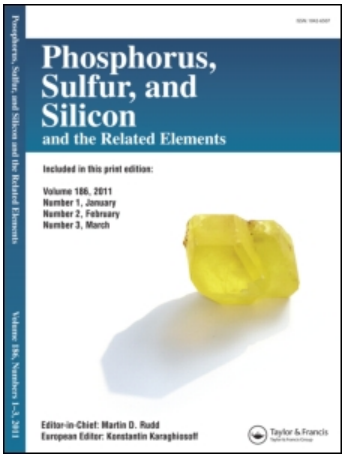

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SYNTHESES, NMR STUDY AND STEREOCHEMISTRY OF NEW P-H TRICYCLOPHOSPHORANES

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SYNTHESES, NMR STUDY AND STEREOCHEMISTRY OF NEW P-H TRICYCLOPHOSPHORANES*

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Keywords: Tricyclophosphoranes; stereoselective synthesis; x-ray diffraction study; ^{31}P; ^{13}C; ^{1}H NMR study and amineborane

Four new tricyclophosphoranes **1b-4b** were synthesized derived from N,N'-bis[2-hydroxy phenyl]ethylenediamine (**1a**), N,N'-bis[2-hydroxyphenyl]oxamide (**2a**), N,N'-bis[(-)-norephedrine]ethylene (**3a**), N,N'-bis[(-)-norpseudoephedrine]oxalyl (**4a**), The syntheses of compounds **3b** and **4b** were completely stereoselective giving only one epimer in each case (epimer helix Δ, **3b**; helix Λ, **4b**). For both the phosphorus configuration was established. The phosphorus atoms in **1b-4b** adopt a trigonal bipyramid geometry with an oxygen and a nitrogen atoms in apical positions as deduced from ^{31}P, ^{13}C, ^{1}H and $^{1}H/^{13}C$ HETCOR NMR studies and confirmed by the x-ray diffraction structure of **3b**. Compound **1b** reacts with BH_3-THF giving the N→BH_3 adduct **1c;** borane coordinates to the tetrahedral apical nitrogen atom. Compound **3b** reacted with BH_3 giving two isomeric adducts, **3c** and **3c'**. The main product **3c** came from attack of BH_3 on the equatorial nitrogen followed by epimerization of the phosphorus atom giving the molecule with the N→BH_3 group in an apical position and heli-

* Dedicated to Professor Robert Wolf.

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coidal structure Λ. The minor isomer **3c'** came directly from addition of BH_3on an apical nitrogen atom giving the Δ helix.

INTRODUCTION

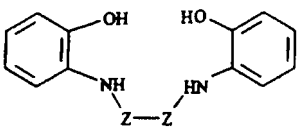
There are few examples of tricyclic P-H phosphoranes derived from bis-ethanolamines[2]. It has been reported that the P-H bond in these compounds reduces carbonyl groups. One nitrogen atom is in an apical position and is a Lewis basic center[2].

In previous reports we have described the synthesis of optically active spirophosphoranes[3-5], bicyclophosphoranes and benzobicyclophosphorane[6-8], we are interested in studying the tautomeric behaviour [P^V-P^{III}] of phosphoranes using BH_3 as a basic probe[8-12]. Also, we are currently studying the synthesis of N-BH_3 adducts of optically active heterocycles[13-18], the preparation of heterocycles with stereogenic nitrogen atoms[19-22], and the synthesis of ligands bearing amides[23]. Therefore, continuing with our work, we decided to synthesize tricyclicphosphoranes by treating ligands bearing amide **2a, 4a** or amine groups **1a, 3a** with hexamethyl phosphorous triamide ($P[N(CH_3)_2]_3$), and to study their structure and reactivity with BH_3THF, (Figure 1).

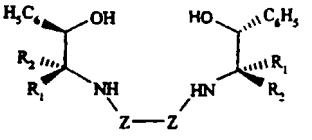
RESULTS AND DISCUSSION

The reaction of $P[N(CH_3)_2]_3$ with N,N'-bis[2-hydroxy)phenyl]ethylenediamine **1a**, and N,N'-bis[(2-hydroxy)phenyl]oxamide **2a** afforded heterocycles **1b** and **2b**, Figure 1. In both cases the reaction gave a phosphorane with a P-H group (^{31}P NMR, $\delta = -38.1$ ppm $J_{P\text{-}H} = 786$ Hz, for **1b** and $\delta = -53.9$ ppm $J_{P\text{-}H}$ 789 Hz for **2b**). Only one set of carbon atoms (Z) was found for **1b** and **2b** indicating symmetric phosphoranes (with phosphorus in a square pyramid geometry or in a trigonal bipyramid tbp in equilibrium between isomers, Figure 2).

