and ion charge. The most significant are in the order of binding affinity $[ReS_4]^- < [MoS_4]^{2-} \simeq [WS_4]^{2-} < [VS_4]^{3-}$ toward $FeCl_2$, the ability of $[VS_4]^{3-}$ to form $[VFe_2S_4L_4]^{3-}$ with either hard ($L = Cl^-$) or soft ($L = PhS^-$) ligands, and the order of Fe–Cl distances $M = V > Mo \simeq W$, which is one measure of charge delocalization in $[MFe_2S_4Cl_4]^{3-,2-}$. The scope of the metal complex chemistry of $[VS_4]^{3-}$ remains to be defined. This point has been partly examined by means of reaction systems containing $(NH_4)_3[VS_4]$ and $(Et_4N)_2[ML_4]$ (M = Mn(II), Co(II), Ni(II), Cu(II) ($L = Cl^-$); Zn(II), Cd(II) ($L = Cl^-$, PhS^-)) in DMF or acetonitrile. Solution color changes were observed, followed by separation of amorphous black solids and decolorization of the solutions. The reaction between $[VS_4]^{3-}$ and AgCN gives a similar result. Evidently in these systems $[VS_4]^{3-}$ acts as a sulfide donor. However, the reaction system containing the mole ratio 3:1 $FeCl_2$:$(NH_4)_3[VS_4]$ in DMF affords in good yield the new cluster core $[VFe_3S_4]^{2+}$, with a cubane-type structure.[49] Clusters of this type will be the subject of our next report on V–Fe–S chemistry.

Acknowledgment. This research was supported by NSF Grant CHE 81-06017 and NIH Grant GM 28856. X-ray diffraction and NMR equipment used in this research was obtained by NSF Grants CHE 80-00670 and CHE 80-08891 and NIH Grant 1 S10 RR 02247.

Supplementary Material Available: X-ray structural data for $(NH_4)_3[VS_4]$, $(n\text{-}Bu_4N)[ReS_4]$, and $(Me_4N)_3[VFe_2S_4Cl_4]{\cdot}DMF$: anisotropic temperature factors, hydrogen atom coordinates and temperature factors, interatomic distances and angles in the cations, and calculated and observed structure factors (44 pages). Ordering information is given on any current masthead page.

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Contribution from the Laboratoire de Chimie Moléculaire, Unité Associée au CNRS, Université de Nice, Parc Valrose, 06034 Nice, France, and Laboratoire de Chimie Organique Physique, LA 321, Département de Recherches Fondamentales, Centre d'Etudes Nucléaires 85X, Université Scientifique et Médicale, 38041 Grenoble, France

Dibasic Character of a Bicyclic Aminophosphane. Formation and Crystal Structure of $H_3B{\cdot}\overline{P(OCMe_2CH_2)_2N}{\cdot}BH_3$

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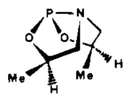
Phosphorus-bound borane adducts form first when diborane is allowed to react with the bicyclic aminophosphanes **1**–**3**. Then, notably, a second borane group is coordinated to the nitrogen site unless it is sterically hindered. All the compounds formed were isolated in good yields. The bis(borane) adducts are unusually stable. $H_3B{\cdot}\overline{P(OCMe_2CH_2)_2N}{\cdot}BH_3$ crystallizes in the monoclinic systems $P2_1/n$ with unit cell dimensions a = 7.803 (1) Å, b = 16.650 (1) Å, c = 10.431 (1) Å, β = 95.1 (1)°, and Z = 4. The dibasic character of ligand **2** is established by the existence of a B–P bond (1.873 (7) Å) and of a B–N bond (1.655 (8) Å). The P–N bond length (1.757 (4) Å) indicates the absence of π-bonding. The almost identical five-membered rings display a N-flap envelope conformation and are assembled in a helicoidal exo–endo arrangement (B–N–P–B dihedral angle 21.7°). NMR data (^{11}B and ^{31}P) establish that the B–P and B–N coordination bonds on **2b** and related bis(borane) adducts are preserved in solution. The basicity of the nitrogen atom of these cyclic aminophosphanes is further illustrated by the formation of the N-bonded BF_3 adduct $\overline{P(OCHMeCH_2)_2N}{\cdot}BF_3$ (**1c**).

