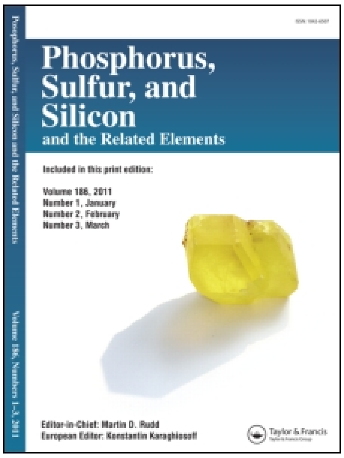

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SYNTHESES AND REACTIVITY OF NEW P-H DIBENZOBICYCLIC PHOSPHORANES BEARING HYDROXY-, ALKOXY-, OXO-, AMIDO-, AND DIHYDRIDO-FUNCTIONS AT THE PHOSPHORUS ATOM

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SYNTHESES AND REACTIVITY OF NEW P–H DIBENZOBICYCLIC PHOSPHORANES BEARING HYDROXY-, ALKOXY-, OXO-, AMIDO-, AND DIHYDRIDO-FUNCTIONS AT THE PHOSPHORUS ATOM

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A series of new dibenzophosphoranes (**1–6**) bearing uncommon functions such as hydroxy-, alkoxy-, oxo-, amide- and dihydride- attached to the phosphorus atom have been prepared and characterized. The reactivities of the alkoxy derivative **1** and the amide **2** towards alcohols, amines, water and borane were studied mainly by ^{31}P NMR. The structure of the diphenoxyamine-*bis*-phoshorane **4** was established by single crystal X-ray diffraction studies.

Key words: (P–H) dibenzobicyclic phosphoranes; substituted phosphoranes.

INTRODUCTION

In this paper we report six new phoshoranes (**1–6**, Figure 1) which constitute an interesting series of pentacoordinated phoshorus compounds. A few aliphatic analogues, briefly described in the literature,[1,2] are known as being very unstable. The major interest of compounds **1–6** is related to their planar bicyclic framework, a fact that might help to add some information to the structure and chemical behavior of phosphoranes. Due to their unstability, most of the phoshoranes **1–6** and some of their derivatives were characterized mainly by phosphorus-31, hydrogen-1 and carbon-13 NMR. However, the structure of compound **4** could further be secured by X-ray diffraction studies. Bicyclic phosphoranes can be in tautomeric equilibrium between P(V) and P(III) species through two routes (Figure 2). One of these involves rupture of the phosphorus–nitrogen bond (a) and the other involves loosing the H–X fragment (b). The first equilibrium (a) was found to occur in compound **8**[3], Figure 3. The second equilibrium (b) is not feasible when X is an organyl group due to the stability of the P–C bond, but it is possible for phosphorus compounds being substituted with labile HX groups.

The P-phenylphosphorane **7**[4,5] was found to be very stable as compared to its aliphatic analogue **8**. This fact is attributed to the absence of tautomerization in **7** as a consequence of the electronic behavior of the nitrogen atom, which precludes protonation[5] to produce the more reactive tricoordinated tautomer[3] (a, Figure 2).

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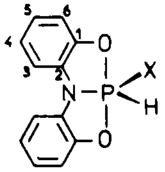
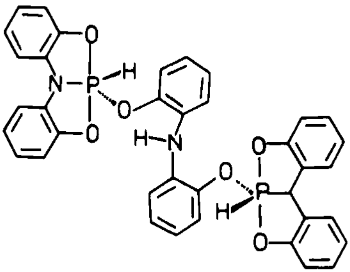


1 X = OMe

2 X = NMe_2

3 X = $O^-H\overset{+}{N}R_3$

6 X = H



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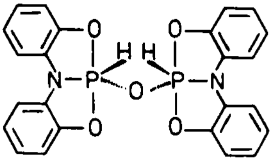

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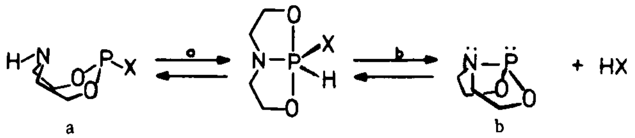
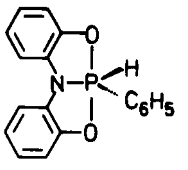
FIGURE 1 New phosphorane compounds.



a b

FIGURE 2 Equilibrium between P(III) and P(V) species.



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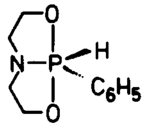

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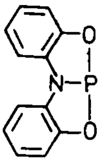
FIGURE 3 Examples of aromatic[5] and aliphatic[3] P-phenyl phosphoranes.



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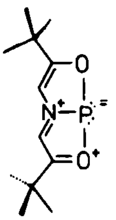

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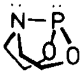

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FIGURE 4 Examples of aromatic and aliphatic phosphanes.[1,6,7]

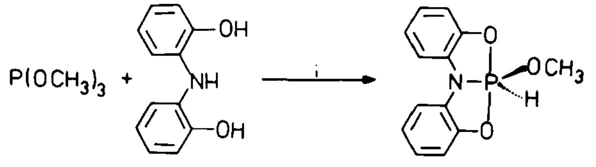
Furthermore, a monocyclic form (a) would be extremely unfavorable due to the rigid structure of the aromatic ligand. The equilibrium (b) is attractive for understanding the chemistry of phosphoranes and for a potential route to the unknown phosphane **9**. Such a dibenzobicyclic structure should reinforce a T-shaped geometry as in **10**[6], instead of a bent geometry **11** shown by saturated compounds[1,7] (Figure 4).

RESULTS AND DISCUSSION

Syntheses of phosphoranes 1–6

We have prepared and studied six dibenzobicyclic phosphoranes **1–6**.

