IR and NMR properties of N-base:PH$_2$F:BeX$_2$ ternary and corresponding binary complexes stabilised by pnicogen and beryllium bonds

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ABSTRACT

Ab initio MP2/aug-cc-pVTZ calculations have been performed to determine selected stretching frequencies and chemical shieldings for ternary complexes N-base:PH$_2$F:BeX$_2$ and the corresponding binary complexes, with NH$_3$, H$_2$C$\equiv$NH, and HCN as the nitrogen bases and H, F, and Cl as the substituents X. Be-F and P-F stretching frequencies depend on the Be-F and P-F distances, respectively, while P and F chemical shieldings depend on the N-P and P-F distances, respectively. The graph of the P chemical shieldings versus the P-F distance bears a remarkable resemblance to the graph of the P-F stretching frequencies versus that same distance. EOM-CCSD spin–spin coupling constants have also been evaluated for binary and ternary complexes. $^{1}$P$\mathbf{J}$(N-P) is negative at the longer N-P distances found in ternary complexes with HCN in which the N···P bond is a traditional pnicogen bond with some phosphorous-shared character, gains phosphorus-shared character as the N-P distance continues to decrease, and then becomes a phosphorous-transferred bond with ion-pair character at the shorter distances in the complexes with NH$_3$ and H$_2$C$\equiv$NH. $^{1}$J(P-F) values are large and negative in complexes with HCN, but increase and become positive in complexes with H$_2$C$\equiv$NH and NH$_3$ as the P-F distance increases.

1. Introduction

In a recent study [1], we reported the structures, binding energies, and bonding properties of two series of binary complexes represented as N-base:PH$_2$F and PH$_2$F:BeX$_2$, and the corresponding ternary complexes N-base:PH$_2$F:BeX$_2$, with NH$_3$, HN$\equiv$CH$_2$, and NCH as the nitrogen bases, the phosphorous molecule fluorophosphane PH$_2$F, and five beryllium derivatives BeH$_2$, BeF$_2$, BeCl$_2$, BeCO$_3$, and BeSO$_4$. Two equilibrium isomers labelled A and B were found on the potential surfaces having BeH$_2$, BeF$_2$, and BeCl$_2$ as the acids, and these are illustrated in Figure 1 for NH$_3$:PH$_2$F:BeH$_2$. In isomer A, the BeH$_2$ molecule lies in the symmetry plane of the complex, with the F···Be bond cis to the bisector of the H-P-H angle with respect to the P-F bond. Isomer B has no symmetry in point group C$_1$, since BeH$_2$ assumes
what might be described as a sideways approach to F relative to the plane defined by the bisector of the H-P-H angle and the P-F bond. The presence of the N···P pnicogen bond and the Be···F beryllium bond in the ternary complexes leads to large, synergistic cooperative effects on the binding energies and the geometries of these complexes. In ref. 1 it was concluded that as the strength of the nitrogen base as an electron-pair donor and the beryllium acid as an electron pair acceptor increases, the nature of the pnicogen bond changes from traditional, to phosphorus-shared, to phosphorus-transferred. Significant changes are also found for the Be···F and P-F bonds in the ternary complexes.

The study of non-covalent interactions is a very active field of research. The hydrogen bond was the first to be investigated, and is the best known and most important of these interactions [2–5]. In recent years other interactions have been described [6]. They have been named based on the atom directly involved in the interaction as the Lewis acid [7]. Thus, aerogen (atoms of column 18 of the periodic table) [8], halogen (column 17) [9,10], chalcogen (column 16) [11–13], pnicogen (column 15) [14–16], tetrel (column 14) [17–19], triel (column 13) [20], spodum (column 12) [21], regium (column 11) [22–24], alkaline-earth (column 2) [25,26] and alkaline (column 1) [27–29] bonds have been described in the literature. The ability of these molecules to act as Lewis acids has been attributed to the presence of positive regions of their electrostatic potential, denoted as σ or π-holes [30].

In previous studies we have demonstrated that spin–spin coupling constants across hydrogen [31], halogen [32], chalcogen [33], pnicogen [34], and tetrel bonds [35] provide a fingerprint of the nature of the intermolecular bond in a related series of complexes. These coupling constants increase in absolute value as the intermolecular distance decreases in complexes with traditional intermolecular bonds, may reach a maximum as the bond length decreases and the bonds become atom-shared bonds, and then further decreases as atom transfer occurs. As a follow-up to ref. 1, we have now carried out EOM-CCSD calculations to evaluate spin–spin coupling constants $^{1}pJ(N-P)$ across the pnicogen bond, $^{1}beJ(\text{Be-F})$ across the beryllium bond, and $^{1}J(\text{P-F})$ in the equilibrium ternary complexes N-base:PH$_2$F:BeX$_2$ isomers A and B and the corresponding binary complexes N-base:PH$_2$F and PH$_2$F:BeX$_2$. We have also examined computed IR vibrational frequencies and chemical shieldings in both binary and ternary complexes. It is the purpose of this paper to report these NMR and IR properties, and to interpret them in light of the changing nature of the intermolecular N···P and F···Be bonds and the covalent P-F bond of fluorophosphane.

