ , could yield a stabilized primary adduct **1m**.

**The  $H_2PN + BH_2F$  System.** The corresponding results are recorded in Figures 7 and 8. Again we consider only the migratory aptitude of the fluorine atom. Compared with the unsubstituted system, it is clear that F exerts some remarkable modifications on the shape of the potential energy surface. There is a significant electronic redistribution between both partners in the primary complex **1f** as evidenced by the bond distances: while the B–N bond becomes longer (1.607 Å), the P–N bond becomes much shorter (1.509 Å). A Mulliken analysis of the electron population indicates, in fact, that F mainly plays the role of an electron donor. As in the previous cases, **1f** is unstable with respect to a H-migration, giving **2f**, but remains stable with respect to a 1,2-F shift. Moreover, the fluoramine **2f** is dramatically destabilized, being now much higher in energy

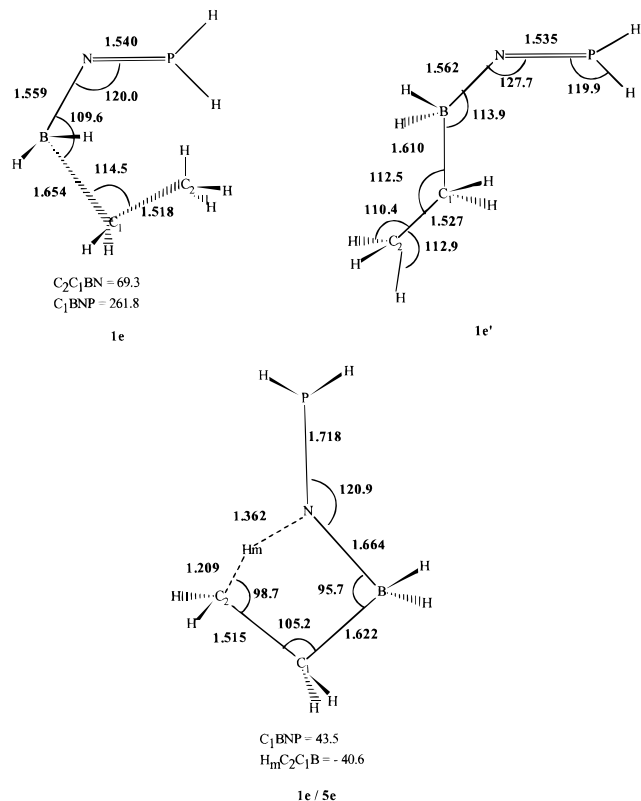


**Figure 7.** Selected MP2/6-31G(d,p) geometries for the points on the  $\text{H}_2\text{PN} + \text{BH}_2\text{F}$  reaction pathways.



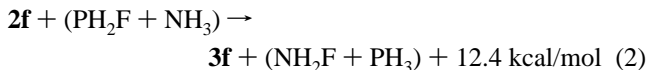
**Figure 8.** Schematic energy profiles for the  $\text{H}_2\text{PN} + \text{BH}_2\text{F}$  reaction. Relative energies were obtained from MP2/6-31G(d,p) + ZPE calculations. In parentheses are given the QCISD/6-311G(d,p) + ZPE values.

than **1f**. The instability of **2f** is likely due to the weakness of the N–F bond whose energy<sup>8</sup> in  $\text{NF}_3$  amounts only to 57 kcal/mol. The F atom can migrate, connecting **2f** and **3f**, but such a F-migration requires a significant activation energy. In contrast, the 1,3-shift of F directly converting **1f** into the more



**Figure 9.** Selected MP2/6-31G(d,p) geometries for the points on the  $\text{H}_2\text{PN} + \text{BH}_2\text{C}_2\text{H}_5$  reaction pathways.

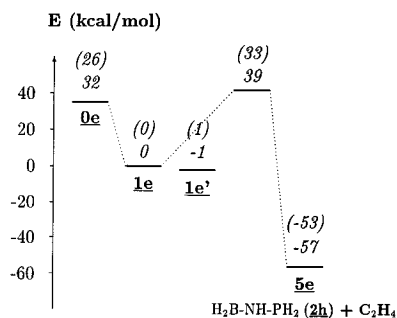
stable phosphorane **3f** is only inhibited by a moderate energy barrier (less than 20 kcal/mol) through TS **1f/3f**. In this context, it is reasonable to admit that, in the case where only F can migrate (such as in  $\text{BF}_3$  or  $(\text{CH}_3)_2\text{BF}$  for example), the primary adduct **1** could again be stabilized as a distinct equilibrium structure and subsequently undergo a preferential 1,3-F shift producing the corresponding iminophosphorane **3**. This result corroborates the experimental observation shown in Scheme 2 (reaction b) where  $(\text{Mes})_2\text{BF}$  was used as the starting material. Similar to methyl, phenyl is inherently a poor migrating group; mesityl is in addition much bulkier. Overall, the migration of F is in this case favored both thermodynamically and sterically and results in the formation of a (borylimino)phosphorane **3**, which is the most stable isomer according to our calculations (Figure 8). The higher stability of **3f** can simply be understood by the peculiar strength of the P–F bond (132 kcal/mol for the P–F bond energy in  $\text{PF}_3$ <sup>8</sup>). Owing to this property, fluorine has been demonstrated to stabilize preferentially many phosphorus compounds.<sup>3,9</sup> To probe further this point, we have calculated the isodesmic reaction (2) at the QCISD/6-311G-