Introduction

Although the description of the P–N bond and the extent of P_π–d_π interaction between the two atoms remains a subject of controversy,[1] it is a well-established experimental fact that aminophosphanes generally behave as P-donors only.[2] Restoration of the basicity of a tricoordinated nitrogen atom directly bonded to a phosphorus center appears to require constrained structures capable of forcing the nitrogen to retain its pyramidal geometry.[3,4] However, this nonplanarity is not in itself sufficient to induce coordination of the P-bound nitrogen to Lewis acids such as BH_3 or BF_3.[3] Finally, a few P- and N-bonded bis(borane) adducts have been obtained, and these were generally reported to be unstable.[3,5] The harder BF_3 is more inclined to coordinate at nitrogen, and N-bonded BF_3 adducts have indeed been reported to form with F_2PNMe_2[6] and $\overline{FPN(Me)(CH_2)_2N}Me$.[7] The recent obtainment of a stable adduct in which two borane groups are coordinated to two nitrogen atoms occupying apical positions on a five-coordinated bipyramidal phosphorus atom must also be mentioned.[8]

The bicyclic aminophosphanes **1**–**3**[9] are attractive because their bicyclic structure forces the P-bonded nitrogen atom to remain pyramidal; **1** is obtained as a mixture of meso and racemic diastereiosomers in 80:20 ratio and **3** as a pair of enantiomers.



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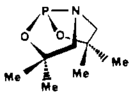

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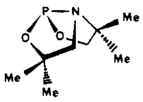

3

The basicity of the nitrogen site in the bicyclic aminophosphanes **1** and **2** has now been confirmed by the formation of unusually

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stable bis(borane) adducts as well as of a N-coordinated BF_3 adduct. $H_3B\cdot\overline{P(OCMe_2CH_2)_2N}\cdot BH_3$ appears to be the first compound with a P-bonded N coordinated to a borane group for which X-ray data are being reported. Part of this work has appeared as a preliminary communication.[10]

Experimental Section

All manipulations were carried out under argon, with use of Schlenk tubes or vacuum line techniques. Solvents were purified by standard procedures. Diborane[11] and the bicyclic phosphanes[9] were prepared according to the literature. The NMR spectra were recorded on a Bruker WH-90 spectrometer operating in the Fourier transform mode. Chemical shifts (Table IV) are given as positive for downfield shifts with respect to 85% H_3PO_4 for ^{31}P, $F_3B\cdot OEt_2$ for ^{11}B as external references, and CCl_3F for ^{19}F as internal reference. The infrared spectra were recorded on a Perkin-Elmer 577 spectrometer as Nujol mulls, and the mass spectra on a VG Micromass 70-70F spectrometer. The mass spectra and the elemental analyses were performed by the Service Central de Microanalyses of the CNRS.

Synthesis of 3,7-Dimethyl-2,8-dioxa-5-aza-1-phosphabicyclo[3.3.0]octane–1-Borane (1a). Diborane (10.7 mg, 0.713 mmol) was condensed at −196 °C in an ampule containing ligand **1** (230 mg, 1.43 mmol) in 3 mL of toluene; the ampule was sealed under vacuum and then allowed to warm to room temperature. After 24 h the solution was cooled to −30 °C; transparent crystals grew after a few hours, and crystallization appeared to be complete after 48 h. The volatile fractions were distilled on a vacuum line, while the crystals were dried for 24 h under vacuum, to yield 225 mg (90%) of air-sensitive compound **1a**: mp 75 °C, dec pt 85–90 °C. IR: νB–H(asym) 2400 (s) cm^{-1}; ν_{B-H}(sym) 2345 (w) cm^{-1}. Mass spectrum (70 eV, 90 °C): M = $C_6H_{15}BNO_2P$; *m*/*e* (relative intensity) 176 (35) [MH], 162 (63) [M − CH_3], 147 (19) [MH − BH_3 − CH_3], 132 (47) [MH − BH_3 − 2 CH_3], 117 (100) [C_4H_8NOP]. Anal. Calcd for $C_6H_{18}NBNO_2P$: C, 41.19; H, 8.58; B, 6.18; N, 8.01; P, 17.73. Found: C, 41.64; H, 8.64; B, 6.14; N, 8.07; P, 17.14.

Synthesis of 3,3,7,7-Tetramethyl-2,8-dioxa-5-aza-1-phosphabicyclo[3.3.0]octane–1-Borane (2a). The same experimental procedure applied to 26 mg (0.94 mmol) of diborane and 396 mg (2.08 mmol) of ligand **2** gave, after recrystallization in toluene, 285 mg (67%) of the mono(borane) adduct **2a** as white air-sensitive crystals, mp 130 °C. IR: ν_{B-H}(asym) 2400 (s) cm^{-1}; ν_{B-H} (sym) 2350 (w) cm^{-1}. Mass spectrum (70 eV, 200 °C): M = $C_8H_{19}BNO_2P$; *m*/*e* (relative intensity) 295 (32) [$(M - 4CH_2)_2 + H$], 230 (30) [$(M - 4CH_2)_2 - H_3PO_2$], 204 (4) [MH], 6.2 (100) [C_2H_7P or CH_3OP]. Anal. Calcd for $C_8H_{19}BNO_2P$: C, 47.29; H, 9.43; B, 5.32; N, 6.90; P, 15.26. Found: C, 47.80; H, 9.66; B, 5.16; N, 6.80; P, 14.98.