2. Methods

The structures of the isolated monomers; the binary complexes N-base:PH$_2$F and PH$_2$F:BeX$_2$; and the ternary complexes N-base:PH$_2$F:BeX$_2$, for N-base equal to NH$_3$, H$_2$C=NH, and HCN, and BeX$_2$ equal to BeH$_2$, BeF$_2$, and BeCl$_2$ for structures A and B, had been optimised previously at second-order Møller-Plesset perturbation theory (MP2) [36–39] with the aug'-cc-pVTZ basis set [40]. These structures are reported in ref. 1. Vibrational frequencies were computed to ensure that these structures are equilibrium structures on their potential energy surfaces, and to examine the variation in selected stretching frequencies in the binary and ternary complexes. MP2/aug'-cc-pVTZ absolute chemical shieldings have also been calculated using the GIAO approximation [41]. These calculations were carried out with the Gaussian 16 programme [42].

Spin–spin coupling constants for these complexes have been evaluated using the equation of motion coupled cluster singles and doubles (EOM-CCSD) method in the CI (configuration interaction)-like approximation [43,44] with all electrons correlated. For these calculations, the Ahlrichs [45] qzp basis set was placed on $^{13}$C, $^{15}$N, and $^{19}$F, the qz2p basis set on $^{31}$P and $^{35}$Cl, and the hybrid basis set introduced previously on $^{9}$Be [46]. The Dunning cc-pVDF basis was placed on $^{1}$H atoms. All terms that contribute to the total coupling constant, namely, the paramagnetic spin orbit (PSO), diamagnetic spin orbit (DSO), Fermi contact (FC) and spin dipole (SD) have been evaluated for the binary complexes and ternary complexes with C$_{2v}$ symmetry. Computing the SO and SD terms was not feasible for some of the larger ternary complexes with C$_{1}$ symmetry. For three of these we have estimated the values of $^{1}pJ(N-P)$ and $^{1}beJ(\text{Be-F})$ from the computed FC terms and values of the SO and SD terms taken from similar complexes. Coupling constant calculations were performed using ACES II [47] on the HPC cluster Owens at the Ohio Supercomputer Center.
Table 1. P-F stretching frequencies and distances, and intermolecular Be-F and P-N stretching frequencies [ν(X-Y), cm⁻¹] and X-Y distances [R(X-Y), Å] in binary and ternary complexes.

| System                  | ν(P-F), cm⁻¹ | R(P-F), Å | ν(Be-F), cm⁻¹ | R(Be-F), Å | ν(P-N), cm⁻¹ | R(P-N), Å |
|-------------------------|--------------|----------|---------------|-----------|--------------|----------|
| PH₂F                   | 807.9        |          |               |           |              |          |
| H₃N:PH₂F               | 740.4        | 145.2    | 1.622         |           |              |          |
| H₂CHN:PH₂F             | 733.0        | 153.9    | 1.650         |           |              |          |
| HCN:PH₂F               | 755.9        | 106.5    | 1.635         |           |              |          |
| PH₂F:BeH₂ A            | 696.8        | 335.4    | 1.681         | 1.783     |              |          |
| PH₂F:BeH₂ B            | 711.6        | 378.2    | 1.694         | 1.747     |              |          |
| PH₂F:BeF₂ A            | 678.9        | 392.5    | 1.689         | 1.75      |              |          |
| PH₂F:BeF₂ B            | 669.0        | 403.4    | 1.698         | 1.736     |              |          |
| PH₂F:BeCl₂ A           | 680.5        | 557.6    | 1.702         | 1.697     |              |          |
| PH₂F:BeCl₂ B           | 669.6        | 568.0    | 1.713         | 1.679     |              |          |
| H₃N:PH₂F:BeH₂          | 443.1        | 540.4    | 240.8         | 1.805     | 1.645        | 2.214    |
| H₃N:PH₂F:BeCl₂         | 448.1        | 542.8    | 241.2         | 1.809     | 1.64         | 2.231    |
| H₃N:PH₂F:BeF₂ A        | 463.6        | 526.0    | 267.6         | 1.835     | 1.624        | 2.172    |
| H₃N:PH₂F:BeF₂ B        | 469.3        | 525.3    | 262.8         | 1.835     | 1.624        | 2.187    |
| H₃N:PH₂F:BeCl₂ A       | 457.0        | 746.4    | 309.6         | 1.902     | 1.565        | 2.104    |
| H₃N:PH₂F:BeCl₂ B       | 457.9        | 763.8    | 302.8         | 1.899     | 1.566        | 2.121    |
| HCN:PH₂F:BeH₂ A        | 432.1        | 571.3    | 260.3         | 1.821     | 1.635        | 2.116    |
| HCN:PH₂F:BeH₂ B        | 439.3        | 574.6    | 231.0         | 1.825     | 1.631        | 2.132    |
| HCN:PH₂F:BeCl₂ A       | 450.2        | 543.7    | 259.3         | 1.852     | 1.616        | 2.08     |
| HCN:PH₂F:BeCl₂ B       | 457.8        | 539.6    | 259.0         | 1.853     | 1.616        | 2.093    |
| HCN:PH₂F:BeF₂ A        | 463.2        | 776.4    | 294.5         | 1.925     | 1.557        | 2.019    |
| HCN:PH₂F:BeF₂ B        | 469.3        | 777.3    | 283.7         | 1.924     | 1.557        | 2.032    |
| HCN:PH₂F:BeCl₂ A       | 568.5        | 446.7    | 124.3         | 1.726     | 1.704        | 2.481    |
| HCN:PH₂F:BeCl₂ B       | 553.7        | 473.9    | 131.4         | 1.736     | 1.689        | 2.489    |
| HCN:PH₂F:BeF₂ A        | 590.1        | 466.0    | 137.7         | 1.742     | 1.678        | 2.428    |
| HCN:PH₂F:BeF₂ B        | 583.0        | 475.2    | 132.2         | 1.748     | 1.673        | 2.437    |
| HCN:PH₂F:BeCl₂ A       | 554.6        | 667.6    | 132.1         | 1.776     | 1.621        | 2.341    |
| HCN:PH₂F:BeCl₂ B       | 547.6        | 676.0    | 130.2         | 1.782     | 1.615        | 2.354    |