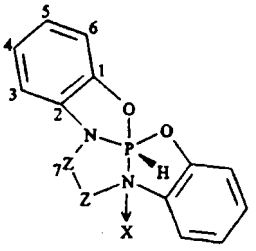
The expected more stable phosphoranes were those with three rings each occupying an equatorial-apical with one oxygen and one nitrogen in apical position. Examination of the NMR data reveled that **1b** and **2b** have enantiomeric helicoidal structures which are interconverted by a Berry pseudorotation process (Figure 2). Assignment of ^1H and ^{13}C NMR data of compounds **1b** and **2b** was made by comparison with those of the free ligand (Figure 1) and with the spirophosphorane obtained from o-aminophenol **5b**, (Figure 3). The coupling constants $^3J_{P\text{-}C}$ in spirophosphorane **5b** indicate the position of the carbon atom, C-2 *ipso* to the N-equatorial (15.4 Hz) or C-1 *ipso* to the O-apical (5.6 Hz). The



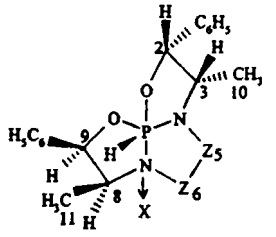
1a) Z=CH_2
2a) Z=CO



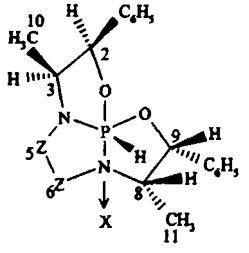
	R_1	R_2
3a) Z=CH_2	CH_3	H
4a) Z=CO	H	CH_3



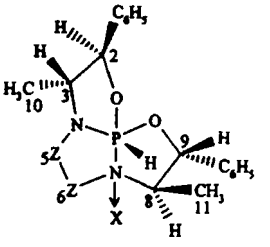
1b) Z=CH_2 ; X=lone pair
2b) Z=CO ; X=lone pair
1c) Z=CH_2 ; X=BH_3



3b) Z=CH_2 ; X=lone pair
3c') Z=CH_2 ; X=BH_3

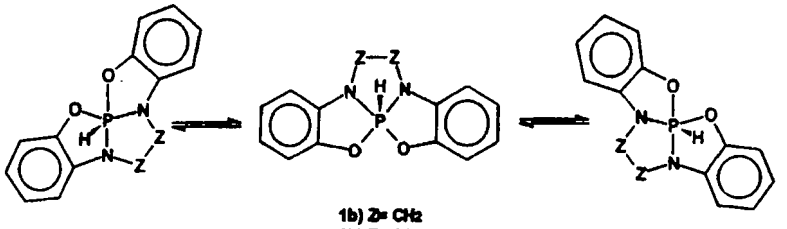


3c) Z=CH_2 ; X=BH_3



4b) Z=CO ; X=lone pair

FIGURE 1 Compounds **1b**, **2b** and **1c** are racemic, only one enantiomer is shown



1b) Z= CH_2
2b) Z= CO

FIGURE 2

$^3J_{P\text{-}C}$ of the aromatic carbon atoms of **1b** show an averaged value, thus supporting the equilibria depicted in Figure 2.

We are able to detect the phosphorane basic sites[9-12] (apical nitrogen atoms) by adding borane. The BH_3 coordination may anchor the molecule avoiding the pseudorotation in two ways, one making the isomer with N→BH_3 in an apical position more stable than the other with N→BH_3 in an equatorial position and avoiding the inversion of apical nitrogen atom which is necessary in order to epimerize the molecule. Thus, when compound **1b** was treated with three equivalents of BH_3, only one BH_3 group reacted to form a N→BH_3 adduct **1c** [Figure 1, ^{11}B NMR $\delta = -13.2$, $J_{B\text{-}H} = 98$ Hz]. The NMR data show that adduct **1c** is no longer in pseudorotational equilibrium. By ^{13}C and ^1H NMR two different phenolamine rings were observed. In ^1H NMR the four methylenic hydrogen atoms appear at different chemical shift indicating a strong N→BH_3 coordination and that the nitrogen atom becomes a stereogenic center with a stable configuration. The NMR assignment of phosphorane N-borane adduct **1c** was made by comparison with **1b** and with data from N-BH_3 anilines[24].

Compound **2b** did not form any borane adduct, because of the amidic and anilinic nature of nitrogen atoms which make them a very weak base.

The reaction of N,N'-bis[(-)norephedrine]ethylene (**3a**) and N,N'-bis[(-)norpseudoephedrine]oxalyl **4a** with $P[N(CH_3)_2]_3$ afforded exclusively one epimer [**3b** (helix △) and **4b** (helix Λ)] of the corresponding phosphoranes, (Figure 1). The ^{31}P NMR spectra indicated a phosphoranic P-H structure in both cases [δ = -40.7 ppm $J_{P\text{-}H}$ = 714 Hz for **3b** and δ -62.36 ppm, $J_{P\text{-}H}$ = 736 Hz for **4b**]. A double set of signals in the ^1H NMR spectrum of each compound indicate two differently bonded fragments of each ligand according to a bpt geometry and without pseudorotation at room temperature. The structure was confirmed by the x-ray diffraction study of **3b**, Figure 4. The stable configuration at phosphorus atom indicates that the epimerization energy is very high or that the equilibrium is completely shifted to one isomer. An explanation for the stereoselectivity came from examination of the stereochemistry of **3b** and **4b**. In both cases the methyl group α to the axial nitrogen atom is found in the wider dihedral angle of the molecule (*exo* position), in the absent isomers the methyl group would be in a crowded *endo* position. The methyl groups near the equatorial nitrogen atom do not encounter a steric hindrance owing to its sp^2 hybridation. The wide variation of the ^{31}P NMR chemical shifts between compounds **1b** and **2b** and **3b** and **4b**, can be explained by the different nature of the nitrogen atoms; in **2b** and **4b** the amidic nitrogen atoms are bonded more weakly to the phosphorus atom since they denote less electronic density.

