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Phosphorus Heterocycles from 2-(2-Hydroxyphenyl)-1*H*-benzimidazole

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ABSTRACT: *Sixteen different P(III) and P(V) heterocycles derived from 2-(2-hydroxyphenyl)-1H-benzimidazole (***1***) are reported. In these heterocycles the phosphorus atom is part of a six-membered unsaturated ring. They were mainly studied by multinuclear NMR. The X-ray diffraction of 3,4-benzimidazole-5,6-benzo-2-dimethylamino-2-seleno-1,3,2-oxazaphosphorinane is reported. Phosphoranes derived from* **1** *and 3,5-di-tert-butylcatechol, and bearing Cl, NMe_2, or phenyl as substituent at phosphorus are presented.* © 2004 Wiley Periodicals, Inc. Heteroatom Chem 15:307–320, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20021

INTRODUCTION

Here we report the synthesis of phosphorus heterocycles derived from 2-(2-hydroxyphenyl)-1*H*-benzimidazole (**1**) which has a phenol ring linked to C2 of a benzimidazole unit with two acidic hydrogen atoms which can be substituted by main group atoms giving heterocycles. The main interest is the preparation of six-membered unsaturated phosphorus heterocycles, which are scarcely studied.

We have recently determined the solid state structure of compound **1** by X-ray diffraction [Esparza Ruiz, A.; Hernández-Díaz, J.; Flores-Parra; Contreras, R. (in preparation)]. The molecule has a planar conformation, a π electronic delocalized system, and a strong hydrogen bond between the phenolic proton and the N lone pair (1.57 Å). In DMSO-d_6 solution, **1** presents a different behavior from the solid state, its ^{1}H and ^{13}C spectra show a symmetrical pattern for the benzimidazole fragment, seven signals for ^{1}H and ten for ^{13}C. This behavior is consequence of the benzymidazole protonation giving a zwitterion as is deduced by comparison with the spectra of protonated benzimidazole [1].

We expected that compound **1** would be an excellent chelating compound, the two labile hydrogen atoms could be substituted in different ways by 15 group atoms as is shown in Scheme 1. Some previous results indicate that **1** forms stable heterocycles with boron compounds [Esparza Ruiz A. Hernández-Díaz, J. Flores-Parra; Contreras, R. (in preparation)]. Tavman and Ülküseven [2] have reported the syntheses of spirocyclic zinc complexes of **1**. We have assumed that its chemistry would be similar to that found for *o*-aminophenol [3,4a] and spirocyclic structures could be possible [IV, Scheme 1], therefore we undertook this research. Phosphorus heterocycles derived from 2-(2-aminophenyl)-1*H*-benzimidazole are described in this journal [4b].

We have reacted compound **1** with $P(NMe_2)_3$, PCl_3, and $PhPCl_2$, in order to obtain tri- (II) or pentacoordinated compounds (IV), Scheme 1. We have also investigated the oxidative addition of 3,5-di-*tert*-butyl-1,2-benzoquinone to P(III) compounds in order to give phosphoranes, as well as

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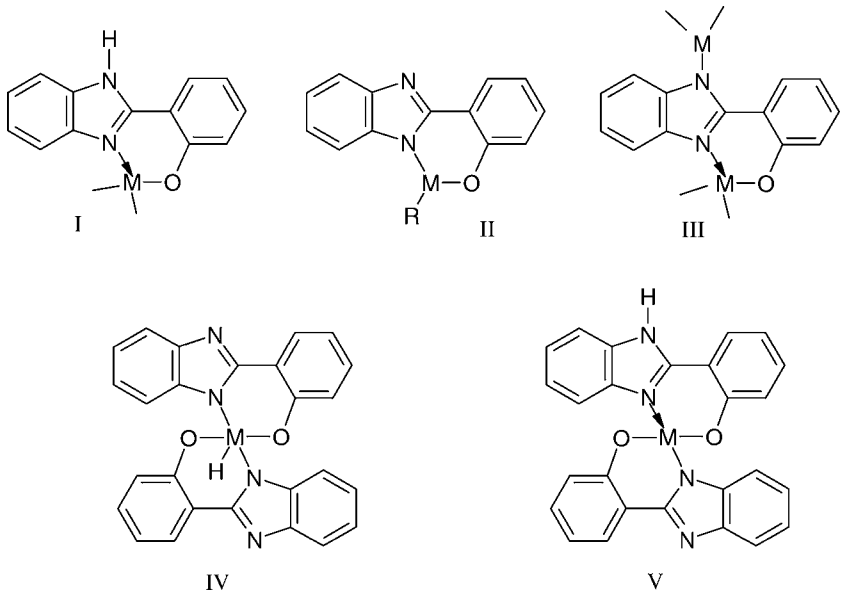


SCHEME 1 Possible heterocycles from compound **1**.

the P(III) heterocycles oxidation with sulfur and selenium.

RESULTS AND DISCUSSION

Reaction with $P(NMe_2)_3$

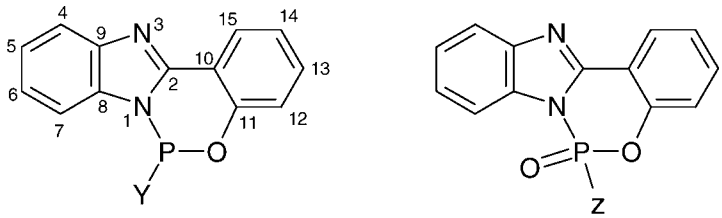
Transamination of **1** with one equivalent of $P(NMe_2)_3$ in refluxing toluene for 2 h produces almost quantitatively heterocycle **2**, as a yellow oil. The ^{31}P spectrum shows a heptet at +104.2 ppm [$^3J(^{31}P, ^1H) = 10$ Hz], that confirms the presence of one P-NMe_2 group [5], Scheme 2. Compound **2** reacts rapidly with traces of moisture to give the phosphorus oxide **4** [6].

Reaction with PCl_3

Compound **1** reacts with one equivalent of PCl_3 in toluene and NEt_3 to give quantitatively the tetracyclic compound **5** (^{31}P +127.2 ppm) [5,6], Scheme 2. Compound **5** is a very reactive beige solid characterized in $CDCl_3$ by NMR; it is easily oxidized and hydrolyzed to give the phosphoric ester **6** [7,8].

Reaction with $PhPCl_2$

The reaction of compound **1** with one equivalent of $PhPCl_2$ in toluene and NEt_3 gave quantitatively **7** as a yellow oil, Scheme 2. ^{31}P NMR spectrum presents a triplet by coupling with *ortho* hydrogen atoms [$^3J(^{31}P, ^1H)$ 6.2 Hz]. There are few examples of structures similar to compound **7**, one of them reported by Fischer et al. [5]. Compound **7** is very reactive to oxygen and moisture and is easily transformed into its oxide **8**, that is a white solid, also characterized by MS. Saturated six-membered phosphorus oxides derived from aminoalcohols are known [9].



	Y	δ ^{31}P (ppm)
2	NMe_2	+ 104.2
5	Cl	+ 127.2
7	Ph	+ 109.7

	Z	δ ^{31}P (ppm)
4	H	+ 4.0 [$^1J(^{31}P, ^1H)$ 650 Hz]
6	OH	+ 3.2
8	Ph	+ 8.0

SCHEME 2 ^{31}P NMR data of compounds **2** and **4–8**.

In order to obtain pure compounds, the syntheses of **5** and **7** were performed in a suspension of **1** in toluene, followed by addition of NEt_3, and then by the phosphorus reagent.

The ^{31}P NMR data of compounds **2, 5**, and **7** are in the expected range for P(III) compounds [5]. Comparison of their ^{31}P chemical shifts reveals the electron withdrawing effect of chlorine, and the electron donating effect of phenyl and N-Me_2 groups. The unequivocal assignment of ^{1}H and ^{13}C signals was based on two dimensional experiments, COSY, HETCOR, COLOC, HMBC, and HMQC [10]. Tables 1 and 2 show ^{1}H and ^{13}C NMR data for **1, 2, 5**, and **7**. Labile proton substitution by phosphorus breaks the equivalence of the benzimidazole carbon atoms, C4 and C9 neighbors of the N3 lone pair are shifted to higher frequencies [1,11,12]. C10, C12, and C14 atoms *ortho* and *para* to oxygen are shifted to higher frequencies, and C11 to lower frequencies with respect to the starting compound **1** as a consequence of the P—O bond formation. The equivalence of N-Me groups in **2** indicates the P—N bond fast rotation. ^{1}H NMR spectra of compounds **1, 2, 5**, and **7** show eight signals for heterocycles **2, 5**, and **7** [1,11]. Resonances of H4 and H15 in **2, 5**, and **7** are strongly deshielded by their close position to the N-lone pair effect [1,11–13].