3. Results and discussion

3.1. Stretching frequencies in binary and ternary complexes

Table 1 provides the P-F, Be-F, and P-N stretching frequencies and corresponding bond distances in binary and ternary complexes. The P-N stretching frequencies range from 107 cm⁻¹ at a P-N distance of 2.77 Å in the binary complex HCN:PH₂F, to 310 cm⁻¹ at a P-N distance of 2.10 Å in the ternary complex H₃N:PH₂F:BeCl₂ A. These frequencies are intermolecular stretching frequencies across the P···N nitrigen bond. As expected, the P-N distances are longest in the binary complexes and the ternary complexes HCN:PH₂F:BeX₂, and these complexes have the smallest P-N stretching frequencies. The P-N distances are shorter in the ternary complexes with NH₃ and H₂C=NH as the nitrogen bases, and these complexes have greater stretching frequencies. The P-N stretching frequencies exhibit a second order dependence on the charge on the nitrogen base in the ternary complexes, with a correlation coefficient of 0.986. However, these frequencies are relatively small and should be significantly anharmonic. They will not be discussed further in this paper.

There are two bonds of interest which have greater stretching frequencies, namely, the intermolecular Be···F bond and the intramolecular P-F bond. The data of Table 1 show that the Be-F stretching frequencies across the Be···F bond vary from 335 cm⁻¹ in the binary complex H₂PF:BeH₂ to 777 cm⁻¹ in the ternary complex H₂C=N:PH₂F:BeCl₂. B. In the two series of ternary complexes with the strongest nitrogen bases, Be-F stretching frequencies increase with respect to the substituent in the order F < H < Cl. In the binary complexes, this order is H < F < Cl, with the frequencies in the A isomer lower than those in the corresponding B isomer.

The most interesting relationship is found for the Be-X stretching frequencies in the binary and ternary complexes when these are analysed as a function of the substituent X, as illustrated in Figure 2. For each BeX₂ acid, the Be-F stretching frequency across the beryllium bond increases linearly as the Be-F distance decreases. The correlation coefficients of the trendlines are greater than 0.990. The trendlines for the complexes with BeH₂ and BeCl₂ are essentially parallel, while that for the complexes with BeF₂ has a reduced slope. There are eight points for each set of complexes, but values of the stretching frequencies for ternary complexes with NH₃ and H₂C=NH as the nitrogen bases and BeF₂ and BeCl₂ as the beryllium acids may have values for the A and B isomers which are indistinguishable in the graph.