In compounds **3b** and **4b**, the phosphorus and apical nitrogen atoms are stereogenic centers of stable configuration. The unequivocal assignment of their configuration and of their chemical shifts in ^1H and ^{13}C NMR spectra was based on

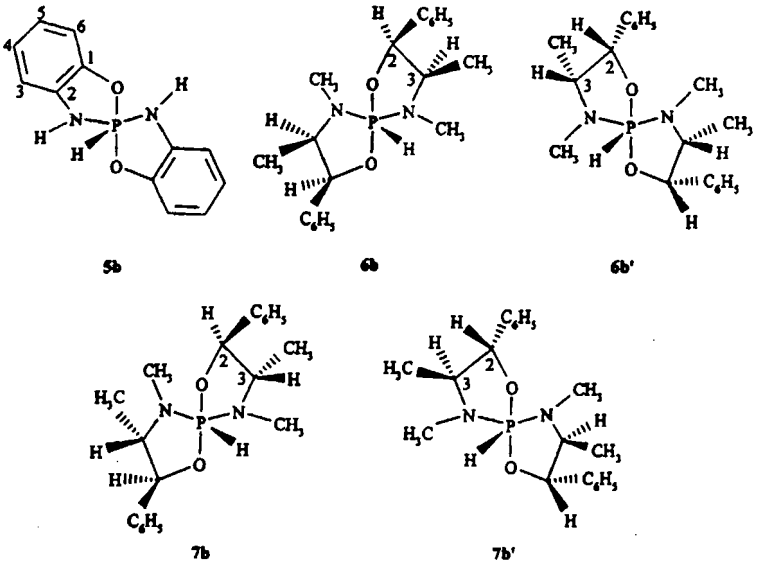


FIGURE 3 **5b** is a racemic compound, only one enantiomer is shown

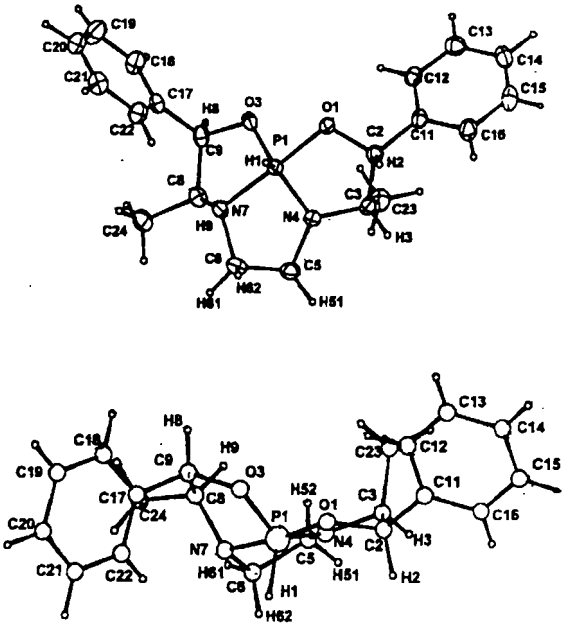


FIGURE 4 Two views of the X-ray diffraction structure of compound **3b**

HETCOR experiments, coupling constant data, evaluation of steric effects and comparison with spirophosphoranes derived from ephedrines **6b, 6b', 7b,** and **7b**'[26] (Figure 3).

TABLE I Selected interatomic distances (Å) and bond angles (deg.)

P1-O1	1.693(2)	N4-C3	1.454(4)	C3-C23	1.514(5)
P1-O3	1.615(2)	N4-C5	1.451(4)	C5-C6	1.527(5)
P1-N4	1.656(2)	N7-C6	1.466(4)	C8-C9	1.522(5)
P1-N7	1.772(3)	N7-C8	1.457(4)	C8-C24	1.520(5)
O1-C2	1.414(4)	C2-C3	1.546(4)	C9-C17	1.510(4)
O3-C9	1.446(4)	C2-C11	1.490(4)		
O1-P1-O3	86.8(1)	P1-N4-C5	118.6(2)	N4-C5-C6	102.4(2)
O1-P1-N4	88.9(1)	P1-N7-C6	107.9(2)	N7-C6-C5	107.3(3)
O1-P1-N7	175.2(1)	P1-N7-C8	107.8(2)	N7-C8-C9	102.8(2)
O3-P1-N4	129.8(1)	O1-C2-C3	105.5(2)	N7-C8-C24	114.3(3)
O3-P1-N7	90.2(1)	O1-C2-C11	111.0(3)	C3-N4-C5	122.0(2)
N4-P1-N7	90.3(1)	03-C9-C8	105.2(2)	C6-N7-C8	113.6(2)
P1-O1-C2	114.0(2)	03-C9-C17	109.4(3)	C3-C2-C11	114.9(3)
P1-O3-C9	116.9(2)	N4-C3-C2	100.7(2)	C2-C3-C23	114.3(3)
P1-N4-C3	118.4(2)	N4-C3-C23	112.0(3)	C9-C8-C24	114.1(3)
C8-C9-C17	118.1(3)				

X-Ray diffraction structure of compound 3b

Compound **3b** was recrystallized from benzene and the x-ray diffraction structure was obtained. The phosphorus atom has a slightly distorted tbp. There are three, five-membered rings in apical-equatorial positions and with one nitrogen and one oxygen atoms in apical positions. The apical bonds [P-N(7) 1.772(3), P-O(1) 1.693(2)] are longer than the corresponding equatorial ones [P-N(4) 1.656(2), P-O(3) 1.615(2)], the P-H bond length is 1.3795(8). N-7 has sp^3 hybridation as deduced from the acute angles around the nitrogen atom (C6-N7-C8 = 113.6°). The methyl and phenyl groups adjacent to the apical nitrogen have the substituents in the *exo*-dihedral angle whereas the methyl and phenyl group closest to the equatorial nitrogen are *endo*. The x-ray diffraction information agrees with the proposed structure of **3b** suggested in solution by the NMR data, (Figure 1).

