Heteroatom Chemistry
Volume 15, Number 4, 2004

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

Julio Hernández-Díaz, Angelina Flores-Parra, and Rosalinda Contreras

Departamento de Química, Centro de Investigación y de Estudios Avanzados del IPN, A.P. 14-740, México D. F., CP 07000 México

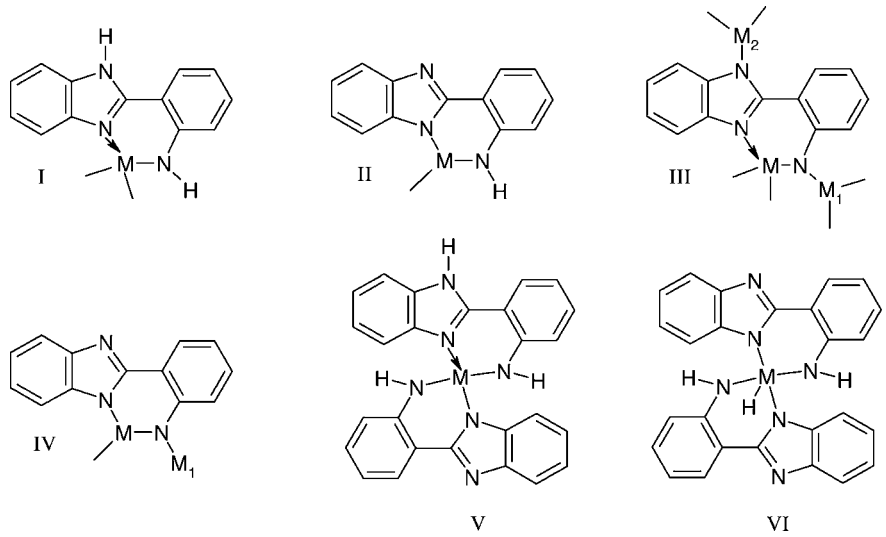
Received 27 August 2003; revised 23 February 2004

ABSTRACT: *We report the syntheses of unsaturated six-membered heterocycles bearing tri-, tetra-, and pentacoordinated phosphorus atoms derived from 2-(2-aminophenyl)-1H-benzimidazol (**1**). The presence of three different N—H protons allowed to prepare different compounds by selective substitution. Molecules with two (endo and exocyclic) phosphorus atoms were prepared. The free anilinic proton is the most reactive to substitution reactions, followed by the benzimidazolic, and then the anilinic proton involved in the hydrogen bond. Substitution of the exo-anilinic proton of* **1** *by Ph_2PCl leads a precursor with a hydrogen bond forming a six-membered ring, which could be substituted by other groups giving more complex molecules. A pentacoordinated phosphorus compound was obtained after oxidative addition of 3,5-di-tert-butyl-1,2-benzoquinone to P(III) heterocycle.* © 2004 Wiley Periodicals, Inc. Heteroatom Chem 15:321–332, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20022

INTRODUCTION

2-(2-Aminophenyl)-1*H*-benzimidazole (**1**) is a polyfunctional molecule of pharmacological and chemical interest. Compound **1** presents antipoliomielitic [1], triquinocide [2], and fungicide [3] activities and benzimidazoquinazolines derived from **1** have antinflamatory [4] and antitumoral [5,6] activities. Compound **1** has one basic pyridinic type nitrogen and three labile hydrogen atoms, which can be substituted by heteroelements. Because of these features, compound **1** is a good candidate to prepare new heterocycles by substitution of the N—H protons and N-coordination by atoms of 15 group as is shown in Scheme 1. Some coordination compounds derived from **1** are known (Sn(IV) [7], U(VI) [8], Fe(II) [9], Sn(IV), Ti(IV), and V(IV) [10], Fe(III) [11], Ni(II) and Pd(II) [12]) as well as some boron heterocycles [13]. But, to our knowledge there are no reports of phosphorus compounds derived from **1**, this and the complexity of the ligand guarantees interesting results, in particular that uncommon unsaturated six-membered ring phosphorus heterocycles could be prepared. Therefore, we decided to explore reactions of **1** and phosphorus reagents in order to prepare heterocycles bearing tri-, tetra-, and pentacoordinated phosphorus atoms. The structures were assigned from the ^{31}P NMR data and 2D $^{1}H/^{1}H$ COSY, $^{1}H/^{13}C$ HETCOR, $^{1}H/^{13}C$ COLOQ, and $^{1}H/^{13}C$ HMBC experiments. In DMSO-d_6, ^{1}H and ^{13}C NMR spectra of **1** show 8 and 13 signals for aromatic protons and carbon atoms respectively, this means that the structure of **1** in solution is the same that in the solid state and that the hydrogen bond is very strong [Esparza Ruiz, A.; Hernández-Díaz, J.; Flores-Parra, A.; Contreras, R. (paper in preparation)]. Two broad ^{1}H signals at 7.32 and 12.72 ppm in a 2:1 ratio were

Correspondence to: Rosalinda Contreras; e-mail: rcontrer@mail.cinvestav.mx.
Contract grant sponsor: Conacyt-Mexico.
Contract grant sponsor: Conacyt and Cinvestav-Mexico.



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

observed and therefore assigned to anilinic NH_2 and imidazole N—H protons respectively.

X-ray diffraction structure of **1** was recently determined by us [Esparza Ruiz, A.; Hernández-Díaz, J.; Flores-Parra, A.; Contreras, R. (paper in preparation)]. In the solid state, compound **1** exists as an almost planar molecule with a strong hydrogen bond. Phosphorus heterocycles derived from 2-(2-hydroxyphenyl)-1*H*-benzimidazole are reported in this journal [14].