Table 1 also presents the P-F stretching frequencies and the P-F distances in the monomer PH₂F₂, the binary complexes N-base:PH₂F₂ and PH₂F₂:BeX₂, and the ternary complexes N-base:PH₂F₂:BeX₂. The P-F stretching frequency in the monomer PH₂F₂ is 808 cm⁻¹. Complex formation reduces the P-F stretching frequency, which has its smallest value of 406 cm⁻¹ in the ternary complex with H₂C=NH as the base and Cl as the substituent, and its largest value of 756 cm⁻¹ in the binary complex with HCN as the base. From Table 1, it is apparent that the P-F stretching frequencies depend on the nature of the complex, that is, whether it is a binary complex with PH₂F as the electron-pair donor or acceptor, or a ternary complex with HCN, H₂C=N(H)N, or NH₃ as the nitrogen base. Thus, the order of decreasing P-F stretching frequencies is PH₂F > N-base:PH₂F > PH₂F:BeX₂ > HCN:PH₂F:BeX₂ > H₃N:PH₂F:BeX₂ ≈ H₂C=N(=)N:PH₂F:BeX₂.

There is also some dependence on the nature of X in these complexes. These relationships can be readily seen in Figure 3 which is a plot of the P-F stretching frequencies versus the P-F distance. The third-order trendline has a correlation coefficient of 0.956.
3.2. Chemical shieldings in binary and ternary complexes

Table 2 presents the N, P, F, and Be chemical shieldings in the binary and ternary complexes. The Be chemical shieldings in the binary complexes PH₂F₂BeX₂ are 87, 110, 100 ppm for X = H, F, and Cl, respectively. In the ternary complexes N-base:PH₂F₂BeX₂ for X = H, these shieldings increase to about 95 ppm. Smaller increases of no more than 3 ppm are found in the ternary complexes with X = F and Cl. Thus, the formation of ternary complexes has little effect on these Be chemical shieldings. However, the Be chemical shieldings in the binary and ternary complexes do exhibit a second order correlation with the charge on Be, with a correlation coefficient of 0.98.

The N chemical shieldings in H₃N:PH₂F₂, H₂C(H)N:PH₂F₂, and HCN:PH₂F₂ have values of 267, −44, and +16 ppm. These shieldings decrease upon the formation of ternary complexes with NH₃, but vary over a narrow range from 247 to 251 ppm. The chemical shieldings increase to between −9 and −22 ppm when H₂C = NH is the base, and to between 26 and 34 ppm when HCN is the base. Once again, these are relatively small changes associated with the formation of ternary complexes.
Table 2. Chemical shieldings (\(\sigma, \text{ppm}\)) in PH2F and the binary and ternary complexes.

| System / Atom = | N  | P  | F  | Be |
|-----------------|----|----|----|----|
| PH2F            | 372.8 | 524.5 |     |     |
| H3N:PH2F        | 266.9 | 349.5 | 431.5 |     |
| H3N:PH2F        | -43.7 | 346.5 | 425.9 |     |
| HCN:PH2F        | 15.6 | 304.6 | 472.0 |     |
| PH2F:BeH2 A     | 213.3 | 474.1 | 86.7 |     |
| PH2F:BeH2 B     | 229.7 | 471.9 | 86.7 |     |
| PH2F:BeF2 A     | 214.2 | 489.5 | 110.5 |     |
| PH2F:BeF2 B     | 215.8 | 489.6 | 110.5 |     |
| PH2F:BeCl2 A    | 206.0 | 466.1 | 100.3 |     |
| PH2F:BeCl2 B    | 210.2 | 463.2 | 100.3 |     |
| H3N:PH2F:BeH2 A | 250.3 | 403.3 | 325.5 | 94.4 |
| H3N:PH2F:BeH2 B | 251.4 | 418.3 | 340.9 | 95.5 |
| H3N:PH2F:BeF2 A | 248.7 | 429.0 | 352.3 | 111.0 |
| H3N:PH2F:BeF2 B | 249.6 | 429.3 | 357.8 | 111.2 |
| H3N:PH2F:BeCl2 A | 246.9 | 433.0 | 324.4 | 103.5 |
| H3N:PH2F:BeCl2 B | 247.8 | 440.6 | 329.5 | 103.7 |
| H3N:PH2F:BeF2 A | -22.4 | 394.0 | 325.4 | 94.7 |
| H3N:PH2F:BeF2 B | -21.7 | 408.2 | 334.4 | 95.8 |
| H3N:PH2F:BeCl2 A | -18.8 | 416.8 | 347.2 | 111.0 |
| H3N:PH2F:BeCl2 B | -17.4 | 417.0 | 352.8 | 111.1 |
| H3N:PH2F:BeCl2 A | -10.3 | 416.3 | 320.5 | 103.6 |
| H3N:PH2F:BeCl2 B | -8.8 | 424.4 | 325.8 | 103.7 |
| HCN:PH2F:BeH2 A | 26.6 | 294.7 | 398.2 | 93.0 |
| HCN:PH2F:BeH2 B | 26.1 | 309.2 | 402.8 | 94.4 |
| HCN:PH2F:BeF2 A | 29.0 | 314.8 | 412.0 | 111.1 |
| HCN:PH2F:BeF2 B | 28.5 | 313.5 | 415.8 | 111.2 |
| HCN:PH2F:BeCl2 A | 33.5 | 327.0 | 378.1 | 103.0 |
| HCN:PH2F:BeCl2 B | 32.8 | 326.7 | 381.8 | 103.3 |