Transamination Reactions

It is established that P—H spirophosphoranes with larger than five-membered rings are unstable [14,15], however the use of electron withdrawing ligands could allow their preparation by producing a more acidic phosphorus atom ready to form extra bonds, as was demonstrated for antranilic and *o*-aminophenol ligands [16]. Therefore, it was of interest for us to check if compound **1** could afford spirocyclic six-membered ring phosphoranes, however the reaction of two equivalents of **1** with one of $P(NMe_2)_3$ in refluxing toluene for 12 h afforded only compound **2**, Scheme 3.

TABLE 1 ^{1}H NMR Data of **1, 2, 5**, and **7**

Compds	**1**[a]	**2**[b]	**5**	**7**[c]
H4	7.69	7.87	7.89	7.93
H5	7.28	7.33	7.40	7.30
H6	7.28	7.28	7.38	7.35
H7	7.69	7.49	7.57	7.56
H12	7.07	7.10	7.25	7.02
H13	7.37	7.36	7.49	7.24
H14	7.02	7.16	7.35	7.16
H15	8.10	8.37	8.43	8.29

For numbering see Scheme 2.
[a] δ NH = 13.26.
[b] δ NMe_2: 2.57 [^{3}J(PH) = 9.7 Hz].
[c] δ Ph: H_o 7.08, H_m 7.12, H_p 7.18.

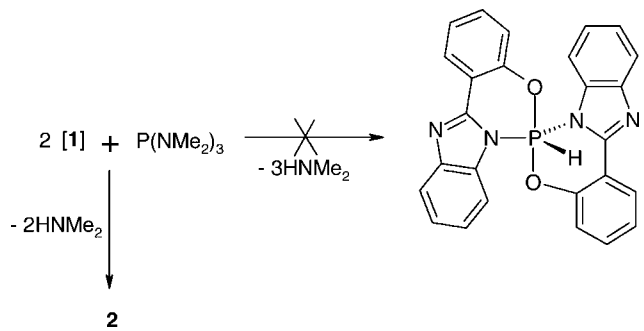
TABLE 2 ^{13}C NMR Data δ (ppm) and ^{n}J(P–C) (Hz) of **1, 2, 5**, and **7**

Compds	**1** δ	**2**[a] δ[^{n}J(P–C)]	**5** δ[^{n}J(P–C)]	**7**[b] δ[^{n}J(P–C)]
C2	152.3	148.0[2.4]	145.1[1.0]	147.1[1.4]
C4	115.6	119.5	120.3	119.9
C5	123.4	123.6	124.7	123.8
C6	123.4	123.3	124.5	123.6
C7	115.6	110.9[7.4]	110.7[7.9]	110.8[6.9]
C8	137.9	134.8[13.4]	133.2[15.2]	135.6[16.2]
C9	137.9	144.6[3.0]	144.4[3.3]	144.4[2.7]
C10	113.4	116.3[5.5]	117.3[6.9]	118.5[5.7]
C11	158.7	151.4[13.3]	147.6[11.6]	150.1[11.2]
C12	117.8	118.8[2.0]	120.2[2.8]	120.0[1.4]
C13	132.2	132.1	132.5[1.1]	132.0
C14	119.6	123.3	125.8	124.2
C15	126.8	126.3	126.7	126.5

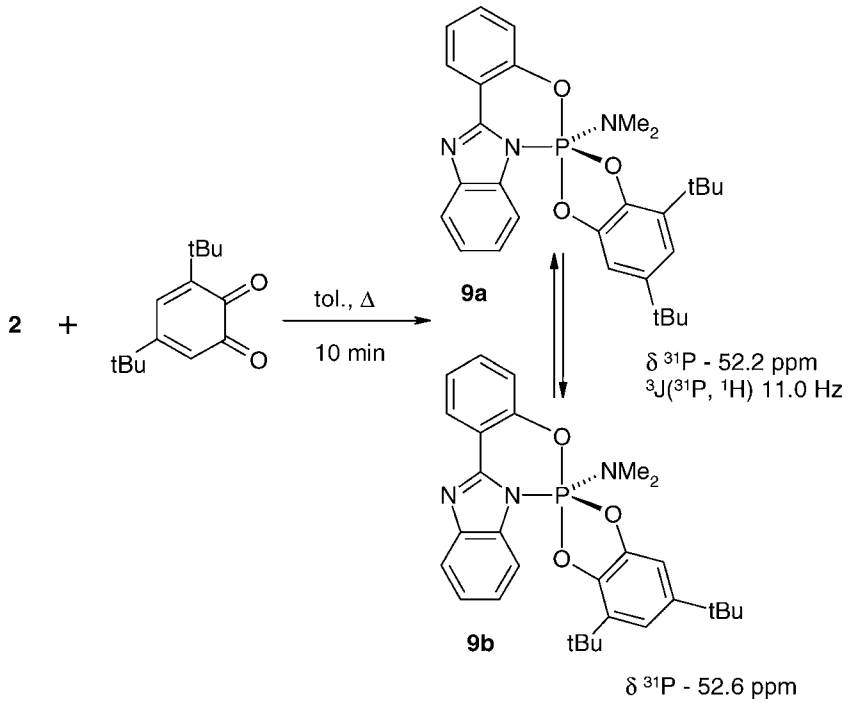
For numbering see Scheme 2.
[a] δ NMe_2 = 36.8 [^{2}J(PC) = 20.8 Hz].
[b] δ PPh: C_i 137.8 [^{1}J(PC) = 31.8 Hz], C_o 129.3 [^{2}J(PC) = 21.3 Hz], C_m 128.7 [^{3}J(PC) = 5.3 Hz], C_p 131.2.

Oxidative Addition of 3,5-Di-tert-butyl-1,2-benzoquinone

We decided to explore the use of a highly electron withdrawing ligand in order to obtain spirophosphoranes derived from **1**, therefore we have investigated the oxidative addition of 3,5-di-*tert*-butyl-1,2-benzoquinone to heterocycles **2, 5**, and **7**. Quinone addition to a solution of **2** in toluene gave a yellow solid (92%). The $^{31}P\{^{1}H\}$ spectrum in $CDCl_3$ indicates a phosphoranes mixture **9a** and **9b** in a 84:16 ratio respectively, Scheme 4. The δ ^{31}P of **9a** and **9b** are similar to data of a reported phosphorane with the same connectivity [17]. In the ^{31}P-^{1}H coupled spectrum, two heptets appeared [^{3}J(^{31}P, ^{1}H) 11.0 Hz] indicating the presence of one P-NMe_2 group. Isomers



SCHEME 3 Reaction of compound **2** with $P(NMe_2)_3$.



SCHEME 4 Synthesis of spirocyclic compounds **9**.

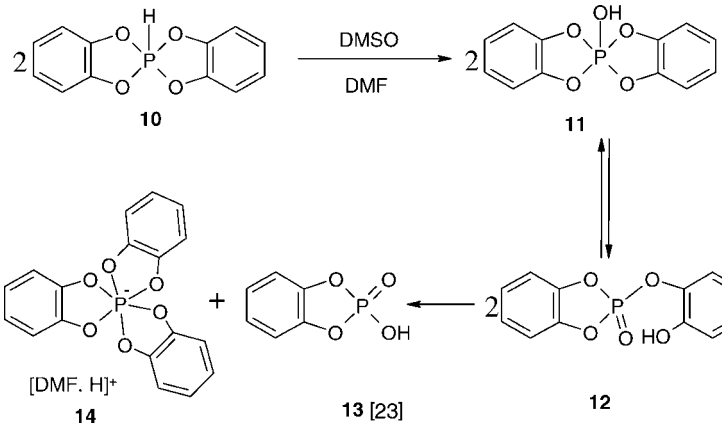
come from the two ways that quinone can be linked. A phosphorus tbp geometry is assumed with catechol and ligand **1** bonded in the most stable apical-equatorial way [18,19]. On the other hand, it is expected that nitrogen atoms must occupy the equatorial positions that favor electronic donation to phosphorus [20]. Although enantiomers for **9a** and **9b** exist, we will not depict them [21]. The structure of the favored isomer **9a** could be predicted from the steric hindrance observed at the calculated models (PC-Spartan Plus 1.5 [22]). Isomer **9a** has a *tert*-butyl group *ortho* to oxygen in equatorial position, the same group in **9b** generates a steric tension with the benzimidazole group. A small signal (−138.1, 5%) also found in the ^{31}P spectrum was assigned for an hexacoordinated compound and is discussed below.