Borane addition to compounds 3b and 4b

Borane addition to **3b** gave two N-BH_3 monoadducts, **3c** and **3c'** in a 88:12 ratio respectively (Figure 5). The NMR data of ^{31}P, ^{1}H and ^{13}C spectra show that iso-

mers **3c** and **3c'** are tbp structures with the $N\rightarrow BH_3$ group in an apical position. The ^{31}P chemical shifts were shifted to high frequency compared with the parent phosphoranes (about 16 ppm), and the coupling constants J_{P-H} were increased (**3c** δ = -24.42 ppm; J_{P-H} = 822 Hz and **3c'** δ = - 27.58 ppm, J_{P-H} = 807 Hz). The latter changes were attributed to the electronic withdrawal of BH_3 group. The major isomer arises from BH_3 addition to the equatorial nitrogen from the *exo* face (Figure 5). This prompts epimerization at the phosphorus atom, in order to move the electroattractive $N\rightarrow BH_3$ group to an apical position; the methyl group close to the BH_3 remains in the *endo* face. The minor isomer **3c'** comes from direct addition of BH_3 at the apical nitrogen of **3b** without epimerization in **3c'**; BH_3 and CH_3 group are the *exo* face and are *cis* (Figure 5).

The assignment of the chemical shifts of **3c** and **3c'** was based on HECTOR experiments, coupling constants, evaluation of steric effects, and comparison with phosphorane **3b**. The ring next to borane can be identified because the ^{13}C chemical shifts change significantly. In the ^{1}H NMR spectrum the methylene groups are assigned based on the fact that protons cis to BH_3 are shifted to high frequencies[25].

Compound **4b** reacts very slowly with BH_3-THF and gives some polymeric material; therefore, we decided to follow the reaction by ^{31}P NMR. To a sample of **4b** dissolved in C_7D_8 an equivalent of BH_3THF was added and the reaction products observed. In addition to the signal of compound **4b** several new resonances appear in the range of P^V. Two of them (^{31}P NMR δ = –18.0 and –20.0 ppm) were attributed to compounds **4d** and **4d'** which disappear as the reaction evolves. Two other signals arrose which were assigned to compounds **4c** and **4c'** (^{31}P NMR δ = –21.03 and –24.8 ppm respectively). They resulted from reduction of the amide function by borane. A set of small signals appeared around –26 ppm. These were assigned to isomeric phosphoranes with boron oxygen bonds. The assignment of these structures was based on observation in the ^{11}B NMR of a sharp signal at –1.0 ppm of a borate structure in addition to $N\rightarrow BH_3$ groups, which resonated at –14 ppm and –18 ppm. Some $P^{III}\rightarrow BH_3$ adducts were also observed. After heating of the reaction mixture at 80°C in an excess of borane, only the signals of **4c** and **4c'** remained. The solution was evaporated and the solids extracted with a mixture of benzene and toluene in order to separate the polymeric material, and reexamined by ^{31}P NMR. Compounds **4c** and **4c'** were the only species observed together with some $P^{III}\rightarrow BH_3$ adducts. In the ^{13}C NMR spectra two sets of signals of different intensity were recorded and assigned to phosphoranes **4c** and **4c'** (Figure 6).

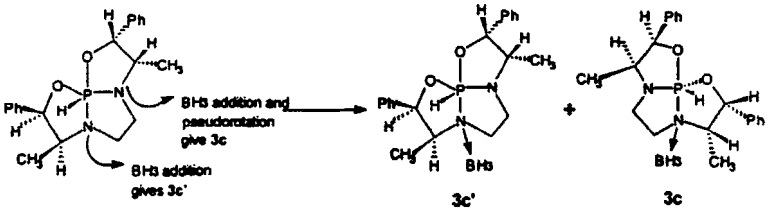


FIGURE 5

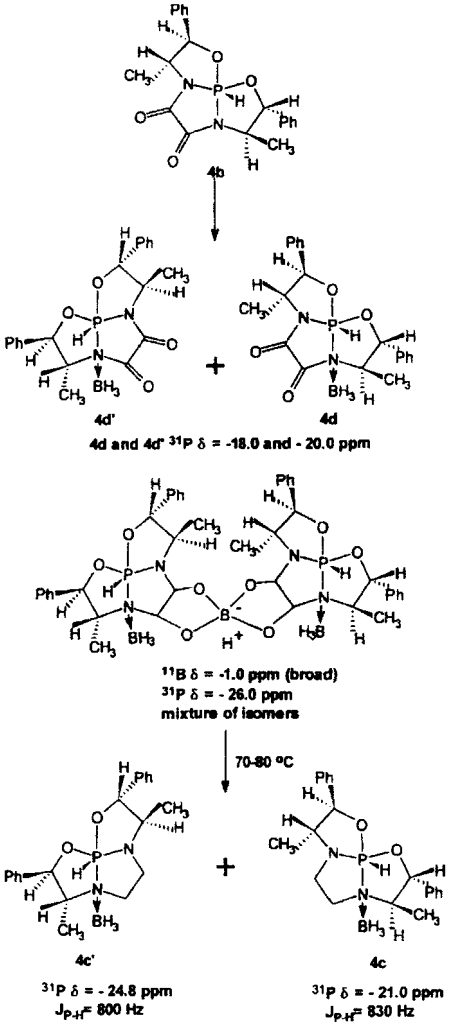


FIGURE 6 Products of the reaction of **4b** and BH_3THF. Compounds **4d** and **4d'** are the first adducts observed. **4c** and **4c'** are produced in an excess of BH_3. The borate structure is proposed as an intermediate