Much greater changes upon binary and ternary complex formation are found for the chemical shieldings of the P and F atoms of PH2F. The chemical shielding of the P atom in the isolated monomer is 273 ppm. The shieldings increase to between 305 and 350 ppm in the binary complexes with the nitrogen bases, but decrease to between 206 and 230 ppm in the binary complexes with the beryllium acids. The values of the P chemical shieldings in the ternary complexes H3N:PH2F:BeX2 are small relative to the values in the binary complexes with the beryllium acids, and then to the ternary complexes. It is also interesting to compare this graph of the F chemical shieldings versus the P-F distance to Figure 3 which illustrates the F-P stretching frequencies versus the P-F distance. Except for the points for the binary complexes N-base:PH2F, these two graphs look remarkably alike. Thus, they emphasise what is an expected result, namely, that as the P-F distance decreases, the P-F stretching frequencies as well as the F chemical shieldings increase.

3.3. Spin–spin coupling constants for binary and ternary complexes

Table S1 of the Supplemental Data provides the components of \(1^J(N-P)\) and \(1^J(P-F)\) for the binary complexes H3N:PH2F, H2C = (H)N:PH2F, and HCN:PH2F; and \(1^J(P-F)\) and \(1^JBe(J(Be-F))\) for the binary complexes PH2F:BeX2 structures A and B, with X = H, F, and Cl. Table S2 provides corresponding data for the ternary complexes H3N:PH2F:BeX2, H2C = (H)N:PH2F:BeX2, and HCN:PH2F:BeX2. When analysing these data, it should be kept in mind that the magnetogyric ratios of \(^{9}\text{Be}\) and \(^{15}\text{N}\) are negative, while those of \(^{19}\text{F}\) and \(^{31}\text{P}\) are positive. The data of Table S1 show that the FC term is a good approximation to \(1^J(N-P)\) for the binary complexes with the three nitrogen bases, but is not a good approximation to \(1^J(P-F)\) since both the PSO and SD terms are non-negligible, as is usually the case for coupling constants involving F [48]. The FC term is a fairly good approximation to \(1^JBe(J(\text{Be-F}))\) since there is a partial cancellation between the negative DSO and SD terms and the positive PSO term, but cancellation is not something that can be relied on. Table S2 provides the components of coupling constants for the ternary complexes. For these, the FC term is generally not a good approximation to total J, except for \(1^J(N-P)\) in complexes with HCN as the nitrogen base. Only total J values will be discussed in this paper.
3.4. Coupling constants for binary complexes.

Table 3 presents P-F and P-N distances and the corresponding coupling constants $^{1}J(P-F)$ and $^{1}J(P-N)$ for the binary complexes $H_3N:PH_2F$, $H_2C=\text(N):PH_2F$, and $HCN:PH_2F$. Table 3 also presents P-F and Be-F distances and $^{1}J(P-F)$ and $^{1}beJ(\text{Be-F})$ coupling constants for the complexes $PH_2F:BeH_2$, $PH_2F:BeF_2$, and $PH_2F:BeCl_2$ structures A and B. For the complexes $H_3N:PH_2F$, $H_2C=(\text{H})N:PH_2F$, and $HCN:PH_2F$, $^{1}J(P-F)$ for the P-F covalent bond is negative as it is in the $PH_2F$ monomer, even though both P and F have positive magnetogyric ratios. Thus, the reduced coupling constant $^{1}K(P-F)$ would also be negative. This is another example of a violation of the Dirac Vector Model [49] which states that all reduced one-bond coupling constants are positive.

As noted above, values of $^{1}J(P-F)$ are negative in the N-base:$PH_2F$ complexes, and increase in absolute value as the P-F distance decreases, as illustrated in Figure 6. The linear trendline has a correlation coefficient of 0.995. Different patterns are observed for this coupling constant.
Table 3. Distances (R, Å) and spin-spin coupling constants (J, Hz) for binary complexes.

| Binary complex       | R(P-F) | 1pJ(N-P) | R(N-P) | 1J(P-F) |
|----------------------|--------|----------|--------|---------|
| H₂N:PH₂F            | 1.648  | −535.5   | 2.609  | −65.6   |
| H₂C = (H)N:PH₂F     | 1.650  | −516.6   | 2.490  | −58.1   |
| HCN:PH₂F            | 1.635  | −609.6   | 2.769  | −46.9   |

