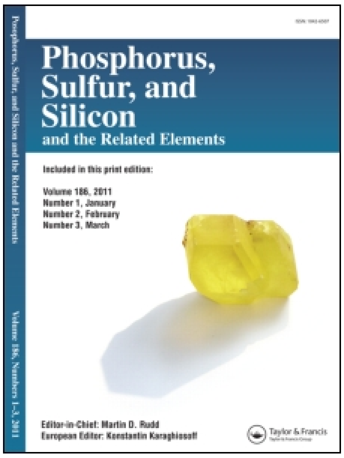

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE SYNTHESIS AND CHARACTERIZATION OF BORANE(3) COMPLEXES OF 1,3-DI(TERTBUTYL)2,4-DIFLUORODIAZADIPHOSPHETIDINE. THE CRYSTAL AND MOLECULAR STRUCTURE OF THE BIS BORANE(3) COMPLEX

J. S. Jessup[a]; R. T. Paine[a]; C. F. Campana[a]
[a] Department of Chemistry, The University of New Mexico, Albuquerque, NM

To cite this Article Jessup, J. S. , Paine, R. T. and Campana, C. F.(1981) 'THE SYNTHESIS AND CHARACTERIZATION OF BORANE(3) COMPLEXES OF 1,3-DI(TERTBUTYL)2,4-DIFLUORODIAZADIPHOSPHETIDINE. THE CRYSTAL AND MOLECULAR STRUCTURE OF THE BIS BORANE(3) COMPLEX', Phosphorus, Sulfur, and Silicon and the Related Elements, 9: 3, 279 — 284

To link to this Article: DOI: 10.1080/03086648108078251
URL: http://dx.doi.org/10.1080/03086648108078251

Phosphorus and Sulfur, 1981, Vol. 9, pp. 279–284
0308-664X/81/0903-0279$06.50/0

THE SYNTHESIS AND CHARACTERIZATION OF BORANE(3) COMPLEXES OF 1,3-DI(TERTBUTYL)2,4-DIFLUORODIAZADIPHOSPHETIDINE. THE CRYSTAL AND MOLECULAR STRUCTURE OF THE BIS BORANE(3) COMPLEX

J. S. JESSUP, R. T. PAINE,* and C. F. CAMPANA

Department of Chemistry, The University of New Mexico, Albuquerque, NM 87131

(*Received January 9, 1980; in final form March 31, 1980*)

The 1:0.5 and 1:1 combinations of 1,3-di(tert-butyl)-2,4-difluorodiazadiphosphetidine with diborane (6) result in the formation of monoborane (3) and bis borane (3) complexes. The new complexes have been characterized by mass, infrared and NMR spectroscopic techniques. The crystal and molecular structure of $FPN(Bu^t)P(F)N(Bu^t) \cdot (BH_3)_2$ has been established by single crystal X-ray diffraction analysis. The compound crystallizes in the monoclinic space group $P2_1/m$ with $a = 6.328(4)$ Å, $b = 12.183(5)$ Å, $c = 10.627(4)$ Å, $\beta = 100.56(1)°$, $Z = 2$, $\rho_{\text{calcd}} = 1.11$ g cm^{-3}, mol. wt. = 269.84, $F(000) = 288$ (25°, Cu Kα). The structure was solved using direct methods and refined to $R = 0.093$ on 996 independent reflections with $I \geq 2\sigma(I)$. The P_2N_2 ring is planar with the borane (3) groups coordinated to the phosphorus atoms in an *exo*, *cis* configuration; the P—N, P—F, and P—B bond distances are 1.657(5) Å and 1.661(5), 1.558(5) Å, and 1.836(11) Å, respectively.

INTRODUCTION

Diazadiphosphetidine ligands of the general type

$XPN(R)P(X)NR$ (R = alkyl group, X = halogen, NR_2, OR)

have been known for some time; however, the coordination chemistry of these ligands has not been extensively explored.[1–3] Like numerous other diphosphines, the diazadiphosphetidines are expected to act as multifunctional ligands as a consequence of the several sites of reactivity present in the ring system. Specifically, the potential reaction sites include the phosphorus atom and nitrogen atom lone pairs, the P—N bonds and the P—X bonds. Stimulated by several fruitful studies of the coordination properties of the acyclic aminodiphosphine, $CH_3N(PF_2)_2$,[4–7] we have undertaken an investigation of the coordination chemistry of

$FPN(Bu^t)P(F)NBu^t$,

1,

toward borane(3), metal carbonyl fragments, and organometallic nucleophiles.[8] In this report we describe the reaction chemistry of this ligand with B_2H_6 and the molecular structure of the bis-borane(3) adduct. Later reports will relate the rather extensive chemistry shown by this ligand in combination with metal carbonyl and organometallic compounds.