1-Methoxy derivative **1**. Compound **1** was prepared from diphenolamine **12** and methyl phosphite in boiling benzene, Figure 5. It was isolated by evaporation of the solvent to afford a pale brown solid, moderately stable under anhydrous conditions and inert atmosphere ($\delta\ ^{31}P = -35.0$ ppm, J(P–H) 898 Hz, see Tables



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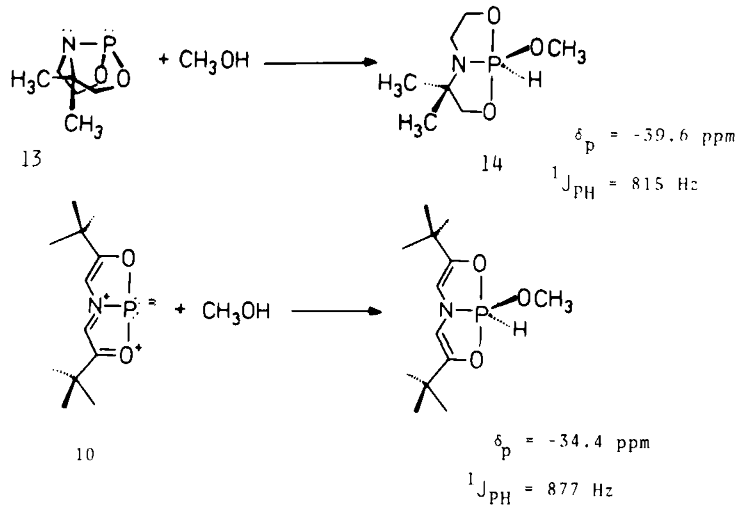
1

i: C_6H_6, 80°C, 5h

$\delta_P = -35.0$ ppm

$^1J_{PH} = 898$ Hz

FIGURE 5 Synthesis of compound **1**.



13

14

$\delta_P = -39.6$ ppm

$^1J_{PH} = 815$ Hz

10

$\delta_P = -34.4$ ppm

$^1J_{PH} = 877$ Hz

FIGURE 6 Reported[2,6] analogues of compound **1**.

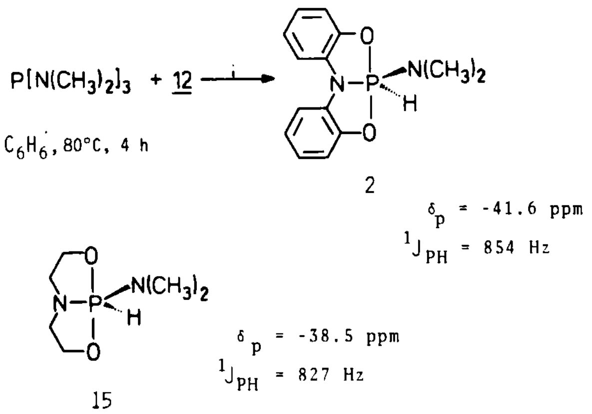


FIGURE 7 Synthesis of compound **2**, and comparison with its aliphatic analogue.[1]

II and III for ^{1}H and ^{13}C NMR). The phosphorane structure of compound **1** is clearly established by the NMR data. When the proton at the phosphorus atom is exchanged by a deuterium in the presence of D_2O, the ^{31}P NMR signal shows an isotope shift of +0.2 ppm and a $^1J_{P-D}$ of 137 Hz. The aliphatic analogue **14** has been observed in solution as the result of oxidative addition of methanol to the phosphane[2] **13**. A similar unsaturated compound was observed as an unstable intermediate by Arduengo[6] (Figure 6).

Dimethylamide derivative **2**. Compound **2** was synthesized after heating tris(dimethylamino)phosphane with **12** in benzene which causes elimination of dimethylamine, (Figure 7). It is characterized by its NMR ($\delta\ ^{31}P = -41.6$ ppm, $J(P-H) = 854$ Hz; see Tables II and III for ^{1}H and ^{13}C NMR). This is a very unstable and reactive compound that could not be isolated, but was identified in solution as being similar to its aliphatic analogue[1] **15**, Figure 7.

TABLE I

^{31}P NMR chemical shifts; δ ppm *J* (Hz) in C_6D_6

Compound	δ	$^1J_{P-H}$ (Hz)	
1	−35.0	898	$^2J_{POCH_3} = 15$
2	−41.6	854	$^2J_{PNCH_3} = 11$
3	−39.0	839	
4	−36.4	916	
5	−42.9	complex	
6	−49.3	709	

TABLE II

Proton NMR (δ, ppm and *J* Hz)

1	3.1 (d, *J* = 16); 8.0 (d, *J* = 900); 6.5(m) and 7.4(m).
2	2.3 (d, *J* = 12); 8.35 (d, *J* = 855); 6.8–7.2(m).
3	0.9 (t, *J* = 7); 2.36 (q, *J* = 7); 8.33 (d, *J* = 840); 6.9(m); 7.2(m) and 7.5(m).

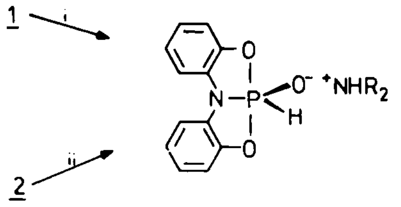
TABLE III

^{13}C NMR (δ, ppm; J, Hz) data

Compounds		C-1	C-2	C-3	C-4	C-5	C-6	x	
1[a]	δ	146.4	128.6	111.1	121.1	120.9	111.1	53.5	—
	J	5.8	*	14.6				7.8	
2[b]	δ	147.0	129.2	110.8	121.7	120.6	110.5	38.3	—
	J	4.8	21.4	13.6			5.8	5.8	
3[b]	δ	149.4	128.5	110.3	120.7	118.3	109.8	46.7	12.0
	J	6.0		13.4			6.0		
5[b]	δ	145.6	128.8	111.3	122.2	121.0	111.1	—	—
	J	6.0		10.9			12.1		
6[b]	δ	148.4	128.9	111.2	122.4	120.5	110.8	—	—
	J	5.8		17.5			8.7		

[a] = In $CDCl_3$; [b] = in C_6D_6.