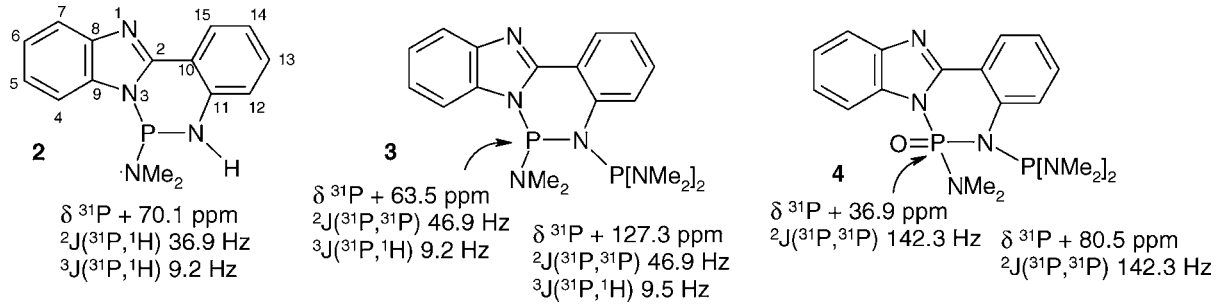
RESULTS AND DISCUSSION

Tricoordinated Phosphorus Compounds

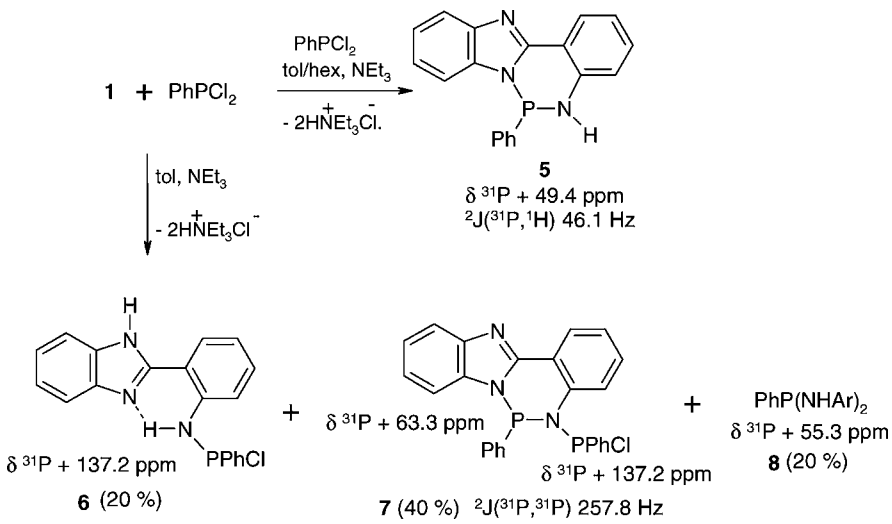
Reaction of **1** *with* $P(NMe_2)_3$. Transamination reactions of **1** with $P(NMe_2)_3$ in equimolar ratio and in excess of the phosphorus reagent yield heterocycles **2** and **3** respectively as red oils, sensitive toward oxygen and moisture, Scheme 2. ^{31}P NMR spectrum of **2** showed a doublet of heptets by phosphorus coupling to NH and NMe_2. Compound **3** presented two doublets at the $^{31}P\{^1H\}$ spectrum. The signal at +127.3 ppm presents a 2 × 13 pattern resulting from coupling with the ring phosphorus atom and with 12 isochronous NMe_2 protons [$^3J(^{31}P,^1H) = 9.5$ Hz] for the exocyclic phosphorus, whereas the signal at +63.5 ppm was a doublet of heptets [$^3J(^{31}P,^1H) = 9.2$ Hz]. Similar coupling constants were reported for tris- [15–18] and tetraphosphazanes [19]. After some days, compound **3** produced the new species **4** as result of the endocyclic phosphorus oxidation, Scheme 2.

Reactions with $PhPCl_2$. Because of the lower N—H proton reactivity toward a second substitution by another phosphorus atom in compound **2**, it was expected that equimolar reaction of **1** with $PhPCl_2$ could give exclusively heterocycle **5**, which effectively was observed in the reaction performed in *n*-hexane–toluene (90:10), its ^{31}P resonance is similar to that reported for a diazaphosphorinone with the same phosphorus connectivity [20], Scheme 3.

When a similar reaction was made in toluene and NEt_3, three new compounds were observed, **6,**



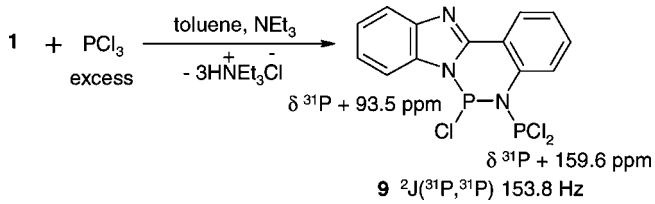
SCHEME 2 ^{31}P NMR data of compounds **2–4**.



SCHEME 3 Synthesis and ^{31}P NMR data of compounds **5–7**.

7, and PhP(NHAr)$_2$(**8**). One singlet at +137.2 (20%) is characteristic for a PhPClN group and was assigned to compound **6** (for example PhPClNMe$_2$, δ ^{31}P + 141.0 ppm [21]). Another singlet at +55.3 (20%) corresponds to **8** according to similarity with reported *bis*-(benzimidazol-1-yl)-phenylphosphine (δ ^{31}P = +50.2 ppm [22]) and *bis*(anilide)phenyl phosphine {PhP(NHPh$_2$)$_2$, δ ^{31}P = + 46.8 ppm [23]}. The two doublets at +137.2 and +63.3 ppm [40%, ^2J(^{31}P, ^{31}P)] = 257.8 Hz correspond to the heterocycle **7**, Scheme 3.

Reaction with PCl$_3$. Addition of one equivalent or an excess of PCl$_3$ to ligand **1**, at rt (or at −78°C), in toluene (or in a 90:10 *n*-hexane–toluene mixture) and NEt$_3$ affords only one product, which presents in the ^{31}P{^{1}H} spectrum two doublets that correspond to **9**, Scheme 4. Exocyclic phosphorus atom has a similar chemical shift to Cl$_2$P-N(Me)Ph [24]. The large ^2J(^{31}P, ^{31}P) coupling constant values of **4** (142.3 Hz), **7** (127.8 Hz), and **9** (153.8 Hz) suggest a *trans* conformation derived from the P-lone pair orientation with regard the endocyclic phosphorus atom [15–19], as can be modeled in the PM3 program for **9** [25], Fig. 1.



SCHEME 4 Synthesis and ^{31}P NMR data of compound **9**.

Compound **9** is not stable, after solvent elimination a complex mixture of non identified products with δ ^{31}P between +162 and +50 ppm was obtained.

Reaction with Ph$_2$PCl. Equimolar reaction, at rt, of **1** and Ph$_2$PCl in toluene and NEt$_3$ affords a main product whose ^{31}P spectra showed a singlet at +28.7 ppm. ^{1}H NMR spectrum presented two N<u>H</u> resonances, a singlet at 10.77 ppm and a doublet at 10.59 ppm with a coupling ^2J(^{31}P, ^{1}H) of 7.32 Hz, from these observations we concluded that the structure of compound **10** results from phosphorus substitution of the exo-anilinic N—H, Scheme 5. ^{31}P NMR data of **10** are similar to those of the aminophosphine [Ph$_2$PNHPh, δ ^{1}H = 4.18 ppm (d, ^2J[^{31}P, ^{1}H] = 7.70 Hz), δ ^{31}P = 29.4 ppm] [26]. The ^{1}H chemical shift of the P—N—<u>H</u> suggests a strong intermolecular hydrogen bond. Because of the presence of two N—H protons and a Ph$_2$P— acting