If the mixture of compounds **9a** and **9b** in $CDCl_3$ is set aside for some days the signals of the phosphoranes decrease and two other (+14.8 and −138.1) emerge together in a 1:1 ratio. After 10 days, the new ones are the only signals at the spectrum, they are attributed to hydrolysis of **9a** and **9b**, as it was checked by addition of small amounts of water to other samples. Muñoz et al. [23] have reported that oxidation of phosphorane **10** with DMSO in DMF gave a mixture of the anion **14** and the ester **13**, via phosphorane **11** in equilibrium with **12**, Scheme 5. Using the same argument, Schmutzler explained the oxidation of **15** to produce **16** [24], Scheme 6.

With this information we have explained the structure of compounds **20** and **21**, with signals at +14.8 and −138.1, formed from **9a** and **9b**, Scheme 7. The mechanism implies formation of the hydroxyphosphorane **17** by hydrolysis with traces of moisture. Compound **17** is in equilibrium with the tetracoordinated compound **18**. The attack of **18** to another molecule of **17** gives the hexacoordinated complex **19**, that after water elimination is rearranged to species **20** and **21**. The chemical shift of **21** is similar to that of compound **13** [δ ^{31}P +11.3] [23,25], Scheme 5.

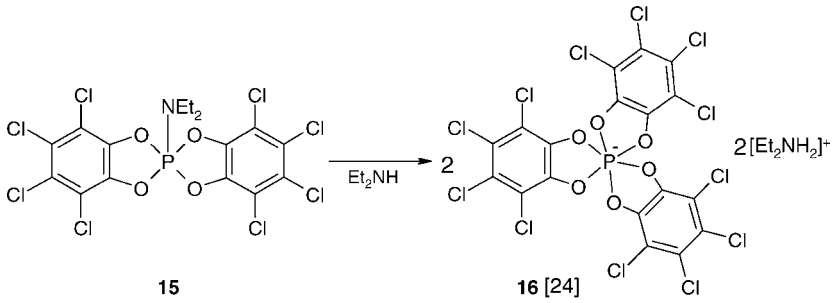
Opening of phosphorane **17** through the six-membered ring is supported by the report of Meyer et al. [26], which describes that hydrolysis of a spirophosphorane with 5- and 7-membered rings proceeds by opening of the largest ring to give compound **21** assigned by X-ray diffraction, Scheme 8. Only one ^{31}P resonance was observed for **20** which could indicate that there is a preferred isomer or that the stable isomers are in equilibrium. Compound **20** is similar to reported hexacoordinated species derived from aromatic phenolamines [27,28].

Compound **5** reacted in $CDCl_3$ with one equivalent of the 3,5-di-*tert*-butyl-1,2-benzoquinone in an NMR tube and gave instantaneously one signal at −36.3 ppm which corresponds to the mixture of phosphoranes **22a** and **22b** [5]. The chemical shift



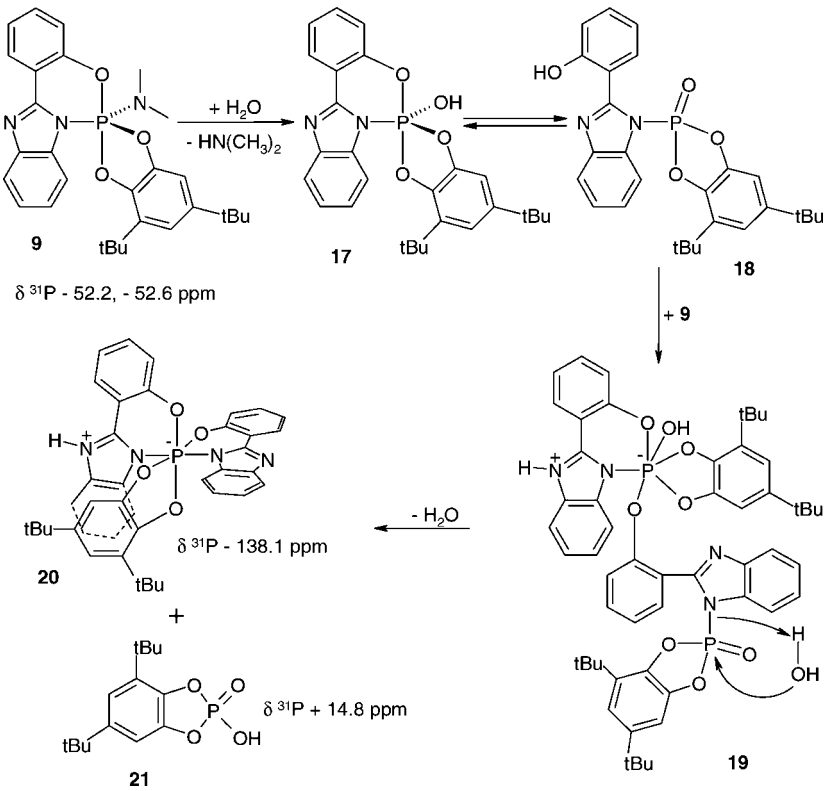
10 **11** **12** **13** [23] **14**

SCHEME 5 Hydrolysis of dicatechol phosphorane **10**.



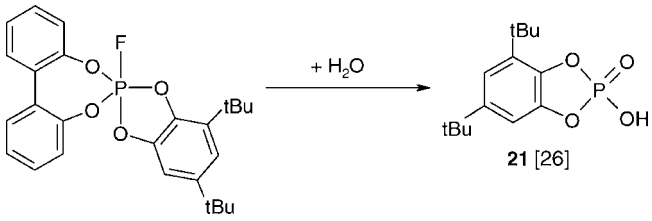
15 **16** [24]

SCHEME 6 Deproportionation of spirocyclic compound **15**.



9 **17** **18** **19** **20** **21**

SCHEME 7 Hydrolysis of compound **9**.



SCHEME 8 Hydrolysis of a fluoro phosphorane.

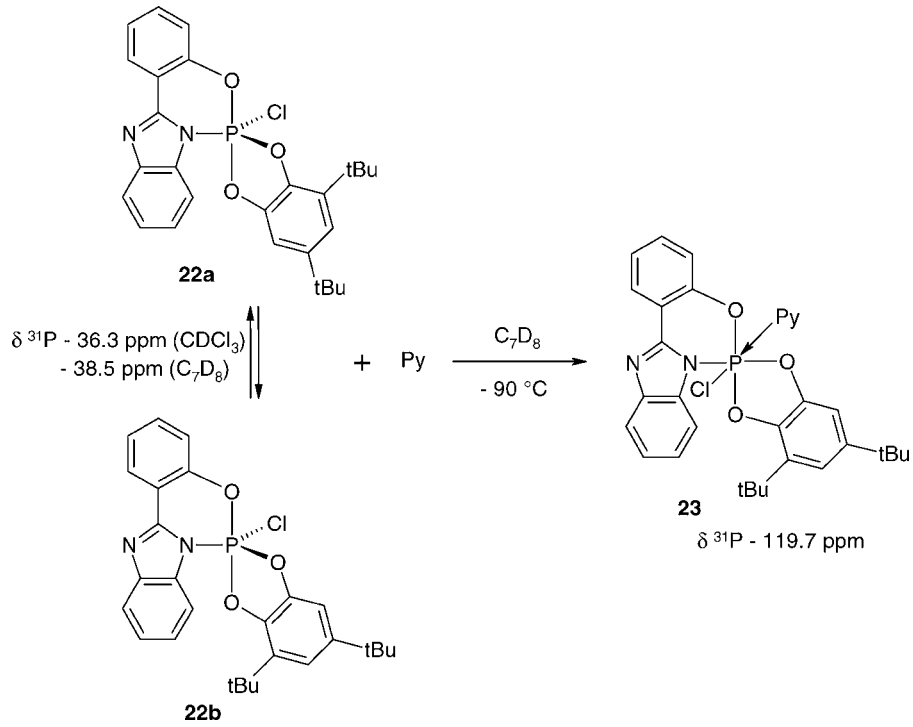
is close to those of compounds with the same connectivity [6,29], Scheme 9.