EXPERIMENTAL

General Information and Materials

Standard high vacuum synthetic techniques were used for the manipulations of the volatile compounds. Mass spectra were recorded on a Dupont Model 21–491 spectrometer operating at 70 eV. Infrared spectra were recorded on a Perkin Elmer Model 621 infrared spectrometer using a mull cell fitted with KBr windows. The NMR spectra were recorded on a Varian XL-100 NMR spectrometer operating at 32.1 MHz (^{11}B), 24.2 MHz (^{13}C), 94.1 MHz (^{19}F), and 40.4 MHz (^{31}P). These spectra were collected in the pulse-Fourier transform mode using a Nicolet TT-100 data system. ^1H NMR spectra were recorded on a Varian EM-390 spectrometer. Samples were contained in sealed 5 mm tubes rigidly placed in a 12 mm tube containing a deuterated lock sample. Standards used were $BF_3O(C_2H_5)_2$ ^{11}B, $CFCl_3$ ^{19}F, 85% H_3PO_4 ^{31}P, TMS ^1H, ^{13}C. *All* downfield shifts from the standards are reported as $+\delta$.

The $ClPN(Bu^t)P(Cl)N(Bu^t)$ was prepared by a literature procedure[9] and the fluoro analog **1** was prepared by fluorination with SbF_3. Diborane (6) was prepared as described in the literature.[10]

Preparation of $FPN(Bu^t)P(F)N(Bu^t) \cdot BH_3$, **2** Typically a 3.0 mmol sample of ligand was syringed into a dry nitrogen filled

Schlenk flask. The flask was evacuated, a 1.5 mmol sample of B_2H_6 was condensed onto the ligand and the contents of the flask were warmed to 25°C. After thirty minutes the flask was cooled to 0°C and the volatile materials were distilled from the flask. The borane complex was retained in the flask. Mass spectrum [m/e, assignment, relative intensity]:[11] 256–254, $F_2P_2N_2C_8H_{18}\cdot BH^+_{3-1}$, total intensity 2; 242, $F_2P_2N_2C_8H^+_{18}$, 16; 241, $F_2P_2N_2C_8H^+_{17}$, 13; 227, $F_2P_2N_2C_7H^+_{15}$, 100; 171, $F_2P_2N\text{-}C_4H^+_9$, 20; 114, $F_2P_2N^+$, 13; 106, $FPNC_3H^+_6$, 68; 102, $PNC_4H^+_9$, 38; 57, $C_4H^+_9$, 73; 41, $NC_2H^+_3$, 43. Infrared spectrum (cm^{-1}) (liquid thin film):[12] 3000–2825(s, br), 2408(s), 2360(m), 2240(w), 2200(w), 1750(vw), 1620(vw), 1468(m), 1403(m), 1373(s), 1313(w), 1258(s), 1235(m), 1203(s), 1155(w), 1128(m), 1065(s), 1050(s), 940(s), 920(s), 875(w), 840(s), 815(s), 760(s), 728(m), 695(m), 595(m), 558(m), 538(m), 480(m), 430(w), 390(m), 350(w). NMR spectra ($CDCl_3$), 30°C: ^1H, δ 1.3 ppm; $^{11}B\{^1H\})$ δ -36.8 ppm, $J_{BP} = 61.2$ Hz, $J_{BH} = 96.0$ Hz, $^{13}C\{^1H\}$ δ 30.5 ppm, δ 54.0 ppm; ^{19}F δ -37.15 ppm; $J_{PF} = 1220.7$ Hz, $J_{PP'} = 55.7$ Hz, δ -22.6 $J_{PF} = 1252$ Hz, $J_{PP'} = 56.0$; $^{31}P\{^1H\}$ δ 139.8 ppm $J_{PF} = 1217.2$ Hz, δ 134.6 ppm, $J_{PF} = 1252.3$ Hz, $J_{PB} = 55.7$ Hz.