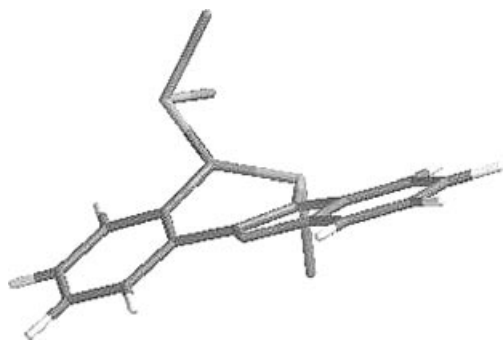
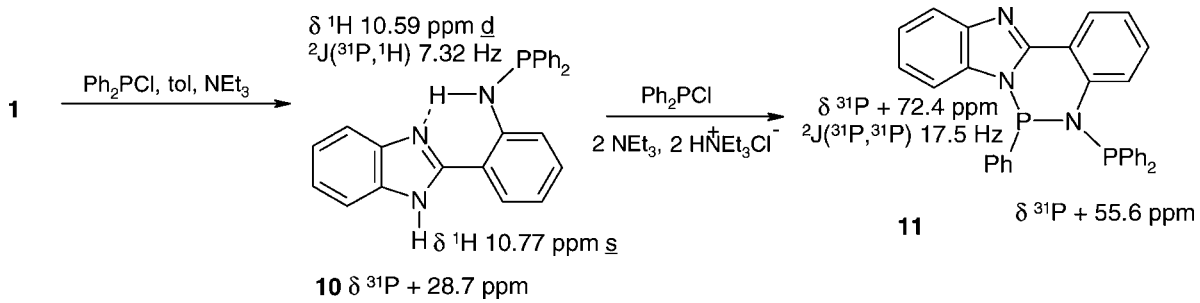


FIGURE 1 Model of compound **9** calculated using the PM3 program [25].



SCHEME 5 Synthesis and ^{31}P NMR data of compounds **10** and **11**.

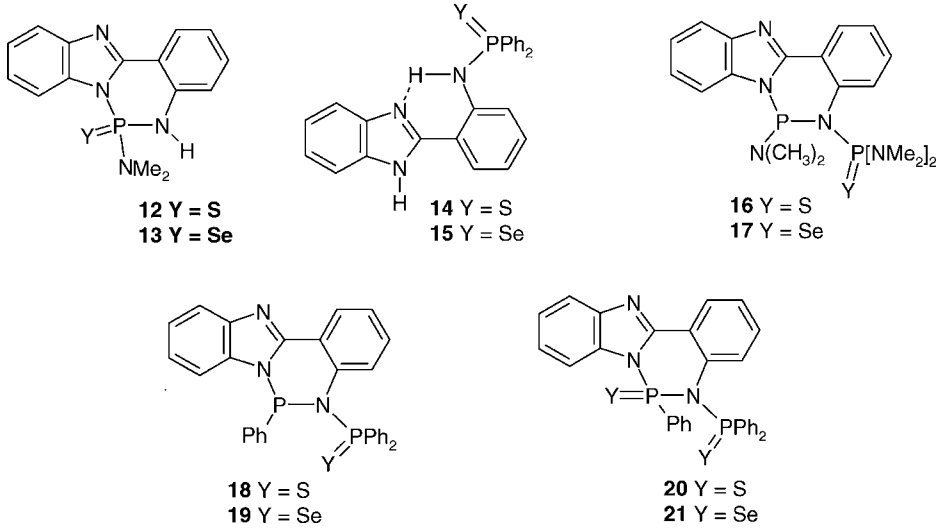
as a protecting group, compound **10** could be an excellent precursor to selectively synthesize six-membered ring heterocycles by proton substitution. Equimolar reaction of **10** and $PhPCl_2$ in NEt_3 affords quantitatively heterocycle **11**, Scheme 5. ^{31}P NMR spectrum showed two doublets, the structure was confirmed by the absence of the N–H in the ^{1}H spectrum and the mass spectrometry ($m/z = 499.30$). Similar data was found for $Ph\underline{P}_{(a)}$-[$NEtP_{(b)}$-Ph_2]$_2$ δ $^{31}P_{(a)} = +104.3$ and δ $^{31}P_{(b)} = 52.8$ ppm [27].

Tetracoordinated Phosphorus Compounds

Next step in this research was to synthesize tetracoordinated phosphorus compounds oxidized with sulfur and selenium, which are more stable to moisture. Additional NMR information can be obtained from the selenium derivatives.

Addition of equimolar amounts of elemental sulfur or selenium powder to compound **2** in refluxing toluene produces **12** or **13** derivatives, Scheme 6. ^{31}P{^{1}H} NMR spectra showed singlets at +48.1 (**12**) and +44.1 ppm [$^1J(^{31}P, ^{77}Se) = 896.6$ Hz] (**13**). In the ^{1}H coupled ^{31}P NMR spectra, **12** and **13** gave heptets in the spectrum range observed for one of the few known examples of unsaturated six-membered phosphorus ring, as reported by Neda et al. [28]. ^{77}Se NMR spectra of **13** showed a doublet at −161.3 ppm with $^1J(^{77}Se, ^{31}P) = 895.3$ Hz. Because of their high stability, compounds **12** and **13** were completely characterized by NMR and mass spectrometry ($m/z = 314.25$ for **12** and $m/z = 362.20$ for **13**).

Compound **10** was instantaneously and quantitatively oxidized at rt to **14** [+49.5 ppm] and **15** [+45.3 ppm, $^1J(^{31}P, ^{77}Se) = 774.4$ Hz], Scheme 6. In the ^{31}P ^{1}H-coupled spectra both signals displayed a doublet of multiplets [$^2J(^{31}P, ^1H)$ of 11.4 and 9.4 Hz for **14** and **15** respectively]. A doublet at −249.1 ppm, $^1J(^{31}P, ^{77}Se) = 774.0$ Hz in the ^{77}Se spectra confirmed phosphorus oxidation in **15**. ^{1}H resonances of the NH protons indicate the hydrogen bond and phosphorus coupling [$\delta = 12.30$ ppm, $^2J(^{31}P, ^1H) = 10.2$ Hz for **14** and $\delta = 12.32$ ppm, $^2J(^{31}P, ^1H) = 9.9$ Hz for **15**]. The IR spectra showed characteristic bands for N–H