It was assumed that P—Cl bonds make phosphoranes very acidic and suitable to give hexacoordinated phosphorus atoms. In order to check the acidity of **22a** and **22b**, we have added an excess of pyridine to their solution in C_7D_8. Addition made the P(V) signals to disappear and to emerge a new one at −119.7, which corresponds to P(VI) compound **23**, Scheme 9. At −90°C, the ^{31}P resonance at −119.7 was split into five other signals, at −118.9, −120.4, −122.2, −123.8, and −124.8, assigned to isomers of hexacoordinated species. The same experiment for compound **9** failed due to the lesser acidity of phosphorus atom.

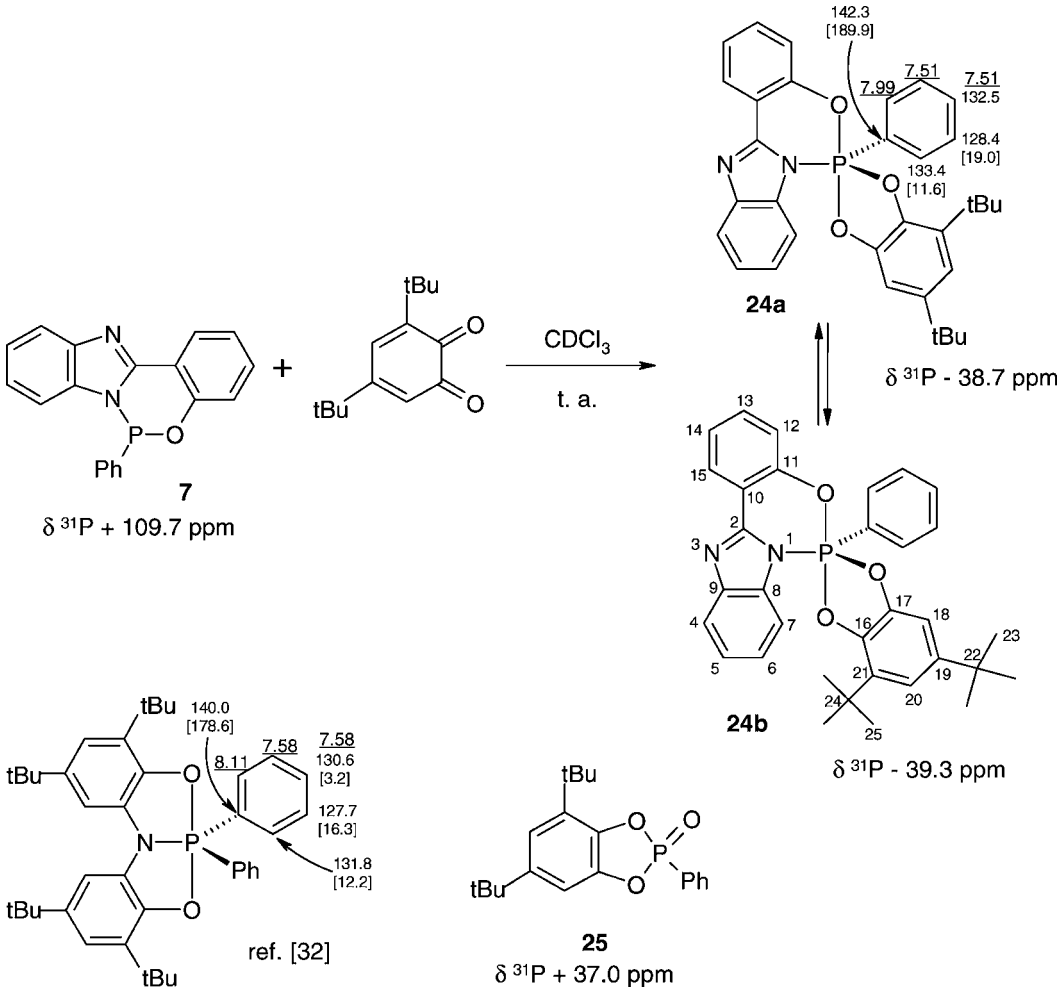
The reaction between compound **7** and 3,5-di-*tert*-butyl-1,2-benzoquinone, in refluxing toluene, gave a mixture of compounds after 10 min. In the $^{31}P\{^1H\}$ spectrum in $CDCl_3$, signals for phosphoranes **24a** and **24b** were found at −38.7 (90%) and −39.3 (10%) respectively. Their ^{31}P chemical shifts are similar to those reported for a phosphorane with the same connectivity [6,30]. Models show that isomer **24a** is the most stable. Two oxides **25** and **8** were found in a solution when the mixture was set aside for some time [31], Scheme 10.

The δ ^{13}C values of the preferred isomers of **9, 22**, and **24** do not change significantly with respect to those of the P(III) compounds **2**, **5**, and **7**, however there are changes in their coupling constants, Tables 2 and 3. It is evident that $^3J(^{31}P, ^{13}C)$ of C12 and C9 increase with the phosphorus coordination number. The opposite was found for $^2J(^{31}P, ^{13}C)$ of C8. C_{ipso}-11 resonances are shifted to higher frequencies with respect to those of the precursors **2, 5**, and **7**, revealing a lesser electronic donation from the phenolic ring to the phosphorus atom. This behavior is in accord with the electroattractive nature of oxygen atom in the apical position of the tbp. Carbon atoms C2 and C8 α to N1 are shifted to higher frequencies, which suggests that they are donating electronic density to the phosphorus through the imidazolic nitrogen, which in consequence must be located at the tbp equatorial position, in order to favor electronic donation from nitrogen to phosphorus.

The shift to higher frequencies of the N-Me_2 group and the small coupling constant $[^2J(^{31}P, ^{13}C)]$ in phosphoranes **9** indicate that this group is in



SCHEME 9 Lewis acid-base reaction of spirocyclic compounds **22**.

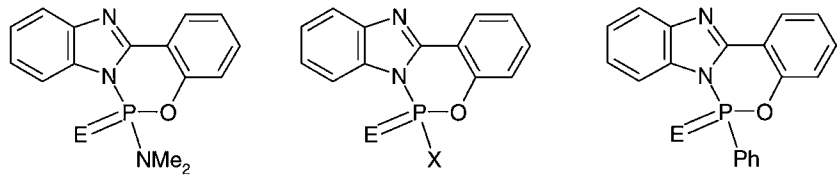


SCHEME 10 Synthesis of compounds **24**.

equatorial position. In phosphorane **24**, the phenyl group is also in equatorial position as is deduced from its coupling constant P-*Cipso* [$^1J(^{31}P, ^{13}C)$ = 189.9 Hz], characteristic for P(V) with an equatorial phenyl group [33,34]. Phenyl NMR data of phosphorane **24** are very similar to that of diphenylbicyclophosphorane, whose structure was determined by X-ray diffraction analyses [32].

^{1}H NMR data of phosphoranes **9, 22**, and **24** are in Table 4. One of the relevant changes with respect of the starting material is the shift to higher frequencies of H7, which is close to the apical oxygen and is probably forming a hydrogen bond. Equivalence of the methyl resonances of the N-Me_2 group in **9** indicates the fast rotation of P—N bond. Chemical shift and coupling constants $^3J(^{31}P, ^1H)$ are characteristic of its equatorial position [35]. On the other hand, the shift of the P-phenyl protons in **24** with respect to its P(III) precursor **7** reveals P-phenyl equatorial position [20], which is in accord with data of diphenylbicyclophosphorane of Scheme 10 [32].

The interest in preparing sulfur and selenium oxidized compounds derived from heterocycles **2, 5**, and **7** was based in their higher stability to hydrolysis and in their ^{77}Se NMR data. Compound **2** was dissolved in toluene and sulfur or selenium added and refluxed for 8 h to give quantitatively compounds **26** and **27**, Scheme 11. They are stable to moisture orange solids. Their ^{1}H coupled ^{31}P resonances are heptets, the signal for **27** presents a coupling constant with selenium [$^1J(^{31}P, ^{77}Se)$ = 963.7]. These ^{31}P data are similar to those reported for an oxazaphosphorinanone [36]. ^{1}H and ^{13}C NMR data are in Tables 5 and 6. Slow evaporation of a solution of **27** in $CDCl_3$ produced suitable single crystals for X-ray diffraction analyses, Figs. 1–4 and Tables 7 and 8. In the solid state, compound **27** has a tetracyclic structure (dihedral angle N1-C2-C10-C11 is 7.7°). The six-membered ring has an envelop conformation with the phosphorus atom out of the plane, Fig. 2. The geometry at the phosphorus is distorted tetrahedral, as is seen from the angles, for example



	E	δ ^{31}P (ppm)
26	S	+ 56.1
27	Se	+ 57.6

δ ^{77}Se - 218.5 ppm
$^{1}J(^{31}P, ^{77}Se)$ 963.7 Hz

	E	X	δ ^{31}P (ppm)
28	S	Cl	+ 39.4
29	Se	OH	+ 27.7

δ ^{77}Se - 17.1 ppm
$^{1}J(^{31}P, ^{77}Se)$ 1061.4 Hz

	E	δ ^{31}P (ppm)
30	S	+ 67.2
31	Se	+ 71.5

δ ^{77}Se - 160.9 ppm
$^{1}J(^{31}P, ^{77}Se)$ 929.9 Hz

SCHEME 11 ^{31}P and ^{77}Se NMR data for compounds **26–31**.