Preparation of $\overline{FPN(Bu^t)P(F)N}(Bu^t)\cdot 2BH_3$, **3** A 3.0 mmol sample of ligand was syringed into a Schlenk flask and a two-fold molar excess of B_2H_6 was condensed into the flask. The contents of the flask were maintained at 25°C for thirty minutes. The volatile products were pumped from the flask, and the remaining solid was vacuum sublimed onto a cold finger held at −78°C. Mass spectrum [m/e, assignment, relative intensity]:[11] 270–266, $F_2P_2N_2C_8H_{18}B_2H^+_{6-2}$ total intensity 1; 256–254, $F_2P_2N_2C_8H_{18}BH^+_{3-1}$, 3; 242, $F_2P_2N_2C_8H_8H^+_{18}$, 8; 241, $F_2P_2N_2C_7H^+_{17}$, 8; 227, $F_2P_2N_2C_7H^+_{15}$, 54; 199, $F_2P_2N_2C_4H_{12}B^+$, 5; 171, $F_2P_2NC_4H^+_9$, 8; 114, $F_2P_2N^+$, 5; 106, $FPNC_3H^+_6$, 32; 102 $PNC_4H^+_9$, 20; 57, $C_4H^+_9$, 100; 41, $NC_2H^+_3$, 43. Infrared spectrum (cm^{-1}) (liquid thin film):[12] 300–2850(s, br), 2600(s), 2400(m), 2230(w), 2185(w), 2120(w), 1930(w), 1930(w), 1620(m), 1470(m), 1400(m), 1373(s), 1313(w), 1250(s), 1235(m), 1190(s), 1155(w), 1125(m), 1070(s), 1045(s), 940(s), 920(s), 870(w), 835(s), 810(s), 750(s), 720(s), 720(m), 700(m), 595(s), 558(m), 525(s), 485(m), 420(w), 385(m), 340(w). NMR spectra ($CFCl_3$), 30°C: ^1H δ 1.8 ppm; $^{11}B\{^1H\}$ δ -38.1 ppm, $J_{BP} = 46.5$ Hz; $J_{BH} = 101.2$ Hz; ^{19}F δ -34.0 ppm, $J_{PF} = 1304$ Hz; $^{31}P\{^1H\}$ 128.4 ppm; $J_{PF} = 1298$ Hz.

Crystal data for **3** A crystal of dimensions 0.7 × 0.25 × 0.25 mm was enclosed in a glass capillary under a dry nitrogen atmosphere. The crystal was centered on a Syntex P3/F automated diffractometer. Determinations of the crystal class, the orientation matrix, and accurate unit cell dimensions were performed in a standard manner.[13] The data were collected at 298°K by the θ–2θ technique with monochromatic Cu Ka radiation using a scintillation counter and a pulse height analyzer. Details of the data collection appear in Table I. A survey of the complete data set revealed systematic absences hOl for h + l = 2n + 1 and OkO for k = 2n + 1. The centrosymmetric monoclinic space group $P2_1/m$ was strongly indicated. Corrections for absorption were found to be unnecessary. The redundant and equivalent reflection data were averaged and were converted to unscaled $|F_0|$ values following corrections for Lorentz and polarization effects.

Solution and Refinement of the Structure The crystallographic computations were performed on an in-house Syntex XTL system.[14] The structure was solved by direct methods using the MULTAN package. An initial *E*-map revealed the location of all nonhydrogen atoms. Isotropic refinement of the 11 independent atoms converged at $R = 0.18$. A Fourier map revealed approximate positions for the hydrogen atoms, from which idealized coordinates were calculated using tetrahedral angles and C-H and B-H distances of 1.01 Å. Isotropic refinement was continued with the hydrogen atoms in

TABLE I

Experimental data for the X-ray diffraction study of $\overline{FPN(Bu^t)P(F)N}\text{-}(Bu^t)\cdot(BH_3)_2$

(*a*) *Crystal Parameters at 298°K*[a]

cryst system: monoclinic
space group: $P2_1/m$
a 6.328(4) Å
b 12.183(5) Å
c 10.627(4) Å

$\beta = 100.56(1)°$
V = 805.40 $Å^3$
Z = 2
mol. wt. = 269.84
ρ(calcd) = 1.11 g/cm^3
F(000) = 288

(*b*) *Measurement of Intensity Data*

diffractometer: Syntex P3/F
radiation: Cu $K\alpha(\lambda 1.5418$ Å)
monochromator: highly oriented graphite
reflections measured: +h, +k, ±l
scan type: coupled θ(crystal) – 2θ(counter)
scan range: from $[2\theta(K_{\alpha 1}) - 1.0]°$ to $[2\theta(K_{\alpha 2}) + 1.0]°$
2θ range: 3–120°
scan speed: 3.91–29.30°/min (in 2θ)
bkgd measurement: stationary crystal and counter; at beginning and end of each 2θ scan—each for half the time taken for a 2θ scan standard reflections: 0, 5, 3, and 2, 2, 2, reflections measured every 48 reflections; no significant changes in intensity were observed reflections collected: 1273 total yielding 1147 independent reflections
reflections observed ($I \geq 2\sigma(I)$): 996 (86.8%)
abs. coeff: $\mu = 24.4$ cm^{-1}

---

[a] Unit cell parameters were derived from a least-squares fit to the setting angles of the unresolved Cu $K\alpha$ components of 24 reflections.