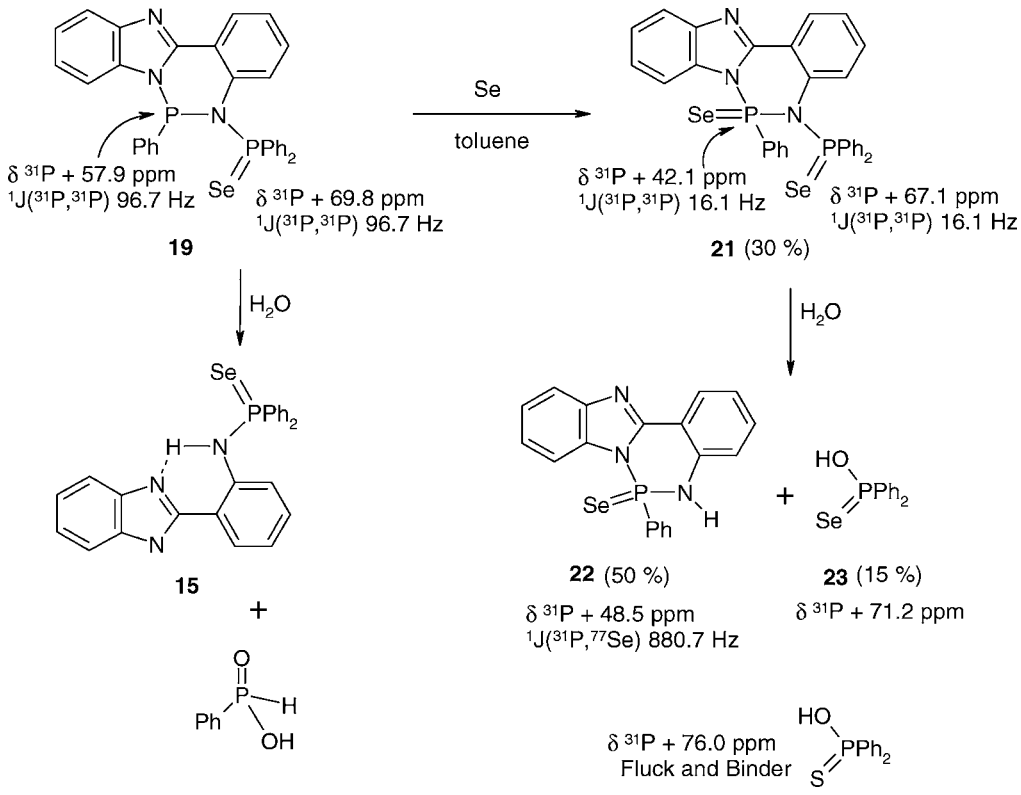
SCHEME 6 Oxidated compounds **12–21**.

protons involved in hydrogen bond at 3207 and 3227 cm^{-1} for **14** and **15** respectively. In addition, **14** and **15** are ideal candidates to build six-membered heterocycles, with the advantage of their stability. It is clear that higher reactivity of **10** toward sulfur and selenium is due to a better P-lone pair availability compared with **2**.

Equimolar addition of S and Se powder to a $CDCl_3$ solution of **3** at rt immediately affords chalcogenides **16** and **17**, which showed two series of doublets at +62.3 and +75.1 ppm [$^2J(^{31}P, ^{31}P) = 95.8$] for **16** and +61.9 and +74.0 ppm [$^2J(^{31}P, ^{31}P) = 96.3$ Hz] for **17** in the $^{31}P\{^1H\}$ spectra, Scheme 6. Analysis of ^{31}P spectrum of **17** revealed that exocyclic phosphorus atom was selectively oxidized, because only the doublet at +74.0 ppm gives the selenium coupling $^1J(^{31}P, ^{77}Se) = 830$ Hz. The signal at +61.9 ppm showed a doublet of heptets by coupling to NMe_2 protons. ^{31}P signals of **16** were assigned by comparison with **17**. Even in an excess of S or Se and stirring at rt for 24 h endocyclic phosphorus atoms were not oxidized. Compounds **16** and **17** were only slightly stable toward oxygen and moisture, because they still have a highly reactive P(III) atom.

On the other hand, reaction of a toluene solution of **11** and sulfur and selenium yielded **18** and **19** after 48 h of stirring at rt. ^{31}P NMR reaction monitoring revealed slow oxidation of **11** even in excess of sulfur or selenium. In both cases only exocyclic phosphorus was selectively oxidized, Scheme 6. The last conclusion originated from $^{31}P\{^1H\}$ NMR spectra analysis, which gives two doublets at +69.8 and +57.9 ppm with $^2J(^{31}P, ^{31}P) = 96.7$ Hz for **18** and at +69.5 [$^1J(^{31}P, ^{77}Se) = 795.2$ Hz] and +57.7 ppm with $^2J(^{31}P, ^{31}P) = 98.8$ Hz for **19**. Low frequency signals produced a broad doublet whereas those at high frequency exhibited a doublet of quintuplets pattern by ^1H coupling. Chemical shifts of ^{31}P, $^2J(^{31}P, ^{31}P)$, and $^1J(^{31}P, ^{77}Se)$ values of **19** are similar to reported diphosphanes selenides [29].

Addition of excess of sulfur to **18** and refluxing in toluene for 1 h gave compound **20** with two doublets at +68.2 and +50.4 ppm and $^2J(^{31}P, ^{31}P) = 12.1$ Hz. By comparison to **18**, signal at +50.4 ppm was assigned to the endocyclic phosphorus. Compound **20** is very stable to environment exposition and therefore it could be a potential candidate to coordinate metal ions [29]. Reaction of **19** with an excess of selenium in refluxing toluene for 1 h produced the diselenium derivative **21** in a 30 % yield, Scheme 7. Hydrolysis of the reaction mixture gave a ^{31}P resonance at +48.5 ppm $^1J(^{31}P, ^{77}Se) = 880.7$ Hz



SCHEME 7 Hydrolysis of compounds **19** and **21**.

(50%) with another singlet at +71.2 ppm (≈15%) [31]. These two products correspond to **22** and **23** respectively, Scheme 7.

Compounds **18** and **19** were unstable to oxygen and moisture. Water addition to a $CDCl_3$ solution of **19** affords $^{31}P\{^1H\}$ signals at +18.2 [$^1J(^{31}P, ^1H)$ = 522.2 Hz] assigned to PhPH(O)OH species [30] and +46.8 ppm $^1J(^{31}P, ^{77}Se)$ = 754.9 Hz which corresponds to compound **15**, Scheme 7.

