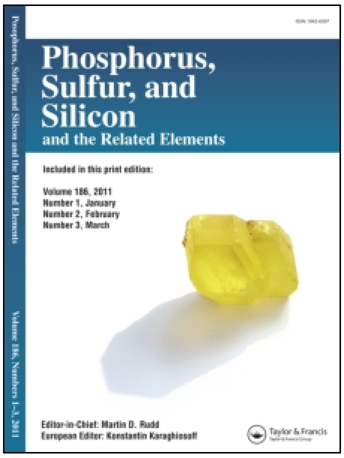

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SYNTHESES AND STRUCTURAL STUDY OF PHOSPHOLIDINES DERIVED FROM AROMATIC AMIDES

Francisco Javier Martínez Martínez[a]; José Luis León-Romo[b]; Itzia I. Padilla-Martínez[a]; Maria De Jesús Rosales-Hoz[b]; Rosalinda Contreras[b]
[a] Departamento de Química, Unidad Profesional Interdisciplinaria de Biotecnologia, México [b] Departamento de Química, Centro de Investigación y de Estudios Avanzados del Instituto Politecnico Nacional, D.F., México

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SYNTHESES AND STRUCTURAL STUDY OF PHOSPHOLIDINES DERIVED FROM AROMATIC AMIDES

FRANCISCO JAVIER MARTÍNEZ-MARTÍNEZ,*† JOSÉ LUIS LEÓN-ROMO,‡
ITZIA I. PADILLA-MARTÍNEZ,† MARIA DE JESÚS ROSALES-HOZ‡ and
ROSALINDA CONTRERAS*‡
†Departamento de Química, Unidad Profesional Interdisciplinaria de Biotecnologia, Av. Acueducto s/n, Barrio la Laguna Ticomán, D.F.C.P. 07340 México; ‡Departamento de Química, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Apartado Postal 14-740, 07000 D.F., México

Dedicated to Prof. John G. Verkade on the occasion of his 60th birthday

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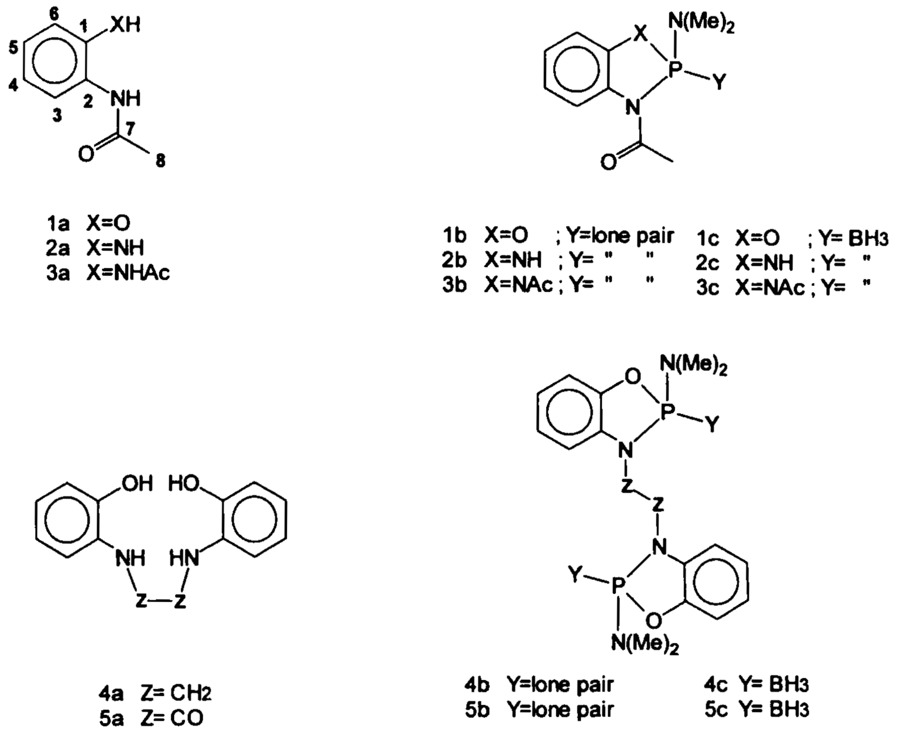
The preparation and structural study in solution by ^1H, ^{13}C and ^{31}P NMR spectroscopy of 2-dimethylamine-N-acetylbenzoxazaphospholidine **1b**, 2-dimethylamine-N-acetylbenzo diazaphospholidine **2b**, 2-dimethyl-N,N′-diacetylbenzoxazaphospholidine **3b**, bis-[(2-dimethylamine)-N,N′-(benzoxazaphospholidine)]-1,2-ethane **4b**, bis-[(2-dimethylamine)-N,N′-(benzoxazaphospholidine)]oxalyl **5b**. The reaction of compounds **1b**–**5b** with BH_3DMS afforded the corresponding P—BH_3 adducts without reducing the heterocycles, **1c**–**5c** were also studied by ^{11}B NMR. The solid state structure determined by x-ray diffraction analysis of **1b** and **3b** shows phosphorus atoms with 45% of sp^3 character and with the NMe_2 group in axial position.