TABLE II

Positional parameters and thermal parameters of $\mathrm{F\overline{PN(Bu^{t})P(F)N}(Bu^{t})\cdot(BH_{3})_{2}}$

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	0.2068(3)	0.6493(1)	0.2318(2)	7.3(1)	4.7(1)	7.1(1)	−0.0(1)	1.7(1)	−0.2(1)
F(1)	−0.0200(7)	0.5963(4)	0.1938(4)	9.9(3)	9.0(3)	12.0(4)	−3.5(3)	2.0(3)	−1.4(3)
N(1)	0.2190(11)	0.7500	0.1287(6)	6.6(5)	4.7(4)	5.4(4)	0.0	1.1(3)	0.0
N(2)	0.1837(11)	0.7500	0.3337(6)	7.0(5)	3.9(4)	6.0(4)	0.0	1.2(4)	0.0
C(1)	0.2662(17)	0.7500	−0.0033(9)	8.3(7)	8.3(7)	6.5(6)	0.0	1.5(6)	0.0
C(11)	0.1659(16)	0.0016(9)	−0.0717(7)	14.9(8)	14.6(9)	6.7(5)	−2.6(7)	1.7(5)	−2.2(6)
C(12)	0.5037(24)	0.7500	0.0011(14)	11.9(10)	13.4(12)	11.2(10)	0.0	4.4(8)	0.0
C(2)	0.1826(16)	0.7500	0.4740(9)	7.9(7)	6.9(6)	6.2(6)	0.0	1.7(5)	0.0
C(21)	0.0684(13)	0.6456(8)	0.5053(8)	10.9(7)	13.5(8)	9.9(6)	−1.5(6)	4.6(5)	1.2(6)
C(22)	0.4112(19)	0.7500	0.5481(10)	10.9(9)	10.4(9)	6.5(7)	0.0	0.9(6)	0.0
B(1)	0.4067(19)	0.5390(8)	0.2671(10)	15.7(10)	7.3(6)	11.1(8)	4.3(7)	3.5(7)	1.0(6)

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
H(11-1)	0.2416	0.5924	−0.0250	H(21-3)	0.0359	0.6586	0.5972
H(11-2)	0.1823	0.6426	−0.1605	H(22-1)	0.4987	0.8101	0.5110
H(11-3)	0.0125	0.6404	−0.0618	H(22-2)	0.4230	0.7500	0.6368
H(21-1)	0.5601	0.8097	0.0347				
H(12-2)	0.5433	0.7500	−0.0858	H(1)	0.4166	0.5107	0.3553
H(21-1)	0.1741	0.6027	0.4894	H(2)	0.3656	0.4832	0.2125
H(21-2)	0.0826	0.3333	0.5792	H(3)	0.5510	0.5638	0.2528

TABLE III

Intramolecular bond distances and angles for $\mathrm{FP\overline{N(Bu^{t})P(F)N}(Bu^{t})\cdot(BH_{3})_{2}}$

(*a*) *Bond Lengths*, Å			
P(1)-N(1)	1.657(5)	N(1)-C(1)	1.487(13)
P(1)-N(2)	1.661(5)	C(1)-C(11)	1.496(11)
P(1)-F(1)	1.558(5)	C(1)-C(12)	1.495(19)
P(1)-B(1)	1.836(1)		
(*b*) *Nonbonded Distances*, Å			
P(1)-P(2)	2.45(1)		
N(1)-N(2)	2.23(1)		
(*c*) *Bond Angles, Deg.*			
F(1)-P(1)-N(1)	106.7(3)	F(1)-P(1)-B(1)	108.5(4)
F(1)-P(1)-N(2)	106.7(3)	N(1)-P(1)-B(1)	124.3(5)
N(1)-P(1)-N(2)	84.5(3)	N(2)-P(1)-B(1)	123.2(4)
P(1)-N(1)-C(1)	132.1(2)	C(11)-C(1)-C(12)	110.5(7)
P(1)-N(1)-P(2)	95.6(4)	C(11)-C(1)-N(1)	108.5(6)
		C(12)-C(1)-N(1)	110.2(8)

fixed ideal positions and with hydrogen isotropic thermal factors set at $\beta = 5.0$ Å^2 to converge at $R = 0.15$. Anisotropic refinement of all nonhydrogen atoms yielded $R = 0.093$ at convergence. The final atomic positional and thermal factors are given in Table II. Important intramolecular distances and angles for **3** are summarized in Table III and least-squares planes are given in Table IV.

