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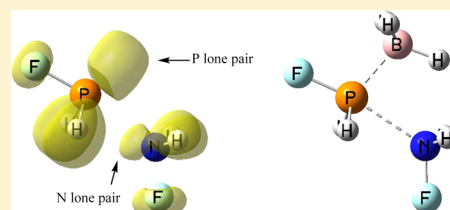
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# Phosphorus As a Simultaneous Electron-Pair Acceptor in Intermolecular P $\cdots$ N Pnicogen Bonds and Electron-Pair Donor to Lewis Acids

Janet E. Del Bene,<sup>\*,†</sup> Ibon Alkorta,<sup>\*,‡</sup> Goar Sánchez-Sanz,<sup>§</sup> and José Elguero<sup>‡</sup><sup>†</sup>Department of Chemistry, Youngstown State University, Youngstown, Ohio 44555, United States<sup>‡</sup>Instituto de Química Médica (C.S.I.C.), Juan de la Cierva, 3, E-28006 Madrid, Spain<sup>§</sup>Institute of Organic Chemistry and Biochemistry, Gilead Sciences Research Center & IOCB, Academy of Sciences of the Czech Republic, Flemingovo nám. 2, 166 10 Praha 6, Czech Republic

## Supporting Information

**ABSTRACT:** Ab initio MP2/aug'-cc-pVTZ calculations have been performed to investigate the structures and energies of binary complexes LA:PH<sub>2</sub>F and LA:PH<sub>3</sub> and of ternary complexes LA:H<sub>2</sub>FP:NHF<sub>2</sub> and LA:H<sub>3</sub>P:NH<sub>3</sub> in which the pnicogen-bonded P atom also acts as an electron-pair donor to a Lewis acid (LA), for LA = BH<sub>3</sub>, NCH, ClH, FH, FCl, and HLi. Hydrogen bonds, halogen bonds, and dative covalent bonds are found at P in some cases, depending on the nature of the Lewis acid. HLi forms a lithium bond with P only in the binary complex HLi:PH<sub>3</sub>. The binding energies of ternary complexes exhibit a classical synergistic effect, although the computed cooperativity may be overestimated due to neglect of the interaction of the Lewis acid with NH<sub>2</sub>F or NH<sub>3</sub> in some cases. The hydrogen-bonding Lewis acids appear to have little effect on the strength of the P $\cdots$ N bond, while the remaining Lewis acids strengthen the pnicogen bond. <sup>31</sup>P absolute chemical shieldings increase in LA:H<sub>2</sub>FP:NHF<sub>2</sub> complexes relative to the corresponding LA:PH<sub>2</sub>F complexes as the positive charge on P decreases, while chemical shieldings decrease in LA:H<sub>3</sub>P:NH<sub>3</sub> relative to the corresponding LA:PH<sub>3</sub> complexes as the positive charge increases. Absolute values of <sup>1</sup>J(P–N) spin–spin coupling constants in complexes LA:H<sub>2</sub>FP:NHF<sub>2</sub> decrease as the P–N distance decreases. It appears that this behavior is associated with the presence of a second intermolecular interaction, whether electron-donation by P or hydrogen bond formation at P–F.



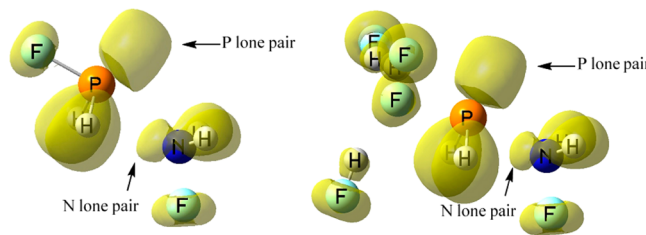
## INTRODUCTION

The pnicogen bond is a Lewis acid–Lewis base interaction in which a pnicogen atom (N, P, or As) acts as the Lewis acid. Although the pnicogen bond has been recognized for several decades,<sup>1–5</sup> it was not among those at the forefront of studies of intermolecular interactions until the landmark paper by Hey-Hawking et al. appeared in 2011.<sup>6</sup> Since then, the pnicogen bond has received a great deal of attention in the literature.<sup>7–28</sup>

The pnicogen bond provides another example of the  $\sigma$ -hole concept proposed by Politzer and Murray.<sup>5</sup> This term refers to the electron-deficient outer lobe of a p orbital, which can act as an electron-pair acceptor from a Lewis base. As with other types of intermolecular interactions, the pnicogen bond is stabilized in part by electrostatic and polarization contributions. However, the present authors and Scheiner in their recent papers have demonstrated that charge-transfer from the lone pair of an atom (Y) of the base to the antibonding  $\sigma^*$  P–X orbital of the acid, with X–P $\cdots$ Y approaching a linear alignment, is a very important component in the stabilization of complexes with pnicogen bonds. The pnicogen bond and its relationship to other types of intermolecular interactions has been discussed in recent review articles.<sup>29–31</sup>

In a recent paper,<sup>32</sup> we examined the effect of the formation of F–H $\cdots$ F hydrogen bonds at P–F and at N–F on the strength of P $\cdots$ N pnicogen bonds in complexes nFH: (H<sub>2</sub>FP:NHF<sub>2</sub>), for n = 1–2, and a selected complex with n = 3.

We observed that the ELF representation of these complexes clearly indicates that the lone pair on the nitrogen is directed toward the P $\cdots$ N region, while the lone pair on phosphorus is not, as illustrated in Figure 1 for the parent complex H<sub>2</sub>FP:NHF<sub>2</sub> and



**Figure 1.** ELF representations at the 0.8 isosurface for H<sub>2</sub>FP:NHF<sub>2</sub> and the same complex hydrogen bonded to three FH molecules at P–F, showing the P lone pairs and the N lone pairs in the P $\cdots$ N basins.

the complex having three FH molecules hydrogen bonded at P–F. In that study, electrons in the intermolecular P–N region were assigned to the P–N basin only in complexes in which hydrogen bonding with FH occurred at P–F. When hydrogen bonding

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occurred at N–F, electrons in the P–N region were described as nitrogen lone pairs.

The existence of a diffuse and relatively exposed lone pair of electrons at P led us to ask to what extent the P atom could act as an electron-pair donor (a base) to a Lewis acid, while at the same time functioning as an electron-pair acceptor (an acid) for the P...N pnictogen bond. To answer this question, we have investigated two series of complexes LA:H<sub>2</sub>FP:NFH<sub>2</sub> and LA:H<sub>3</sub>P:NH<sub>3</sub>, with LA representing the Lewis acids BH<sub>3</sub>, NCH, ClH, FH, FCl, and HLi. In the present article, we present the structures of these complexes, as well as the energies for the reactions that form P...N and P...LA bonds. We investigate the ability of phosphorus to act as a Lewis electron-pair donor in various types of intermolecular interactions, including hydrogen bonds, halogen bonds, and lithium bonds as well as dative covalent bonds. We examine cooperative effects for ternary complexes LA:H<sub>2</sub>FP:NFH<sub>2</sub> and LA:H<sub>3</sub>P:NH<sub>3</sub> due to the presence of P...N and P...LA bonds and estimate the bond energies. We also investigate <sup>31</sup>P and <sup>15</sup>N absolute chemical shieldings and indirect P–N spin–spin coupling constants <sup>1</sup>J(P–N) across the pnictogen bonds. In this article, we report the results of this investigation.