Pentacoordinated Phosphorus Compounds

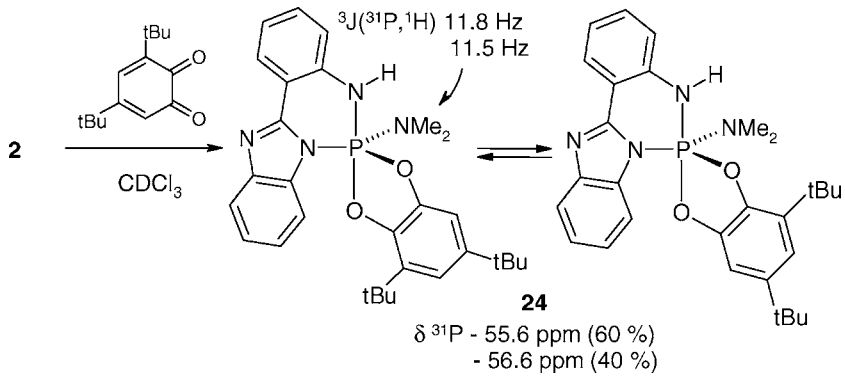
Transamination reaction between two equivalents of **1** and one of $P(NMe_2)_3$ should produce the corresponding hydrospirophosphorane. However, reactions in benzene (stirring 24 h at rt or refluxing for 4 h) were not successful. The only product was the P(III) compound **2**, Scheme 2. A first explanation of the lack of reactivity was found in the report that spirophosphoranes containing a P–H bond are not stable if they are constituted by rings with more than five atoms [32,33]. A second could be the rigidity of the ligand once it is bonded to phosphorus and a third one is the fact that two electrodonor nitrogen atoms, which have a preference for the equatorial sites of the tbp, would be located at the apical positions.

In contrast to transamination reaction, oxidative addition of 3,5-di-*tert*-butyl-1,2-benzoquinone to heterocycle **2** immediately and quantitatively affords phosphoranes **24**, easily identified in the ^{31}P spectrum as two singlets, in a 60:40 ratio, at −55.6 and −56.6 ppm respectively. Asymmetry of 3,5-di-*tert*-butylcatecholate fragment is responsible for observing two signals for **24**. Chemical shifts of **24** are near to those of the reported phosphoranes with the same connectivity [34], Scheme 8.

It is known that in phosphoranes where the phosphorus atom is part of 4–7 membered-rings, the rings prefer an apical-equatorial position in the tbp, independently of the substituents nature [35]. According to this, it is expected that in phosphoranes **24** the two rings keep apical-equatorial position with the N-Me_2 group located at the equatorial site. It has been reported that apicophilicity of a group depends on its electronegativity, π interactions with phosphorus, and steric factors. High electronegativity and small size favor high apicophilicity of a substituent [35]. These facts allow to propose that anilinic nitrogen is located at the apical position of the tbp. This hypothesis was confirmed from the P–H coupling constant analysis through two and three bonds. In the ^{31}P H-coupled spectrum, each signal of **24** was split in an heptet instead of doublet of heptets, with constants $^3J(^{31}P, ^1H)$ = 11.8 and 11.5 Hz. This result means that N–H proton is not coupled to phosphorus. If the N–H would be located in an equatorial position its $^2J(^{31}P, ^1H)$ constant would be similar to those found [$^2J(^{31}P, ^1H)$ = 17.2 Hz] for the phosphorane derived from *o*-aminophenol [36]. On the other hand, the magnitude of the coupling constant $^3J(^{31}P, ^1H)$ between P and N-Me_2 in **24** is practically equal to that of the phosphorane with the same connectivity reported by Neda et al. [28]. According to these facts, it is clear that in **24** the N-Me_2 group is located in the equatorial position of the tbp, whereas anilinic nitrogen is apical due to absence of a coupling between N–H proton and phosphorus. This behavior is similar to that found in the hydrospirophosphorane derived from *o*-aminophenol [36], where coupling $^2J(^{31}P, ^{13}C)$ through equatorial substituent is big [16.5 Hz] and null through the axial one.

CONCLUSION

We have found that compound **1** forms unsaturated six-membered phosphorus heterocycles. The presence of three different N–H protons allowed to prepare different compounds by selective substitution. In compound **1**, the free anilinic proton is most



SCHEME 8 Synthesis and ^{31}P NMR data of spirophosphoranes **24**.

reactive to substitution reactions, followed by the benzimidazolic, and finally the anilinic proton involved in the hydrogen bond.

$P[NMe_2]_3$ was less reactive but more selective in the heterocyclic formation, this behavior could be explained considering that NMe_2 group is not a good leaving group as chlorine is. Substitution of only one proton of **1** by Ph_2PCl leads to a hydrogen bond which could be substituted by other groups giving more complex molecules.

Compound **1** also allows to prepare derivatives with two kind of phosphorus atoms, endo- and exocyclic. This different reactivity can be exploited to prepare mixed compounds which, together with the reported here, can be used as potential ligands in coordination chemistry.

Because of phosphorus acidity in a P(III) derivative, it was possible to prepare pentacoordinated phosphorus compounds by oxidative addition of a quinone heterocycle.

EXPERIMENTAL

All experiments were carried out under dry nitrogen atmosphere. Solvents were dried and freshly distilled under N_2 atmosphere according to reported procedures [37]. NMR spectra were recorded in DMSO-d_6 and $CDCl_3$ on a Jeol GSX-270, Jeol Eclipse 400, and Bruker 300 spectrometers. δ are given in ppm and referred to Me_4Si, H_3PO_4 (aq., 85%) [δ $^{31}P = 0$], and neat Me_2Se [δ $^{77}Se = 0$]. Assignment of ^1H and ^{13}C NMR data were supported by 2D $^1H/^1H$ COSY, $^1H/^{13}C$ HETCOR, $^1H/^{13}C$ COLOQ, and $^1H/^{13}C$ HMBC experiments. IR spectra were taken in KBr disc using 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.

*2-(2-Aminophenyl)-1H-benzimidazol (**1**)*

Compound **1** was prepared according to described method [38]. ^{13}C NMR (DMSO-d_6): δ (ppm) 153.1 (C2), 118.7 (C4), 122.0 (C5), 122.8 (C6), 111.3 (C7), 134.1 (C8), 143.5 (C9), 110.7 (C10), 148.8 (C11), 116.7 (C12), 130.9 (C13), 115.6 (C14), 127.8 (C15). ^1H NMR (DMSO-d_6): δ (ppm) 7.69 (t, J_{HH} 7.04 Hz, H4), 7.22 (br, H5), 7.22 (br, H6), 7.57 (br, H7), 6.90 (d, J_{HH} 7.92 Hz, H12), 7.18 (dd, J_{HH} 7.92 and J_{HH} 7.44 Hz, H13), 6.69 (t, J_{HH} 7.48 Hz, H14), 7.92 (d, J_{HH} 7.92 Hz, H15), 7.32 (br, N—$\underline{H}_2$), 12.72 (br, N—$\underline{H}$).