RESULTS AND DISCUSSION

The combinations of B_2H_6 with the diazadiphosphetidine ligand, **1**, in 0.5: 1 and 1: 1 mole ratios at 25°C produce the respective mono-borane(3) and bis-borane (3) addition complexes. The reactions are summarized by the following equations.

$$1/2\mathrm{B_2H_6} + \underset{\mathbf{1}}{\mathrm{F\overline{PN(Bu^{t})P(F)N}(Bu^{t})}} \longrightarrow \underset{\mathbf{2}}{\mathrm{F\overline{PN(Bu^{t})P(F)N}(Bu^{t})\cdot BH_3}}$$

$$\mathrm{B_2H_6} + \underset{\mathbf{1}}{\mathrm{F\overline{PN(Bu^{t})P(F)N}(Bu^{t})}} \longrightarrow \underset{\mathbf{3}}{\mathrm{F\overline{PN(Bu^{t})P(F)N}(Bu^{t})\cdot 2BH_3}}$$

TABLE IV

Least-squares planes and deviation of atoms from the planes

Plane 1:	P(1)-N(1)-P(2)-N(2)			
	$(-0.9602)x + (-0.0028)y + (-0.2793)z = -1.5231$			
	P(1)	0.026(6)	P(2)	0.026(6)
	N(1)	−0.003(2)	N(2)	−0.004(2)
Plane 2:	P(1)-N(1)-C(1)-P(2)-N(2)-C(2)			
	$(-0.9608)x + (0.0022)y + (-0.2771)z = -1.5179$			
	P(1)	0.002(2)	P(2)	0.002(2)
	N(1)	0.029(6)	N(2)	0.034(6)
	C(1)	−0.098(8)	C(2)	−0.090(8)
Plane 3:	P(1)-F(1)-B(1)-P(2)-F(2)-B(2)			
	$(0.2795)x + (-0.0010)y + (-0.9602)z = -2.0980$			
	P(1)	0.001(2)	P(2)	0.001(2)
	F(1)	−0.003(3)	F(2)	−0.003(4)
	B(1)	−0.012(7)	B(2)	−0.024(10)

The new compounds, **2** and **3**, are a colorless liquid and a colorless solid respectively. Both compounds are stable to thermal decomposition in an atmosphere of dry nitrogen at 25°C and **3** readily sublimes at room temperature. The basic molecular compositions and structures of **2** and **3** were determined from mass, infrared and NMR spectroscopic data. The mass spectra of **2** and **3** show ions with m/e values corresponding to the respective parent ions, and the remainder of the spectra resemble the mass spectrum of the free ligand. The infrared spectra of **2** and **3** are similar to the spectrum of the free ligand with additional bands appearing in the regions 2600–2200 cm^{-1} (B—H stretch), 1150–1050 cm^{-1} (BH_3 deformation) and 550–500 cm^{-1} (B—P stretch).[13]

The multinuclear NMR spectra of **2** and **3** are informative and worthy of discussion. The ^1H NMR spectra for **2** and **3** show a resonance at 1.3 ppm and 1.8 ppm, respectively. These resonances are broadened with respect to the free ligand ^1H resonance centered at 1.5 ppm, and they may be assigned to the protons of the *tert*-butyl groups. The proton resonance for the borane groups are broad and weak and accurate chemical shift determinations were not made. The $^{13}C\{^1H\}$ NMR spectra, **2** δ 30.5, 54.0 ppm, **3** δ 31.2, 58.4 ppm compare favorably with the free ligand resonances, **1** δ 31.6; 52.5 ppm, and the resonances may be assigned to the terminal methyl groups and the tertiary carbon atom. The $^{11}B\{^1H\}$ NMR spectra for **2** and **3** show doublets centered at −36.8 and −38.1 ppm (upfield of $BF_3 \cdot OEt_2$) with $J_{BP} = 61$ and 46 Hz respectively. Restoration of the proton coupling splits each member of the doublets into quartets, $J_{BH} = 96$ and 101 Hz. These spectra are clearly consistent with BH_3 coordination to the phosphorus atom lone pairs. The chemical shifts for the BH_3 groups compare favorably with the chemical shifts for phosphorus bonded BH_3 groups in

$\overline{(CH_3)NCH_2CH_2N(CH_3)P}(F)BH_3$,[15]

$F_2PN(CH_3)P(F_2)BH_3)$[4]

and

$F_2P(BH_3)N(CH_3)PF_2(BH_3'$.[4]