## COMPUTATIONAL METHODS

The structures of isolated monomers, binary complexes LA:PH<sub>2</sub>F and LA:PH<sub>3</sub>, and ternary complexes LA:H<sub>2</sub>FP:NFH<sub>2</sub> and LA:H<sub>3</sub>P:NH<sub>3</sub> for the Lewis acids LA = BH<sub>3</sub>, NCH, ClH, FH, FCl, and HLi, were optimized at second-order Møller–Plesset perturbation theory (MP2)<sup>33–36</sup> with the aug'-cc-pVTZ basis set.<sup>37</sup> This basis set is derived from the Dunning aug-cc-pVTZ basis set<sup>38,39</sup> by removing diffuse functions from H atoms. Frequencies were computed to establish that these optimized structures correspond to equilibrium structures on their potential surfaces. The binary complex HLi:PH<sub>2</sub>F failed to optimize to a structure with a P...Li bond, undergoing an atom transfer reaction instead. This complex was then optimized under the constraint that P...Li–H must be linear. All optimization and frequency calculations were performed using the Gaussian 09 program.<sup>40</sup>

The Natural Bond Orbital (NBO) method<sup>41</sup> has been used to obtain atomic charges using the NBO-5 program<sup>42</sup> within the Gamess program.<sup>43</sup> Absolute chemical shieldings have been calculated at MP2/aug'-cc-pVTZ using the GIAO approximation.<sup>44</sup> Coupling constants were evaluated using the equation-of-motion coupled cluster singles and doubles (EOM-CCSD) method in the CI (configuration interaction)-like approximation,<sup>45,46</sup> with all electrons correlated. For these calculations, the Ahlrichs<sup>47</sup> qzp basis set was placed on <sup>13</sup>C, <sup>15</sup>N, and <sup>19</sup>F, and the qz2p basis set on <sup>31</sup>P, <sup>35</sup>Cl, and hydrogen-bonded <sup>1</sup>H atoms of Lewis acids. A previously developed basis set with the same number of basis functions as the qzp basis was placed on <sup>7</sup>Li and <sup>11</sup>B.<sup>48</sup> The Dunning cc-pVDZ basis set was placed on all other H atoms. Only <sup>1</sup>J(P–N) coupling constants are reported in this article. The EOM-CCSD calculations were performed using ACES II<sup>49</sup> on the IBM Cluster 1350 (Glenn) at the Ohio Supercomputer Center.

## RESULTS AND DISCUSSION

The energies and structures of the binary complexes LA:PFH<sub>2</sub> and LA:PH<sub>3</sub> and the ternary complexes LA:H<sub>2</sub>FP:NFH<sub>2</sub> and LA:H<sub>3</sub>P:NH<sub>3</sub> are reported in Tables S1 and S2, respectively, of the Supporting Information. The structures of the ternary

complexes LA:H<sub>2</sub>FP:NFH<sub>2</sub> and LA:H<sub>3</sub>P:NH<sub>3</sub> have C<sub>s</sub> symmetry and are reported in Table 1 and illustrated in Figure 2.

**Table 1. Distances (R, Å), Angles (∠, deg), and Reaction Energies for the P–N [ $\Delta E(P-N)$ ] and P–LA [ $\Delta E(P-LA)$ , kJ mol<sup>−1</sup>] Reactions which Form the Ternary Complexes LA:H<sub>2</sub>FP:NFH<sub>2</sub> and LA:H<sub>3</sub>P:NH<sub>3</sub>**

LA:H <sub>2</sub> FP:NFH <sub>2</sub>					
complex	R(P–N)	$\Delta E(P-N)$	R(P–LA)	∠	$\Delta E(P-LA)$
H <sub>2</sub> FP:NFH <sub>2</sub>	2.524	−26.67			
LA = BH <sub>3</sub>	2.413	−36.82	1.920 <sup>a</sup>	83 <sup>a</sup>	−144.75
NCH	2.568	−42.55	3.564 <sup>b</sup>	75 <sup>b</sup>	−24.63
ClH	2.541	−42.76	3.580 <sup>c</sup>	13 <sup>c</sup>	−28.52
FH	2.503	−46.33	3.098 <sup>d</sup>	17 <sup>d</sup>	−38.14
FCl	2.274	−58.96	4.019 <sup>e</sup>	1 <sup>e</sup>	−103.43
HLi	2.378	−85.49 <sup>f</sup>	3.489 <sup>g</sup>	43 <sup>g</sup>	−92.22 <sup>f</sup>
LA:H <sub>3</sub> P:NH <sub>3</sub>					
complex	R(P–N)	$\Delta E(P-N)$	R(P–LA)	∠	$\Delta E(P-LA)$
H <sub>3</sub> P:NH <sub>3</sub>	3.292	−7.82			
LA = BH <sub>3</sub>	3.098	−21.52	1.942 <sup>a</sup>	85 <sup>a</sup>	−120.89
NCH	3.332	−18.39	3.730 <sup>b</sup>	16 <sup>b</sup>	−21.98
ClH	3.192	−18.00	3.683 <sup>c</sup>	4 <sup>c</sup>	−25.03
FH	3.194	−20.49	3.185 <sup>d</sup>	8 <sup>d</sup>	−34.06
FCl	2.888	−35.01	4.035 <sup>e</sup>	0 <sup>e</sup>	−78.38
HLi	4.325	−71.09	2.932 <sup>g</sup>	62 <sup>g</sup>	−103.82

<sup>a</sup>The P–B distance and ∠N–P–B. <sup>b</sup>The P–C distance and ∠H–C...P. <sup>c</sup>The P–Cl distance and ∠H–Cl...P. <sup>d</sup>The P–F distance and ∠H–F...P. <sup>e</sup>The P–F distance and ∠Cl–F...P. <sup>f</sup>Energies derived from a constrained optimized HLi:PFH<sub>2</sub> structure with H–Li–P linear. <sup>g</sup>The P–H distance and ∠Li–H...P.

Complexes LA:PH<sub>3</sub> have C<sub>3v</sub> symmetry, with the lone pair of electrons of the sp<sup>3</sup> hybridized P directed toward the acidic site of the Lewis acid. The complexes LA:PH<sub>2</sub>F have reduced C<sub>s</sub> symmetry due to the substitution of F for H but have structures that are similar to the corresponding LA:PH<sub>3</sub> complexes, as evident from Table 2. The P–N and P–LA reaction energies are given in Tables 1 and 2 as the energies for the following reactions, using complexes involving H<sub>2</sub>FP:NFH<sub>2</sub> and PH<sub>2</sub>F as examples. For ternary complexes:

$$\Delta E(P-N) = E(\text{LA:H}_2\text{FP:NFH}_2) - E(\text{LA:PH}_2\text{F}) - E(\text{NH}_2\text{F}) \quad (1)$$

$$\Delta E(P-LA) = E(\text{LA:H}_2\text{FP:NFH}_2) - E(\text{H}_2\text{FP:NFH}_2) - E(\text{LA}) \quad (2)$$