*Dimethyl-(5H-5,6a,11-triaza-6-phospha-benzo-[a]fluoren-6-yl)-amine (**2**)*

To a suspension of 100 mg (0.48 mmol) of compound **1** in 10 ml of toluene, 0.09 ml (78 mg, 0.48 mmol) of $P[NMe_2]_3$ were added. This mixture was heated under reflux until the calculated amount of Me_2NH was evolved and titred with a 1 N HCl solution. The resulting solution was filtered and the solvent evaporated in vacuum to produce 130 mg (96%) of a red oil. ^{13}C NMR ($CDCl_3$): δ 149.8 (d, $^2J_{PC}$ 6.2 Hz, C2), 119.0 (C4), 123.1 (C5), 122.4 (C6), 110.9 (d, $^3J_{PC}$ 11.4 Hz, C7), 136.0 (d, $^2J_{PC}$ 18.7 Hz, C8), 144.6 (d, $^3J_{PC}$ 4.2 Hz, C9), 114.5 (C10), 141.0 (d, $^2J_{PC}$ 10.4 Hz, C11), 117.3 (C12), 131.4 (C13), 120.3 (C14), 126.7 (C15), 37.4 (d, $^2J_{PC}$ 18.7 Hz, N—$\underline{C}H_3$). ^1H NMR ($CDCl_3$): δ 7.82 (d, J_{HH} 7.68 Hz, H4), 7.29 (dd, J_{HH} 6.96 and 8.04 Hz, H5), 7.25 (dd, J_{HH} 7.72 and 7.68 Hz, H6), 7.60 (d, J_{HH} 8.08 Hz, H7), 6.93 (d, J_{HH} 8.44 Hz, H12), 7.23 (t, J_{HH} 7.68 Hz, H13), 6.96 (t, J_{HH} 7.68 Hz, H14), 8.38 (d, J_{HH} 8.32 Hz, H15), 2.39 (d, $^3J_{PH}$ 9.51 Hz, N—C$\underline{H}_3$), 6.58 (d, $^2J_{PH}$ 37.34 Hz, P—N—$\underline{H}$). MS: *m/z* (%): 282.25 (4) $[M]^+$, 238.20 (29), 237.20 (14), 210.35 (17), 209.30 (100), 208.35 (27).

*Dimethyl-(5-[bis(dimethylamino)phosphanyl]-5,6a,11-triaza-6-phospha-benzo[a]fluoren-6-yl)-amine (**3**)*

It was synthesized following the same procedure as for **2** using 300 mg (1.43 mmol) of **1** and five equivalents (1.30 ml, 1.17 g, 7.17 mmol) of $P(NMe_2)_3$. Five hundred and sixty milligrams (97%) of **3** were isolated as a red oil. ^{13}C NMR ($CDCl_3$): δ 149.8 (d, $^2J_{PC}$ 4.2 Hz, C2), 119.2 (C4), 123.1 (C5), 122.3 (C6), 111.1 (d, $^3J_{PC}$ 11.2 Hz, C7), 136.4 (d, $^2J_{PC}$ 20.3 Hz, C8), 144.7 (d, $^3J_{PC}$ 3.3 Hz, C9), 120.4 (C10), 141.7 (dd, $^2J_{PC}$ 13.4 and 6.6 Hz, C11), 121.3 (d, $^3J_{PC}$ 22.3 Hz, C12), 130.8 (C13), 122.4 (C14), 126.9 (C15), 39.3 (d, $^2J_{PC}$ 20.7 Hz, P—N($\underline{C}H_3)_2$), 38.8 (d, $^2J_{PC}$ 18.9 Hz, P—[N($\underline{C}H_3)_2]_2$), 38.7 (d, $^2J_{PC}$ 18.7 Hz, P-[N($\underline{C}H_3)_2]_2$). ^1H NMR ($CDCl_3$): δ 7.87 (d, J_{HH} 7.70 Hz, H4), 7.32 (dd, J_{HH} 8.15 and 7.70 Hz, H5), 7.32 (dd, J_{HH} 8.15 and J_{HH} 7.31 Hz, H6), 7.74 (d, J_{HH} 7.46 Hz, H7), 7.40 (br, H12), 7.39 (br, H13), 7.18 (t, J_{HH} 7.94 Hz, H14), 8.46 (d, J_{HH} 7.99 Hz, H15), 2.41 (d, $^3J_{PH}$ 9.96 Hz, P—N(C$\underline{H}_3)_2$), 2.73 (d, $^3J_{PH}$ 8.99 Hz, P-[N(C$\underline{H}_3)_2]_2$), 2.47 (d, $^3J_{PH}$ 9.11 Hz, P-[N(C$\underline{H}_3)_2]_2$).

*5H-6-Phenyl-5,6a,11-triaza-6-phospha-benzo[a]fluorene (**5**)*

To a suspension of 200 mg (0.96 mmol) of **1** in 15 ml of a 90:10 *n*-hexane–toluene solvent mixture and 0.27 ml (193 mg, 1.91 mmol) of NEt_3, 0.13 ml

(171 mg, 0.96 mmol) of $PhPCl_2$ dissolved in 3 ml of toluene were added at rt. The reaction mixture was stirred overnight at rt. According to ^{31}P NMR spectra of an aliquot, compound **5** was formed in quantitative yield. It was characterized in solution because vacuum solvent elimination produces a white solid, which is a complex mixture of non identified products.

*5-Dichlorophosphanyl-6-chloro-5,6a,11-triaza-6-phospha-benzo[a]fluorene (**9**)*

The synthesis was performed following the described procedure for **5** using 200 mg (0.96 mmol) of **1**, 0.27 ml (193 mg, 1.91 mmol) of NEt_3, and 0.16 ml (262 mg, 1.91 mmol) of PCl_3. ^{31}P NMR of an aliquot of the reaction mixture after overnight stirring showed quantitative formation of **9**. The product was characterized in solution because vacuum solvent elimination affords a complex mixture of non identified compounds.

*[2-(1H-Benzoimidazol-2-yl)-phenyl]-diphenylphosphanyl-amine (**10**)*

It was prepared using the same procedure as for **5** from 200 mg (0.96 mmol) of **1**, 0.27 ml (193 mg, 1.91 mmol) of NEt_3, and 0.17 ml (211 mg, 0.96 mmol) of Ph_2PCl. Resulting mixture reaction after 4 h stirring at rt was filtered to eliminate NEt_3HCl. The liquid portion was concentrated in vacuum to obtain 340 mg (90%) of **10** as a bright red oil. ^{13}C NMR ($CDCl_3$): δ 152.2 (C2), 118.9 (C4), 123.1 (C5), 122.2 (C6), 110.9 (C7), 133.2 (C8), 143.0 (C9), 147.9 (d, $^2J_{PC}$ 16.9 Hz, C11), 116.3 (d, $^3J_{PC}$ 26.1 Hz, C12), 130.9 (C13), 117.8 (C14), 127.1 (C15), 140.7 (d, $^1J_{PC}$ 10.8 Hz, C*i*), 131.4 (d, $^2J_{PC}$ 21.5 Hz, C*o*), 128.6 (d, $^3J_{PC}$ 7.7 Hz, C*m*), 129.0 (C*p*). ^1H NMR ($CDCl_3$): δ 7.33 (d, J_{HH} 6.96 Hz, H4), 7.27 (t, J_{HH} 6.96 Hz, H5), 7.27 (t, J_{HH} 6.96 Hz, H6), 7.66 (d, J_{HH} 8.44 Hz, H7), 7.65 (d, J_{HH} 8.44 Hz, H12), 7.28 (t, J_{HH} 6.96 Hz, H13), 6.77 (dd, J_{HH} 7.68, J_{HH} 7.32, H14), 7.80 (d, J_{HH} 7.72, H15), 10.77 (s, N—H), 10.59 (d, $^2J_{PH}$ 7.32 Hz, P—N—H), 7.74 (ddd, $^3J_{PH}$ 8.04, J_{HH} 7.68 and 1.84 Hz, H*o*), 7.42 (m, H*m*), 7.40 (m, H*p*).