Synthesis of 3,3,6,6-Tetramethyl-2,8-dioxa-5-aza-1-phosphabicyclo[3.3.0]octane–1-Borane (3a). The same procedure applied to 267 mg (140 mmol) of **3** and 17.7 mg (0.65 mmol) of diborane in 5 mL of toluene gave, after 24 h at −20 °C, 198 mg (70%) of a white, air-sensitive crystalline solid (recrystallized in toluene), mp 80 °C. IR: ν_{B-H}(asym) 2400 (s) cm^{-1}; ν_{B-H}(sym) 2350 (w) cm^{-1}. Anal. Calcd for $C_8H_{19}BNO_2P$: C, 47.29; H, 9.43; B, 5.32; N, 6.90; P, 15.26. Found: C, 47.05; H, 9.40; B, 5.10; N, 6.92; P, 15.20.

Synthesis of 3,7-Dimethyl-2,8-dioxa-5-aza-1-phosphabicyclo[3.3.0]octane–1,5-Bis(borane) (1b). Diborane (59.6 mg, 1.16 mmol) was condensed in an ampule containing 350 mg (2.17 mmol) of **1** in 10 mL of toluene. The ampule was sealed under vacuum and allowed to reach room temperature. After 24 h, the volatiles were distilled and the residue yielded, after recrystallization in CH_2Cl_2/pentane, 347 mg (85%) of the white air-sensitive product **1b**, mp 110 °C. IR $\nu_{(P)B-H}$(asym) 2395(vs), cm^{-1}; $\nu_{(P)B-H}$(sym) 2330(w) cm^{-1}; $\nu_{(N)B-H}$(asym) 2460 (vs) cm^{-1}; $\nu_{(N)B-H}$(sym) 2280 (s) cm^{-1}. Mass spectrum (15 eV, 150 °C): M = $C_6H_{18}B_2NO_2P$; *m*/*e* (relative intensity) 346 (8) [2 M − CH_3], 190 (8) [MH], 175 (11) [M − CH_3], 160 (100) [$C_6H_{12}NO_2P$], 117 (28) [C_4H_8NOP]. Anal. Calcd for $C_6H_{18}B_2NO_2P$: C, 38.17; H, 9.61; B, 11.45; N, 7.41; P, 16.40. Found: C, 38.27; H, 9.54; B, 11.47; N, 7.41; P, 16.35.

Synthesis of 3,3,7,7-Tetramethyl-2,8-dioxa-5-aza-1-phosphabicyclo[3.3.0]octane–1,5-Bis(borane) (2b). The same experimental procedure, with 80 mg (2.97 mmol) of diborane and 280 mg (1.47 mmol) of **2**, yielded, after 24 h at −20 °C and recrystallization from toluene, 130 mg (40%) of **2b**, dec pt 110 °C. IR: $\nu_{(P)B-H}$ 2400 (vs), 2350 (w) cm^{-1}; $\nu_{(N)B-H}$ 2460 (vs), 2290 (s) cm^{-1}. Mass spectrum (70 eV, 200 °C): M = $C_8H_{22}B_2O_2P$; *m*/*e* 217 (9) [M], 202 (8) [MH − BH_3], 189 (13) [M − 2BH_3], 174 (15) [M − 2 BH_3 − CH_3], 170 (40) [M − 2 BH_3 − C_2H_5], 154 (17) [$C_6H_5NO_2P$], 131 (100) [$C_4H_6NO_2P$]. Anal. Calcd for $C_8H_{22}B_2NO_2P$: C, 44.25; H, 10.23; B, 9.96; N, 6.47; P, 14.28. Found: C, 45.10; H, 10.08; B, 8.90; N, 6.41; P, 13.05.

Table I. X-ray Crystallographic Data

mol formula	$C_8H_{22}O_2NPB$
mol wt	216.87
monoclinic space group	$P2_1/n$
a	7.803 (1) Å
b	16.650 (1) Å
c	10.431 (1) Å
β	95.1 (1)°
V	1349.7 $Å^3$
Z	4
d_{calcd}	1.068 $g\cdot cm^{-3}$
d_{measd}	1.07 $g\cdot cm^{3}$
Cu Kα radiation	λ = 1.540 51 Å, Ni filtered
cryst size	092 × 0.2 × 0.2 mm
$F(000)$	472
μ(Cu Kα)	16.1
θ range	$3° < \theta < 70°$
reflecns collected	2663
reflecns with $I > 3\sigma(I)$	1758
R	0.104
R_w	0.087

The borane adducts are stable for several months in the solid state. They are generally slightly soluble in toluene, more soluble in chloroform, dichloromethane, or acetonitrile; the solubility increases with the number of methyl groups present on the cyclic frame. Slow decomposition was observed for solutions of **1b** and **2b**, especially in acetonitrile (evolution of ~10% B_2H_6 after 24 h at room temperature).