1-Oxo derivatives **3**. Hydrolysis of **2** with one equivalent of water gives the ammonium salt of phosphoranic diacid **3** (R = CH_3). The absence of ^3J(P–H) and ^2J(PC) couplings to the NMe_2 residue and all other NMR data are in agreement with structure **3**, (Tables I–III). Reaction of compound **1** with one equivalent of dibenzylamine gave the dibenzylammonium salt **16**, as was observed by phoshorus NMR, Figure 8. The acidity of the P–H proton is evidenced by H/D exchange in the presence of D_2O, and the strong acidity of the P–OH is deduced by the formation of ammonium salts, this being attributed to the electron back-donation from the oxygen atoms to the phosphorus atom. Compound **3** is more stable than phosphoranes **1–2** and it does not give substitution reactions of the oxo group by amines of hydrides. Its greater stability compared to the aliphatic compound **17**, which is observed as an intermediate in the hydrolysis of phosphane[2] **18** (Figure 9), can again be attributed to the rigid framework of the aromatic bicycle. Some stable spirohydroxyphosphoranes have been reported.[8,9]



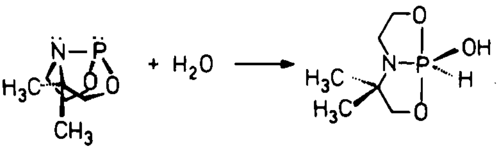
i: $HN(CH_2C_6H_5)_2$; H_2O
C_6H_6, 80°C

ii: H_2O, C_6H_6, 80°C

3 R = Me δ_p = -39.0 ppm
$^1J_{PH}$ = 838 Hz

16 R = $CH_2C_6H_5$ δ_p =-39.5 ppm
$^1J_{PH}$ = 838 Hz

FIGURE 8 Syntheses of compounds **3** and **16**.



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17 δ_P = -42.4 ppm

$^1J_{PH}$ = 799 Hz

FIGURE 9 Phosphorane oxyacid detected during phosphane hydrolysis.[2]

Substitution reactions of compounds **2.** Reactions of compound **2** with some selected reagents were monitored by ^{31}P NMR. The substitution reactions of amide or hydride groups were observed as depicted in Figure 10. Furthermore, reactions of **2** with several reagents were performed:

a) Methanol affords compound **1** ($\delta\ ^{31}P = -35.0$ ppm).

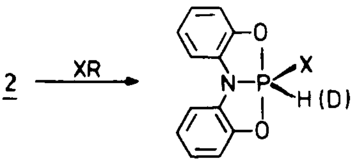
b) Phenol gives the corresponding phenoxy derivative **19** ($\delta\ ^{31}P = -37.3$ ppm, J(P–H) = 912 Hz). This compound was compared with its aliphatic analogue[2] **20**, Figure 11.

c) Acetic anhydride provides the corresponding anhydride **21** which shows a doublet at $\delta\ ^{31}P = -40.1$ ppm (JP–H) = 930 Hz.

d) Dibenzylamine affords compound **22**, $\delta\ ^{31}P = -42.4$ ppm, J(P–H) = 857 Hz.

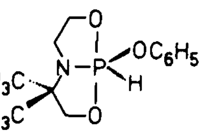
e) One equivalent of water gives the ammonium salt of hydroxy phosphoranes **3**, $\delta\ ^{31}P = -39.0$ ppm, J(P–H) = 839 ppm.

f) One molecule of deuterated water shows that **23** is formed, $\delta\ ^{31}P = -39.4$ ppm, J(P–D) = 128 Hz. The high stability of phosphorane **7** toward ring rupture[4] and the behavior of phosphorane **2** in the substitution reactions shown in Figure 10 suggest that an equilibrium (b, Figure 2) is occurring.



XR		X	δ_p	$^1J_{PH}$
MeOH	1	OMe	-35.0	898
H_2O	3	$O^-H_2\overset{+}{N}Me_2$	-39.0	839
C_6H_5OH	19	OC_6H_5	-37.3	912
Ac_2O	21	OAc	-40.1	930
$HN(CH_2C_6H_5)_2$	22	$N(CH_2C_6H_5)_2$	-42.4	857
D_2O	23	$O^-\ D_2\overset{+}{N}Me_2$	-39.4	128

FIGURE 10 Substitution reactions of compound **2**.



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δ_P = -38.3 ppm

$^1J_{PH}$ = 830 Hz

FIGURE 11 Aliphatic analogue of compound **19**.[2]

Diphenoxyamine-bis-*phosphorane* **4** *and oxy*-bis-*phosphorane* **5**. Compounds **4** and **5** were isolated during our attempts to obtain the 1-chlorodibenzobicyclic derivative by reaction of phosphorus trichloride and **12** in the presence of triethylamine. ^{31}P NMR measurements of the reaction products allow observation of three phosphoranes: δ −42.9 with a complex coupling pattern, $\delta = -39.0\,J$(P–H) = 836 and δ −36.4 J(P–H) = 913. The ratios of compounds varie from one reaction to another, and evidently they depend on very small quantities of moisture in the solvent. Crystallization of the reaction mixture and separation of crystals by decantation, followed, by redissolution in deuterated benzene, gave a sole compound as evidenced by the NMR signal at $\delta = -42.9$, as two multiplets formed each by three signals, which collapse into one signal under proton decoupling conditions. The same coupling pattern was observed by proton NMR. By heating the benzene solution in the presence of an excess of triethylamine, the former signals disappear giving a ^{31}P doublet at $\delta = -39.0$ ppm, which corresponds to the ammonium salt of the hydroxy derivative **24**, (Figure 12). Additional NMR data support that the structure of compound **5** corresponds to an anhydride.