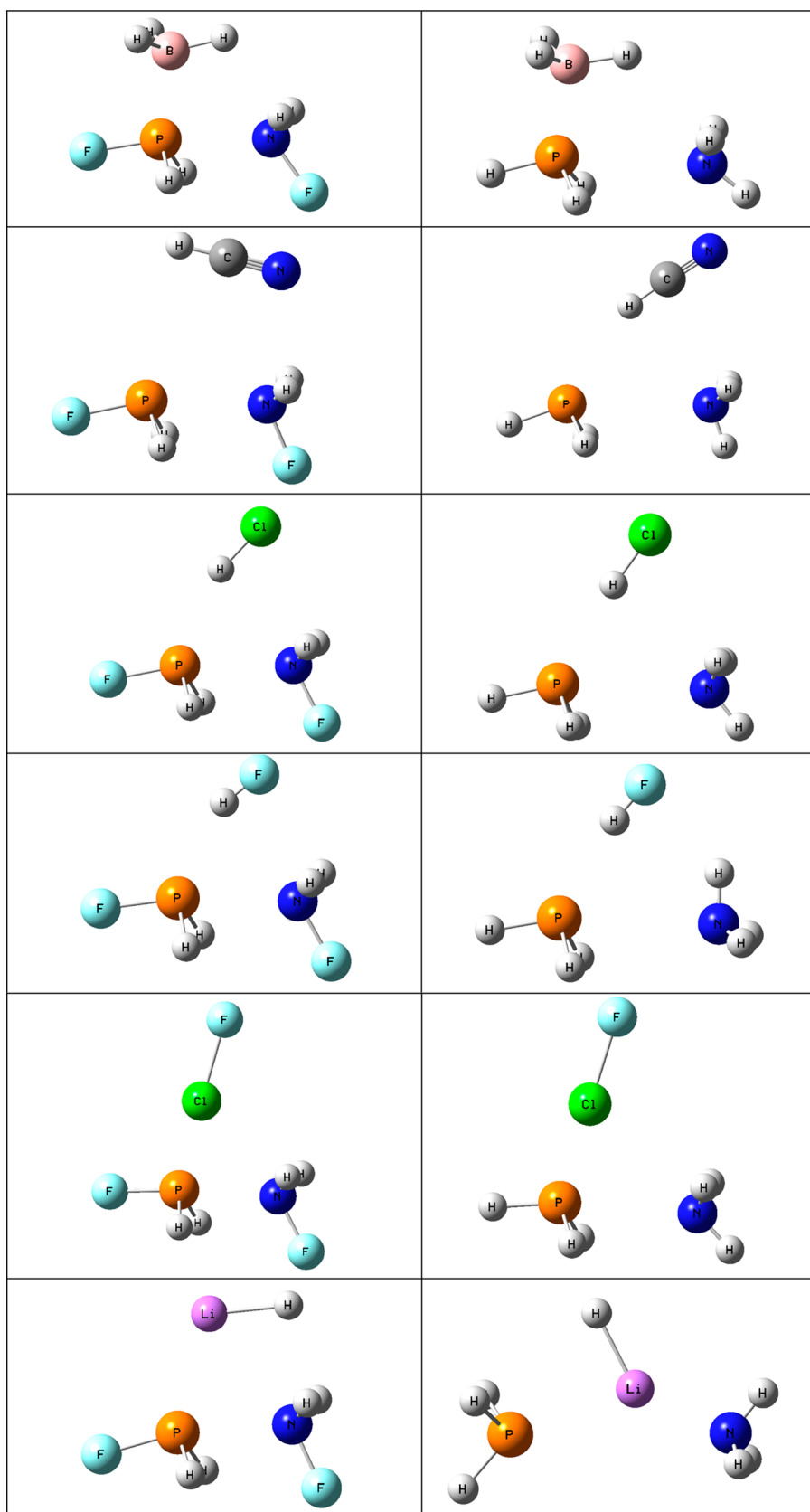
For binary complexes:

$$\Delta E(P-N) = E(\text{H}_2\text{FP:NFH}_2) - E(\text{PH}_2\text{F}) - E(\text{NH}_2\text{F}) \quad (3)$$

$$\Delta E(P-LA) = E(\text{LA:PH}_2\text{F}) - E(\text{PH}_2\text{F}) - E(\text{LA}) \quad (4)$$

It is important to note that eqs 1 and 2 for the formation of a ternary complex from a binary complex and an isolated monomer implicitly assume that the binding energy of the binary complex is unchanged in the ternary complex. Consequences of this assumption will be discussed below.

**Structures of Complexes with Hydrogen Bonding Lewis Acids. X–H...P Hydrogen Bonds.** Of the six Lewis acids considered in this study, three are possible proton donors for



**Figure 2.** Complexes  $\text{LA}:\text{H}_2\text{FP}:\text{NHF}_2$  and  $\text{LA}:\text{H}_3\text{P}:\text{NH}_3$ .

hydrogen bond formation:  $\text{NCH}$ ,  $\text{ClH}$ , and  $\text{FH}$ . An ideal  $\text{X}-\text{H}\cdots\text{Y}$  hydrogen bond is one in which these three atoms are arranged linearly, as measured by the angle  $\text{H}-\text{X}-\text{Y}$ , which has

a value of  $0^\circ$  when the hydrogen bond is linear. Figure 2 and the structural data of Table 1 suggest that the complex  $\text{NCH}:\text{H}_2\text{FP}:\text{NHF}_2$  is not hydrogen-bonded at all since the

**Table 2. Distances ( $R$ , Å), Angles ( $\angle$ , deg), and P–LA Reaction Energies [ $\Delta E(\text{P–LA})$ , kJ mol $^{-1}$ ] for the Formation of the Binary Complexes LA:PH $_2$ F and LA:PH $_3$**

LA:PH $_2$ F			
complex	$R(\text{P–LA})$	$\angle$	$\Delta E(\text{P–LA})$
LA = BH $_3$	1.865 <sup>a</sup>		−134.55
NCH	3.936 <sup>b</sup>	3 <sup>b</sup>	−8.77
ClH	3.836 <sup>c</sup>	3 <sup>c</sup>	−12.33
FH	3.284 <sup>d</sup>	3 <sup>d</sup>	−18.48
FCl	3.942 <sup>e</sup>	3 <sup>e</sup>	−71.11
HLi	4.298 <sup>f</sup>	0 <sup>f</sup>	−33.40 <sup>g</sup>
LA:PH $_3$ <sup>h</sup>			
complex	$R(\text{P–LA})$		$\Delta E(\text{P–LA})$
LA = BH $_3$	1.936		−107.18
NCH	3.881		−11.41
ClH	3.800		−14.86
FH	3.271		−21.39
FCl	4.034		−51.19
HLi	4.270		−40.54

<sup>a</sup>The P–B distance. <sup>b</sup>The P–C distance and  $\angle\text{H–C}\cdots\text{P}$ . <sup>c</sup>The P–Cl distance and  $\angle\text{H–Cl}\cdots\text{P}$ . <sup>d</sup>The P–F distance and  $\angle\text{H–F}\cdots\text{P}$ . <sup>e</sup>The P–F distance and  $\angle\text{Cl–F}\cdots\text{P}$ . <sup>f</sup>The P–H distance and  $\angle\text{Li–H}\cdots\text{P}$ . <sup>g</sup>Energies derived from a constrained optimized HLi:PFH $_2$  structure with H–Li–P linear. <sup>h</sup>All complexes have C $_{3v}$  symmetry.

H–C $\cdots$ P angle is 75°. Rather, NCH appears to be almost parallel to the P $\cdots$ N bond. Moreover, both ClH and FH form distorted X–H $\cdots$ P hydrogen bonds with H $_2$ FP:NFH $_2$ , as indicate by the H–Cl–P and H–F–P angles of 13 and 17°, respectively. The nonlinearity of these bonds may be attributed to secondary interactions involving Cl and F with the positively charged H atoms of NH $_2$ F. This interaction is particularly strong for NCH and is the primary interaction stabilizing this complex.