Key words: Aromatic phospholidines, amides heterocycles, phosphorus-borane adducts, NMR, X-ray diffraction.

INTRODUCTION

We are interested in the synthesis of aromatic phosphorus heterocycles which have more hydrolytic and thermal stability than their analogous aliphatic compounds.[1–4] In addition we are exploring the reactivity of amides as coordinating sites in aromatic compounds with heteroelements and metals.[5,6] The rotation energy of N—CO bond in amines is high and thus preferred rotamers exist. We have investigated the conformational analysis of these amines and we have found by NMR experiments that the preferred conformation of the aromatic amides **1a**–**5a** is planar with the carbonyl group pointing towards the aromatic ring and opposed to the *ortho* substituent as is depicted in Figure 1. This proposition was mainly based on the important deshielding effect that carbonyl group produces at the proton at C3.[5] The planar conformation and the attractive effect of the phenyl and amide group makes the proton on the nitrogen very acidic and available for reaction with phosphorus reagents. Therefore, we wanted to synthesize compounds **1b**–**5b** in order to extend our research on the conformational analysis of phosphorus heterocycles. Also, we have explored the potential of aromatic amides forming phosphorus heterocycles. To our knowledge



1a X=O
2a X=NH
3a X=NHAc

1b X=O ; Y=lone pair
2b X=NH ; Y= " "
3b X=NAc ; Y= " "

1c X=O ; Y= BH3
2c X=NH ; Y= "
3c X=NAc ; Y= "

4a Z= CH2
5a Z= CO

4b Y=lone pair
5b Y=lone pair

4c Y= BH3
5c Y= BH3

FIGURE 1

these amides have not been employed before for these purposes. Nevertheless some aromatic phosphorus six membered heterocycles derived from amides are reported.[7-9] Herein, we describe the reaction of $P[N(CH_3)_2]_2$ with the aromatic amides: N-[(2-hydroxy)phenyl] methylamide **1a**, N-[(2-amine)phenyl)]methylamide **2b**, N,N′-(diacetyl)phenylenediamine **3a**, N,N′-bis[(2-hydroxy) phenyl]-ethylenediamine **4a**, N,N′-bis[(2-hydroxy)phenyl] oxamide **5a**, the reactions afforded phospholidines **1b–5b**, Figure 1.

We were also interested in studying the basic nature and hybridization of the heteroatoms in **1b–5b** using BH_3 as a probe. And to explore the possibility to obtain P—H heterocycles by substitution of a NMe_2 group by a hydride. Therefore, we decided to react compounds **1b–5b** with borane dimethylsulfide, BH_3 DMS, and to examine the products.

RESULTS AND DISCUSSION

The reaction of amides **1a–5a** with hexamethylphosphorous triamide in toluene afforded, by substitution of two P-amide groups, the tricoordinated phospholidine heterocycles bearing a P—NMe_2 group **1b–5b**, Figure 1. The ^1H and ^{13}C NMR data were assigned unequivocally through HETCOR experiments. Two of the compounds **1b** and **3b** crystallized and their x-ray diffraction structure were obtained. Our attempts to synthesize the corresponding phosphoranes directly from hexamethylphos-

TABLE I

^1H NMR chemical shifts of **1a**–**3c** in ppm

Compd.	H-3	H-4	H-5	H-6	OH	NH	CONH	
								COMe
1a	7.69	6.77	6.99	6.89	6.62	---	9.25	2.2
2a	7.18	6.67	6.97	6.74	---	4.1	9.0	2.12
3a	7.60	7.10	7.10	7.60	---	---	9.3	2.08
4a	6.66	6.42	6.65	6.55	9.22	4.96		
5a	8.13	6.89	7.06	7.00	10.43	9.82	---	---
							NMe_2	COMe
1b	8.62	6.88	6.80	6.92	----	----	1.99	1.97
2b	8.68	6.78	6.84	6.38	----	3.70	2.06	2.13
3b	8.7	6.98	6.98	8.7	----	----	1.90	2.07
4b	6.55	6.86	6.70	7.02	----	----	2.16	----
5b	8.67	(6.8	-----	7.0)	----	----	2.25	----
1c	8.45	6.67	6.72	6.76	----	----	1.97	2.12
2c	8.18	6.74	6.89	6.72	----	7.51	2.41	2.65
3c	8.36	6.82	6.82	8.36	----	----	1.96	2.07