The remaining solution, left after isolating compound **3**, was crystallized again, providing crystals that were suitable for X-ray diffraction studies. The data collection was performed in the $\theta:2\theta$ scanning mode using graphite monochromated Cu-K$_\alpha$ radiation ($\lambda = 1.54178$ Å). The data measured were corrected for background, Lorenz and polarization effects, while crystal absorption and decay were negligible. The structure was solved by direct methods using the software provided by the diffractometer manufacturer. For the structural refinements the non-hydrogen atoms were treated anisotropically; the NH and the two PH hydrogen atoms became evident from ΔF synthesis, and the hydrogen atoms bonded to carbons, included in the structure factor calculation, were refined isotropically. The structure of compound **4** was determined as is shown in Figure 13, the corresponding crystallographic data being on Tables IV–VI.

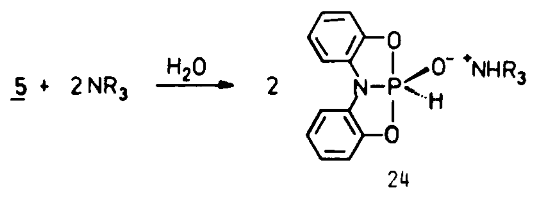

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FIGURE 12 Hydrolysis of anhydride **5**.

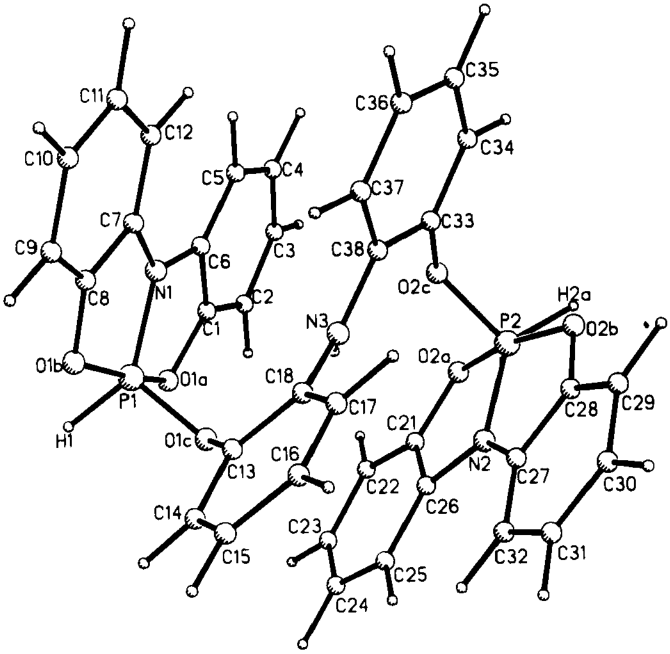

FIGURE 13 X-ray diffraction structure of compound **4**.

Compound **4** is a double ester formed by the combination of one ligand and two phosphoranes. Examination of the angles around the phosphorus atoms shows that the structure is a Berry coordinate,[4] approximately half-way between a trigonal bipyramid and a rectangular pyramid. The assignment of the NMR signal observed at $\delta = -36.4$ ppm; $J(\text{P–H}) = 913$ Hz, is mainly based on analogy to that of the phenol derivative **19** ($\delta = -37.3$ ppm; $J = 912$ Hz).

Reactions of compounds **1** *and* **2** *with borane.* So far, our attempts to obtain compound **9** by elimination of equatorial substituents from phosphoranes **1** and **2** by heating under vacuum or in solution were unsuccessful. In some attempts we observed mixtures of phosphanes and phosphoranes, as evidenced by a ^{31}P NMR signals near 120 ppm.

We have tried to eliminate amine or alcohol from compounds **1** or **2** by reacting these phosphoranes with borane derivatives. The ^{31}P and ^{11}B NMR measurements allowed to follow the reactions. Addition of borane dimethylsulfide to compound **1** causes an intensity decrease in the doublet due to the phosphorane $\delta = -34.9$ while a broadened quartet appeared at $\delta = +120$ ppm, $J(\text{P–B}) = 99$ Hz. In addition, the ^{11}B NMR spectrum shows a doublet of quartets (as a quintet) at $\delta = -45.4$ ppm $J(\text{P–B}) = 97$ Hz and $J(\text{B–H}) = 98$. The NMR data show no evidence for N-borane coordination but support the structure of a P-borane coordination dimer,[7,10] since the $\delta\ ^{31}\text{P} = 120$ ppm value agrees with the chemical shift of a tricoordinated phosphorus[6] **26** (Figure 14). Such dimerization processes are spontaneous for bicyclic aliphatic phosphoranes.[7,10] The resonance

TABLE IV

Crystal data, collection and refinement parameters for **4**

A. Crystal parameters	
chemical formula	$C_{36}H_{27}N_3O_6P_2$
molecular weight	659.5807
crystal system	triclinic
space group	$P\bar{1}$
crystal size, mm	0.7 × 0.5 × 0.25
crystal color	white
cell constants	
a, Å	10.4702(37)
b, Å	10.6877(38)
c, Å	14.6620(44)
α, deg	81.131(27)
β, deg	83.843(27)
γ, deg	73.194(27)
cell volume, $Å^3$	1548.43(91)
ρ (calc), g/cm^3	1.05
Z	2
F (000), e^-	684
B. Data collection parameters	
μ, cm^{-1}	17.12
scan width, below $K_{\alpha 1}$, above $K_{\alpha 2}$, deg	1.1–1.2
2θ limits, deg	3.0–110.0
scan speed (variable), deg min^{-1}	5.0–29.3
exposure time, h	94.58
total no. reflections collected	4164
no. unique reflections	2410
C. Structure refinement	
reflections for final refinement	1996
parameters refined	443
$R(F)$, %	6.0
$R(W)$, %	6.75
goodness of fit for the last cycle	1.161
final G	0.00311
residual electron density ($e^-/Å^3$)	0.3077

signal of **25** is far from the expected value ($^{31}P\ \delta = -187$ ppm) of compound **10**,[6] from the values of compounds **27** and **28**[11] (Figure 14) or from those of phosphane **9** or its borane derivatives. The absence of a borane–nitrogen bond is attributed to the nitrogen planarity, as evidenced by the X-ray diffraction studies of compounds **4** and **7**.[5]