PH₂F:BeF₂           | R(P-F) | 1pJ(N-P) | R(Be-F) | 1beJ(Be-F) |
|---------------------|--------|----------|---------|------------|
| A                   | 1.681  | −729.0   | 1.783   | 39.5       |
| B                   | 1.694  | −498.8   | 1.747   | 33.8       |

PH₂F:BeCl₂          | 1.689  | −714.1   | 1.750   | −3.3       |
| A                   | 1.698  | −536.1   | 1.736   | −5.4       |
| B                   | 1.702  | −751.4   | 1.697   | 8.6        |

PH₂F:BeCl₃          | 1.713  | −499.8   | 1.679   | 3.7        |

a) 1pJ(N-P) in isolated PH₂F is −740.9 Hz at a P-F distance of 1.622 Å.

Table 4. Distances (R, Å) and spin-spin coupling constants ¹J(J(N-P)), 1J(P-F), and 1beJ(Be-F) (Hz) for ternary complexes NH₃:PH₂F:BeX₂, H₂C = (H)N:PH₂F:BeX₂, and HCN:PH₂F:BeX₂.

| NH₃       | R(P-F) | ¹J(N-P) | R(P-F) | ¹J(P-F) | R(Be-F) | 1beJ(Be-F) |
|-----------|--------|---------|--------|---------|---------|------------|
| X = H     | 2.214  | −65.5   | 1.805  | −54.6   | 1.645   | 24.8       |
| B         | 2.231  | −72.6   | 1.809  | −45.0   | 1.640   | 20.7       |
| X = F     | 2.172  | −60.2   | 1.835  | 43.1    | 1.624   | −22.1      |
| B         | 2.187  | −66.6   | 1.835  | 33.1    | 1.624   | −23.0      |
| X = Cl    | 2.104  | −50.0   | 1.902  | 186.5   | 1.565   | −18.3      |
| B         | 2.187  | −58.4   | 1.624  | −19.8   |
| H₂C = NH  | 2.116  | −33.2   | 1.821  | −15.0   | 1.635   | 22.7       |
| B         | 2.132  | −40.5   | 1.825  | −6.8    | 1.631   | 18.6       |
| X = F     | 2.080  | −26.6   | 1.852  | 77.4    | 1.616   | −23.6      |
| B         | 2.093  | −43.4   | 1.616  | −23.8   |

[MOLECULAR PHYSICS]

3.5. Coupling constants for ternary complexes.

Table 4 reports the N-P, Be-F, and P-F distances and the corresponding coupling constants ¹J(J(N-P)), ¹beJ(Be-F), and ¹J(P-F) for the ternary complexes NH₃:PH₂F:BeX₂, H₂C = (H)N:PH₂F:BeX₂, and HCN:PH₂F:BeX₂. Total J values ¹J(J(N-P)) and ¹beJ(Be-F) for the B isomers of NH₃:PH₂F:BeCl₂, H₂C = (H)N:PH₂F:BeCl₂, and HCN:PH₂F:BeCl₂ were approximated based on the computed value of the FC term as modified to take into account the contributions of the SO and SD terms. How this was done can be seen from the footnotes in Table 4 and the values of these terms in related complexes, which are found in Table S2. The three coupling constants ¹J(J(N-P)), ¹beJ(Be-F), and ¹J(P-F) will be discussed in the following three sections.

3.5.1. ¹J(J(N-P))

Table 4 provides N-P distances and coupling constants ¹J(J(N-P)) across the pnicogen bond for the ternary complexes. ¹J(J(N-P)) values are always negative, varying from −73 Hz at an N-P distance of 2.23 Å in H₂N:PH₂F:BeH₂ B, to −27 Hz at a N-P distance of 2.08 Å in H₂C = (H)N:PH₂F:BeF₂ A. Although the N-P distance is considerably shorter in the complexes with NH₃ as the base, ¹J(J(N-P)) values for H₃N:PH₂F:BeH₂ A and B, and H₂N:PH₂F:BeCl₂ B are similar to the values of ¹J(J(N-P)) for the corresponding HCN complexes at much longer N-P distances. Values of ¹J(J(N-P)) for the H₃N:PH₂F:BeH₂ complexes tend to decrease in absolute value as the N-P distance decreases, with H₃N:PH₂F:BeCl₂ A having the least negative value of −50 Hz. The N-P distance in this complex overlaps the N-P distances in the H₂C = (H)N:PH₂F:BeX₂ complexes, but the coupling constants in the later have smaller absolute values, ranging from −43 to −27 Hz. The range of values of ¹J(J(N-P)) coupling constants in the ternary complexes with NH₃ as the base include the coupling constant for the binary complex H₃N:PH₂F. However, ¹J(J(N-P)) for the complexes H₂C = (H)N:PH₂F:BeX₂ have smaller negative values than ¹J(J(N-P)) for the binary complex H₂C = (H)N:PH₂F, while ¹J(J(N-P)) for the ternary complexes HCN:PH₂F:BeX₂ have greater negative values than ¹J(J(N-P)) for HCN:PH₂F. Thus, the presence of the beryllium bond has a significant effect on the value of ¹J(J(N-P)) in the ternary complexes.