TABLE II

CRYSTAL DATA for	$C_{20}H_{25}O_2N_2P$
fw	356.4
space group	$P2_12_12_1$
a (Å) =	10.955(3)
b (Å) =	12.675 (2)
c (Å)	13.149 (3)
α (°) =	90
β (°) =	90
γ (°) =	90
V(Å^3)=	594.9 (6)
Z	4
F(000)	760
systematic absences	h00,h=2n+1 ; 0k01,k=2n+1 ; 001,1=2n+1
Diffractometer	CAD4-Enraf-Nonius
radiation	MoKα (λ = .71069 Å)
linear abs coeff cm^{-1}	1.604
ρ (calc) g cm^{-3}	1.29
scan type	ω/2θ
scan range (°)	0.8+0.345 tg θ
θ limits (°)	1 - 25
temperature of measurement	room temperature
octants collected	0,13;0,15;0,15
no of data collected	1862
no of unique data collected	1839
no of unique data used	1531 $(Fo)^2 > 3\sigma(fo)^2$
R(int)	0.01
decay %	<1
absortion correction	DIFABS (min = 0.94, max = 1.08)
$R = \Sigma\|\|Fo\|-\|Fc\|\|/\Sigma \|Fo\|$	0.030
$Rw = [\Sigma w(\|Fo\| - \|Fc\|)^2/\Sigma wFo^2]1/^2$	0.030 w = 1.0
Goodness of fit s	2.36
no. of variables	227
$\triangle\rho$min (E/Å^3)	-.19
$\Delta\rho$max (e/Å^3)	.15

TABLE III Fractional atomic coordinates

Atom	x/a	y/b	z/c	U(eqv)	Occ
P1	0.41361(8)	0.09515(6)	0.70179(6)	0.0257	1.0000
O1	0.4986(2)	0.1515(2)	0.7946(2)	0.0293	1.0000
O3	0.5187(2).	0.1324(2)	0.6236(2)	0.0303	1.0000
N4	0.4045(3)	-0.0131(2)	0.7718(2)	0.0296	1.0000
N7	0.3360(2)	0.0308(2)	0.6012(2)	0.0277	1.0000
C2	0.4897(3)	-0.1001(3)	0.8896(2)	0.0290	1.0000
C3	0.4757(3)	-0.0184(3)	0.8649(2)	0.0300	1.0000
C5	0.3446(3)	-0.1053(3)	0.7294(3)	0.0364	1.0000
C6	0.2666(3)	-0.0571(3)	0.6447(3)	0.0356	1.0000
C8	0.4265(3)	0.0021(3)	0.5266(3)	0.0322	1.0000
C9	0.5106(3)	0.0937(3)	0.5204(2)	0.0306	1.0000
C11	0.5958(3)	0.1266(2)	0.9560(2)	0.0286	1.0000
C12	0.7062(3)	0.1580(3)	0.9154(3)	0.0330	1.0000
C13	0.8045(3)	0.1782(3)	0.9779(3)	0.0394	1.0000
C14	0.7944(4)	0.1674(3)	1.0816(3)	0.0392	1.0000
C15	0.6851(4)	0.1373(3)	1.1227(3)	0.0445	1.0000
C16	0.5864(4)	0.1168(3)	1.0600(3)	0.0391	1.0000
C17	0.4753(3)	0.1826(3)	0.4503(2)	0.0292	1.0000
C18	0.5616(3)	0.2234(3)	0.3851(3)	0.0417	1.0000
C19	0.5357(4)	0.3056(3)	0.3192(3)	0.0518	1.0000
C20	0.4192(4)	0.3481(3)	0.3182(3)	0.0443	1.0000
C21	0.3330(3)	0.3087(3)	0.3832(3)	0.0396	1.0000
C22	0.3603(3)	0.2274(3)	0.4488(3)	0.0360	1.0000
C23	0.5951(4)	-0.0767(3)	0.8496(3)	0.0420	1.0000
C24	0.3734(4)	-0.0358(3)	0.4250(3)	0.0428	1.0000

EXPERIMENTAL

The reactions were carried out under an atmosphere of dry nitrogen. 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. The NMR spectra were obtained on a JEOL GXS-270 spectrometer in [$^2H_6$]DMSO, C_7D_8 and C_6D_6 solution. ^1H and ^{13}C NMR spectra 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.

Crystal Structure Determination, Some experimental details are given in Table 1. The crystal was mounted in a capillary tube. All calculations were carried out in a Vax 4000 computer using the Molen package.

N,N'-bis[(2-Hydroxy)phenyl]ethylene **1a**. Compound **1a** was prepared as reported[27]. m. p. 230-232 °C.

N,N'-bis[(2-Hydroxy)phenyl]oxalyl **2a.** Compound **2a** was prepared as reported[23]. m.p. 282-284 °C.

N,N'-bis[(1R,2S)-(-)Norephedrine]ethylene **3a.** Compound **3a** was prepared as reported[28].

N,N'-bis[(1R,2R)-(-)Norpseudoephedrine]oxalyl **4a.** Compound **4a** was prepared as reported[23]. m.p. 166 °C.