N1-P2-O1 is 97.7 (1)° and N4-P2-Se1 is 117.43 (9)°. The bond length N1-P2 1.693 (2) Å has some double bond character, whereas P2-N4 is shorter (1.609 Å, single bond P—N is 1.77 A, [35]), this fact was attributed to some double bond character [37] which also explains the planar geometry at N4. The P2—O1 bond length 1.605 Å is characteristic of a P—O single bond in tetracoordinated compounds [36], whereas bond length P═Se (2.0625 Å) is a normal double bond [38].

The cell of **27** showed two intermolecular interactions between two molecules giving a dimer, between the N3 and H16 of the NMe_2 group (2.675 Å), Fig. 2. The intermolecular distance of N3 and C10′ (3.288 Å) indicates a π interaction (graphite is 3.35 Å). Other intermolecular π type interactions were found between H13 with C2, N3, and C9, (distances of 2.799, 2.744, and 2.721 Å respectively), Fig. 3. These short contacts produce a tridimensional arrangement of alternated dimers, Fig. 4.

Reaction of **5** with sulfur or selenium in refluxing toluene for 8 h afforded quantitatively compounds **28** and **29**, Scheme 11. In **29**, the P—Cl bond is hydrolyzed, as was deduced from its ^{31}P spectrum, mass spectrometry confirmed the structure. Compounds **28** and **29** are oxygen and moisture sensitive white solids, they were dissolved in $CDCl_3$ in order to obtain their NMR spectra. Comparison of the ^{31}P data of 28 with reported compounds bearing a six-membered ring supported the assignment [39–41].

Compound **7** was more reactive to sulfur and selenium than the previous compounds, reactions are completed in 1 h in refluxing toluene giving **30** and **31**, Scheme 11. Compounds **30** and **31** are stable solids, their chemical shifts are similar to one of the

TABLE 3 ^{13}C NMR Data δ (ppm) and ^{n}J(P–C) (Hz) of **9a, 22**, and **24a**

Compds	**9a**[a]	**22**	**24a**[b]
C2	151.4	149.9	151.2[3.8]
C4	119.3	119.9	119.4
C5, C6	123.4	124.7	123.9
C7	115.5	116.1	115.9
C8	135.7[5.2]	135.2	135.7[6.0]
C9	143.9[15.6]	143.8[17.8]	144.0[14.8]
C10	117.2	116.7	117.6
C11	153.4[10.4]	151.9[12.2]	153.7[12.2]
C12	119.1[8.3]	119.5[10.9]	119.4[5.5]
C13	131.9	132.7	132.5
C14	123.3	125.2	124.0
C15	126.3	126.7	126.6
C16	143.6	142.9[4.0]	145.8
C17	137.9	137.9[3.7]	137.6
C18	105.4[13.5]	106.2[16.8]	106.0[10.0]
C19	144.9	146.2	146.2
C20	115.1	117.3	115.3
C21	133.5[15.6]	134.3[13.7]	[c]
C22	34.9	35.2	35.0
C23	31.6	31.8	31.7
C24	34.0	34.5	34.1
C25	29.3	29.8	29.3

For numbering see Scheme 10.
[a]δ NMe_2 = 42.3 [^{2}J(PC) = 4.2 Hz].
[b]δ PPh = C_i 142.3 [^{1}J(PC) = 189.9 Hz], C_o 133.4 [^{2}J(PC) = 11.6 Hz], C_m 128.4 [^{3}J(PC) = 19.0 Hz], C_p 132.5.
[c]Not observed.

TABLE 4 ^{1}H NMR Data of **9a, 22**, and **24a**

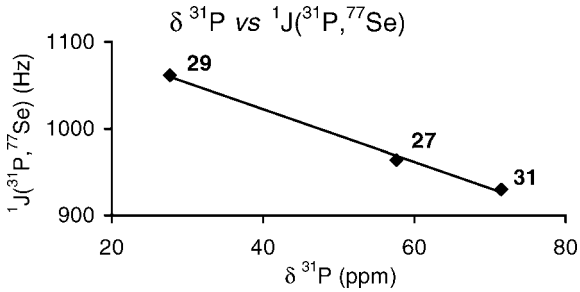
Compds	**9a**[a]	**22**	**24a**[b]
H4	7.78	7.85	7.83
H5, H6	7.33	7.39	7.29
H7	8.02	7.85	7.89
H12	7.20	7.32	7.29
H13	7.44	7.55	7.58
H14	7.17	7.34	7.33
H15	8.21	8.36	8.33
H18	6.72	7.07	6.84
H20	6.71	7.02	6.80
H23	1.18	1.33	1.25
H25	1.06	1.30	1.10

For numbering see Scheme 10.
[a]δ NMe_2 = 3.04 [^{3}J(PH) = 11.24 Hz].
[b]δ PPh = H_o 7.99, H_m and H_p 7.51.

TABLE 5 ^{1}H NMR Data of **26–31**

Compds	**26**[a]	**27**[a]	**28**	**29**	**30**[b]	**31**[b]
H4	7.86	7.86	7.88	7.92	7.86	7.85
H5	7.41	7.41	7.49	7.52	7.37	7.35
H6	7.38	7.38	7.47	7.49	7.24	7.21
H7	7.53	7.52	8.24	8.41	7.49	7.41
H12	7.26	7.26	7.38	7.40	7.26	7.26
H13	7.51	7.50	7.60	7.63	7.49	7.50
H14	7.34	7.35	7.47	7.49	7.36	7.37
H15	8.38	8.38	8.44	8.49	8.46	8.45

[a] δ NMe_2 = 3.00 [^{3}J(PH) = 12.79 Hz] (**26**), 3.04 [^{3}J(PH) = 12.80 Hz] (**27**).
[b] δ Ph = H_o 7.86, H_m 7.46, H_p 7.58 (**30**); H_o 7.91, H_m 7.48, H_p 7.59 (**31**).



SCHEME 12 Correlation between δ ^{31}P and ^{1}J(^{31}P,^{77}Se) for compounds **27, 29**, and **31**.

few known compounds of the same type [42]. ^{31}P NMR signals of compounds **26** (+56.1), **27** (+57.6) and **30** (+67.2), and **31** (+71.5) are at higher frequencies than those of **28** (+39.4) and **29** (+27.7), fact explained by the electron withdrawing effect of chlorine and OH groups [36,39,42], Scheme 11.

^{77}Se chemical shifts for compounds **27, 29**, and **31** are negative, which suggest a substantial contribution of the dipolar mesomeric structure with a negative charge at selenium (R_3P-Se ↔ R_3P^{+}-Se^{-}). Allen and Taylor reported that bigger coupling constant ^{1}J(^{31}P,^{77}Se) corresponds to an increase in electron density donation from sulfur and selenium at phosphorus [43] and with the electronegativity of the phosphorus substituents [44]. The P—O bond produces a considerable deshielding at the selenium in **29** attributed to the oxygen electron donation to phosphorus. Correlation of the δ ^{31}P with ^{1}J(^{31}P,^{77}Se) showed a linear behavior for **27, 29**, and **31**, Schemes 11 and 12.

The P=E (E = S, Se) bonds have some electron withdrawing effect over the phenolic part of the ligand as is deduced from the shift to higher frequencies of C14 and the shielding of C11 *ipso* to oxygen. The value of the coupling constant ^{1}J(^{31}P,^{13}C) for the *ipso* carbon of phenyl group in **30** and **31** increases with oxidation indicating the bigger electroattractor effect of P=E [38].

CONCLUSIONS

The reaction of compound **1** with P(III) compounds afforded six-membered heterocycles. The presence of a leaving group chlorine or NMe_2 makes the compounds useful intermediates for preparation of more complex compounds. Because of the unsaturation of the ligand and the acidic nature of the imidazolic N—H proton, the heterocycles are very sensitive to moisture and oxygen; oxidized compounds with sulfur and selenium gave more stable heterocycles.