The variation of ¹J(J(N-P)) as a function of the N-P distance is illustrated in Figure 7. The vertical axis has been reversed to reflect the negative magnetogyratic ratio of ¹⁵N. The behaviour of ¹J(J(N-P)) as a function of the N-P distance can be interpreted from Figure 7 in terms of the changing nature of the pnicogen bond in these complexes. At the longest N-P distances are the complexes with HCN as the base. These complexes
are stabilised by traditional pnictogen bonds that have significant phosphorus-shared character. As the N-P distance decreases, \( ^1\text{P}(\text{N-P}) \) becomes less negative as the N...P bond in the complexes with \( \text{NH}_3 \) as the base becomes a phosphorus-shared pnicogen bond with some phosphorus-transferred character. At even shorter distances, the N...P bond becomes a phosphorous-transferred bond in the complexes with \( \text{H}_2\text{C}=(\text{H})\text{N}:\text{PH}_2\text{F}:\text{BeF}_2 \) complex. It should be noted that it is unusual for the weak base HCN to form complexes with a high degree of phosphorus-shared character as it does in the \( \text{HCN}:\text{PH}_2\text{F}:\text{BeX}_2 \) complexes. This may be attributed to cooperativity between the beryllium bond and the pnicogen bond.

3.5.2. \( ^{1}\text{Be}J(\text{Be-F}) \)

The Be-F distances and coupling constants \( ^{1}\text{Be}J(\text{Be-F}) \) for the ternary complexes are reported in Table 4. The values of this coupling constant range from \(-24 \text{ Hz}\) at a Be-F distance of 1.616 Å in \( \text{H}_2\text{C}=(\text{H})\text{N}:\text{PH}_2\text{F}:\text{BeF}_2 \) complex and 1.704 Å at a Be-F distance of 1.68 Å in \( \text{HCN}:\text{PH}_2\text{F}:\text{BeCl}_2 \) complex. Figure 8 provides graphical insight into the variation of this coupling constant as functions of the Be-F distance, the substituent X, and the nitrogen base.

From Table 4 and Figure 8 it can be seen that in the ternary complexes which have H as the substituent, \( ^{1}\text{be}J(\text{Be-F}) \) is positive, independent of the nature of the nitrogen base and independent of the structure A or B. Among these complexes, the longest distance found is in \( \text{HCN}:\text{PH}_2\text{F}:\text{BeH}_2 \) complex with \( ^{1}\text{be}J(\text{Be-F}) \) equal to 34 Hz. The shortest Be-F distance is 1.616 Å in \( \text{H}_2\text{C}=(\text{H})\text{N}:\text{PH}_2\text{F}:\text{BeF}_2 \) complex. When X = F, \( ^{1}\text{be}J(\text{Be-F}) \) is negative in complexes \( \text{H}_3\text{N}:\text{PH}_2\text{F}:\text{BeX}_2 \) and \( \text{HCN}:\text{PH}_2\text{F}:\text{BeX}_2 \) when X is F or Cl, independent of the conformation A or B. Among these, the longest Be-F distance of 1.68 Å is found in \( \text{HCN}:\text{PH}_2\text{F}:\text{BeCl}_2 \) complex with \( ^{1}\text{be}J(\text{Be-F}) \) equal to \(-18 \text{ Hz}\).

3.5.3. \( ^1\text{J}(\text{P-F}) \)

Coupling constants \( ^1\text{J}(\text{P-F}) \) and P-F distances for the ternary complexes are reported in Table 4. When HCN is the nitrogen base, \( ^1\text{J}(\text{P-F}) \) values range from \(-365 \text{ Hz}\) to \(-800 \text{ Hz}\).
Figure 7. $^1p_J(N-P)$ versus $R(N-P)$ for ternary complexes as a function of the nitrogen base. Points labelled App were approximated from the FC terms and a factor to account for SO and SD terms, as indicated in Table 2.