TABLE II

^{13}C chemical shifts of **1a**–**3c** in ppm

Compd	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	NMe_2
1a	147.9	126.4	122.4	119.0	124.7	116.0	169.1	23.5	----
2a	140.3	124.9	122.9	115.9	124.5	115.8	167.8	21.9	----
3a	130.4	130.4	124.5	124.7	124.7	124.5	168.5	23.6	----
4a	144.0	137.3	109.5	119.6	115.7	113.4	42.1	----	----
5a	147.2	124.5	119.8	119.3	125.4	115.1	156.9	----	----
1b	145.0	130.6	117.8	122.5	123.9	111.9	168.5	25.1	35.6
2b	138.3	130.6	117.7	119.3	123.5	110.1	171.3	25.6	36.2
3b	121.9	121.9	118.0	124.2	124.2	118.0	169.2	25.5	36.4
4b	150.2	136.8	106.7	121.9	118.7	111.3	41.3	----	35.3
5b	150.8	130.0	112.2	121.8	125.9	118.9	161.7	----	36.6
1c	146.0	131.0	117.9	123.7	124.5	1121	168.5	24.7	35.5
2c	136.0	125.4	117.9	120.3	124.5	111.1	171.0	25.3	36.3
3c	124.2	124.2	117.4	124.6	124.6	117.4	169.0	25.4	35.5

phorous triamide in excess of ligand or from the tricoordinated phosphorus heterocycle with another equivalent of the ligand were unsuccessful denoting a high stability of heterocycles **1b**–**5b**.

Conformation and Structure in Solution of Phospholidine Heterocycles **1b**–**5b**

In the ^1H NMR spectra, the H-3 proton in **1b**–**5b**, remains at higher frequencies, which indicates that the *endo* conformation of the carbonyl group is retained upon coordination to the phosphorus. In this conformation, the oxygen atom produces an important deshielding effect on this proton, Table I.

^{13}C NMR data of compounds **1b**–**5b** (Table II) showed for the acetamide methyl groups a signal near 25 ppm with a $^3J(CCNP)$ = between 15.4–17.6 Hz and doublets for N—Me_2 around 35–36 ppm $^2J(CNP)$ = 17.7–19.6 Hz. The aromatic carbon

TABLE III

${}^{31}P^{a}$ and ${}^{11}B^{b}$ NMR of **1b**–**5c**

Compd.	${}^{31}P$	Compd.	${}^{31}P$	${}^{11}B$	J(P-B)
1b	126	**1c**	125.1	-39.0	60.5
2b	96.4	**2c**	101.1	-37.9	65.2
3b	96.1	**3c**	113.5	-36.8	78.2
4b	131.4	**4c**	124.0	-39.0	----
5b	124.5	**5c**	126.0	-37.0	----

a) external reference 85% H_3PO_4; b) external reference $BF_3.OEt_2$; in ppm and J(P-B) in Hz.

TABLE IV

${}^{n}J$(C—P) and ${}^{1}J$(H—P) coupling constants of **1b**–**3c** in Hz

Comp.	${}^{3}J$(C3-P)	${}^{3}J$(C6-P)	${}^{3}J$(C8-P)	${}^{2}J$(C9-P)	${}^{4}J$(H8-P)	${}^{3}J$(H9-P)	${}^{2}J$(HN-P)
1b	----	----	15.4	19.8	3.74	8.83	
2b	----	----	17.6	18.8	3.67	8.43	36.2
3b	----	----	17.6	17.7	4.39	8.90	----
4b	----	----	----	18.8	----	8.61	----
5b	----	----	----	16.6	----	9.2	----
1c	4.4	5.5	0.0	4.4	1.33	10.56	----
2c	2.2	7.7	6.6	5.6	0.0	10.94	27.35
3c	3.3	3.3	0.0	4.4	0.0	10.50	----

chemical shifts of **1b** were unequivocally assigned from an HETCOR experiment, **2b**–**5b** were assigned by comparison with **1b**.