The reaction of borane dimethylsulfide with compound **2** followed a somewhat different course. The ^{31}P NMR spectrum shows, in addition to the broad signal at +120 ppm for a dimeric borane adduct, a triplet in the phosphorane region. This is assigned to phosphorane **6**, $\delta\ ^{31}P = -49.2$ ppm, $J(P\text{–}H) = 710$ Hz. The chemical shift of the corresponding aliphatic phosphorane **29** is reported to be $\delta = -61.8$ ppm.[12] Separation of the two compounds was unsuccessful. Reaction of compound **2** with catechol borane mainly affords compound **6**, which again could not be isolated. Compound **1** does not react with catechol borane, Figure 15.

TABLE V

Atom coordinates (×10^4) and temperature factors (Å^2 × 10^3) for **4**

Atom	x	y	z	U_{eq}
P(1)	7121(2)	5224(2)	5459(1)	72(1)[a]
O(1a)	6621(5)	6717(4)	5840(4)	88(2)[a]
O(1b)	7346(4)	3860(4)	4940(3)	81(2)[a]
O(1c)	8469(4)	4762(4)	5995(3)	66(2)[a]
N(1)	5802(5)	4836(5)	6103(3)	67(2)[a]
C(1)	5634(7)	6821(7)	6540(5)	79(3)[a]
C(2)	5145(8)	7895(7)	7016(5)	100(4)[a]
C(3)	4081(10)	7869(9)	7665(6)	107(5)[a]
C(4)	3617(9)	6769(10)	7840(6)	106(5)[a]
C(5)	4114(7)	5708(8)	7355(5)	86(4)[a]
C(6)	5130(6)	5729(6)	6697(4)	67(3)[a]
C(7)	5673(7)	3571(6)	6028(4)	70(3)[a]
C(8)	6616(7)	3039(6)	5350(4)	70(3)[a]
C(9)	6743(8)	1805(7)	5122(5)	95(4)[a]
C(10)	5884(9)	1105(8)	5593(6)	108(4)[a]
C(11)	4946(9)	1612(8)	6258(6)	94(4)[a]
C(12)	4832(7)	2875(6)	6498(5)	77(3)[a]
C(13)	9248(6)	3448(6)	6190(4)	58(3)[a]
C(14)	10284(8)	2925(8)	5585(5)	80(4)[a]
C(15)	11065(7)	1648(7)	5803(5)	90(4)[a]
C(16)	10831(7)	925(7)	6646(5)	86(4)[a]
C(17)	9800(7)	1465(7)	7260(5)	73(3)[a]
C(18)	9005(7)	2745(6)	7048(4)	61(3)[a]
N(3)	8002(6)	3408(5)	7648(4)	69(2)[a]
P(2)	7959(2)	5123(2)	9526(1)	83(1)[a]
O(2a)	7541(5)	6713(4)	9047(4)	95(2)[a]
O(2b)	8587(5)	3599(5)	10109(3)	102(3)[a]
O(2c)	6790(4)	4807(4)	9032(3)	67(2)[a]
N(2)	9412(5)	4884(5)	8868(4)	80(3)[a]
C(21)	8352(7)	6961(5)	8298(5)	84(4)[a]
C(22)	8123(10)	8154(8)	7723(7)	111(5)[a]
C(23)	9045(13)	8288(12)	6999(8)	121(6)[a]
C(24)	10138(14)	7253(15)	6860(7)	134(7)[a]
C(25)	10384(9)	6049(11)	7432(7)	105(5)[a]
C(26)	9454(7)	5944(7)	8159(5)	78(3)[a]
C(27)	10270(7)	3605(8)	8993(6)	89(4)[a]
C(28)	9771(8)	2886(8)	9728(6)	108(4)[a]
C(29)	10395(15)	1558(13)	10035(9)	149(7)[a]
C(30)	11596(18)	1028(17)	9567(12)	181(11)[a]
C(31)	12101(14)	1701(13)	8852(10)	166(8)[a]
C(32)	11465(8)	3022(8)	8531(7)	120(5)[a]
C(33)	6592(6)	3558(6)	9043(4)	59(3)[a]
C(34)	5712(7)	3137(7)	9702(5)	72(3)[a]
C(35)	5441(7)	1952(7)	9647(5)	84(4)[a]
C(36)	6025(7)	1237(7)	8944(5)	76(3)[a]
C(37)	6896(7)	1672(6)	8269(5)	68(3)[a]
C(38)	7182(6)	2877(5)	8325(4)	55(3)[a]
H(1)	7355(44)	5817(40)	4628(29)	47(13)
H(2)	5572	8728	6888	116(11)
H(3)	3617	8715	8035	116(11)
H(4)	2825	6739	8383	116(11)
H(5)	3702	4865	7495	116(11)
H(9)	7490	1392	4591	92(10)
H(10)	5963	126	5425	92(10)
H(11)	4279	1045	6605	92(10)
H(12)	4105	3280	7042	92(10)
H(14)	10490	3509	4938	133(13)