In contrast to the complexes with H $_2$ FP:NFH $_2$ , all three possible hydrogen-bonding Lewis acids form hydrogen bonds with H $_3$ P:NH $_3$ . This bond is distorted by 16° when NCH is the acid, a result of the interaction of N with the H atoms of NH $_3$ . The deviation of hydrogen bonds from linearity by 4 and 8° for complexes with ClH and FH, respectively, indicates a weakening of the interaction of Cl and F with the H atoms of NH $_3$ .

Intermolecular hydrogen bond distances in binary complexes with PH $_3$  are shorter than corresponding distances with PH $_2$ F, a reflection of the electron-withdrawing effect of F. These distances in ternary complexes are shorter than those in the corresponding binary complexes, while those in the ternary complexes formed with H $_2$ FP:NFH $_2$  are shorter than those in complexes with H $_3$ P:NH $_3$ . There is also an interesting structural difference between binary and ternary complexes. In all of the binary complexes, P acts as the electron-pair donor through an sp $^3$  hybridized orbital. The P atom is four-coordinated, that is, the geometry around P is tetrahedral, with one intermolecular bond. The hydrogen-bonded LA:H $_2$ FP:NFH $_2$  and LA:H $_3$ P:NH $_3$  complexes may be viewed as involving a five-coordinated P, that is, they have a distorted trigonal bipyramidal geometry, with two intermolecular bonds.

**P–N Phicogen Bonds.** Just as the reaction energies for the ternary complexes, which result in the formation of a bond between P and the Lewis acid, increase in going from the binary to the corresponding ternary complexes, so too do the reaction energies for NCH, ClH, and FH interacting at P lead to greater

P–N reaction energies in the ternary complexes relative to the corresponding binary complexes H $_2$ FP:NFH $_2$  and H $_3$ P:NH $_3$ . However, the differences among these interaction energies in each series of ternary complexes are small.

What is interesting and puzzling at the same time is the variation of the P–N distances in these complexes. If the reaction energies are a measure of the strength of the P $\cdots$ N bond, then it would be expected that the strengthening of this bond in the ternary complexes should lead to a shortening of P–N distances, but this is not necessarily the case. For example, the P–N distance of 2.524 Å in the parent complex H $_2$ FP:NFH $_2$  lengthens to 2.568 and 2.541 Å in the complexes with NCH and ClH, but shortens to 2.503 Å in the complex with FH. Similarly, the P–N distance of 3.292 Å in H $_3$ P:NH $_3$  increases to 3.332 Å in the complex with NCH, but decreases to 3.192 and 3.194 Å in the complexes with ClH and FH, respectively. These structural curiosities will be discussed below following a discussion of the reaction energies and their relationship to the strength of the P $\cdots$ N bond.

### Structures of Complexes with a Halogen Bonding Lewis Acid. P $\cdots$ Cl–F Halogen Bonds.

A P $\cdots$ Cl–F halogen bond may potentially form in binary complexes FCl:PH $_2$ F and FCl:PH $_3$ , and in ternary complexes FCl:H $_2$ FP:NFH $_2$  and FCl:H $_3$ P:NH $_3$ . In the binary complexes FCl:PH $_2$ F and FCl:PH $_3$ , F–P distances are 3.942 and 4.034 Å, and the F–Cl distances are 1.903 and 1.852 Å, respectively, a rather significant elongation relative to the F–Cl distance of 1.638 Å in isolated FCl. The elongation of the F–Cl bond suggests that the P–Cl halogen bonds are quite strong. Moreover, the binding energies of the halogen bonds in the binary complexes FCl:PH $_2$ F and FCl:PH $_3$  are 71.1 and 51.2 kJ mol $^{-1}$ , respectively, significantly stronger than the halogen bonds in the complexes FCl:NH $_2$ F and FCl:NH $_3$ , which are 8.3 and 11.8 kJ mol $^{-1}$ . The F–Cl distances in the nitrogen complexes are also much shorter at 1.688 and 1.713 Å, respectively.<sup>50</sup>

It is also not surprising to see that F–Cl distances elongate further to 1.930 and 1.898 Å, respectively, in the ternary complexes FCl:H $_2$ FP:NFH $_2$  and FCl:H $_3$ P:NH $_3$ . These distance changes result in P–Cl distances of 2.089 and 2.137 Å, respectively, which are similar to the covalent P–Cl bond distances in PFCIH and PH $_2$ Cl of 2.057 and 2.076 Å, respectively, computed at the same level of theory. Thus, in both ternary complexes, but particularly in FCl:H $_2$ FP:NFH $_2$ , formation of a halogen bond results essentially in Cl transfer to P. A similar situation was found in binary FCl:CNH and some ternary FCl:CNH:Z complexes for Z an electron-donating substituent.<sup>51</sup>

**P $\cdots$ N Phicogen Bonds.** The formation of a P–Cl bond with significant covalent character has a dramatic effect on the P $\cdots$ N bond. Thus, the P–N distance of 2.524 Å in H $_2$ FP:NFH $_2$  decreases to 2.274 Å in FCl:H $_2$ FP:NFH $_2$ . This shortening is reminiscent of the effect of the formation of three F–H $\cdots$ F hydrogen bonds at P–F in 3FH:H $_2$ FP:NFH $_2$ , a complex that has an even shorter P–N distance of 2.143 Å.<sup>32</sup>

### Structures of Complexes with a Lithium Bonding Lewis Acid. P $\cdots$ Li–H Lithium Bonds.

HLi does not form a stable binary complex with an H–Li $\cdots$ P lithium bond with PH $_2$ F since an atom-transfer reaction occurs. An optimized structure with H–Li $\cdots$ P constrained to be linear has an H–P distance of 4.298 Å. HLi does form a stable binary complex with PH $_3$  with an H–P distance of 4.270 Å.

The ternary complexes of HLi with H $_2$ FP:NFH $_2$  and H $_3$ P:NH $_3$  are equilibrium structures, but neither HLi:H $_2$ FP:NFH $_2$  nor HLi:H $_3$ P:NH $_3$  has an H–Li $\cdots$ P lithium bond, as can be seen from



Figure 2 and the data of Table 1. The Li–H⋯P angles for a lithium bond should also be near 0° but have values of 43 and 62° in these two complexes, respectively. Interaction of HLi with H<sub>2</sub>FP:NFH<sub>2</sub> leads to a complex with a structure similar to that of the complex NCH:H<sub>2</sub>FP:NFH<sub>2</sub>, with HLi nearly parallel to the P⋯N bond. Thus, it would appear that there is a stabilizing electrostatic interaction between the hydridic H of HLi and the very positively charged H atoms of NH<sub>2</sub>F. Interaction of HLi with H<sub>3</sub>P:NH<sub>3</sub> leads to a complex in which HLi essentially inserts into the P⋯N bond and appears to interact more strongly with N than with P.

**P⋯N Bonds.** The P–N distance in HLi:H<sub>2</sub>FP:NFH<sub>2</sub> is short at 2.378 Å. In contrast, the P–N distance in HLi:H<sub>3</sub>P:NH<sub>3</sub> is very long at 4.325 Å since the insertion of HLi essentially destroys the P–N bond.