The ${}^{31}P$ NMR data (Table III) of phospholidines **1b**–**5b** showed a signal near 125 ppm for the oxygen-phosphorus compounds and near 96 ppm for the phosphorus with three nitrogen atoms, the shifts found to lower frequencies are indicative of a better electron donating N—P bonding. All the chemical shifts are characteristic of tricoordinated phosphorus compounds. Compound **2b** showed a ${}^{2}J$(PNH) of 36 Hz due to the coupling between phosphorus and anilinic proton, Table IV. In the ${}^{1}H$ NMR the signals of the acidic protons of **1a**–**5a** were lost and a doublet in the range 1.9–2.3 ppm [${}^{3}J$(PNCH)] was observed for **1b**–**3b** and assigned to the N-Me_2 group (Table I). The resonances at 2.0–2.2 ppm with a ${}^{4}J$(PNCCH) coupling constant of 3.6–4.4 were attributed to the acetyl group.

Solid State Structure of Phospholidine Heterocycles **1b** *and* **3b**

The x-ray diffraction structure of compounds **1b** and **3b** (Figures 2–4 and Tables V–VII) showed the phosphorus atom in a five membered ring with an envelope conformation, where the phosphorus atom occupies the apical position. The carbonyl acetamide group is in an *endo* conformation, pointing towards the aromatic ring and in the plane of the molecule.

We confirmed that in the solid state the compounds have the same preferred conformation as that established in the solution experiments. The dimethyl amide group is oriented along the molecule axis perpendicular to the molecular plane, with the N(10)—P(3)—O(2)—C(1) dihedral angle of −97° in **1b**, Figure 2. The phosphorus atom has closed angles N(10)—P(3)—O(2) 104.6(2), N(4)—P(3)—N(10) 102.2(2)

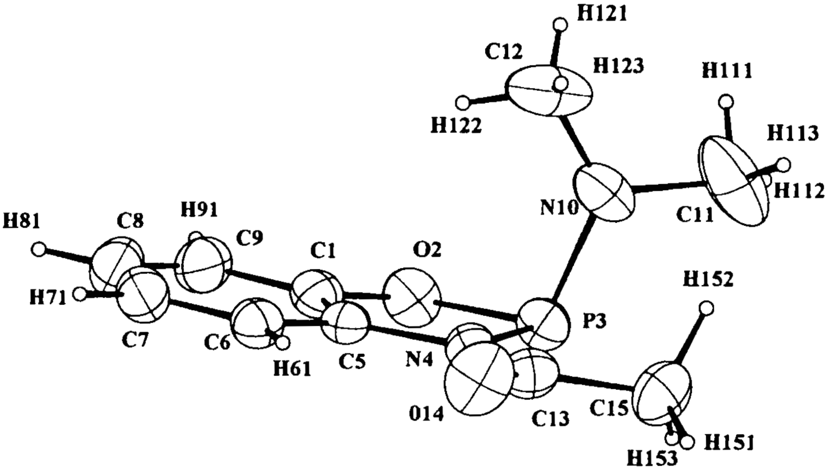


FIGURE 2 X-ray diffraction structure of **1b**.

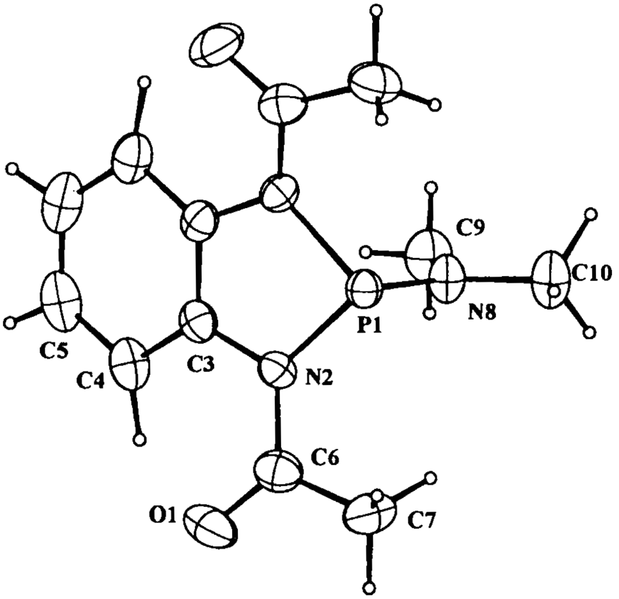


FIGURE 3 X-ray diffraction structure of compound **3b**.

and N(4)—P(3)—O(2) 89.6(1) which denote that the phosphorus atom has a 45% of a sp^3 character. The P(3)—N(10) length of 1.632(3) Å is shorter than a single P—N bond length[10] (1.77 A), but larger than a P═N double bond length (1.56 A) showing a partial double bond attributed to pπ-dπ contributions.[10] This is confirmed by the planar character of the exocyclic nitrogen atom. Whereas the endocyclic P—N bond is a single P—N bond [1.774(3) A].