TABLE 6 ^{13}C NMR Data [δ,^{n}J(P—C)] of **31–36**

Compds	**26**[a]	**27**[a]	**28**	**29**	**30**[b]	**31**[b]
C2	149.2[1.5]	148.9	146.9	146.3	148.2	147.7[2.4]
C4	120.2	120.2	120.3	120.4	120.2	120.1
C5	124.7	124.8	125.7	125.9	124.8	124.7
C6	124.6	124.7	125.6	125.6	124.8	124.6
C7	112.1	112.1	113.7	114.0	113.1	113.0
C8	132.7[5.4]	132.6[6.1]	132.7[7.7]	132.8[8.2]	133.5[6.6]	133.2[6.2]
C9	144.5[13.1]	144.6[12.3]	144.0[15.4]	143.9[14.6]	144.8[11.5]	144.7[11.5]
C10	115.4[3.9]	115.5[4.6]	116.0[4.6]	116.0[5.6]	116.0[4.8]	116.0[5.4]
C11	150.3[10.0]	150.0[10.0]	149.5[13.8]	149.6[17.1]	149.7[11.6]	149.2[12.3]
C12	119.3[8.5]	119.5[8.5]	119.4[9.2]	119.5[9.4]	119.6[8.2]	119.7[7.7]
C13	132.6	132.7	133.3	133.5	133.0	132.9
C14	125.2	125.3	126.7	126.9	125.6	125.6
C15	126.9	127.0	127.3	127.6	127.2	127.1

[a] δ NMe_2 = 37.4 [^{2}J(PC) = 6.2 Hz] (**26**), 37.7 [^{2}J(PC) = 6.2 Hz] (**27**).
[b] δ PPh = C_i 131.4 [^{1}J(PC) = 137.2 Hz], C_o 131.5 [^{2}J(PC) = 13.6 Hz], C_m 129.2 [^{3}J(PC) = 15.8 Hz], C_p 134.2 [^{4}J(PC) = 3.2 Hz] (**30**); C_i 131.7 [^{1}J(PC) = 79.2 Hz], C_o 131.7 [^{2}J(PC) = 13.8 Hz], C_m 129.0 [^{3}J(PC) = 16.0 Hz], C_p 134.3 [^{4}J(PC) = 3.1 Hz] (**31**).

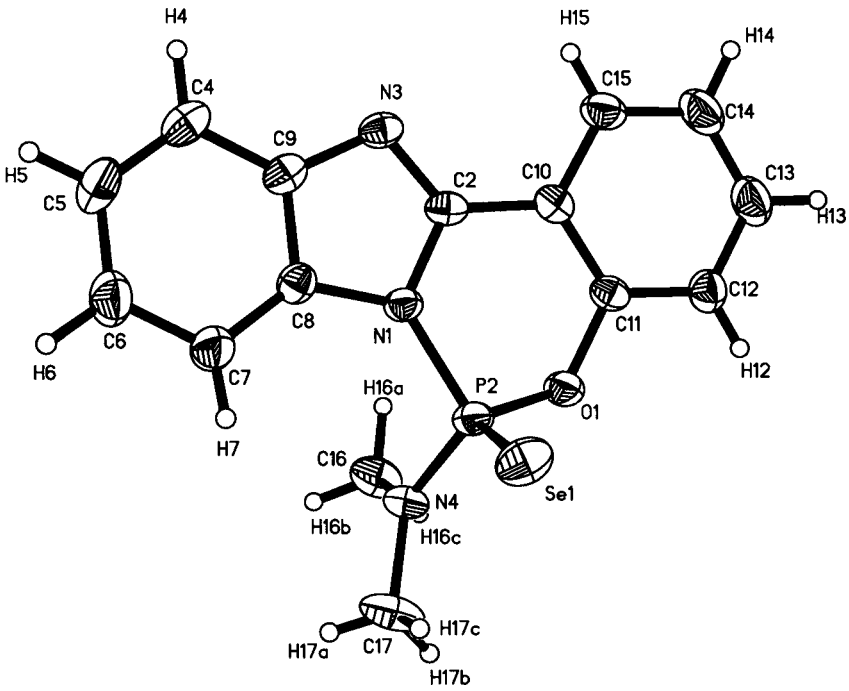


FIGURE 1 ORTEP representation of compound **27**.

The formation of hydrospirophosphoranes with two molecules of ligand **1** was not successful, an explanation is that two six-membered rings bonded to phosphorus do not give stable structures. However, spirophosphoranes can be prepared by combining a catechol with ligand **1**.

EXPERIMENTAL

All experiments were carried out under dry nitrogen atmosphere. Solvents were dried and freshly distilled under N_2 atmosphere according to reported procedures [45]. NMR spectra were recorded in

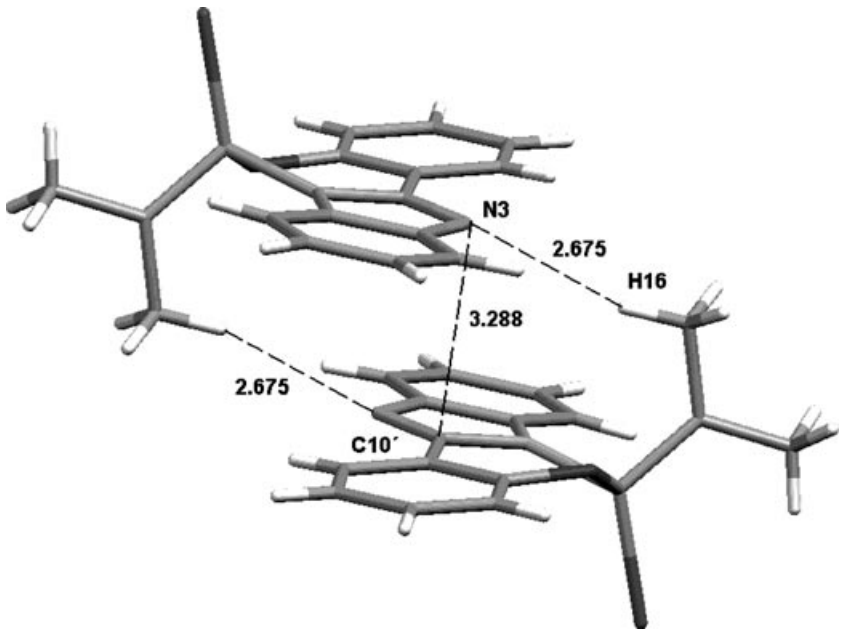


FIGURE 2 Dimeric rearrangement of compound **27** in the crystalline cell.

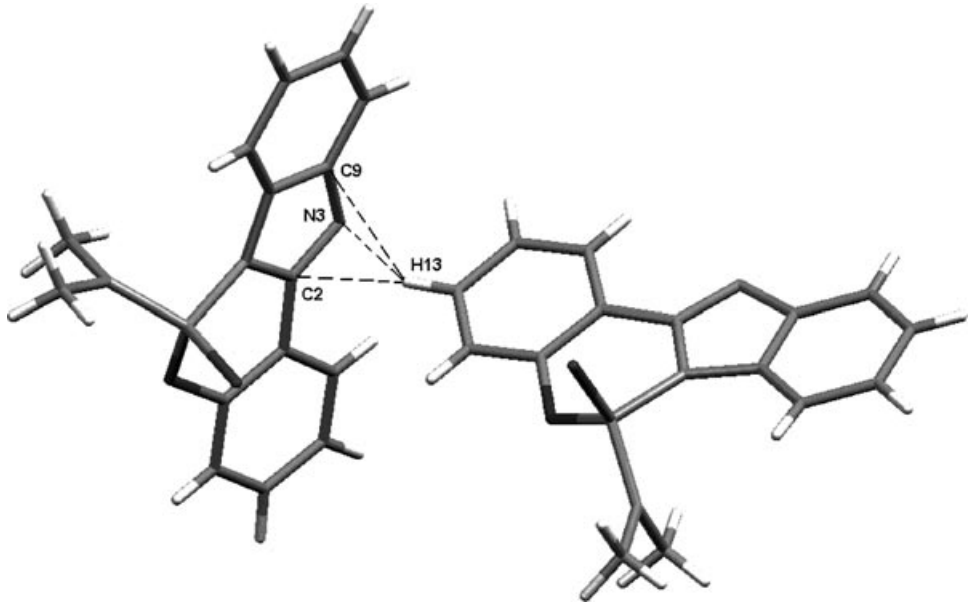


FIGURE 3 π-Interactions between H13 and the atoms C2–N3–C9 in the solid structure of compound **27**.