**Interaction with a Covalent Bonding Lewis Acid. P–B Bonds.** Since BH<sub>3</sub> is an electron-deficient molecule, it may be anticipated that electron-pair donation by P results in a dative P–B covalent bond. This can be seen by comparing the computed P–B distances in the molecules H<sub>2</sub>P–BH<sub>2</sub> (1.865 Å) and FHP–BFH (1.927 and 1.936 Å in the *Z* and *E* forms, respectively) with the distances in the binary complexes. The P–B distances in BH<sub>3</sub>:PH<sub>2</sub>F and BH<sub>3</sub>:PH<sub>3</sub> are similar at 1.865 and 1.936 Å, respectively, with the shorter distance found in the complex with PH<sub>2</sub>F. In contrast to the usual trend of decreasing distance in going from the binary to the ternary complexes, the B–P distances increase to 1.920 and 1.942 Å, respectively, in the complexes BH<sub>3</sub>:H<sub>2</sub>FP:NFH<sub>2</sub> and BH<sub>3</sub>:H<sub>3</sub>P:NH<sub>3</sub>.

**P⋯N Bonds.** The formation of the P–B bond shortens the P–N distances in the ternary complexes. Thus, the P–N distances in the parent complexes H<sub>2</sub>FP:NFH<sub>2</sub> and H<sub>3</sub>P:NH<sub>3</sub> of 2.524 and 3.292 Å, respectively, decrease in BH<sub>3</sub>:H<sub>2</sub>FP:NFH<sub>2</sub> and BH<sub>3</sub>:H<sub>3</sub>P:NH<sub>3</sub> to 2.413 and 3.098 Å, respectively.

**Energies.** The energies reported in Table 1 are the reaction energies for the formation of ternary complexes from the corresponding binary complex and monomer. Thus, these are not the bond energies for either the P⋯N or P⋯LA bonds in the ternary complexes. Rather, the computed values are interdependent. Their interdependence can be derived and easily demonstrated by computing the change in the P–N and P–LA reaction energies in the ternary complexes relative to the corresponding binary complexes. Using H<sub>2</sub>FP:NFH<sub>2</sub> and PH<sub>2</sub>F as an example

$$\begin{aligned} \delta\Delta E(\text{P–N}) &= \Delta E[(\text{P–N}), \text{LA:H}_2\text{FP:NFH}_2] \\ &\quad - \Delta E[(\text{P–N}), \text{H}_2\text{FP:NFH}_2] \end{aligned} \quad (5)$$

$$\begin{aligned} \delta\Delta E(\text{P–LA}) &= \Delta E[(\text{P–LA}), \text{LA:H}_2\text{FP:NFH}_2] \\ &\quad - \Delta E[(\text{P–LA}), \text{LA:PFH}_2] \end{aligned} \quad (6)$$

For a given Lewis acid,  $\delta\Delta E(\text{P–N}) = \delta\Delta E(\text{P–LA})$ . Thus, neither the reaction energies nor the change in the reaction energies for ternary complexes relative to the corresponding binary complexes provide information about the strengths of the P⋯N or P⋯LA bonds in these ternary complexes. What other approaches might provide some insight into the energetics of these complexes?

**Cooperativity.** As evident from Table 1, the formation of a ternary complex from the corresponding binary complex and monomer is an exothermic process. The classical cooperative effect,  $\Delta E_i$ , computed as

$$\Delta E_i = \Delta E(\text{ternary}) - \sum \Delta E(\text{binary}) \quad (7)$$

is always negative, as evident from Table 3. Thus, these data suggest that the formation of these two bonds has a synergistic effect.

**Table 3. Classical ( $\Delta E_i$ ) Cooperativity (kJ mol<sup>−1</sup>) for All Ternary Complexes and Estimated P⋯N [ $\Delta E'(\text{P⋯N})$ ] and P⋯LA [ $\Delta E'(\text{P⋯LA})$ , kJ mol<sup>−1</sup>] Bond Energies for Complexes LA:H<sub>2</sub>FP:NFH<sub>2</sub>**

LA:H <sub>2</sub> FP:NFH <sub>2</sub>	$\Delta E_i^a$	$\Delta E'(\text{P⋯N})^b$	$\Delta E'(\text{P⋯LA})^c$
LA = BH <sub>3</sub>	−10.16	−31.9	−129.3
NCH	−15.88	−23.8	−11.6
ClH	−16.09	−24.9	−14.1
FH	−19.67	−26.6	−18.5
FCI	−32.29	−43.1	−54.7
HLi	−58.88 <sup>d</sup>	−34.3	−25.8
<hr/>			
LA:H <sub>3</sub> P:NH <sub>3</sub>	$\Delta E_i$		
LA = BH <sub>3</sub>	−13.70		
NCH	−10.57		
ClH	−10.18		
FH	−12.67		
FCI	−27.19		
HLi	−63.27		

<sup>a</sup>Computed from eq 7. <sup>b</sup>Equation 8 gives a P⋯N bond energy of −25.6 kJ mol<sup>−1</sup> for H<sub>2</sub>FP:NFH<sub>2</sub>, which is about 1 kJ mol<sup>−1</sup> less than the energy of −26.7 kJ mol<sup>−1</sup> computed from eq 3. <sup>c</sup>Computed from eq 9. <sup>d</sup>Based on a constrained optimized HLi:PH<sub>2</sub>F complex.

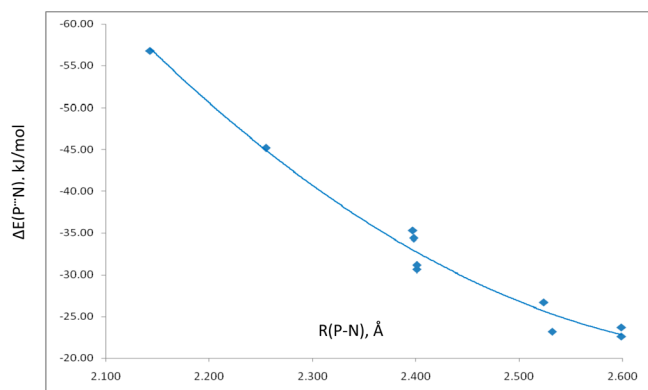
However, the nonadditivity may not be as large as computed since this calculation ignores any interaction of the Lewis acid with the NH<sub>2</sub>F or NH<sub>3</sub> molecules. These interactions appear to be significant in complexes of the Lewis acids NCH, ClH, FH, and HLi with H<sub>2</sub>FP:NFH<sub>2</sub>, and even with H<sub>3</sub>P:NH<sub>3</sub>, but to a less extent, as noted above.

**Estimating P⋯N and P⋯LA Bond Energies in Complexes LA:H<sub>2</sub>FP:NFH<sub>2</sub>.** Although we have computed second-order interaction energies employing the many-body interaction energy model of Stillinger et al.,<sup>52</sup> in an attempt to assess the strength of all bonds (P⋯N, P⋯LA, and N⋯LA), this analysis is appropriate only for weak interactions<sup>53</sup> and not strong ones such as those involving the Lewis acids BH<sub>3</sub>, FCI, and HLi. In addition, this analysis indicates that in each series the strongest P⋯N bond is found in the parent complexes H<sub>2</sub>FP:NFH<sub>2</sub> and H<sub>3</sub>P:NH<sub>3</sub>, even though the P–N distance can be significantly shorter in complexes containing the Lewis acid. This result is contrary to distance–energy relationships in general.