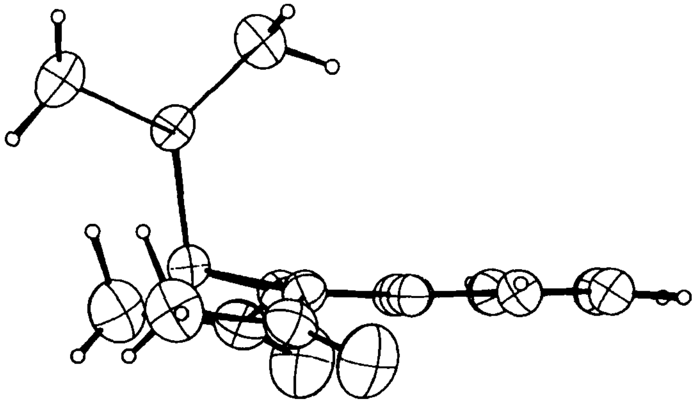


FIGURE 4 View of compound **3b**, showing the acetyl groups out of the phenyl plane.

TABLE V

Selected interatomic distances (A), bond angles (deg), and selected torsional angles (deg) of **1b**

P(3)-N(4)	1.774(3)	P(3)-N(10)	1.632(3)
P(3)-O(2)	1.658(2)	N(4)-C(5)	1.412(4)
N(4)-C(13)	1.371(4)	N(10)-C(11)	1.488(8)
N(10)-C(12)	1.448(7)	O(2)-C(1)	1.378(4)
O(14)-C(13)	1.215(4)	C(1)-C(5)	1.377(5)
C(1)-C(9)	1.383(5)	C(5)-C(6)	1.391(5)
C(6)-C(7)	1.389(6)	C(7)-C(8)	1.366(7)
C(8)-C(9)	1.388(7)	C(13)-C(15)	1.492(6)
N(4)-P(3)-N(10)	102.2(2)	N(4)-P(3)-O(2)	89.6(1)
N(10)-P(3)-O(2)	104.6(2)	P(3)-N(4)-C(5)	111.6(2)
P(3)-N(4)-C(13)	122.8(2)	C(5)-N(4)-C(13)	125.3(3)
P(3)-N(10)-C(11)	115.5(4)	P(3)-N(10)-C(12)	125.6(3)
C(11)-N(10)-C(12)	118.3(5)	P(3)-O(2)-C(1)	114.5(2)
O(2)-C(1)-C(5)	114.1(3)	O(2)-C(1)-C(9)	122.9(4)
C(5)-C(1)-C(9)	123.0(4)	N(4)-C(5)-C(1)	109.8(3)
N(4)-C(5)-C(6)	130.7(3)	C(1)-C(5)-C(6)	119.5(3)
C(5)-C(6)-C(7)	118.2(4)	C(6)-C(7)-C(8)	120.9(4)
C(7)-C(8)-C(9)	122.1(4)	C(1)-C(9)-C(8)	116.3(5)
N(4)-C(13)-O(14)	122.2(4)	N(4)-C(13)-C(15)	116.4(3)
O(14)-C(13)-C(15)	122.4(4)		
C(11)-N(10)-P(3)-N(4)	130.94	C(15)-C(13)-N(4)-C(5)	-178.69
C(12)-N(10)-P(3)-N(4)	-39.65	C(6)-C(5)-N(4)-C(13)	2.27
C(15)-C(13)-N(4)-P(3)	-4.82	C(5)-C(1)-O(2)-P(3)	-5.13
O(14)-C(13)-N(4)-C(5)	-0.33	N(10)-P(3)-O(2)-C(1)	-96.95
P(3)-N(4)-C(5)-C(1)	2.88		

The same structural features were observed in the structure of **3b**, Figures 3 and 4. In order to avoid the van der Waals repulsion between the oxygen of the carbonyl group and the H-3 aromatic proton (atom notation of Figure 1), the amide group is bent as is shown in Figure 4 for compound **3b**. The distance between H-61 and O14 in **1b** is 2.95 A, whereas in **3b** H-4-O1 is 2.26 A.