The $^{31}P\{^1H\}$ NMR spectrum for **2** shows two resonances centered at 139.8 and 134.6 ppm. The lower field resonance is split into a doublet, $^1J_{PF} = 1217$ Hz while the upfield resonance is split into a doublet of quartets, $^1J_{PF} = 1252$ Hz and $^1J_{PB} = 55$ Hz. The spectrum closely resembles the spectrum of the monoborane(3) complex of $CH_3N(PF_2)_2$,[4] and the spectrum is interpreted by assigning the low field resonance to an uncoordinated phosphorus atom and the high field resonance to a BH_3 coordinated phosphorus atom. The $^{31}P\{^1H\}$ NMR spectrum of **1** shows a complex XAA′X′ system with δ 165.3 ppm.[16] The $^{31}P\{^1H\}$ NMR spectrum for **3** shows one resonance centered at 128.4 ppm which is split into a doublet by fluorine coupling $^1J_{PF} = 1298$ Hz, and each member of the doublet is further split into a broad quartet, $^1J_{PB} \sim 40$ Hz. This spectrum is consistent with each phosphorus atom being coordinated by a BH_3 group. The ^{19}F NMR spectrum of **2** is consistent with the ^{31}P NMR spectrum: $\delta - 37.15$ ppm, $^1J_{PF} = 1220$ Hz (doublet), $J_{PP'} = 57$ Hz (doublet) which may be assigned to the fluorine atom bonded to the uncoordinated phosphorus atom, and $\delta = 22.6$ ppm, $^1J_{PF} = 1252$ Hz (doublet) $^2J_{PP'} = 56$ Hz (doublet). The latter doublet of doublets is broad by comparison to the high field doublet of doublets, and it is assigned to the fluorine atom bonded to the coordinated phosphorous atom. The two bond J_{FB} coupling and three bond J_{FH} coupling are commonly not resolved in this type of complex. The ^{19}F observed chemical shift and coupling parameters are also consistent with the parameters from the free ligand: $\delta - 22.2$ ppm, $^1J_{PF} = 1190$ Hz, $2J_{PP'} = 92.5$ Hz, $^3J_{PF'} = 25.5$ Hz, $^4J_{FF'} = 29.0$ Hz. The ^{19}F NMR spectrum of **3** is consistent with the respective ^{31}P NMR spectrum: $\delta - 34.0$ ppm, $^1J_{PF} = 1304$ Hz. Only one fluorine environment is found and each member of the widely spaced doublet is a complex multiplet which is poorly resolved.

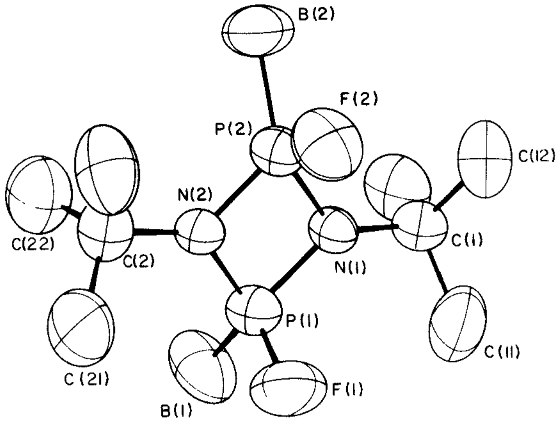

FIGURE 1 Molecular structure of $FPN(Bu^t)P(F)N(Bu^t)\cdot(BH_3)_2$ showing atom labeling scheme (50% probability ellipsoids).

The above characterization data establish the basic connectivities of complexes **2** and **3**. As expected for an aminophosphine ligand[4,15] the borane groups are bonded to the phosphorus base sites. However, the spectroscopic data do not unambiguously determine the *cis* or *trans* borane (3) stereochemistry of the complex **3**. Since the stereochemical predilection adopted by **3** is expected to transfer to the structure of metal carbonyl complexes of **1** prepared in our laboratory,[16] we elected to determine the single crystal structure of **3** by X-ray diffraction methods. The molecular structure of the uncomplexed ligand **1** has not been determined; however, the structures of the chloro analogue

$ClPN(Bu^t)P(Cl)N(Bu^t)$[17] **4**

and the chlorophosphoryl derivative

$Cl(O)PN(Bu^t)P(Cl)(O)N(Bu^t)$[18] **5**

have been determined by X-ray diffraction methods.