In order to obtain more realistic P⋯N bond energies, we have estimated these energies for complexes LA:H<sub>2</sub>FP:NFH<sub>2</sub> from distances and P⋯N energies of complexes nFH:H<sub>2</sub>FP:NFH<sub>2</sub>.<sup>32</sup> These complexes have F–P⋯N–F linear as do the LA:H<sub>2</sub>FP:NFH<sub>2</sub> complexes and are appropriate for comparison purposes. Figure 3 presents the plot of  $\Delta E(\text{P⋯N})$  versus the P–N distance [ $R(\text{P–N})$ ] for these complexes. The equation of the trendline is

$$\begin{aligned} \Delta E'(\text{P⋯N}) &= -97.75R(\text{P–N})^2 + 538.7R(\text{P–N}) - 762.6 \\ n &= 10, R^2 = 0.980 \end{aligned} \quad (8)$$

The P⋯N bond energies in complexes LA:H<sub>2</sub>FP:NFH<sub>2</sub> estimated from this equation are given in Table 3. These energies are significantly less than the reaction energies computed from eq 1, as they should be. It is important to note the significant reduction in the P⋯N bond energies in complexes with the



**Figure 3.**  $\Delta E(\text{P}\cdots\text{N})$  versus  $R(\text{P}-\text{N})$  for complexes  $\text{nFH}:\text{H}_2\text{FP}:\text{NFH}_2$ . Data taken from ref 32.

potential hydrogen-bonding Lewis acids, NCH, ClH, and FH. As noted above, NCH does not form a hydrogen bond with P, and both ClH and FH form very nonlinear hydrogen bonds due to interaction with  $\text{NH}_2\text{F}$ . Of these three acids, only FH strengthens the  $\text{P}\cdots\text{N}$  bond relative to the parent, but by only  $1 \text{ kJ mol}^{-1}$ .

We have also estimated the strength of the bond between P and the Lewis acid using the equation

$$\Delta E'(\text{P}\cdots\text{LA}) = \Delta E(\text{ternary}) - \Delta E_i - \Delta E'(\text{P}\cdots\text{N}) \quad (9)$$

where  $\Delta E(\text{ternary})$  is the total binding energy of the ternary complex relative to the corresponding isolated monomers,  $\Delta E_i$  is the cooperativity, and  $\Delta E'(\text{P}\cdots\text{N})$  is the P–N bond energy estimated from eq 8. The  $\Delta E'(\text{P}\cdots\text{LA})$  values, which are also reported in Table 3, are overestimated since interaction between LA and the  $\text{NH}_2\text{F}$  molecule has been neglected. Nevertheless, it is interesting to note that for the hydrogen-bonding Lewis acids, the order of interaction energies is  $\text{NCH} < \text{ClH} < \text{FH}$ , even though the interaction of NCH with P does not involve hydrogen-bond formation, and the hydrogen bonds in the complexes with ClH and FH are nonlinear due to interaction with  $\text{NH}_2\text{F}$ . The strongest interaction occurs with  $\text{BH}_3$  when a covalent bond forms between P and B. Next in order of bond energies is that between P and FCl, in which case partial Cl transfer occurs to form a P–Cl bond with significant covalent character. The interaction energy of HLi with P is also most probably overestimated, as implied by the structure of this complex.

Because complexes  $\text{LA}:\text{H}_3\text{P}:\text{NH}_3$  have H–P $\cdots$ N–H linear and much longer P–N distances than found in Figure 3, eq 8 cannot be used to estimate P $\cdots$ N bond energies for these complexes. Unfortunately, we do not have other data that would suffice for this purpose.

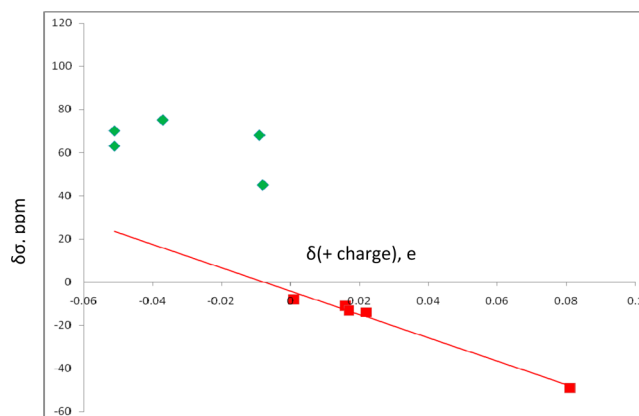
**Absolute Chemical Shieldings.** The absolute chemical shieldings of  $^{31}\text{P}$  and  $^{15}\text{N}$  atoms are reported in Table 4. The presence or absence of a fluorine atom in the complexes determines the regions in which these NMR signals appear.

All  $^{31}\text{P}$  shieldings for the  $\text{LA}:\text{H}_2\text{FP}:\text{NFH}_2$  ternary complexes are greater than shieldings for the  $\text{LA}:\text{PH}_2\text{F}$  binary complexes. In contrast, shieldings for ternary complexes  $\text{LA}:\text{H}_3\text{P}:\text{NH}_3$  are reduced relative to the corresponding  $\text{LA}:\text{PH}_3$  shieldings. These trends are consistent with the NBO charges on P in binary and ternary complexes. An increase in the positive charge on P leads to decreased shielding, while a decrease in the positive charge on P leads to an increased shielding. A linear correlation is found between the change in the  $^{31}\text{P}$  chemical shielding and the change in the positive charge on P in going from  $\text{LA}:\text{PH}_3$  to  $\text{LA}:\text{H}_3\text{P}:\text{NH}_3$ ,

**Table 4.**  $^{31}\text{P}$  and  $^{15}\text{N}$  Absolute Chemical Shieldings (ppm)

	$\text{LA}:\text{PH}_2\text{F}$		$\text{LA}:\text{H}_2\text{FP}:\text{NFH}_2$	
	$^{31}\text{P}$		$^{31}\text{P}$	$^{15}\text{N}$
parent			339.7	79.9
LA = $\text{BH}_3$	285.8		330.8	84.1
NCH	276.4		339.0	76.8
ClH	278.5		353.1	66.3
FH	278.7		349.0	80.7
FCl	313.7		381.4	75.8
	$\text{LA}:\text{PH}_3$		$\text{LA}:\text{H}_3\text{P}:\text{NH}_3$	
	$^{31}\text{P}$		$^{31}\text{P}$	$^{15}\text{N}$
parent			623.9	271.6
LA = $\text{BH}_3$	500.1		492.2	266.0
NCH	625.4		614.5	267.1
ClH	621.1		607.1	267.2
FH	615.1		602.5	270.1
FCl	515.3		466.0	250.3

as illustrated in Figure 4. Although the shielding of  $^{31}\text{P}$  increases as the positive charge on P decreases in going from the binary



**Figure 4.**  $^{31}\text{P}$  chemical shielding in ternary complexes  $\text{LA}:\text{H}_2\text{FP}:\text{NFH}_2$  and  $\text{LA}:\text{H}_3\text{P}:\text{NH}_3$  minus that in the corresponding binary complexes  $\text{LA}:\text{PH}_2\text{F}$  and  $\text{LA}:\text{PH}_3$  ( $\delta\sigma$ ) versus the positive charge on P in the corresponding ternary complexes minus that in the corresponding binary complexes [ $\delta(+ \text{ charge})$ ]. ♦,  $\text{LA}:\text{H}_2\text{FP}:\text{NFH}_2$ ; ■,  $\text{LA}:\text{H}_3\text{P}:\text{NH}_3$ . The correlation coefficient  $R^2$  of the trendline for  $\text{LA}:\text{H}_3\text{P}:\text{NH}_3$  complexes is 0.982.

complex  $\text{LA}:\text{PH}_2\text{F}$  to the corresponding ternary complex  $\text{LA}:\text{H}_2\text{FP}:\text{NFH}_2$ , Figure 4 indicates that these two variables are not well correlated for this series. Changes in  $^{15}\text{N}$  chemical shieldings do not correlate with changes in the negative charges on N in going from the binary to the corresponding ternary complexes.