Figure 8. $^1be_J(Be-F)$ versus $R(Be-F)$ for ternary complexes $\text{NH}_3: \text{PH}_2\text{F}:\text{BeX}_2$, $\text{H}_2\text{C} = \text{(H)N}: \text{PH}_2\text{F}:\text{BeX}_2$, and $\text{HCN}: \text{PH}_2\text{F}:\text{BeX}_2$, structures A and B.

at a P-F distance of 1.73 Å, to −195 Hz at a P-F distance of 1.78 Å. These values are found for the complexes $\text{HCN}: \text{PH}_2\text{F}:\text{BeH}_2$ A and $\text{HCN}: \text{PH}_2\text{F}:\text{BeCl}_2$ A, respectively. $^1p_J(P-F)$ values are available for only three complexes with $\text{H}_2\text{C} = \text{NH}$ as the base. Complexes $\text{H}_2\text{C} = \text{(H)N}: \text{PH}_2\text{F}:\text{BeH}_2$ A and B have values of $^1J(P-F)$ of −15 and −7 Hz at P-F distances of 1.82 Å. $^1J(P-F)$ for $\text{H}_2\text{C} = \text{(H)N}: \text{PH}_2\text{F}:\text{BeF}_2$ A is 77 Hz at a P-F distance of 1.85 Å. In complexes with $\text{NH}_3$ as the base, $^1J(P-F)$ for complexes with $\text{H}$ as the substituent are negative, with values of −55 and −45 Hz at P-F distances of 1.81 Å in structures A and B, respectively. When F is the substituent, $^1J(P-F)$ becomes positive, with values of 43 and 33 Hz at a P-F distance of 1.84 Å in isomers A and B.
respectively. When $X = \text{Cl}$, $^{1}J(P-F)$ increases to 187 Hz at a P-F distance of 1.90 Å in isomer A. Thus, the value of $^{1}J(P-F)$ for $\text{H}_3\text{N}:\text{PH}_2\text{F}:\text{BeCl}_2$, $\text{H}_2\text{C} = (\text{H})\text{N}:\text{PH}_2\text{F}:\text{BeCl}_2$, and $\text{HCN}:\text{PH}_2\text{F}:\text{BeCl}_2$ respectively. When $X = \text{Cl}$, $^{1}J(P-F)$ increases to 187 Hz at a P-F distance of 1.90 Å in isomer A. Thus, the value of $^{1}J(P-F)$ for $\text{H}_3\text{N}:\text{PH}_2\text{F}:\text{BeCl}_2$, $\text{H}_2\text{C} = (\text{H})\text{N}:\text{PH}_2\text{F}:\text{BeCl}_2$, and $\text{HCN}:\text{PH}_2\text{F}:\text{BeCl}_2$

### 4. Conclusions

Ab initio calculations have been performed to evaluate IR stretching frequencies, NMR chemical shieldings, and NMR spin–spin coupling constants involving the atoms N, P, F, and Be in ternary complexes N-base:PH$_2$F:BeX$_2$ and the corresponding binary complexes N-base:PH$_2$F and PH$_2$F:BeX$_2$. The nitrogen bases are NH$_3$, H$_2$C = NH, and HCN, and the substituents X are H, F, and Cl. The main results of this study are summarised in the following points.

1. Intermolecular Be-F stretching frequencies in binary and ternary complexes depend on the substituent X. For each substituent, the Be-F stretching frequencies exhibit a linear dependence on the intermolecular Be-F distance.

2. P-F stretching frequencies show a third-order dependence on the P-F distance in binary and ternary complexes.

3. P chemical shieldings exhibit a second-order dependence on the N-P distance, while F chemical shieldings show a third-order dependence on the P-F distance. The graph illustrating the dependence of the F shieldings on the P-F distance bears a remarkable resemblance to the graph of the P-F stretching frequencies versus the P-F distance.

4. Values of $^{1}J(N-P)$ in the ternary complexes are always negative. At the longest N-P distances in complexes with HCN, $^{1}J(N-P)$ values indicate that the N···P bond has some phosphorus-shared character. As the N-P distance shortens, $^{1}J(N-P)$ begins to
The nitrogen base and the structure of the isomer
dependent of the nature of the hydrogen base and the structure
of the isomer.

5. Values of $^{1\text{be}}J(\text{Be}-\text{F})$ are positive in binary complexes
and in ternary complexes with $\text{BeH}_2$ as the acid, independent
of the nature of the hydrogen base and the structure of the isomer $\text{A}$ or $\text{B}$. Values of this coupling constant are always negative when $\text{BeF}_2$ and $\text{BeCl}_2$ are the acids.

6. $^{1}\text{J}(\text{P-F})$ values are large and negative in complexes
with HCN as the hydrogen base. In the complexes with
$\text{H}_2\text{C} = \text{NH}$ and $\text{NH}_3$, $^{1}\text{J}(\text{P-F})$ increases and becomes
large and positive as the N-P distance increases. There is
an excellent correlation between increasing N-P distance and increasing $^{1}\text{J}(\text{N-P})$.

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Data availability statements

The authors confirm that the data supporting the findings of
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Disclosure statement

No potential conflict of interest was reported by the author(s).

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