3, 4 : 9, 10-dibenzo-5, 8-diazo-2, 11-dioxa-1 (H)-phospha (V)tricyclo[6. 3.0.0] undecane **1b.**

N',N-bis[(2-hydroxy)phenyl)]ethylenediamine **1a** (0.2 g, 0.819 mmol) and $P[N(CH_3)_2]_3$ (0.15 ml, 0.819 mmol) in toluene (5 ml), were heated and stirred to the reflux temperature for 2 h. The dimethylamine 2.46 mmol was eliminated with a nitrogen stream and titred with an aq. solution of HCl. The phosphorane **1b** was obtained after elimination of toluene under reduced pressure (95 mg, 42 %). m.p.=dec. 160 °C. NMR (C_7D_8) δ (ppm), J (Hz),^1H (270 MHz): H3 6.27 (d, J_{H3H4}=7.3), H4 6.89 (dd, J_{H4H3}=7.4, J_{H4H5}=7.6), H5 6.72 (dd, J_{H5H4}=7.7, J_{H5H6}=7.7), H6 7.01 (d, J_{H6H5}=7.6) H7 2.36-2.55 (m, AA'BB'X) and PH 8.2 (d, J_{PH} 788) ppm. NMR ^{13}C (67.94 MHz): C1 145.9, C2 134.3 (d, J_{CP} 19.8), C3 108.3 (d, $^3J_{CP}$ 11), C4 121.5, C5 119.6, C6 110.5 (d, $^3J_{CP}$ 11) and C7 36.7 (d, $^2J_{CP}$ 12.1) ppm, ^{31}P NMR (109.25 MHz), -38.1 ppm (d, J_{PH} 786). I.R (KBr), υ (cm^{-1}), 2366, 1134, 1018, 918, 844. Compound **1b** is unstable, it hydrolizes under the mass spectrum conditions giving the M^+ plus 18 of a water molecule. MS, m/e (% relative intensity), [M^++ 18] 284.5 (1.0), 256.4 (2.0), 185.4 (1.0), 149.2 (2.0), 129.2 (4.0), 97.2 (6.0), 69.1(15.0), 55.1 (28.0), 43.0 (52.0), 28.0 (39.0), 18.0 (100.0)

3, 4:9, 10-Dibenzo-5, 8-diazo-6, 7-dicarboxy-2, 11-dioxa-1(H)-phospha(V)tricyclo[6. 3.0.0.] undecane **2b**. N',N-bis[(2-hydroxyphenyl)]oxalyl **2a** (0.2 g, 0.734 mmol) and $P[N(CH_3)_2]_3$ (0.13 ml, 0.734 mmol) in toluene (10 ml), were heated and stirred to the reflux temperature for 9 h. The dimethylamine was eliminated with a nitrogen stream and titred with HCl. The phosphorane **2b** was obtained after elimination of toluene under reduced pressure. Compound **2b** is very reactive to oxydation and hydrolisis. (75 mg, 25 %). NMR (C_7D_8) δ (ppm),

J (Hz), ^{1}H, H3 8.10 (d), H4-H6 6.7-6.9 (m), PH 6.94 (d, J_{PH} 785) ppm. ^{31}P NMR (109.25 MHz), -53.9 ppm, (J_{PH} 789).

(4S, 9S)-4, 9-Dimethyl-(3R, 10R)-3, 10-diphenyl-2, 11-dioxa-5, 8-diazo-1 (H)-phospha(V)tricyclo[6.3.0.0]undecane **3b**. N'N-bis[(-)-1R,2S-norephedrine]ethylene **3a** (0.499 g, 1.52 mmol) and $P[N(CH_3)_2]_3$ (0.276 ml, 1.52 mmol) in toluene (50 ml), were heated and stirred to the reflux temperature. The dimethylamine (4.5 mmol) was eliminated and titred with a solution 0.1 M of HCl. The phosphorane **3b** was obtained after elimination of toluene under reduced pressure. Recrystallization from benzene gave **3b** (0.491 g, 90.69 %). NMR (C_7D_8) δ (ppm), J (Hz) ^{13}C NMR: (67.94 MHz) C2 74.0 (d, J_{CP} 4.4), C3 53.1 (d, J_{CP} 13.2), C5 39.8 (d, J_{CP} 16.2), C6 44.2 (d, J_{CP} 5.5), C8 55.7 (d, J_{CP} 6.6), C9 76.3 (d, J_{CP} 3.3), C10 14.8, C11 16.6 (d, $^{3}J_{CP}$5.5), $2C_6H_5$ [*i*-C, 140.67 (d, J_{CP} 9.9), *i*-C 140.1 (d, J_{PC} 8.8), 2 *o*-C, 128.2, *p*-C, 127.3, *p*-C 127.2, *m*-C, 127.0, *m*-C 126.5]. ^{1}H NMR: (270.0 MHz) H2 4.97 (dd, $J_{HH,}$ 5.87, J_{HP} 3.12), H3 3.03 (m), H5 2.82 (m), 2.63 (m), H6 2.94 (m), 2.67 (m), H8 3.07 (m), H9 5.01 (dd, J_{HH} 6.4, J_{HP} 6.4), H10 0.639 (d, J_{HH} 6.23), H11 0.69 (d, J_{HH} 6.6), $2C_6H_5$ 7.04-7.42 (m), PH 7.47 (d, J_{PH} 714); ^{31}P NMR: (109.25 MHz), -40.7 (d, J_{PH} 714). IR (KBr), υ (cm^{-1}) 1228, 1066, 986; $[\alpha]_D$ = -217.5 (conc. 34.23 mM, toluene, 31 °C); mp 120-123 °C; MS, m/e (% relative intensity), M^+ 356.2 (33), 249.3 (51), 159.2 (68), 117.2 (85), 118.2 (65), 132.2 (100). Anal. calcd. for $C_{20}H_{25}O_2N_2P.1/4(H_2O)$, C 66.56; H, 6.98, N, 7.76. Found: C, 66.55; H, 7.04; N, 7.57.