TABLE VI

Selected interactomic distances (A) and bond angles (deg) of **3b**

P(1)-N(2)	1.752(4)	P(1)-N(8)	1.637(6)
N(2)-C(3)	1.414(5)	N(2)-C(6)	1.368(6)
N(8)-C(9)	1.438(9)	N(8)-C(10)	1.455(9)
C(3)-C(C3′)	1.375(9)	C(3)-C(4)	1.395(6)
C(4)-C(5)	1.375(7)	C(5)-C(5′)	1.350(1)
C(6)-C(7)	1.502(6)	C(6)-O(1)	1.205(6)
N(2)-P(1)-N(2′)	87.3(3)	N(2)-P(1)-N(8)	104.5(2)
P(1)-N(2)-C(3)	113.8(3)	P(1)-N(2)-C(6)	122.3(2)
C(3)-N(2)-C(6)	123.2(4)	P(1)-N(8)-C(9)	127.1(5)
P(1)-N(8)-C(10)	119.5(5)	C(9)-N(8)-C(10)	113.5(5)
N(2)-C(3)-C(3′)	111.7(2)	N(2)-C(3)-C(4)	127.1(4)
C(3′)-C(3)-C(4)	121.0(3)	C(3)-C(4)-C(5)	116.9(5)
C(4)-C(5)-C(5′)	121.1(3)	N(2)-C(6)-C(7)	116.9(5)
N(2)-C(6)-O(1)	123.1(5)	C(7)-C(6)-O(1)	120.0(5)

TABLE VII

Crystallographic data of **1b** and **3b**

Compound	1b	3b
Crystal Date for	$C_{10}H_{13}N_2O_2P$	$C_{12}H_{16}N_3O_2P$
fw	224.19	265.25
space group	$P2_1/a$	P m c n
a (A)	9.447(1)	11.945(6)
b (A)	12.887(2)	12.216(4)
c (A)	10.18	9.086(3)
α(°)	90.0	90.0
β(°)	116.0	116.0
γ(°)	90.0	90.0
V(A^3)	1115	1325.8(9)
Z	4	4
radiation	MoKα (λ=0.71069 A)	MoKα (λ=0.71069 A)
linear abs coeff cm^{-1}	2.21	1.99
ρ (calc) g cm^{-1}	1.33	1.33
scan type	ω/2θ	ω/2θ
scan range (°)	0.67 + 1.15 tg θ	0.8 + 0.345 tg θ
θ limits ($^{o)}$	3 - 27	1 - 25
temperature of measurement	room temperature	room temperature
octans collected	-10, 12; 0, 16; -12, 0	0, 14; 0, 14; 0, 10
no of data collected	2414	1373
no of unique data collected	1424	1224
no of unique data used (Fo)^2>3σ(Fo)^2	1427	554
R (int)	0.08	
decay %	<1	<1
absorption correction	DIFABS (min= 0.72, max= 1.27)	DIFABS (min= 0.91, max= 1.05)
R=Σ|| Fo| - |Fc|)/ Σ|Fo|	0.047	0.039
Rw= |Σw(|Fo| -| Fc|)^2/Σ wFo^2 |$^{1/2}$	0.044 w=1.0	0.038 w=1.0
Goodness of fit s	3.69	2.12
no of variables	176	89
Δρmin (e/A^3)	-0.21	-0.30
Δρmax (e/A^3)	0.20	0.22

Phospholidine-P-Borane Adducts **1c–5c**

We reacted compounds **1b–5b** with borane dimethylsulfide in order to form the borane adducts or to reduce the molecule. The reactions were very clean and afforded the phospholidine P-borane adducts **1c–5c** as the only products. This means that the phosphorus atom is more basic than the nitrogen atoms in the molecule. No other compounds were obtained, the P—N(CH_3)$_2$ and the carbonyl groups were preserved. The ^{11}B NMR spectra showed a multiple signal between −36 and −39 ppm, characteristic of P → B coordination.

Some changes in the phosphorus coupling constants indicates conformational and hybridization changes at the phosphorus atoms upon coordination. Coupling constants with amide-methyl hydrogens ^4J(PNCCH) diminishes from 3.7 Hz in **1b** to 1.3 Hz in **1c** and in **2c–3c** it takes a value near of zero. The ^3J(PNCH) coupling constants of the phosphorus atom (Table IV) with N-methyl hydrogen atoms is 2 Hz larger in the borane adducts than in the free compounds. C3 and C6 in the borane adducts, appear to be coupled with the phosphorus atom with ^3J(PXCC) of 3.3–7.7 Hz (X = O, N) and ^3J(PNCC) of 2.2–4.4 Hz. It is known that ^3J(PNCC) coupling constants are dependent on the dihedral angle. They became larger as the dihedral angle approaches 0° and 180°. These changes suggest that the phosphorus atom in the borane adducts lies practically in the plane of the ring. The ^{31}P NMR spectra presented broad signals due to the boron coupling, with ^1J(P—B) coupling constants between 60 and 79 Hz. It is interesting to note that ^{31}P chemical shifts are not a good probe for P—BH_3 coordination because they do not change in **1c** and **5c**, whereas in **2c** and **3c** they are shifted to higher frequencies (5–7 ppm) and in **4c** to lower frequencies (7 ppm). The carbonyl *endo* conformation of the amide-carbonyl remained upon coordination, as was shown by the H-3 resonances at higher frequencies.