Synthesis of 3,7-Dimethyl-2,8-dioxa-5-aza-1-phosphabicyclo[3.3.0]octane–5-Trifluoroborane (1c). By the procedure used for the synthesis of **1a**, a solution of the bicyclic aminophosphane **1** (217 mg, 1.35 mmol) in 7 mL of toluene was allowed to react with boron trifluoride (189.5 mg, 2.79 mmol) at −30 °C for 24 h. The formation of a supernatant precipitate was immediately observed. The sealed ampule was left for 3 more days at room temperature, and the volatile fractions were then distilled on a vacuum line. The crude solid was sublimed (80 °C, 10–5 mmHg) to yield 275 mg (89%) of white air-sensitive crystals (dec pt 155 °C) soluble in dichloromethane, chloroform, and toluene. IR: ν_{B-F} 1200 (s), 1155 (m) cm^{-1}. Mass spectrum: (200 °C, chemical ionization with NH_3): M = $C_6H_{12}F_3BNO_2P$; *m*/*e* 229 (0.5) [M], 209 (3) [M − HF], 180 (22) [M − CF_2], 162 (100) [MH − BF_3].

Crystallographic Data for 2b. The compound crystallized from the mother solution as colorless parallelepipedic needles. The space group was determined from Weissenberg photographs with Cu Kα radiation. The extinctions ($h0l$, $h + l = 2n$; $0k0$; $k = 2n$) indicated the $P2_1/n$ space group with $Z = 4$.

Unit cell parameters were determined by "least-squares fit" of the reflecting position of 25 reflections measured on a Nonius CAD 4 automatic diffractometer, with Ni-filtered Cu Kα radiation. The crystal data are reported in Table I.

The intensities of 2663 reflections ($3° < \theta < 70°$) were collected. Three check reflections (063, 150, 402) were recorded periodically and showed a time-dependent decay of the intensities that amounted to about 25% at the end of data collection. The data were corrected for Lorentz and polarization factors and time-dependent decay but not for absorption.

Structure Determination and Refinement. The structure was solved by direct methods (MULTAN).[12] The *E* map was calculated with 148 reflections ($E > 1.50$), and the solution with the best figure of merit revealed the positions of P, N, O, B, and two carbon atoms. Fourier synthesis allowed the location of all carbon atoms and some hydrogen atoms; the others were calculated. Least-squares refinement based on 1758 reflections ($F_o > 2\sigma$ and $F_o > 3\sigma$) with XFLSN[13] of non-hydrogen atom positions with anisotropic temperature factors converged with R = 10.4% ($R = \sum||F_o| - |F_c|/\text{"um}|F_o||$) and R_w = 8.7% ($R_w = [\sum_w(|F_o| - |F_c|)^2/\sum_w F_o^2]^{1/2}$). Hydrogen atoms were introduced into the refinement with an isotropic temperature factor of 6.0 $Å^2$ but were kept fixed. The poor quality of the crystal as well as the time-dependent decay precluded the obtainment of better reliability indices.

The final atomic parameters are collected in Table II, and bond distances and angles are reported in Table III.

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Table II. Atomic Parameters (with Standard Deviations in Parentheses)

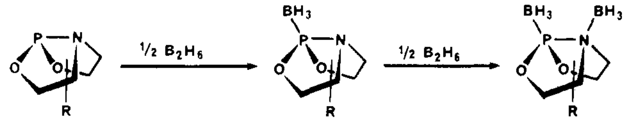
	x	*y*	*z*
P	248 (2)	8779 (1)	2455 (2)
N	−1434 (5)	8074 (3)	2314 (5)
B1	2600 (9)	8532 (5)	2626 (9)
B2	−817 (10)	7183 (5)	2887 (9)
O1	−350 (5)	9229 (2)	1193 (4)
O2	−339 (5)	9255 (3)	3632 (4)
C1	−1606 (7)	8831 (4)	264 (6)
C2	−1987 (8)	8040 (4)	905 (6)
C3	−2818 (7)	8432 (4)	3121 (7)
C4	−2065 (8)	9088 (4)	4021 (7)
C5	−3102 (8)	9418 (4)	36 (7)
C6	−756 (10)	8654 (4)	−946 (7)
C7	−3089 (9)	9837 (5)	3840 (8)
C8	−1846 (12)	8853 (6)	5371 (9)

Table III. Selected Bond Lengths and Angles (with Estimated Standard Deviations in Parentheses)