TABLE V (*Continued*)

Atom	*x*	*y*	*z*	U_{eq}
H(15)	11866	1206	5314	133(13)
H(16)	11466	−73	6823	133(13)
H(17)	9608	885	7913	133(13)
H(3a)	7865(43)	4251(40)	7593(29)	49(13)
H(2a)	7496(67)	5419(62)	10443(46)	128(23)
H(22)	7236	8963	7843	157(14)
H(23)	8903	9213	6538	157(14)
H(24)	10852	7373	6278	157(14)
H(25)	11263	5232	7309	157(14)
H(29)	9959	990	10601	161(15)
H(30)	12155	15	9792	161(15)
H(31)	13043	1211	8500	161(15)
H(32)	11894	3564	7945	161(15)
H(34)	5236	3721	10256	94(9)
H(35)	4760	1594	10167	94(9)
H(36)	5807	309	8910	94(9)
H(37)	7351	1098	7705	94(9)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE VI

Bond lengths (Å) and angles (deg.) for **4**

P(1)-O(1a)	1.692(5)	P(1)-O(1b)	1.692(5)
P(1)-O(1c)	1.603(5)	P(1)-N(1)	1.703(5)
O(1a)-C(1)	1.368(9)	O(1b)-C(8)	1.358(9)
O(1c)-C(13)	1.408(6)	N(1)-C(6)	1.379(8)
N(1)-C(7)	1.418(9)	C(1)-C(2)	1.378(11)
C(1)-C(6)	1.393(11)	C(2)-C(3)	1.389(12)
C(3)-C(4)	1.377(16)	C(4)-C(5)	1.375(13)
C(5)-C(6)	1.360(9)	C(7)-C(8)	1.387(9)
C(7)-C(12)	1.377(10)	C(8)-C(9)	1.377(11)
C(9)-C(10)	1.393(13)	C(10)-C(11)	1.363(12)
C(11)-C(12)	1.416(12)	C(13)-C(14)	1.368(9)
C(13)-C(18)	1.401(8)	C(14)-C(15)	1.382(10)
C(15)-C(16)	1.391(11)	C(16)-C(17)	1.378(10)
C(17)-C(18)	1.389(8)	C(18)-N(3)	1.395(8)
N(3)-C(38)	1.403(8)	P(2)-P(2a)	1.685(5)
P(2)-O(2b)	1.699(5)	P(2)-O(2c)	1.625(5)
P(2)-N(2)	1.688(6)	O(2a)-C(21)	1.356(9)
O(2b)-C(28)	1.366(9)	O(2c)-C(33)	1.406(8)
N(2)-C(26)	1.421(8)	N(2)-C(27)	1.399(8)
C(21)-C(22)	1.388(10)	C(21)-C(26)	1.360(9)
C(22)-C(23)	1.376(15)	C(23)-C(24)	1.364(17)
C(24)-C(25)	1.396(17)	C(25)-C(26)	1.379(12)
C(27)-C(28)	1.372(12)	C(27)-C(32)	1.382(10)
C(28)-C(29)	1.405(14)	C(29)-C(30)	1.378(21)
C(30)-C(31)	1.328(23)	C(31)-C(32)	1.406(15)
C(33)-C(34)	1.378(9)	C(33)-C(38)	1.363(9)
C(34)-C(35)	1.392(12)	C(35)-C(36)	1.362(11)
C(36)-C(37)	1.392(10)	C(37)-C(38)	1.420(10)
O(1a)-P(1)-O(1b)	168.1(3)	O(1a)-P(1)-O(1c)	93.6(3)
O(1b)-P(1)-O(1c)	98.2(2)	O(1a)-P(1)-N(1)	88.5(3)
O(1b)-P(1)-N(1)	88.3(3)	O(1c)-P(1)-N(1)	113.1(2)

TABLE VI (*Continued*)