EXPERIMENTAL

The reactions were carried out under a dry nitrogen atmosphere. All solvents were freshly distilled and dried before use according to established procedures. Melting points were measured on a Gallenkamp apparatus and are uncorrected. The IR spectra were taken in KBr disc using a Perkin Elmer 16F PC IR spectrometer. All the NMR spectra were obtained on a JEOL GXS-270 spectrometer in C_6D_6 and C_7D_8 solution. ^{1}H and ^{13}C NMR were measured with TMS as internal reference, ^{31}P NMR spectra are referenced to external 85% H_3PO_4 and ^{11}B NMR spectra are referenced to external BF_3. OEt_2. Mass spectra were obtained on a Hewlett-Packard HP-5989A. Elemental analyses were performed by Oneida Research Services. Compounds **1a**, **4a** and **5a** were prepared following established procedures.

Crystal Structure Determination

Crystallographic data and experimental details are given in Tables VI and VII. Corrections were made for Lorentz and polarization effects. An instrument Enraf-nonius CAD4 was employed. Empirical absorption corrections (DIFABS) were applied. Computations were performed by using CRYSTALS. The structures were solved by direct methods and subsequent fourier maps. Hydrogen atoms were located in Fourier maps in structure **3c** and fixed and refined in structure **1b**.

N-((2-hydroxy)phenyl)methylamide **1a**. Compound **1a** was prepared as reported.[5] I.R. ν_{max}(KBr) cm^{-1} CO 1658, NH 3404. m.p. 204–206°C.

N-((2-amine)phenyl)methylamide **2a**. A suspension of 3.00 g (21.7 mmol) of *o*-nitroaniline **2** in 4 ml of acetic acid were treated with 3.7 ml of acetic anhydride at room temperature under vigorous stirring. The reaction mixture was heated at 100°C for 2 hours, then the reaction mixture was treated with 2 ml of water, the suspension was filtered and 3.37 g (86.27%) of a yellow solid was obtained m.p. 87–90.6°C (*o*-nitroacetanilide). A suspension of 1.00 g (5.55 mmol) of *o*-nitrocetanilide and 7 mg of Pd/C 10% in 7 ml of MeOH was treated with H_2 (500 lb/in^2) at room temperature for 2 hours. The suspension was filtered and the volatile materials were removed at reduced pressure to give a beige solid. The recrystallization from methanol yield 0.67 g (80.4%) of a beige crystalline solid. I.R. ν_{max}(KBr) cm^{-1} CO 1650, NH 3288. m.p. 122–124°C.

N,N'-(diacetyl)phenylendiamine **3a**. A procedure identical to that used to prepare **1a** was followed using *o*-phenylenediamine. (90.1% yield), I.R. ν_{max}(KBr) cm^{-1} CO 1666, NH 1540. m.p. 206–207°C.

N,N'-bis((2-hydroxy)phenyl)ethylenediamine **4a**. Compound **4a** was prepared as reported.[11] m.p. 230–232°C.

N,N'-bis(2-hydroxy)phenyl)oxamide **5a**. Compound **5a** was prepared as reported,[5] m.p. 282–284°C.

2-Dimethylamine-N-acetylbenzoxazaphospholidine **1b**. A suspension of 0.5 g (5 mmol) *o*-hydroxyacetanilide **1a** in 8 ml of dry toluene was treated with 0.6 ml (5 mmol) of hexamethylphosphorus triamide at room temperature under vigorous stirring. The reaction mixture was heated at 100°C for 10 hours. Then, the solution was filtered and the volatile materials were removed at reduced pressure to give a yellow solid. The recrystallization in toluene yield 0.65 g (87.3%) of a yellow crystalline solid, I.R. ν_{max}(KBr) cm^{-1} CO 1680 PN 976, 842, PO 1180. mp 123–124°C. Elemental analysis calc. for $C_{10}H_{13}N_2O_2P$: C, 52.97, H, 5.84, N 12.5; found C, 52.97, H, 5.84, N, 12.22.