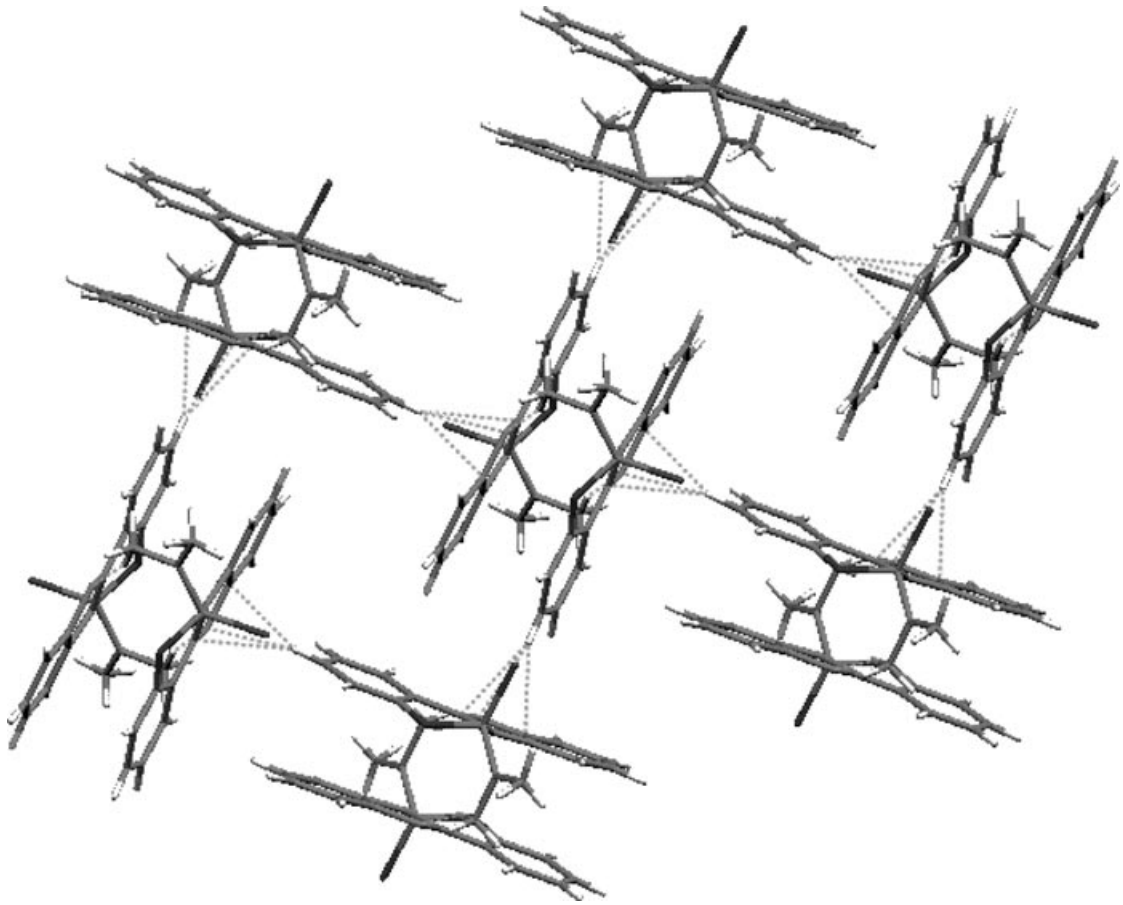


FIGURE 4 View of the dimeric rearrangement of compound **27**.

TABLE 7 Crystal Data and Data Collection Parameters of Compound **27**

Chem. formula	$C_{15}H_{14}N_3OPSe$
Formula wt.	362.22
Cryst. size (mm)	0.40 × 0.375 × 0.3
Cryst. system	Orthorhombic
Space group	*Pbca*
A (Å)	14.400(3)
B (Å)	12.758(3)
C (Å)	16.940(3)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
V (Å^3)	3112.1(11)
Z	8
ρ (calcd.) (mg/m^3)	1.546
μ (mm^{-1})	2.517
F(000)	1456
Index range	$0 \le h \le 18$; $0 \le k \le 16$; $-21 \le l \le 0$
2θ (°)	54.96
Temp. (K)	293(2)
Refl. collected	2305
Refl. unique	2305
Refl. observed (4□)	2305
R (int.)	0.0000
No. variables	190
Weighting scheme[a] *x*/*y*	0.0172/3.1659
Goodness-of-fit	1.097
Final *R* (4σ)	0.0358
Final w*R*2	0.0682
Larg. res. peak (e/Å^3)	0.465

[a] $w^{-1} = \sigma^2 F_o{}^2 + (xP)^2 + yP$; $P = (F_o{}^2 + 2F_c{}^2)/3$.

TABLE 8 Bond Lengths (Å) and Angles (°) for Compound **27**

Se(1)–P(2)	2.0625(8)	P(2)–O(1)	1.605(2)
P(2)–N(4)	1.609(2)	P(2)–N(1)	1.693(2)
N(3)–C(2)	1.304(4)	N(3)–C(9)	1.403(4)
N(1)–C(2)	1.395(3)	N(1)–C(8)	1.408(4)
O(1)–C(11)	1.393(3)	C(2)–C(10)	1.449(4)
C(11)–C(10)	1.392(4)	N(4)–C(16)	1.467(4)
N(4)–C(17)	1.464(4)	C(9)–C(8)	1.395(4)
O(1)–P(2)–N(4)	104.16(13)	O(1)–P(2)–N(1)	97.73(11)
N(4)–P(2)–N(1)	105.37(13)	O(1)–P(2)–Se(1)	115.29(9)
N(4)–P(2)–Se(1)	117.43(9)	N(1)–P(2)–Se(1)	114.49(9)
C(2)–N(3)–C(9)	104.6(2)	C(2)–N(1)–C(8)	105.6(2)
C(2)–N(1)–P(2)	125.3(2)	C(8)–N(1)–P(2)	127.7(2)
C(11)–O(1)–P(2)	124.1(2)	C(12)–C(11)–C(10)	122.1(3)
C(12)–C(11)–O(1)	117.2(3)	C(10)–C(11)–O(1)	120.6(3)
N(3)–C(2)–N(1)	113.8(3)	N(3)–C(2)–C(10)	126.9(3)
N(1)–C(2)–C(10)	119.3(2)	C(17)–N(4)–C(16)	115.1(3)
C(17)–N(4)–P(2)	123.5(2)	C(16)–N(4)–P(2)	120.4(2)
C(8)–C(9)–N(3)	111.0(2)	C(4)–C(9)–N(3)	129.1(3)
C(11)–C(10)–C(2)	120.3(2)	C(8)–C(7)–C(6)	117.0(3)
C(9)–C(8)–N(1)	104.9(2)		

$CDCl_3$, C_6D_6 (C_7D_8) dried with molecular sieves 4 Å in a Jeol GSX-270, Jeol Eclipse 400, and Bruker DPX 300 spectrometers. Chemical shifts are referenced to $(CH_3)_4Si$, H_3PO_4 (85%) [$\Xi(^{31}P) = 40.480747$ MHz] and $(CH_3)_2Se$ [$\Xi(^{77}Se) = 19.071523$ MHz]. IR spectra were taken in KBr disc in a FT spectrum GX Perkin Elmer spectrometer. EI mass spectra were performed in a Hewlett-Packard HP 5989A spectrometer. Melting points were determined on a Mel Temp II equipment in an open capillar tube and are not corrected. Elemental analyses were carried out in a Flash 1112 Thermo Finnigan analyzer. The glassware, syringes, and needles were dried in the oven for 12 h at 250°C. Toluene was selected as a solvent because phosphorus compounds are inert in it, and that compound **1** is only slightly soluble, whereas the reaction products are completely soluble, therefore the unreacted starting material is easily eliminated by filtration. PCl_3, $PhPCl_2$, 3,5-di-*tert*-butyl-1,2-benzoquinone, sulfur, and selenium are commercial and were used without purification, with exception of $P(NMe_2)_3$ that was previously distilled to be used. Compound **1** was prepared according to the reported method [46]. X-ray data collection for compound **27** was performed in a Enraf Nonius Kappa CCD diffractometer using Mo radiation ($\lambda = 0.71073$ Å) at 293°K. The structure was solved by direct methods and anisotropic refinement in F^2 [47]. Crystallographic data of the structural analysis (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC: 237994. Copies of this information may be obtained free of charge from The director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

*3,4-Benzimidazole-5,6-benzo-2-dimethylamino-1,3,2-oxazaphosphorinane (**2**)*

Compound **1** (100 mg, 0.48 mmol) was suspended in 10 ml of toluene, then 0.09 ml (78 mg, 0.48 mmol) of $P(NMe_2)_3$ was added. The reaction mixture was refluxed until the calculated amount of $NHMe_2$ was evolved and titred with 1N, HCl (2 h). The resulting orange solution was filtered and concentrated in vacuum to give 130 mg of compound **2** as a yellow oil, 95%.