	Distances (Å)		
B1–P	1.873 (7)	N–C3	1.547 (6)
B2–N	1.655 (8)	C1–C2	1.518 (8)
P–N	1.757 (4)	C4–C3	1.523 (8)
P–O1	1.550 (4)	C1–C5	1.525 (8)
P–O2	1.564 (4)	C1–C6	1.507 (9)
O1–C1	1.472 (6)	C4–C7	1.485 (9)
O2–C4	1.468 (6)	C4–C8	1.456 (10)
N–C2	1.495 (7)		
	Angles (deg)		
B1–P–O2	112.9 (3)	N–C2–C1	110.4 (5)
B1–P–O1	113.9 (3)	N–C3–C4	111.2 (4)
O1–P–O2	109.5 (2)	C2–C1–O1	104.2 (4)
O1–P–N	95.0 (2)	C3–C4–O2	106.2 (5)
O2–P–N	97.7 (2)	P–O1–C1	118.2 (3)
N–P–B1	125.4 (3)	P–O2–C4	117.5 (4)
C3–N–B2	110.1 (5)	O1–C1–C6	108.8 (5)
C2–N–B2	111.7 (5)	O2–C4–C8	106.7 (6)
C2–N–C3	113.3 (4)	C5–C1–C6	112.5 (6)
C2–N–P	104.5 (3)	C7–C4–C8	111.3 (7)
C3–N–P	104.5 (3)	C5–C1–C2	116.6 (5)
		C7–C4–C3	110.5 (6)

Results and Discussion

Synthesis of Mono- and Bis(borane) Adducts. Smooth and quantitative reactions were observed at room temperature between the bicyclic aminophosphanes (L) **1**–**3** and 1 or 2 equiv of borane. After crystallization at low temperature both the mono(borane) adducts **1a**, **2a**, **3a** and the bis(borane) adducts **1b** and **2b**, depending on the stoichiometry, were isolated in high yields as white crystalline air-sensitive solids (eq 1) soluble in the usual solvents.



(1)

The addition of 1 molar equiv of B_2H_6 to **3** led only to the mono(borane) adduct **3a** along with unreacted diborane. The lack of formation of a stable bis(borane) adduct in this case may be attributed to the steric hindrance introduced by the two methyl groups in **3** of the N-site rather than to a notable decrease in basicity of its nitrogen atom.

Elemental analysis, infrared and ^{31}P and ^{11}B NMR (Table IV) spectroscopy and mass spectrometry support the formulations of these new compounds as mono- or bis(borane) adducts. X-ray analysis was achieved on the bis(borane) compound **2b**.

Both the mono- and the bis(borane) adducts are stable and can be stored in the solid state at room temperature for at least 2 months without noticeable decomposition. This stability—unusual for the bis(borane) adducts—is also evidenced by their rather high decomposition points (115 and 110 °C for **1b** and **2b**, respectively); it is noteworthy that these are higher than those of the corresponding mono(borane) adducts (85 and 75 °C for **1a** and **2a**, respectively). This thermal stability is further illustrated by the observation of the molecular peak in the mass spectra of all the adducts isolated and permitted the X-ray diffraction pattern of **2b** to be measured.

Table IV. NMR Data on the BH_3 and BF_3 Adducts

		chem shifts, ppm		
compd	solvent	$^{31}P\{^1H\}$	$^{11}B\{^1H\}$	J_{B-P}, Hz
1a	CD_3CN	143.2 (q)	−41.8 (d)	92
2a	$CDCl_3$	150.8 (q)	−38.7 (d)	92
3a	CD_3CN	152 (q)	−39.5 (d)	93
1b	$CDCl_3$	143.2 (q)	−41.7 (d) −10 (s)	89
2b	$CDCl_3$	151.5 (q)	−39.2 (d) −8.7 (s)	90
1c	$CDCl_2$	144.5 (qd), 155.4 (qd) (4:1) ($^3J_{P-F}$ = 28.5)	−0.9 (qd) ($^1J_{B-F}$ = 15.4 Hz)	4.5 (^2J)

[a] Adducts of the meso and racemic forms of **1** (no separate signals observed for ^{11}B or ^{19}F NMR). ^{19}F NMR of **1c**: −95.6 (qd) ppm; $^3J_{P-F}$ = 28.5; $^1J_{B-F}$ = 15.4 Hz.

No immediate evolution of B_2H_6 is observed upon dissolution of **1b** or **2b** in CD_3CN, and the compounds remain long enough in solution to permit all the spectral analyses to be performed; B_2H_6 (≃10%) and a new, unidentified phosphorus species appear, however, in solutions of **1b** or **2b** in CD_3CN allowed to age 24 h.