(d,p) level corrected for zero-point energies. This reaction gives an indication of the PF and NF relative bond strengths in  $\text{PH}_2\text{F}$  and **3f** and in  $\text{NH}_2\text{F}$  and **2f**, respectively. The small endothermicity (+12.4 kcal/mol) of this reaction indicates that the P–F bond strength seems to be the dominating factor in the exchange process and is more pronounced in  $\text{PH}_2\text{F}$  than in **3f**. Compared

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(9) (a) Nguyen, M. T.; Vansweevelt, H.; Vanquickenborne, L. G. *Chem. Ber.* **1992**, *125*, 923. (b) Fitzpatrick, N. J.; Brougham, D. G.; Groarke, P. J.; Nguyen, M. T. *Chem. Ber.* **1994**, *127*, 969.



**Figure 10.** Schematic energy profiles for the  $\text{H}_2\text{PN} + \text{BH}_2\text{C}_2\text{H}_5$  reaction. Relative energies from MP2/6-31G(d,p) + ZPE calculations. In parentheses are the QCISD/6-31G(d,p) + ZPE values.

with the other complexes, **2f** is by far the most stable entity relative to the reactants; we conclude that the stability of **2f** or **3f** is not so much dependent on its conformation as it is on the presence of a strong P–F bond.

**The  $\text{H}_2\text{PN} + \text{BH}_2\text{C}_2\text{H}_5$  System.** In this system, we consider only the mechanism of a retro–ene reaction of the primary adduct (Figures 9 and 10). Due to its larger size, only calculations with the 6-31G(d,p) basis set are available for this system. This primary complex may exist in two distinct configurations **1e** (gauche) and **1e'** (trans) that have nearly identical energies. The gauche form **1e** possesses an appropriate nuclear position for a hydrogen transfer from its terminal methyl group. Regarding the retro–ene mechanism, Alcaraz et al.<sup>4</sup> suggested an initial hydrogen transfer from the methyl group to the phosphorus end through a six-membered transition state giving phosphorane **3** even though the final product identified is an amine derivative of type **2**. In spite of extensive attempts, we have not been able to locate such a six-membered transition structure; instead, all geometry optimizations converged to TS **1e/5e** (Figure 9), which has a five-membered cyclic form. In **1e/5e**, the methyl hydrogen is actually transferred to the nitrogen, giving in a single step the amine product **2h** ( $\text{H}_2\text{BNHPH}_2$ ). This is in agreement with the experimental facts (Scheme 2, reaction c) and appears to be logical since amine **2h** represents a more stable isomer than phosphorane **3h** ( $\text{H}_2\text{B}-\text{N}=\text{PH}_3$ ) (cf. Figure 2). It is worth noting that in **1e/5e**, while the transfer of the hydrogen  $\text{H}_m$  is already engaged, the C–B bond is not at all

broken. The C–B distance in **1e/5e** becomes even shorter than that in **1e**. In contrast, both B–N and P–N bonds of the fragment product are appreciably stretched. Such geometrical changes apparently induce an electronic stabilization of the compact five-membered transition structure **1e/5e**. The corresponding height of the energy barrier is as a matter of fact not very large, namely about 30 kcal/mol.

## Summary

In the present theoretical paper, we have examined the transformation of the primary adducts resulting from the reaction of phosphanylnitrenes and boranes. The stability and rearrangements of these adducts are very much dependent on the substituents on the boranes. When borane bears a hydrogen atom ( $\text{HBR}_2$ ), the H-migration is almost spontaneous; the primary adduct **1** is therefore not stable and tends to collapse to the corresponding amine derivative **2**. In the cases of methyl- and fluoroboranes, ( $\text{CH}_3\text{BR}_2$  and  $\text{FBR}_2$ ), both fluorine and methyl migrations are difficult processes to achieve and as a consequence the primary adducts are stabilized relative to the reactants. The fluorophosphorane species **3** becomes the most favored one. These findings allow us to interpret most of the available experimental observations. When tertiary boranes such as  $(\text{CH}_3)_3\text{B}$  or  $\text{F}_3\text{B}$  could be used as starting materials, the corresponding primary adducts could be formed as discrete intermediates. The fluorine atoms on the nitrene ( $\text{F}_2\text{PN}$ ) show no significant qualitative effects on the reaction pathways. Proceeding in the opposite direction, in the addition of a hydrogen compound to a phosphinoiminoborane ( $\text{HX} + \text{R}-\text{B}\equiv\text{N}-\text{PR}_2$ ), both 1,2-addition to B and N and 1,3-addition to B and P could occur, also in agreement with experiment. In the last system we have considered, the retro–ene reaction of the adduct of  $\text{H}_2\text{PN} + \text{BH}_2\text{C}_2\text{H}_5$  results in an amine product ( $\text{H}_2\text{B}-\text{NH}-\text{PH}_2 + \text{C}_2\text{H}_4$ ) through a five-membered transition structure. Again, the most stable structure found, is in line with the experimental results.

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