(4R, 9R)-4, 9-Dimethyl-(3R, 10R)-3, 10-diphenyl-2, 11-dioxa-5, 8-diazo-6, 7-dicarboxy-1-(H)-phospha(V)tricyclo[6.3.0.0]undecane **4b**. N'N-bis[(-)-Norpseudoephedrine]ethylene **4a** (0.473 g, 1.23 mmol) and $P[N(CH_3)_2]_3$(0.223 ml, 1.23 mmol) in toluene (5 ml), were heated and stirred to the reflux temperature. The dimethylamine 3.6 mmol was eliminated and titred with HCl. The phosphorane **4b** was obtained after elimination of toluene under reduced pressure. Recrystallization from benzene gave **4b** (0.43 g, 90%). NMR (C_7D_8), δ (ppm), J (Hz). ^{13}C NMR: C2 80.4 (s), C3 52.4 (d, J_{CP} 13.3), C5 157.8 (d, J_{CP} 8.8), C6 158.5 (d, J_{CP} 12), C8 53.2 (d, J_{CP}15.4), C9 79.8 (s), C10 17.0 (s), C11 19.0 (s) and C_6H_5 *i*-C 139.9 (d, J_{CP} 6.6), *i*-C 139.7 (d, J_{CP} 6.6), 128.96, 128.93, 128.67, 126.7, 125.99). ^{1}H NMR: H2 4.43 (dd, J_{HH} 12.65, J_{HP} 1.72), H3 3.80 (dqdd, J_{HH} 12.46, J_{HH} 6.21, J_{HP} 1.38), H8 3.644 (dqd, J_{HH} 12.44, J_{HH} 6.22, J_{HP} 1.38), H9 4.42 (dd, J_{HH} 12.54, J_{HP} 3.11), H10 1.34 (d, J_{HH} 6.22), H11 1.17 (d, J_{HH} 6.57), $2C_6H_5$ 6.98-740 (m), PH 6.97 (d, $J_{H\text{-}P}$ 736). ^{31}P NMR: -62.36 (d, J_{PH} 736). IR (KBr), ν cm^{-1}, 3392, 3304, 1738, 1714, 1680, 1314, 954. $[\alpha]_D$= -40.5, (conc. 12.35 mM, toluene, 25-26 °C); m.p = dec 137 °C. Anal. Calcd. for: $C_{20}H_{21}O_4N_2P.1/4H_2O$; C, 58.48; H, 5.84; N, 7.17. Found: C, 58.39; H, 6.12; N, 6.81.

2,3:7, 8-dibenzo-4, 9-diazo-1, 6-dioxa-5(H)-phospha(V)spiro[4.4]nonane **5b**. Compound **5b** was prepared as reported[27a]. NMR (C_6D_6), δ (ppm), J (Hz). ^{13}C NMR: C1 148.2, C2 131.0 (d, J_{PC} 16.5), C3 110.1 (d, $^3J_{PC}$ 15.4), C4 121.0, C5 120.0, C6 109.9 (d, $^3J_{PC}$ 5.6) ; ^1H NMR, H3 6.25 (d, J_{H3H4}=7.2), H4 6.76 (dd, J_{H4H3}=7.4, J_{H4H5}=7.6), H5 6.70 (dd, J_{H5H4}=7.59, J_{H5H6}=7.4), H6 6.82 (d, J_{H6H5}=7.23), NH 4.3 (d, $^2J_{PH}$ 19), PH 8.48 (d, J_{PH} 829). ^{31}P NMR -47.8 (dt J_{PH} 829, $^2J_{PH}$ 17.6)

2(S), 7(S)-diphenyl-3(R), 8(R), 4, 9-tetramethyl-4,9-diazo-1,6-dioxa-5(H)-phospha(V)spiro-[4.4]nonane **6b** (helix Δ), **6b'** (helix Λ). Compounds **6b** and **6b'** were prepared as reported[26b]. **6b**: NMR (C_6D_6), δ (ppm), J (Hz). ^{13}C NMR: C2 74,2 (d, J_{CP} 4.4), C3 58.6 (d, J_{CP} 11), C3-CH_3 13.7 (s), NCH_3 (32.8, J_{CP} 6.6). ^{31}P NMR -67.7 (d, J_{PH} 769.3). **6b'**: NMR (C_6D_6), δ (ppm), J (Hz). ^{13}C NMR: C2 73.6 (d, J_{CP} 3.3), C3 59.2 (d, J_{CP} 15.4), C3-CH_3 14.6 (s), NCH_3 34.2 (d, J_{CP} 4.4). ^{31}P NMR -64.3 (d J_{PH} 741)

2(S), 7(S)-diphenyl-3(S),8(S)-4, 9-tetramethyl-4, 9-diazo-1, 6-dioxa-5(H)-phospha(V)spiro-[4.4]nonane **7b** (helix Λ), **7b'**(helix Δ). Compounds **7b** and **7b'** were prepared as reported[26b]. **7b** NMR (C_6D_6), δ (ppm), J (Hz). ^{13}C C2 80.4 (d, J_{CP} 4.4), C3 51.4 (d, J_{CP} 12.1), C3-CH_3 17.2 (d, J_{CP} 5.5), N-CH_3 32.5 (d, J_{CP} 6.6). ^{31}P NMR, -58.2 (J_{PH} 757). **7b'** NMR (C_6D_6), δ (ppm), J (Hz). ^{13}C C2 78.8 (d, J_{CP} 5.5), C3 61.5 (d, J_{CP} 15.4), C3-CH_3 16.8 (d, J_{CP} 9.9), N-CH_3 33.1 (d, J_{CP} 3.3). ^{31}P NMR, -61.2 (J_{PH} 744).