*5-Diphenylphosphanyl-6-phenyl-5,6a,11-triaza-6-phospha-benzo[a]fluorene (**11**)*

To a toluene solution of 376 mg (0.96 mmol) of **10** and 0.27 ml (193 mg, 1.91 mmol) of NEt_3, 0.13 ml (171 mg, 0.96 mmol) of $PhPCl_2$ were added at rt. After 1 h of stirring, the reaction mixture was filtered and the solvent evaporated to give 470 mg (98%) of a brown oil. ^{13}C NMR ($CDCl_3$): δ 149.6 (C2), 119.6 (C4), 123.5 (C5), 123.5 (C6), 111.2 (d, $^3J_{PC}$ 7.3 Hz, C7), 136.3 (d, $^2J_{PC}$ 18.7 Hz, C8), 144.4 (C9), C10 (not observed.), 143.6 (dd, $^2J_{PC}$ 19.7, $^2J_{PC}$ 5.2, C11), 124.6 (d, $^3J_{PC}$ 16.6 Hz, C12), 130.6 (C13), 124.6 (C14), 127.1 (C15), 137.8 (d, $^1J_{PC}$ 18.7 Hz, C*i*), 133.5 (d, $^2J_{PC}$ 23.9 Hz, C*o*), 129.1 (d, $^3J_{PC}$ 8.3 Hz, C*m*), 129.7 (C*p*) (P—Ph), 137.7 (d, $^1J_{PC}$ 17.6 Hz, C*i*), 131.2 (d, $^2J_{PC}$ 18.7 Hz, C*o*), 128.6 (d, $^3J_{PC}$ 5.2 Hz, C*m*), 128.5 (d, $^3J_{PC}$ 5.2 Hz, C*m*), 129.5 (C*p*), 129.2 (C*p*) (P—Ph_2). ^1H NMR ($CDCl_3$): δ 7.93 (d, J_{HH} 7.92 Hz, H4), 7.33 (dd, J_{HH} 7.91 and 6.26 Hz, H5), 7.36 (dd, J_{HH} 7.59 and 6.26 Hz, H6), 7.47 (d, J_{HH} 7.59 Hz, H7), 7.59 (d, J_{HH} 8.23 Hz, H12), 7.49 (m, H13), 7.15 (m, H14), 8.29 (d, J_{HH} 7.27 Hz, H15), 7.78–7.85 (m, H*o*), 7.49 (m, H*m*), 7.06 (m, H*p*) (P—Ph), 7.23 (m, H*o*), 7.12 (m, H*m*), 6.98 (dd, J_{HH} 6.94 and 7.59 Hz, H*m*), 6.62 (t, J_{HH} 6.94 Hz, H*p*) (P—Ph_2). MS: *m/z* (%): 499.30(5) $[M]^+$, 422.30 (2), 391.30 (13), 315.20 (16), 314.20 (16), 263.25 (20), 262.30 (100), 238.20 (33), 220.20 (24), 209.30 (27), 201.25 (39), 183.20 (38), 154.35 (24).

*Dimethyl-(5H-6-thioxo-5,6a,11-triaza-6-phospha-benzo[a]fluoren-6-yl)-amine (**12**)*

General Procedure. In a 25 ml round bottomed flask equipped with a reflux condenser, 270 mg (0.96 mmol) of **2** was dissolved in 10 ml of toluene and 31 mg (0.96 mmol) of sulfur was added. This mixture was heated for 2 h at toluene reflux. Then, it was filtered to eliminate the excess of sulfur. Filtrate was concentrated in vacuum. Two hundred and ninty milligrams (97%) of a yellow solid was obtained. mp 196–200°C. ^{13}C NMR ($CDCl_3$): δ 150.4 (C2), 119.7 (C4), 124.5 (C5), 123.9 (C6), 113.0 (C7), 133.2 (d, $^2J_{PC}$ 7.3 Hz, C8), 144.5 (d, $^3J_{PC}$ 12.5 Hz, C9), 112.8 (C10), 138.9 (d, $^2J_{PC}$ 3.1 Hz, C11), 117.3 (d, $^3J_{PC}$ 11.4 Hz, C12), 132.0 (C13), 122.3 (C14), 127.3 (C15), 37.8 (d, $^2J_{PC}$ 6.2 Hz, N—CH_3). ^1H NMR ($CDCl_3$): δ 7.85 (d, J_{HH} 7.27 Hz, H4), 7.39 (ddd, J_{HH} 7.27, 7.59, and 1.65 Hz, H5), 7.33 (ddd, J_{HH} 7.59, 6.92, and 1.30 Hz, H6), 7.77 (dd, J_{HH} 6.92, and 1.65 Hz, H7), 6.91 (d, J_{HH} 8.27 Hz, H12), 7.28 (ddd, J_{HH} 7.24, 8.24, and 1.30 Hz, H13), 7.09 (dd, J_{HH} 7.24, and 7.92 Hz, H14), 8.40 (dd, J_{HH} 7.92. and 1.32 Hz, H15), 2.83 (d, $^3J_{PH}$ 12.54 Hz, N—CH_3), 6.50 (d, $^2J_{PH}$ 8.56 Hz, P—N—H). MS: *m/z* (%): 314.25 (60) $[M]^+$, 270.20 (9), 255.95 (10), 239.20 (15), 238.20 (100), 209.30 (15), 160.10 (6), 91.15 (44). IR (KBr), ν (cm^{-1}): 3395, 3221, 2918, 2849, 1690, 1615.