*3,4-Benzimidazole-5,6-benzo-2-chloro-1,3,2-oxazaphosphorinane (**5**)*

200 mg (0.95 mmol) of **1** was suspended in 10 ml of toluene and 0.3 ml (218 mg, 1.1 mmol) of NEt_3, 0.08

ml (131 mg, 0.95 mmol) of PCl_3 was dissolved in 5 ml of toluene and added at r.t. The mixture was stirred overnight. NEt_3HCl was filtered and the solution concentrated to dryness, 240 mg of a beige solid was obtained, 90%. MS: *m/z* (%): 272.25 (39), 256.25 (17), 211.30 (15), 210.30 (100), 182.30 (31), 181.30 (30).

*3,4-Benzimidazole-5,6-benzo-2-phenyl-1,3,2-oxazaphosphorinane (**7**)*

Compound **7** was prepared following the same procedure as for **5** using 200 mg (0.95 mmol) of **1**, 0.3 ml (218 mg, 1.1 mmol) of NEt_3, and 0.13 ml (170 mg, 0.95 mmol) of $PhPCl_2$. Three hundred milligrams of compound **7** was obtained as a yellow oil in quantitative yield. MS: *m/z* (%): 332.25 (5) $[M]^+$, 256.40 (5), 211.30 (16), 210.30 (100), 182.30 (29), 181.30 (21).

*3,4-Benzimidazole-5,6-benzo-2-dimethylamino-8,9-(11,13-di-tert-butyl-benzo)-1,3-oxaza-7,10-dioxa-2-λ^5-phosphaspiro-[4,5]decane (**9**)*

To a solution of 40 mg (0.14 mmol) of **2** in $CDCl_3$ (0.7 ml) placed in an NMR tube, 30 mg (0.14 mmol) of 3,5-di-*tert*-butyl-1,2-benzoquinone was added. Compound **9** was formed after heating the mixture in a water bath at 50°C for 3 h. It was not isolated due to its fragility, the 92% yield was calculated from the ^{31}P NMR spectrum. MS: *m/z* (%): 459.25 (16) $[M-NMe_2]^+$, 284.30 (17), 270.25 (15), 269.20 (100), 210.25 (86), 207.35 (22), 182.25 (26), 181.25 (21).

*3,4-Benzimidazole-5,6-benzo-2-chloro-8,9-(11,13-di-tert-butyl-benzo)-1,3-oxaza-7,10-dioxa-2-λ^5-phosphaspiro-[4,5]decane (**22**)*

Thirty milligrams (0.11 mmol) of **5** and 20 mg (0.11 mmol) of 3,5-di-*tert*-butyl-1,2-benzoquinone were mixed. The reaction was instantaneous, 67% yield.

*3,4-Benzimidazole-5,6-benzo-2-phenyl-8,9-(11,13-di-tert-butyl-benzo)-1,3-oxaza-7,10-dioxa-2- λ^5-phosphaspiro-[4,5]decane (**24**)*

Thirty milligrams (0.09 mmol) of **7** and 20 mg (0.09 mmol) of 3,5-di-*tert*-butyl-1,2-benzoquinone were mixed. The reaction was over in 10 min, 81% yield. MS: *m/z* (%): 344.25 (25), 330.25 (22), 329.25 (100), 273.25 (15), 210.30 (58).

*3,4-Benzimidazole-5,6-benzo-2-dimethylamino-2-thio-1,3,2-oxazaphosphorinane (**26**)*

To a solution of 135 mg (0.48 mmol) of **2** in 10 ml of toluene, 30 mg (0.96 mmol) of sulfur was added. The mixture was refluxed for 8 h. Then it was cooled and filtered in order to eliminate the sulfur and the solvent was evaporated in vacuum. An orange solid was obtained, (145 mg) in quantitative yield. Mp 166–168°C. MS: *m/z* (%): 315.10 (59) $[M]^+$, 272.10 (24), 255.85 (11), 240.15 (17), 239.15 (100). IR (KBr): ν (cm^{-1}) 2918, 2850, 1613, 1583, 1538, 1462, 1205, 1177, 1001, 921, 777, 739, 666. Anal. calcd. ($C_{15}H_{14}N_3OPSe$) [362.26]: C, 49.73; H, 3.89; N, 11.60. Found: C, 49.38; H, 4.35; N, 11.73.

*3,4-Benzimidazole-5,6-benzo-2-dimethylamino-2-seleno-1,3,2-oxazaphosphorinane (**27**)*

A mixture of 135 mg (0.48 mmol) of **2** and 75 mg (0.96 mmol) of Se in powder gave 165 mg of an orange solid in quantitative yield, Mp 212–214°C. MS: *m/z* (%): 363.10 (27) $[M]^+$, 361.10 (13), 283.20 (9), 282.20 (11), 240.15 (29), 239.15 (100), 192.20 (9). IR (KBr): ν (cm^{-1}) 2917, 2850, 1613, 1583, 1538, 1462, 1205, 1175, 1134, 995, 917, 742, 694. Anal. calcd. ($C_{15}H_{14}N_3OPSe$) [362.26]: C, 49.73; H, 3.89; N, 11.60. Found: C, 49.38; H, 4.35; N, 11.73.

*3,4-Benzimidazole-5,6-benzo-2-chloro-2-thio-1,3,2-oxazaphosphorinane (**28**)*

From 261 mg (0.95 mmol) of **5** (freshly prepared) and 45 mg (1.40 mmol) of sulfur, a moisture sensitive yellow solid was obtained in quantitative yield (280 mg). MS: *m/z* (%): 308.20 (44), 307.20 (17), 306.20 (100) $[M]^+$, 271.25 (21), 239.30 (22), 225.30 (11), 224.30 (53). IR (KBr): ν (cm^{-1}) 2918, 2849, 2477, 1621, 1476, 1243, 1184, 1105, 995, 751, 515.

*3,4-Benzimidazole-5,6-benzo-2-chloro-2-seleno-1,3,2-oxazaphosphorinane (**29**)*

From 211 mg (0.77 mmol) of **5** and 70 mg (0.90 mmol) of selenium, a moisture sensitive yellow solid was obtained in quantitative yield (260 mg). MS: *m/z* (%): 336.15 (23) $[M]^+$, 334.15 (11), 273.20 (13), 257.20 (16), 256.20 (100), 210.30 (11), 181.30 (20). IR (KBr): ν (cm^{-1}) 2918, 2849, 2470, 1623, 1476, 1245, 1104, 977, 751, 515.

*3,4-Benzimidazole-5,6-benzo-2-phenyl-2-thio-1,3,2-oxazaphosphorinane (**30**)*

Compound **7** (300 mg, 0.95 mmol) and sulfur (40 mg, 1.25 mmol) were refluxed for 1 h. A yellow solid was obtained in quantitative yield (322 mg). Mp 112–115°C. MS: *m/z* (%): 349.15 (24), 348.15 (100) $[M]^+$, 347.15 (33), 332.20 (25), 269.25 (8), 239.15 (23), 224.15 (16), 210.24 (40).

*3,4-Benzimidazole-5,6-benzo-2-phenyl-2-seleno-1,3,2-oxazaphosphorinane (**31**)*

From 300 mg (0.95 mmol) of **7** and 90 mg (1.14 mmol) of selenium refluxed for 1 h, a yellow solid was obtained in quantitative yield (363 mg). Mp 176–178°C. MS: *m/z* (%): 396.00 (58) $[M]^+$, 394.00 (29), 332.15 (97), 316.15 (29), 272.10 (22), 269.20 (22), 239.15 (62), 210.20 (100), 182.25 (42). IR (KBr): ν (cm^{-1}) 2919, 2849, 1624, 1560, 1478, 1187, 1137, 1034, 748, 696, 543. Anal. calcd. ($C_{19}H_{13}N_2OPSe \cdot CH_3COCH_3$) [453.33]: C, 58.28; H, 4.22; N, 6.17. Found: C, 57.97; H, 4.45; N, 6.53.

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