The coordination of the BH_3 moiety to phosphorus in **1a**, **2a**, and **3a** is established by the presence of a single 1:1:1:1 quartet ($\delta = +150.8$, $^1J_{P-B} = 92$ Hz for **2a**, for instance), in the $^{31}P\{^1H\}$ spectrum, and of a doublet ($\delta = -38.7$, $^1J_{P-B} = 92$ Hz) in the $^{11}B\{^1H\}$ spectrum. The bis(borane) adducts **1b** and **2b** are characterized by an additional broad singlet in the $^{11}B\{^1H\}$ spectrum at $\delta \simeq 10$—a region usually found for the N-coordinated BH_3 groups[14] —and by a small downfield shift (≃1 ppm) of the ^{31}P resonances. The magnetic equivalence of the OCH groups in **1b** excludes coordination through the oxygen atom. No exchange of the BH_3 moiety between the phosphorus and nitrogen donor sites has been observed for the mono(borane) adducts. No disproportionation of **1a** to **1b** and **1** was detected in its CD_3CN solution, although the reaction between 1 equiv of BH_3 and **1** was observed to be displaced toward the less soluble **1b** when the reaction was conducted in toluene at −30 °C.

The IR spectra of the borane adducts show ν_{B-H} absorption bands in the expected region. For instance, for **2b** they are found at 2400 and 2350 cm^{-1} for $\nu_{(P)B-H}$ and at 2460 and 2290 cm^{-1} for $\nu_{(N)B-H}$, in agreement with the data reported on borane–phosphane[15] and borane–amine adducts,[16] respectively.

An interesting observation is that, while the bicyclic aminophosphane **1** initially consists of two diastereoisomers in a 80:20 ratio (meso and racemic forms, respectively),[9] only the meso form was identified for the BH_3 adducts. Careful ^{31}P and ^1H NMR monitoring established that both isomers are consumed during the BH_3 coordination reaction, but only the adducts of the meso isomer are detected on the resulting solutions. This observation, added to the fact that the adducts **1a** and **1b** of the sole meso form were isolated in 90% and 85% yields, respectively, implies that the BH_3 group induces rapid epimerization of the bicyclic frame, with the cleavage of a C–O, C–C, or C–H bond. This phenomenon was also observed to occur, though at a lower rate, in the presence of small amounts (5%) of B_2H_6. The marked tendency of uncoordinated bicyclic phosphanes to undergo oligomerization reactions also indicates the existence of ring-cleavage processes.[9]

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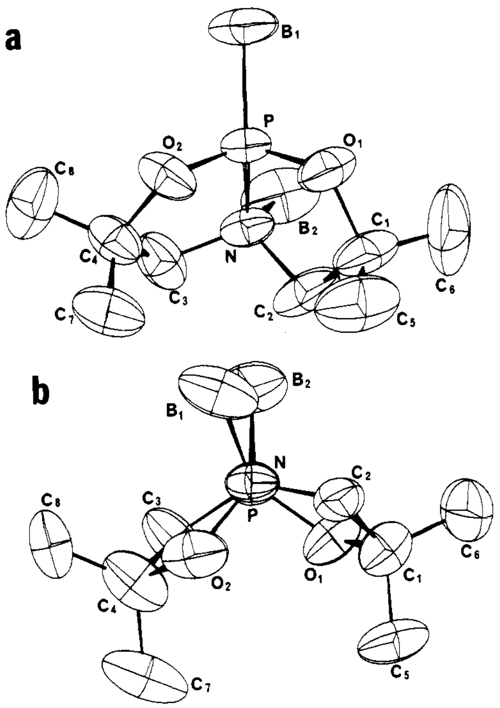
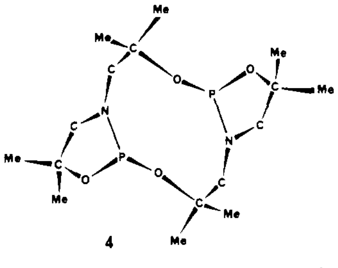


Figure 1. Molecular structure of $H_3B\cdot\overline{P(OCMe_2CH_2)_2N}\cdot BH_3$: (a) showing the flap envelope conformation of the five-membered rings; (b) showing the B–N–P–B dihedral angle.

The epimerization was not observed in the presence of boron trifluoride (see below) or aluminum chloride.

Crystal Structure of 2b. The stability of the isolated crystals of **2b** allowed the first X-ray diffraction data to be obtained on a bis(borane) aminophosphane adduct. The crystal structure of **2b** consists of discrete molecules whose configuration is depicted in Figure 1, with labeling of atoms. Pertinent bond distances and angles are collected in Table III.