P(1)-O(1a)-C(1)	114.0(5)	P(1)-O(1b)-C(8)	114.4(4)
P(1)-O(1c)-C(13)	125.1(4)	P(1)-N(1)-C(6)	114.8(5)
P(1)-N(1)-C(7)	114.8(4)	C(6)-N(1)-C(7)	129.9(5)
O(1a)-C(1)-C(2)	124.7(7)	O(1a)-C(1)-C(6)	112.2(6)
C(2)-C(1)-C(6)	123.1(7)	C(1)-C(2)-C(3)	117.0(8)
C(2)-C(3)-C(4)	119.6(8)	C(3)-C(4)-C(5)	122.5(8)
C(4)-C(5)-C(6)	118.7(8)	N(1)-C(6)-C(1)	109.4(5)
N(1)-C(6)-C(5)	131.6(7)	C(1)-C(6)-C(5)	119.0(6)
N(1)-C(7)-C(8)	107.8(6)	N(1)-C(7)-C(12)	131.4(6)
C(8)-C(7)-C(12)	120.8(7)	O(1b)-C(8)-C(7)	113.5(6)
O(1b)-C(8)-C(9)	125.0(6)	C(7)-C(8)-C(9)	121.5(7)
C(8)-C(9)-C(10)	117.7(7)	C(9)-C(10)-C(11)	121.8(8)
C(10)-C(11)-C(12)	120.3(8)	C(7)-C(12)-C(11)	117.9(6)
O(1c)-C(13)-C(14)	120.1(5)	O(1c)-C(13)-C(18)	118.2(5)
C(14)-C(13)-C(18)	121.5(5)	C(13)-C(14)-C(15)	119.3(7)
C(14)-C(15)-C(16)	120.2(7)	C(15)-C(16)-C(17)	120.3(6)
C(16)-C(17)-C(18)	120.1(6)	C(13)-C(18)-C(17)	118.6(6)
C(13)-C(18)-N(3)	117.0(5)	C(17)-C(18)-N(3)	124.3(6)
C(18)-N(3)-C(38)	128.1(5)	O(2a)-P(2)-O(2b)	169.5(3)
O(2a)-P(2)-O(2c)	92.4(3)	O(2b)-P(2)-O(2c)	98.0(3)
O(2a)-P(2)-N(2)	88.7(3)	O(2b)-P(2)-N(2)	87.9(2)
O(2c)-P(2)-N(2)	112.4(3)	P(2)-O(2a)-C(21)	113.4(4)
P(2)-O(2b)-C(28)	114.5(5)	P(2)-O(2c)-C(33)	126.2(4)
P(2)-N(2)-C(26)	114.0(4)	P(2)-N(2)-C(27)	115.2(4)
C(26)-N(2)-C(27)	129.7(6)	O(2a)-C(21)-C(22)	124.1(6)
O(2a)-C(21)-C(26)	114.3(6)	C(22)-C(21)-C(26)	121.6(7)
C(21)-C(22)-C(23)	118.3(8)	C(22)-C(23)-C(24)	119.6(10)
C(23)-C(24)-C(25)	122.9(11)	C(24)-C(25)-C(26)	116.5(8)
N(2)-C(26)-C(21)	108.0(6)	N(2)-C(26)-C(25)	130.8(6)
C(21)-C(26)-C(25)	121.2(7)	N(2)-C(27)-C(28)	109.2(6)
N(2)-C(27)-C(32)	131.4(7)	C(28)-C(27)-C(32)	119.4(7)
O(2b)-C(28)-C(27)	112.3(6)	O(2b)-C(28)-C(29)	124.2(9)
C(27)-C(28)-C(29)	123.5(8)	C(28)-C(29)-C(30)	115.0(12)
C(29)-C(30)-C(31)	122.7(14)	C(30)-C(31)-C(32)	122.5(12)
C(27)-C(32)-C(31)	116.9(9)	O(2c)-C(33)-C(34)	120.0(6)
O(2c)-C(33)-C(38)	117.0(5)	C(34)-C(33)-C(38)	122.6(7)
C(33)-C(34)-C(35)	118.8(6)	C(34)-C(35)-C(36)	120.2(7)
C(35)-C(36)-C(37)	121.1(7)	C(36)-C(37)-C(38)	118.9(6)
N(3)-C(38)-C(33)	119.4(6)	N(3)-C(38)-C(37)	122.2(5)
C(33)-C(38)-C(37)	118.3(6)		

CONCLUSIONS

The use of 2,2′-diphenolamine[13] allows the isolation and study of new phosphoranes oxyacids of very interesting structure and reactivity,[14] some of them having very unstable aliphatic analogues. The aromatic phosphoranes **1–6** show no tautomeric equilibrium between the monocyclic P(III) and bicyclic P(V) species (Figure 2a), as has been deduced from the lack of reaction of borane with compound **7**.[4] A tautomeric equilibrium (Figure 2b) between the tricoordinated bicyclic compound and the phosphorane seems to be in agreement with exchange

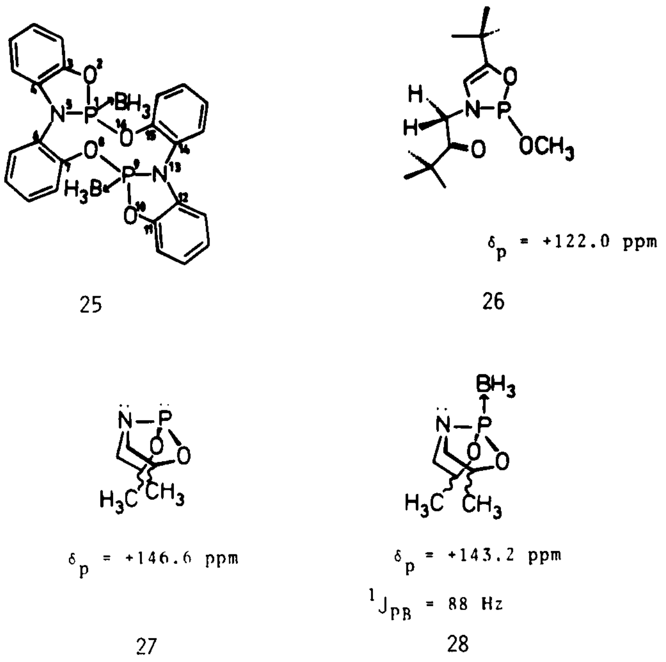

FIGURE 14 Comparison between phosphanes and phosphane–borane adducts.

reactions of equatorial substituents. A very interesting result, is the observation that the stability of the aromatic phosphane **9** appears to be unsufficient for shifting the equilibrium to a P(III) species (Figure 2b). Similarly, phosphane **9** adds methanol to give the phosphorane **1**, but elimination of methanol does not lead back to **9**. The deshielding of ^{31}P nuclei in the aromatic phosphoranes, with respect to the aliphatic systems, indicates electronic delocalization in the unsaturated derivatives.