3, 4:9, 10-dibenzo-5, 8-diazo-2, 11-dioxa-1 (H)-phospha(V)tricyclo[6. 3.0.0] undecane-N-borane adduct **1c**. Compound **1b** (20 mg, 0.073 mmol) was placed in an NMR tube and BH_3-THF 1.59 M (0.047 ml, 0.073 mmol) and toluene-d_8 (0.4 ml) were added and the NMR spectra were obtained. Compound **1c** decomposes on standing. NMR (C_6D_6) δ (ppm) J (Hz), ^1H, $2C_6H_4$ 6.6-7.4 (m), BH_3-N-$C\underline{H}_2$ 3.05-3.28 (m), N-CH_2 2.26-2.42 (m), PH 8.57 (d, J_{PH} 887). ^{13}C NMR, C1 146.4, C2 139.1, C3 121.7 (d, $^3J_{PC}$ 4.4), C4 124.2, C5 127.5, C6 113.7 (d, $^3J_{PC}$ 12), C7 55.9 (d, ^{2}JPC 6.6), C8 37.4 (d, ^{2}JPC 7.7), C9 136.0, C10 110.4 (d, $^3J_{PC}$ 12), C11 122.3, C12 121.1, C13 110.8 (d, $^3J_{PC}$ 7.7), C14 146.1. ^{31}P NMR, -14.3 (dm J_{PH} 887). ^{11}B NMR-13.1(q, J_{BH} 98)

(4S, 9S)-4, 9-Dimethyl-(3R, 10R)-3, 10-diphenyl-2, 11-dioxa-5, 8-diazo-1(H)-phospha(V) tricyclo [6.3.0.0]undecane-N-borane adduct **3c**.

Compound **3b** (0.14g, 0.0394 mmol) and BH_3-THF 1.59 M (0.246 ml, 0.0394 mmol) in toluene (10 ml), were stirred for 35 min. The toluene was eliminated under reduced pressure, **3c** (0.145 g, 100%), two diastereomers **3c** and **3c'** were found in a ratio 88:12 respectively.

Compound **3c** NMR (C_6D_6) δ (ppm) J (Hz), ^{13}C C2 74.8 (d, J_{CP} 2.2) C3 55.8 (d, J_{CP}12.1) C5 40.2 (d, J_{CP} 10) C6 46.1 (d, J_{CP} 6.6), C8 59.81 (d, J_{CP} 11), C9 78.25 (s), C10 13.4 (s), C11 11.4(s), $2C_6H_5$ i-C 138.8 (s), i-C 138.5 (d, $J_{C,P}$ 11),

m-C 126.66 (s), m-C 126.2 (s) o-C 128.2 (s), o-C 127.7 (s). ^{1}H: NMR H2 5.38 (d, J_{HH} 5.8), H3 (ddq, J_{HH} 6.25, J_{HH} 6.25, J_{HP} 19.199), H5 3.26 (1H, m), 2.3 (1H,m), H6 2.46 (2H, m) H8 3.55 (dq, J_{HH}7.17, J_{HH} 7.17), H9 4.81 (dd, J_{HH} 7.63, J_{HP} 19.6), C_6H_5 7-7.3 (m), HP 7.73 (d, $J_{H,P}$ 821). ^{31}P: NMR -24.42 (d, J_{PH} 822). ^{11}B NMR -15 ppm.

Compound **3c'**: NMR (C_6D_6) δ (ppm) J (Hz): ^{13}C NMR: C2 74.0 (d, J_{CP} 4.4), C3 53.98 (d, J_{CP} 16.5), C5 38.85 (d, J_{CP} 9.9) C6 52.54 (d, J_{CP} 4.4), C8 64.1 (d, $J_{C,P}$ 6.6), C9 76.0 (s), C10 13.73 (s), C11 14.82 (s), $2C_6H_5$ i-C 137.85, i-C 137.55 (d, J_{PC} 12.52), m-C 125.65, m-C 125.60, o-C 128.1, o-C 127.86. ^{1}H: NMR H2 5.138 (d, J_{HH} 4.73), H9 4.9 (d, J_{HH} 4.73), H10 0.492 (d, J_{HH} 6.26), H11 1.114 (d, J_{HH} 7.33), HP 7.88 (d, J_{HP} 807). ^{31}P NMR (C_6D_6) -27.58 (d, J_{PH} 807), ^{11}B NMR-18.

Data of the mixture **3c/3c'** (88/12). IR, 3418, 1314, 1148, 1088, 1054, 1018, 972, m.p. 123-129 °C; MS, m/e (% relative intensity), M^+ 370.25 (9), 369.25 (40), 356.25 (15), 249.25 (34), 159.25 (74), 132.20 (100), 118.25 (50).

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