The molecular structure definitely establishes the coordination of a borane group to the nitrogen atom. The N–B bond is not particularly long (1.655 (8) Å) and falls within the range, though at the higher limit, of those usually measured for N–BH_3 bonds (1.56–1.66 Å).[8,17,18] The P–N bond length (1.757 (4) Å) is typical of those expected between singly bound tetrahedrally connected phosphorus and nitrogen atoms (1.77 Å).[1,19] This bond is significantly longer than the P–N bond found in the dimer **4** (1.70 (1) Å),[20] which results from oligomerization of the uncoordinated ligand **2** and in which both the planar, sp^2-type configuration of the nitrogen and the involvement of its lone pair in p_π–d_π bonding with phosphorus are thought to contribute to shortening the bond. It is also longer than in ligand **1** (1.692 (4) Å) in the complex $(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_6H_5)(CO)Fe[\overline{P(OCH_2CH_2)_2N}]$ (**5**), where it is coordinated by its phosphorus atom.[21]



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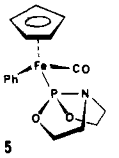


5

The nitrogen atom of **2b** is clearly pyramidal (sum of the angles around N $\sum N = 322.2$). Comparison with the data available on ligand **1** in complex **5** ($\sum N = 333.6°$) indicates a definite increase in the pyramidal character by N-coordination.

The rather short P–B bond (1.873 (7) Å) is consistent, within the usual range reported for P–B bonds (1.84–1.96 Å),[17,22-24] with the values expected for a phosphorus atom bearing electronegative substituents.[2]

The P–O bond lengths (1.557 (4) Å average) are slightly but significantly shorter than those observed for typical single P–O bonds (1.62 Å) as for example in the related structures **4** (1.63 (1) and 1.66 (1) Å for the P–O bonds in the 5- and 10-membered rings, respectively)[20] and **5** (1.61 (1) average.[21] The decrease in P–O bond length while the P–N bond length increases may indicate a compensatory response in the phosphorus's electronic balance.

Conformational analyses performed on ligand **1** and related bicyclic aminophosphanes in solution have shown that the five-membered rings take a C-flap envelope conformation, and a blocked endo–endo conformation has been proposed (Figure 2a).[9] An envelope conformation is also found for these cycles in the solid (Figure 2b), but in contradistinction with the conformation found in solution, it is the nitrogen atom that definitely stands out of these planes. These two almost identical envelopes could a priori be assembled along their common P–N edge in symmetrical endo–endo or exo–exo arrangements or in an asymmetrical exo–endo conformation. The large B–N–P–B dihedral angle (21.7°), which relieves the interaction between the two BH_3 groups, in fact destroys any symmetry and induces the observed helicoidal exo–endo conformation. The highly asymmetrical

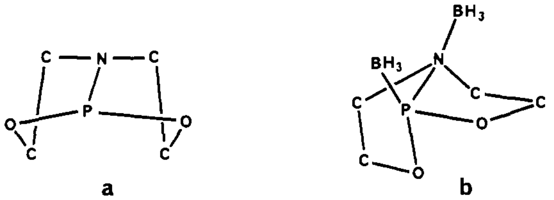
Table V. Conformational Ring Parameters of **2b** (Standard Deviations in Parentheses)

Least-Squares Planes and Deviations

plane PO1C1C2 (A)
$-[6.12\ (4)]x + [7.516\ (7)]y + [5.37\ (4)]z = 7.45\ (7)$
dev, Å: N, 0.44
plane PO2C4C3 (B)
$-[2.64\ (7)]x + [11.72\ (4)]y + [6.18\ (3)]z = 8.70\ (3)$
dev, Å: N, −0.29
dihedral angle between planes A and B, deg: 73.20

Torsion Angles (deg)

Five-Membered Ring			
P–O1–C1–C2	1.3 (6)	P–O2–C4–C3	1.6 (7)
P1–C1–C2–N	17.5 (6)	O2–C4–C3–N	10.3 (7)
C1–C2–N–P	−27.2 (5)	C4–C3–N–P	−16.6 (6)
C2–N–P–O1	24.5 (4)	C3–N–P–O2	15.6 (4)
N–P–O1–C1	−15.8 (4)	N–P–O2–C4	−10.9 (5)
Eight-Membered Ring			
C1–C2–N–C3	86.1 (5)	C4–C3–N–C2	−130.1 (6)
C1–O1–P–O2	−115.9 (4)	C4–O2–P–O1	87.2 (5)



a b

Figure 2. Conformation of the five-membered rings: (a) in solution for the free ligand; (b) in the solid state for **2b**.

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torsion angles around the phosphorus and nitrogen atoms in both the five- and the eight-membered rings are in agreement with such an arrangement.

The constraints imposed on the bicyclic aminophosphane ligand are illustrated by the numerous short intramolecular contacts observed within the frame (Table VI, supplementary material). The distance between the two boron atoms (3.515 (11) Å) is close to the sum of the van der Waals radii.