**Spin–Spin Coupling Constants  $^{10}\text{J}(\text{P}-\text{N})$ .** Values of  $^{10}\text{J}(\text{P}-\text{N})$  and its components for the binary parent complexes  $\text{H}_2\text{FP}:\text{NFH}_2$  and  $\text{H}_3\text{P}:\text{NH}_3$ , the ternary complexes  $\text{LA}:\text{H}_3\text{P}:\text{NH}_3$ , and selected complexes  $\text{LA}:\text{H}_2\text{FP}:\text{NFH}_2$ , are reported in Table 5. These data indicate that the FC term is an excellent approximation to  $^{10}\text{J}(\text{P}-\text{N})$  for these complexes. Therefore, only the FC terms have been computed for the remaining complexes  $\text{LA}:\text{H}_2\text{FP}:\text{NFH}_2$ . It is the FC terms that will be compared below.

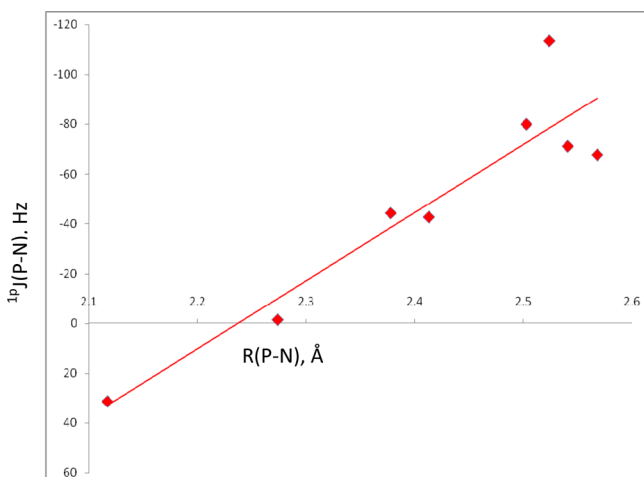
Our previous studies of  $^{10}\text{J}(\text{P}-\text{P})$  for complexes  $(\text{PH}_2\text{X})_2$  and  $(\text{PFHX})_2$  and  $^{10}\text{J}(\text{P}-\text{N})$  for complexes  $\text{H}_2\text{XP}:\text{NXH}_2$  with a variety of substituents X indicate that both of these coupling constants increase with decreasing P–P or P–N distance. This is a general relationship for two-bond coupling constants across

**Table 5.**  $^1J(\text{P-N})$  and Its Components (Hz) and the P–N Distance [ $R(\text{P-N})$ , (Å)] for Complexes  $\text{LA:H}_2\text{FP:NFH}_2$  and  $\text{LA:H}_3\text{P:NH}_3$ <sup>a</sup>

LA:H <sub>2</sub> FP:NFH <sub>2</sub> complexes						
	$R(\text{P-N})$	PSO	DSO	FC	SD	$^1J(\text{P-N})$
parent	2.524	−0.1	−0.1	−113.5	0.0	−113.6
LA = BH <sub>3</sub>	2.413	−0.2	−0.1	−42.7	−0.1	−43.1
NCH	2.568			−67.6		
ClH	2.541			−71.1		
FH	2.503	−0.1	−0.1	−79.9	0.1	−80.1
FCl	2.274			−1.3		
HLi	2.378			−44.4		
LA:H <sub>3</sub> P:NH <sub>3</sub> complexes						
	$R(\text{P-N})$	PSO	DSO	FC	SD	$^1J(\text{P-N})$
parent	3.292	0.0	0.0	−117.5	0.0	−117.5
LA = BH <sub>3</sub>	3.098	0.0	0.0	−112.6	0.1	−112.5
NCH	3.332	0.0	0.0	−112.8	0.1	−112.7
ClH	3.192	0.0	0.0	−119.4	0.1	−119.3
FH	3.194	0.0	0.0	−120.6	0.1	−120.5
FCl	2.888	−10.1	0.0	−113.7	0.1	−113.7
HLi	4.325	0.0	0.0	0.6	0.0	0.6

<sup>a</sup>For an optimized cationic complex  $(\text{H}_2\text{ClFP})^+:\text{NH}_2\text{F}$ , the P–N distance is 2.117 Å, FC = 31.2 Hz, and total  $^1J(\text{P-N}) = 29.4$  Hz.

intermolecular bonds in a related series of complexes, as extensively demonstrated for  $^2J(\text{X-Y})$  versus the X–Y distance for coupling across X–H...Y hydrogen bonds.<sup>54</sup> However, it is apparent from the data of Table 5 that this is not the case for the complexes  $\text{LA:H}_2\text{FP:NFH}_2$  and  $\text{LA:H}_3\text{P:NH}_3$ . Figure 5 presents a plot of

**Figure 5.**  $^1J(\text{P-N})$  vs  $R(\text{P-N})$  for complexes  $\text{LA:H}_2\text{FP:NFH}_2$  and including  $(\text{H}_2\text{ClFP})^+:\text{NH}_2\text{F}$ . The correlation coefficient  $R^2 = 0.857$ .

$^1J(\text{P-N})$  versus the P–N distance for complexes  $\text{LA:H}_2\text{FP:NFH}_2$ , clearly illustrating that  $^1J(\text{P-N})$  decreases as the P–N distance decreases. The parent complex  $\text{H}_2\text{FP:NFH}_2$  has one of the longer P–N distances but the largest absolute value (−114 Hz) of  $^1J(\text{P-N})$ , while  $\text{FCl:H}_2\text{FP:NFH}_2$  has the shortest P–N distance but the smallest absolute value of  $^1J(\text{P-N})$  (−1 Hz).

Some insight into this unusual behavior for coupling across these pnictogen bonds can be obtained from two previous studies in which  $(\text{PH}_2\text{F})_2$  and  $\text{H}_2\text{FP:NFH}_2$  were hydrogen-bonded to 1, 2, or 3 FH molecules at P–F or N–F.<sup>26,32</sup>

For complexes  $n\text{FH}:(\text{PH}_2\text{F})_2$ ,  $^1J(\text{P-P})$  decreased in absolute value and  $R(\text{P-P})$  also decreased as the number of FH molecules bonded to the same P–F bond increased. In these complexes  $^1J(\text{P-P})$  was shown to approach  $^1J(\text{P-P})$  for the covalent P–P bond in the molecule  $\text{P}_2\text{H}_4$ . A similar situation occurred but to a lesser extent in  $3\text{FH}:(\text{H}_2\text{FP:NFH}_2)$  when all FH molecules were bonded to the same P–F bond. Once again,  $^1J(\text{P-N})$  approaches  $^1J(\text{P-N})$  for  $\text{H}_2\text{P-NH}_2$ .