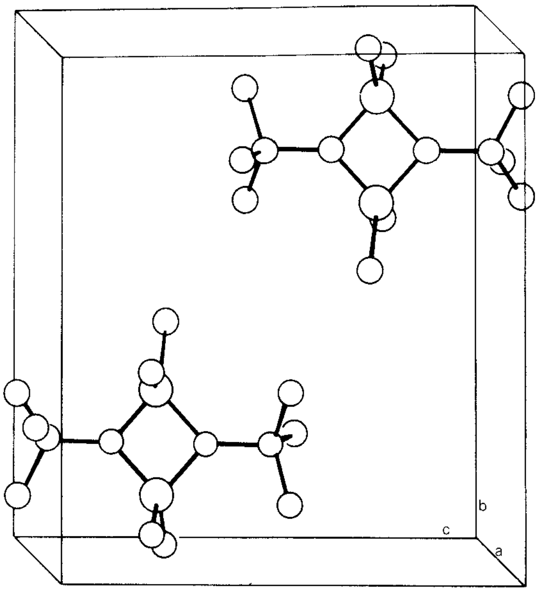

FIGURE 2 Packing diagram showing two molecules in the monoclinic unit cell.

The molecular structure of **3** is shown in Figure 1, a packing diagram appears in Figure 2 and the significant bond angles and distances are summarized in Table III. The crystal structure contains isolated monomeric units of **3** with no intermolecular nonhydrogen atom distances shorter than 4.0 Å. Each molecule of **3** possesses crystallographic $C_s - m$ symmetry with N(1), N(2), C(1), C(2), C(12), and C(22) lying on the mirror plane. The molecule conforms to an approximate $C_{2v} - 2\,mm$ geometry with the two borane groups in a cis configuration. The $(P—N)_2$ diazaphosphetidine ring is nearly planar; the slight puckering of the ring is represented by a planes calculation shown in Table IV. The P—N bond distances are nearly identical, P—N(1) 1.657(5) Å and P—N(2) 1.661(5) Å, and the internal ring angles are N(1)—P—N(2) 84.5(3)° and P(1)—N—P(2) 95.6(4)°. The mean P—N bond distance, 1.659 Å is very similar to the P—N bond distance in **5**, 1.661 Å, and shorter than the distance in **4**, 1.689 Å, which is consistent with the presence of both a fluorine atom and BH_3 group on the phosphorus atom. In each case the P—N bond distance is significantly shorter than the commonly accepted single P—N bond distance in $H_3NPO_3^-$, 1.75 Å,[19] and this bond shortening is taken as evidence for partial multiple bond character in the diazaphosphetidine ring.

The nonbonded N(1) ··· N(2) separations, **3**, 2.23(1) Å, **4**, 2.23 Å, and **5**, 2.25 Å are nearly constant and shorter than the sum of van der Waal radii, 3.0 Å. The nonbonded P(1) ··· P(2) separations are subject to greater variation in this series: **3**, 2.45(1) Å, **4**, 2.53 Å, and **5**, 2.44 Å. The separations also are shorter than the sum of the van der Waal radii, 3.8 Å. This trend is further reflected in the internal ring angles: N—P—N, 84.5°, 82.5°, and 85.5° and P—N—P 95.4°, 97.3°, and 94.5°. The geometries of $(P—N)_2$ rings have been discussed in some detail.[18,20] It has been suggested that the nearly planar ring geometries are a result of balanced N ··· N and P ··· P repulsions. Based upon the available data it appears that inductive variations on the ring substituents are reflected by variations in the P···P nonbonded distance and internal ring angles.

The remaining important bond distances include the P—F distance, 1.558(5) Å and the P—B distance, 1.836(10) Å. These distances are significantly shorter than the respective distances bound in $(CH_3)_2NPF_2 \cdot B_4H_8$, P — F, 1.583 Å, and P—B, 1.856 Å.[21] It is also interesting that the stereochemical configurations in the borane complex **3** and the free chloro ligand **4** are *cis* while the configuration of the phosphoryl derivative is *trans*. The *trans* configuration of **5** was unexpected,[1,8] and the determination of structures for metal carbonyl and organometallic complexes of **1** should prove to be revealing with regard to this stereochemical point. Lastly, it is appropriate to note that the two PFB groups and the two N—C (tertiary) groups lie in mutually perpendicular planes (Table IV, planes 2 and 3). The eclipsed tertiary carbon atoms of the *t*-butylamine groups are displaced out of the $(P—N)_2$ plane by 0.098(8) Å toward the two fluorine atoms. A larger displacement, 0.28 Å, is found in **5**. The origin of this displacement may be a response to steric or packing forces in the crystal.