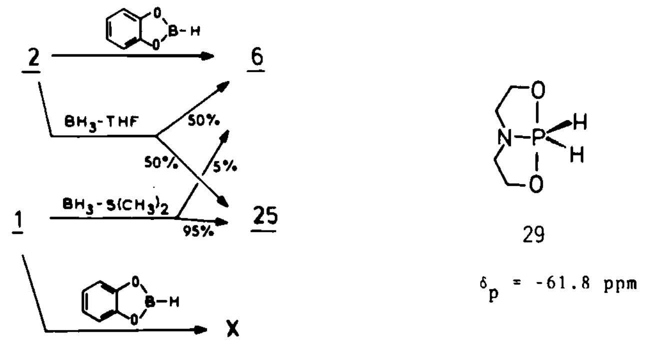

FIGURE 15 Reactions of compounds **1** and **2** with boron reagents, and comparison of compound **6** with its aliphatic analogue **29**.[12]

EXPERIMENTAL SECTION

^1H, ^{13}C, ^{31}P and ^{11}B NMR spectra were recorded on a Jeol FX90Q spectrometer at 89.55, 22.49, 36.23 and 28.69 MHz, respectively. All chemicals shifts are in ppm and coupling constants are in Hertz. ^1H and ^{13}C NMR spectra are referenced to internal Me_4Si, ^{31}P NMR and ^{11}B NMR spectra are referenced to external 85% H_3PO_4 and to external $BF_3:OEt_2$, respectively. Mass spectra (70 eV) were obtained on a Hewlett Packard 5985-A spectrometer. The single crystal X-ray diffraction studies were performed on a Nicolet R3m four circle automatic diffractometer. Melting points were taken on a Gallenkamp apparatus and are uncorrected. The solvents were dried over sodium, distilled and kept over 4 Å molecular Sieve.

1-Methoxy-5-aza-2,8-dioxa-1-phospha^V-dibenzo[c,f]bicyclo[3.3.0]octane (**1**). A 100 ml flask equipped with a dry ice condenser, a magnetic stirring bar and a mercury bubbler, under a nitrogen atmosphere, was charged with 0.35 g (1.74 mmol) of 2,2-diphenolamine[13] in 20 ml of dry benzene at 80°C. After addition of 0.41 ml (3.48 mmole) of trimethylphosphite, the mixture was refluxed for 5 h, the solvent, the excess of trimethyl phosphite and the formed MeOH were removed by distillation at reduced pressure. This yielded 0.42 g (1.6 mmole, 91%) of a crystalline solid. m.p. 114–118°C (decomposes); mass spectrum *m/e* 261 (calcd, 261).

1-Dimethylamine-5-aza-2,8-dioxa-1-phospha^V-dibenzo[c,f]bicyclo[3.3.0]octane (**2**). A 250 ml flask equipped with a dry ice condenser, a magnetic stirring bar and a gas exit valve was charged with 0.5 g (2.5 mmole) of 2,2-diphenolamine in 10 ml of dry benzene at 80°C. After adding 0.54 ml (2.99 mmole) of hexamethylphosphorus triamide, the reaction mixture was refluxed for 4 h under a nitrogen atmosphere. The dimethylamine that eliminated (85%) was titrated with HCl (0.1 M). Elimination of benzene under reduced pressure afforded 0.64 g (2.3 mmole, 92%) of a solid, m.p. 64–95°C (decomposes); mass spectrum m/e 275 (calcalc, 274).

1-Triethylammonium salt-1-oxy-5-aza-2,8-dioxa-1-phospha^V-dibenzo[c,f]bicyclo[3.3.0]octane (**24**), *1,1'-diphenoxyamine-di[1-hydro-5-aza-2,8-dioxa-1-phospha^V-dibenzo[c,f]bicyclo[3.3.0]octane]* (**4**) *and 1-oxo-bis[1-hydro-5-aza-2,8-dioxa-1-phospha^V-dibenzo[c,f]bicyclo[3.3.0]octane]* (**5**). A 100 ml flask equipped with a dropping funnel, a magnetic stirring bar and a mercury bubbler was charged with a solution of 0.5 g (2.5 mmole) of 2,2-diphenolamine and 0.69 ml (4.9 mmole) of triethylamine in 10 ml of dry benzene. After 20 min a solution of phosphorus trichloride 0.2 ml (2.4 mmole) in 15 ml of dry benzene was added at 0°C under a nitrogen atmosphere. The reaction mixture was stirred at 0°C for 1 h and then at 20°C for 2 h. The solution was filtered to remove the formed $HCl{\cdot}NEt_3$ and the solvent was evaporated at reduced pressure. The residue was washed with dry hexane, dissolved in benzene and stirred for 24 h. The crystals that formed (92 mg, 0.19 mmoles, 8%) were separated and characterized as compound **5**. Half of the liquid portion was heated at 80°C for 1 h with an excess of triethylamine. The reaction product was identified as compound **24** (167 mg, 0.42 mmole, 19%). The other half of the filtrate was crystallized again to afford compound **4** (158 mg, 0.24 mmole, 10%) which was characterized by X-ray diffraction studies.

1-Dihydro-5-aza-2,8-dioxa-1-phospha^V-dibenzo[c,f]bicyclo[3.3.0]octane (**6**) *and P,P'-diborane-3,6,11,14-tetradibenzo-2,8,10,16-tetraoxa-5,13-diaza-1,9-diphospha[11,3,0,0^{5,9}]tricyclohexadecano* (**25**). Both compounds were obtained by two procedures:

A) From compound **1**. A 100 ml flask equipped with a magnetic stirring and a mercury bubbler flushed with nitrogen was charged with 0.324 g (1.24 mmole) of **1** in 5 ml of benzene. After addition of 1.0 ml (3.10 mmol) of $BH_3:S(CH_3)_2$ (2.84 M), the reaction mixture was stirred at 0°C for 1 h and then at 80°C for 5 h. The volatile materials were removed at reduced pressure to leave a white solid (240 mg) constituted by compounds **6** and **25** in a 5:95 ratio.

B) From compound **2**. A 100 ml flask equipped with a magnetic stirring bar and a mercury bubbler, under nitrogen, was charged with 0.291 g (1.06 mmole) of **2** in 5 ml of dry benzene. After addition of 1.23 ml (2.86 mmol) of $BH_3:THF$ (2.33 M) the reaction mixture was stirred for at 0°C for 1 h and at 20°C for 16 h. Removal of the volatile materials at reduced pressure gave 143 mg of a mixture of **6** and **25** in a 1:1 ratio.

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