The smallest absolute value of  $^1J(\text{P-N})$  is found for the complex  $\text{FCl:H}_2\text{FP:NFH}_2$ , which has the shortest P–N distance. As noted above, the P–Cl bond in this complex has significant covalent character as indicated by its short P–Cl and long Cl–F distances of 2.089 and 4.019 Å, respectively. The computed NBO charge on F of FCl is −0.66e. To further investigate the small value of  $^1J(\text{P-N})$  in this complex, we optimized the structure of the cation  $(\text{H}_2\text{ClFP})^+$  and the cationic complex  $(\text{H}_2\text{ClFP})^+:\text{NH}_2\text{F}$ . In these, the P–Cl distances are 1.930 and 1.979 Å, respectively. The P–N distance decreases to 2.117 Å in  $(\text{H}_2\text{ClFP})^+:\text{NH}_2\text{F}$ , and  $^1J(\text{P-N})$  is +31.2 Hz with total  $J$  equal to 29.4 Hz. The data point for this cationic complex has been included in Figure 5. Thus, it appears that if  $\text{H}_2\text{FP:NFH}_2$  acts as a Lewis base either at P–F or at P, the interaction tends to produce decreasing absolute values of  $^1J(\text{P-N})$  with decreasing P–N distance.

$^1J(\text{P-N})$  values have also been computed for complexes  $\text{LA:H}_3\text{P:NH}_3$ . In this series,  $^1J(\text{P-N})$  values vary by only 8 Hz if the complex  $\text{HLi:H}_3\text{P:NH}_3$  is omitted since it does not have a P...N bond. There is no correlation between P–N distances and  $^1J(\text{P-N})$  values in this series.  $\text{FCl:H}_3\text{P:NH}_3$ , which has the shortest P–N distance of 2.888 Å, has neither the largest nor the smallest coupling constant. The very different behavior of  $^1J(\text{P-N})$  in these two series must be due in large part to the stabilizing effect of the linear F–P...N–F alignment in complexes  $\text{LA:H}_2\text{FP:NFH}_2$  compared to the linear H–P...N–H alignment in  $\text{LA:H}_3\text{P:NH}_3$ . The F–P...N–F alignment promotes ground-state charge transfer from the N lone pair to the antibonding  $\sigma^*$  P–F orbital. This interaction influences the s electron densities on P and N both in the ground state and in those excited states which couple to it through the Fermi-contact operator.

## CONCLUSIONS

In this study, we have carried out ab initio MP2/aug-cc-pVTZ calculations to investigate the structures and energies of complexes  $\text{LA:H}_2\text{FP:NFH}_2$  and  $\text{LA:H}_3\text{P:NH}_3$  in which a pnictogen-bonded P also acts as an electron-pair donor to a Lewis acid (LA), for LA = BH<sub>3</sub>, NCH, ClH, FH, FCl, and HLi. We have also examined the effect of interaction of P with the Lewis acid on  $^{31}\text{P}$  and  $^{15}\text{N}$  absolute chemical shieldings and spin–spin coupling constants  $^1J(\text{P-N})$  across pnictogen bonds. These calculations support the following statements.

(1)  $\text{H}_3\text{P:NH}_3$  forms hydrogen bonds at P with the Lewis acids NCH, ClH, and FH. ClH and FH form distorted hydrogen bonds at P with  $\text{H}_2\text{FP:NFH}_2$  due to interaction of these two acids with the positively charged H atoms of  $\text{NFH}_2$ . NCH does not form a hydrogen bond with  $\text{H}_2\text{FP:NFH}_2$ .

(2) BH<sub>3</sub> interacts with the P atoms of  $\text{H}_2\text{FP:NFH}_2$  and  $\text{H}_3\text{P:NH}_3$  by forming a covalent bond. The interaction of FCl with these complexes leads to significant Cl transfer to P and a P–Cl bond with significant covalent character.

(3) The geometries of these complexes change from tetrahedral about P in the binary complexes, to distorted trigonal bipyramidal about the P, which acts as the Lewis base in the ternary complexes.



(4) Neither  $\text{H}_2\text{FP:NHF}_2$  nor  $\text{H}_3\text{P:NH}_3$  forms an  $\text{H}\cdots\text{Li}\cdots\text{P}$  lithium bond. Rather, in  $\text{HLi:H}_2\text{FP:NHF}_2$ ,  $\text{HLi}$  is nearly parallel to the  $\text{P}\cdots\text{N}$  bond, with the hydridic  $\text{H}$  interacting with the  $\text{H}$  atoms of  $\text{NH}_2\text{F}$ .  $\text{HLi}$  inserts into the  $\text{P}\cdots\text{N}$  bond of  $\text{H}_3\text{P:NH}_3$  and interacts more strongly with  $\text{N}$ .

(5) The classical cooperativity indicates that the  $\text{P}\cdots\text{N}$  and  $\text{P}\cdots\text{LA}$  binding energies have a synergistic effect, although this effect is most probably overestimated due to the neglect of the interaction of the Lewis acid with  $\text{NH}_2\text{F}$ , which can be significant in some cases. It appears that the hydrogen-bonding acids  $\text{NCH}$ ,  $\text{ClH}$ , and  $\text{FH}$  have little effect on the energy of the  $\text{P}\cdots\text{N}$  bond in complexes  $\text{LA:H}_2\text{FP:NHF}_2$ , while interaction with the Lewis acids  $\text{BH}_3$ ,  $\text{FCl}$ , and  $\text{HLi}$  strengthens the  $\text{P}\cdots\text{N}$  bond.

(6) The absolute chemical shieldings of  $^{31}\text{P}$  increase in going from binary  $\text{LA:PH}_2\text{F}$  to ternary  $\text{LA:H}_2\text{FP:NHF}_2$  complexes as the positive charge on  $\text{P}$  decreases. In contrast, chemical shieldings decrease in ternary complexes  $\text{LA:H}_3\text{P:NH}_3$  relative to  $\text{LA:PH}_3$  as the positive charge on  $\text{P}$  increases. Changes in  $^{15}\text{N}$  chemical shieldings and changes in negative charges on  $\text{N}$  in going from binary to the corresponding ternary complexes do not correlate.

(7) For complexes  $\text{LA:H}_2\text{FP:NHF}_2$ ,  $^{1\text{p}}\text{J}(\text{P}\cdots\text{N})$  coupling constants vary by more than 100 Hz and decrease as the  $\text{P}\cdots\text{N}$  distance decreases. The smallest absolute value of  $^{1\text{p}}\text{J}(\text{P}\cdots\text{N})$  is found for  $\text{FCl:H}_2\text{FP:NHF}_2$ , which has the shortest  $\text{P}\cdots\text{N}$  distance. Its value approaches the value of  $^{1\text{p}}\text{J}(\text{P}\cdots\text{N})$  for the cationic complex  $(\text{H}_2\text{ClFP})^+:\text{NH}_2\text{F}$ . These coupling constants decrease with distance in a manner similar to those of complexes in which intermolecular interactions occur through hydrogen-bond formation at  $\text{P}\cdots\text{F}$ . There is little variation in  $^{1\text{p}}\text{J}(\text{P}\cdots\text{N})$  for complexes  $\text{LA:H}_3\text{P:NH}_3$  and no correlation between the values of this coupling constant and the  $\text{P}\cdots\text{N}$  distance.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

MP2/aug'-cc-PVTZ structures and energies of binary and ternary complexes, and full refs 40, 43, and 49. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [jedelbene@ysu.edu](mailto:jedelbene@ysu.edu) (J.E.D.B.); [ibon@iqm.csic.es](mailto:ibon@iqm.csic.es) (I.A.).

### Notes

The authors declare no competing financial interest.

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