ACKNOWLEDGEMENT

RTP wishes to acknowledge the financial assistance of the University of New Mexico Research Allocations Committee and the National Science Foundation for an instrumentation grant (#CH-780921) which facilitated the purchase of the P3/F diffractometer and R3 structure determination and refinement systems.

SUPPLEMENTARY MATERIAL

Structure factors (4 pages) can be obtained from R.T.P.

REFERENCES AND NOTES

1. Reviews outlining some aspects of diazadiphosphetidine ligand chemistry have appeared: I. Haiduc, *The Chemistry of Inorganic Ring Systems*, J. Wiley: New York, 1970, Part 2; R. A. Shaw, *Phosphorus and Sulfur*, **4**, 101 (1978).
2. P. N. Hawker, L. S. Jenkins, and G. R. Willey, *J. Organomet. Chem.*, **118**, C14 (1976).
3. W. Zeiss and C. H. Feldt, *J. Organomet. Chem.*, **127**, C5 (1977).
4. R. T. Paine, *Inorg. Chem.*, **16**, 2996 (1977).
5. T. R. Johnson and J. F. Nixon, *J. Chem. Soc.*, A, 2518 (1969).
6. R. B. King and J. Gimeno, *Chem. Commun.*, 142 (1977); M. G. Newton, R. B. King, M. Chang, and J. Gimeno, *J. Amer. Chem., Soc.*, **99**, 2802 (1977); R. B. King, M. G. Newton, J. Gimeno, and M. Chang, *Inorg. Chim. Acta*, **23**, L35 (1977); R. B. King and K. N. Chen, *Inorg. Chim. Acta*, **23**, L19 (1977); M. G. Newton, R. B. King, M. Chang, N. S. Pantaleo, and J. Gimeno, *Chem. Commun.*, 531 (1977); M. G. Newton, R. B. King, M. Chang, and J. Gimeno, *J. Amer. Chem. Soc.*, **100**, 1632 (1978); M. Chang, M. G. Newton, and R. B. King, *Inorg. Chim. Acta*, **30**, L341 (1978); R. B. King and J. Gimeno, *Inorg. Chem.*, **17**, 2390 (1978); R. B. King and J. Gimeno, *Inorg. Chem.*, **17**, 2396 (1978) and R. B. King, J. Gimeno, and T. J. Lotz, *Inorg. Chem.*, **17**, 2401 (1978).
7. R. W. Light and R. T. Paine, *Inorg. Chem.*, **18**, 2345 (1979).
8. R. W. Light, Ph.D. Thesis, University of New Mexico, Albuquerque (1979).
9. O. J. Scherer and P. Klusmann, *Angew. Chem. Intl. Ed.*, **8**, 752 (1969).
10. M. J. Klein, B. C. Harrison, I. J. Soloman, *J. Am. Chem. Soc.*, **80**, 4149 (1958).
11. The parent ion regions of the borane complexes are not intense or well resolved. The ion intensities for the parent ion minus hydrogen from the borane group are integrated together.
12. The infrared spectrum (cm^{-1}) for a liquid thin film of **1** shows the following absorption: 3000–2825(s, br), 1463(m), 1393(m), 1368(s), 1310(w), 1245(m), 1210(s), 1130(w), 1040(s), 933(s), 912(s), 850(w), 810(sh), 800(m), 750(s), 718(s), 640(m), 590(m), 540(w), 440(m), 385(m), 355(w). The B-P stretching modes can be tentatively assigned at 538 cm^{-1} for **2** and 525 cm^{-1} for **3**. These frequencies are about 50 cm^{-1} lower than the frequencies observed in the mono-borane(3) and bis-borane(3) complexes of $(F_2P)_2NCH_3$.[4]
13. C. F. Campana, D. F. Sheppard, and W. N. Litchman, submitted to *Inorg. Chem.*
14. All X-ray structure calculations were performed using the Syntex XTL Structure Determination Package.
15. S. Fleming, M. K. Lupton, and K. Jekot, *Inorg. Chem.*, **11**, 2534 (1972).
16. J. Jessup, D. Byers, and R. T. Paine, unpublished results.
17. K. W. Muir, *J. Chem. Soc.* (*Dalton*), 259 (1975).
18. L. Manojlovic-Muir and K. W. Muir, *J. Chem. Soc.* (*Dalton*), 2395 (1974).
19. D. W. J. Cruickshank, *Acta Cryst.*, **17**, 671 (1964).
20. M. B. Peterson and A. J. Wagner, *J. Chem. Soc.*, (*Dalton*), 106 (1973).
21. M. D. LaPrade and C. E. Nordman, *Inorg. Chem.*, **8**, 1669 (1969).