The phospholidines **2b**–**3b** were prepared following the procedure detailed for **1b**.

2-Dimethylamine-N-acetylbenzodiazaphospholidine **2b**. *o*-Phenylenediamine-N-monoacetamide **2a** afforded compound **2b** in 81%. I.R. ν_{max}(KBr) cm^{-1} CO 1642, NH 3248, PN 980, 868. m.p. 89–90°C. Elemental analysis calc. for $C_{10}H_{14}N_3OP\frac{1}{2}H_2O$: C, 51.72, H, 6.50, N 18.09; found C, 51.96; H, 6.27, N, 17.97.

2-Dimethyl-N,N'-diacetylbenzoxazaphospholidine **3b**. N,N-diacetyl-*o*-phenylenediamine **3a** afforded compound **3b** in 76%. The compound crystallized from benzene as a crystalline yellow solid, I.R. ν_{max}(KBr) cm^{-1} CO 1680, PN 980, 868. m.p. 128–129°C. Elemental analysis calc. for $C_{12}H_{16}N_3O_2P$: C, 54.33, H 6.03, N 15.84; found C 54.66, H 6.25, N 16.07.

Bis[(2-Dimethylamine)-N,N'-(benzoxazaphospholidine)]-1,2-ethane **4b**. Compound **4a** (0.200 g, 0.734 mmol) in 10 ml of dry toluene was heated at 100°C under N_2 atmosphere and treated with 0.26 ml of hexamethylphosphorous triamide (1.46 mmol). The reaction was heated at 110°C for 5 hours. The solution was filtered and the volatile materials were removed under reduced pressure at 50°C to yield 150 mg (52%) of a beige solid. I.R. ν_{max}(KBr) cm^{-1}. PN 978, 850, PO 1175. MS (EI) m/z M^+ 390.20(38), 346.25(14), 152.20(100), 137.20(33) and 77.20(15).

Bis-[(2-dimethylamine)-N,N'-(benzoxazaphospholidine)]oxalyl **5b**. A procedure identical to that used to prepare **4b** using **5a** yielded **5b** in 25%. I.R. ν_{max}(KBr) cm^{-1} CO 1688, PO 1162.

2-Dimethylamine-N-acetylbenzoxazaphospholidine-P-borane adduct **1c**. A suspension of 0.48 g (2.14 mmol) of 2-dimethylamine-N-acetylbenzoxazaphospholidine **1b** in 8 ml of dry toluene was treated with $BH_3 \cdot DMS$ 2.6 ml (1 M, 2.6 mmol) under stirring. After one hour at room temperature the solution was filtered and the volatile materials were removed under reduced pressure to yield 0.47 g (93%) of a white solid, I.R. ν_{max}(KBr) cm^{-1} CO 1702, PN 870, PO 126, BH 2450, 2400. m. p. 88–89°C. Elemental analysis calc. for $C_{10}H_{16}BN_2O_2P$: C 50.45, H 6.72, N 11.77; found C 49.53, H 6.88, N 11.46.

The phospholidines adducts **2c**–**3c** were prepared following the procedure detailed for **1c**.

2-Dimethylamine-N-acetylbenzodiazaphospholidine-P-borane adduct **2c**. 2-Dimethylamine N-acetylbenzodiazaphospholidine **2b** afforded adduct **2c** as a white solid in 92%. I.R. ν_{max}(KBr) cm^{-1} CO 1668, NH 3226, PN 990, BH 2436, 2390. mp 79°–80°C. Elemental analysis calc. for $C_{10}H_{17}BN_3OP\frac{1}{5}$ $(B(OH)_3$: C 48.18, H 7.10, N 16.84; found: C 48.32, H 6.81, N 11.46.

2-Dimethyl-N,N'-diacetylbenzoxazaphospholidine-P-borane adduct **3c**. 2-Dimethyl-N,N'-diacetylbenzoxazaphospholidine **3b** afforded adduct **3c** as a white sticky solid in 60%. I.R. ν_{max}(KBr) cm^{-1} CO 1668, PO 988, BH 2434, 2388.

Bis((2-dimethylamine)-N,N'-benzoxazaphospholidine)1,2-ethane-P-borane adduct **4c**, *and bis-((2-dimethylamine)-N,N'-benzoxazaphospholidine)oxalyl-P-borane adduct* **5c**. We have prepared compounds **4c** and **5c** in a NMR tube by adding 1.2 equivalents of BH_3 DMS and observing directly by NMR without isolation. Compounds **4c** and **4b** are unstable and polymerize on standing.

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