Synthesis of a Boron Trifluoride Adduct. The basicity of the nitrogen atom of the bicyclic aminophosphane ligands is also illustrated by the formation of the stable, sublimable mono(trifluoroborane) adduct **1c** when 1 equiv of BF_3 is allowed to react with **1**. No further addition of BF_3 to **1c** was observed.

The coordination of BF_3 to the nitrogen site is established by the NMR parameters (Table IV). The $^{11}B\{^1H\}$ NMR spectra of **1c** in CD_2Cl_2 solutions show a doublet of quadruplets centered at +0.9 ppm ($^1J_{B-F} = 15.4$ Hz, $^2J_{B-P} = 4.5$ Hz). The ^{19}F spectra are characterized by the presence at −95.6 ppm of a pattern that appears as a sextuplet (relative intensity 1:1:2:2:1:1; $^1J_{B-F} = 15.4$ Hz, $J_{F-P} = 28.5$ Hz). In contrast with the observation made in the case of the borane adducts, the $^{31}P\{^1H\}$ spectra indicate that the meso and racemic forms of ligand **1** are preserved during the addition of BF_3 (broad quadruplets (1:3:3:1) at 144.5 and 155.4 ppm, relative intensity 4:1; $J_{P-F} = 28.5$ Hz). The low value of the J_{P-B} constants (4.5 Hz) excludes coordination of the BF_3 moiety to the phosphorus atom, the commonly quoted $^1J_{P-B}$ coupling constants for trialkylphosphane–BF_3 adducts being around 160 Hz.[25] The small value of the J_{P-F} coupling constant, which also lies far outside the usual range of 117–300 Hz[25] of the $^2J_{P-F}$ coupling constants, supports the absence of P-coordination. No evidence was found for an exchange of the BF_3 group between the two potential donor sites of **1**. No ionic spectra were detected.

Donor Character of the Bicyclic Aminophosphanes. The $^1J_{P-B}$ coupling constants are often considered to reflect the Lewis π-acidity of the phosphorus atom,[26,27] and consequently the extent of N p_π–P d_π back-bonding. The values of $^1J_{P-B}$ observed for the mono(borane) adducts **1a**–**3a** (92–93 Hz) are only slightly affected by the ring substituents and are comparable to those observed for acyclic derivatives in which the phosphorus atom bears substituents of similar electronegativity (97.2 Hz for $(Me_2O)_3P{\cdot}BH_3$, 99 Hz for $(Me_2N)(t\text{-}BuO)_2P{\cdot}BH_3$).[28] The values of $^1J_{P-B}$ for the bis(borane) adducts **1b** and **2b** (89 and 90 Hz) as well as for the N-bound $WO(OMe)_4$ adduct of **2a** (89 Hz),[29] raise a question, since they are *not* significantly different.

According to common interpretation this would then mean that the extent of π-bonding in the P–N bond is the same in both P-bound monoadducts and P- and N-bound bisadducts, i.e. effectively zero since, in the latter case, the nitrogen's lone pair is no longer available for π-bonding.

However, on going from the N- and P-coordinated complex **2b** to the solely P-coordinated complex **5**,[21] there is a large decrease in P–N bond length, of 0.08 Å, which implies a considerable change in P–N bond character, i.e. probably in the extent of N p_π–P d_π bonding. It is also difficult to reconcile the absence of N p_π–P d_π interaction with the low coordination ability of this nitrogen toward transition-metal derivatives, even in high oxidation states.[29] The strong π-acceptor character of the phosphorus atom found for the bicyclic aminophosphanes (as shown by the high ν(CO) frequencies of their adducts with group VI (6[31]) hexacarbonyls),[30] with respect to comparable acyclic ligands, indicates that the situation is intermediate. It is likely that some compensatory mechanism sets in which equilibrates the π interactions between phosphorus and all its substituents. This discussion suggests that the $^1J_{P-B}$ coupling data should be handled with care.

The coordination of the BF_3 moiety to the nitrogen atom only is in agreement with observations previously made on cyclic fluoro(dialkylamino)phosphanes such as $\mathrm{FP\overline{N(Me)CH_2N}Me}$, for which coordination takes place on the phosphorus atom only in the presence of B_2H_6, while the formation of an unstable molecular N-adduct only is observed with BF_3.[7]

Registry No. **1a**, 75194-95-5; **1b**, 75194-97-7; **1c**, 99268-67-4; **2a**, 75194-96-6; **2b**, 75194-98-8; **3a**, 99280-65-6; B_2H_6, 19287-45-7.

Supplementary Material Available: Short intramolecular contacts (Table VI), thermal parameters (Table VII), and observed and calculated structure factors (Table VIII) for **2b** (12 pages). Ordering information is given on any current masthead page.

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