*Dimethyl-(5H-6-selenoxo-5,6a,11-triaza-6-phospha-benzo[a]fluoren-6-yl)-amine (**13**)*

To a solution of 270 mg (0.96 mmol) of **2** in toluene, 76 mg (0.96 mmol) of selenium was added and the suspension refluxed for 4 h. Three hundred and thirty milligrams (96%) of a yellow solid were obtained. mp 190–192°C. ^{13}C NMR ($CDCl_3$): δ 149.9 (C2), 119.8

(C4), 124.5 (C5), 123.9 (C6), 113.1 (C7), 133.2 (d, $^2J_{PC}$ 8.3 Hz, C8), 144.6 (d, $^3J_{PC}$ 11.4 Hz, C9), 112.9 (C10), 138.5 (d, $^2J_{PC}$ 5.2 Hz, C11), 117.4 (d, $^3J_{PC}$ 10.4 Hz, C12), 132.0 (C13), 122.5 (C14), 127.3 (C15), 38.0 (d, $^2J_{PC}$ 5.2 Hz, N-($\underline{C}H_3)_2$). ^{1}H NMR ($CDCl_3$): δ (ppm) 7.84 (dd, J_{HH} 6.59 and 1.32 Hz, H4), 7.39 (ddd, J_{HH} 6.94, 7.59, and 1.65 Hz, H5), 7.34 (ddd, J_{HH} 6.92, 7.59, and 1.32 Hz, H6), 7.78 (dd, J_{HH} 6.92, and 1.65 Hz, H7), 6.91 (d, J_{HH} 7.92 Hz, H12), 7.28 (dd, J_{HH} 7.59, and 7.92 Hz, H13), 7.09 (dd, J_{HH} 7.59, and 7.92 Hz, H14), 8.39 (dd, J_{HH} 7.92, and 1.65 Hz, H15), 2.87 (d, $^3J_{PH}$ 12.86 Hz, N($C\underline{H}_3)_2$), 6.47 (br, P─N─$\underline{H}$). ^{77}Se NMR: −161.3 (d, $^1J_{PSe}$ 895.3 Hz). MS: *m/z* (%): 362.20 (14) $[M]^+$, 282.25 (3), 239.20 (16), 238.20 (100), 237.25 (37). $C_{15}H_{15}N_4PSe.2$ (C_3H_6O) (477.40) calcd.: C, 52.83; H, 5.69; N, 11.73. Found: C, 53.10; H, 5.69; N, 12.30. IR (KBr), ν (cm^{-1}): 3381, 3249, 2918, 2849, 1677, 1618.

*[2-(1H-Benzoimidazol-2-yl)-phenyl]-diphenylthiophosphinoyl-amine (***14***)*

To a solution of 1.88 g (4.78 mmol) of **10** in 15 ml of toluene, 153 mg (4.78 mmol) of sulfur was added and the suspension stirred for 5 min at rt. Compound **14** precipitated as beige solid, which was filtered, washed with acetone, and dried in vacuum; 1.95 g (96 %) of **14** were obtained. mp 268–272°C. ^{13}C NMR (DMSO-d_6): δ 151.8 (C2), 118.3 (C4), 123.5 (C5), 122.4 (C6), 111.6 (C7), 135.5 (C8), 142.1 (C9), 115.7 (d, $^3J_{PC}$ 7.3 Hz, C10), 141.6 (C11), 119.1 (d, $^3J_{PC}$ 7.3 Hz, C12), 130.2 (C13), 120.4 (C14), 127.6 (C15), 133.9 (d, $^1J_{PC}$ 11.4 Hz, C*i*), 131.5 (d, $^2J_{PC}$ 11.4 Hz, C*o*), 129.0 (d, $^3J_{PC}$ 13.5 Hz, C*m*), 132.2 (d, $^4J_{PC}$ 3.1 Hz, C*p*). ^{1}H NMR (DMSO-d_6): δ 7.33 (d, J_{HH} 7.24 Hz, H4), 7.22 (dd, J_{HH} 7.24 and 7.56 Hz, H5), 7.19 (t, J_{HH} 7.56 Hz, H6), 7.50 (br, H7), 7.31 (d, J_{HH} 8.24 Hz, H12), 7.13 (dd, J_{HH} 8.24 and 6.92 Hz, H13), 6.97 (t, J_{HH} 7.27 Hz, H14), 8.08 (m, H15), 12.87 (s, N─$\underline{H}$), 12.30 (d, $^2J_{PH}$ 10.21 Hz, P─N─$\underline{H}$), 8.08 (m, H*o*), 7.52 (br, H*m*), 7.52 (br, H*p*). MS: *m/z* (%): 425.10 (34) $[M]^+$, 393.20 (18), 392.20 (62), 349.15 (21), 348.15 (94), 317.15 (22), 316.15 (100), 285.15 (8), 269.15 (11), 238.15 (26), 217.15 (37), 139.00 (26). $C_{25}H_{20}N_3PS$ (425.50) calcd.: C, 70.57; H, 4.74; N, 9.88; S, 7.54. Found: C, 70.38; H, 4.90; N, 9.75; S, 7.51. IR (KBr), ν (cm^{-1}): 3207, 3055, 2917, 2849, 1585.

*[2-(1H-Benzoimidazol-2-yl)-phenyl]-diphenylselenophosphinoyl-amine (***15***)*

It was prepared in the same way as **14** using 1.88 g (4.78 mmol) of **10** and 378 mg (4.78 mmol) of selenium; 2.18 g (97%) of a beige solid were obtained. mp 270–274°C. ^{13}C NMR (DMSO-d_6): δ 151.8 (C2), 118.3 (C4), 123.5 (C5), 122.4 (C6), 111.6 (C7), 134.8 (C8), 142.0 (C9), 116.0 (d, $^3J_{PC}$ 7.3 Hz, C10), 141.6 (C11), 119.2 (d, $^3J_{PC}$ 7.3 Hz, C12), 130.0 (C13), 120.5 (C14), 127.6 (C15), 133.6 (d, $^1J_{PC}$ 18.7 Hz, C*i*), 131.7 (d, $^2J_{PC}$ 12.5 Hz, C*o*), 128.9 (d, $^3J_{PC}$ 12.5 Hz, C*m*), 132.3 (d, $^4J_{PC}$ 2.1 Hz, C*p*). ^{1}H NMR (DMSO-d_6): δ 7.29 (d, J_{HH} 7.24 Hz, H4), 7.20 (dd, J_{HH} 7.27 and 7.59 Hz, H5), 7.17 (dd, J_{HH} 7.56 and 7.27 Hz, H6), 7.49 (br, H7), 7.28 (d, J_{HH} 8.24 Hz, H12), 7.14 (dd, J_{HH} 8.27 and 7.24 Hz, H13), 6.98 (dd, J_{HH} 7.24 and 7.92 Hz, H14), 8.05 (m, H15), 12.84 (s, N─$\underline{H}$), 12.32 (d, $^2J_{PH}$ 8.89 Hz, P─N─$\underline{H}$), 8.07 (m, H*o*), 7.52 (br, H*m*), 7.52 (br, H*p*). ^{77}Se NMR: −249.1 (d, $^1J_{PSe}$ 770.0 Hz). MS: *m/z* (%): 473.05 (16) $[M]^+$, 409.20 (6), 393.15 (28), 392.15 (90), 391.15 (24), 332.15 (9), 317.15 (22), 316.10 (100), 265.00 (14), 238.15 (35), 209.15 (43). $C_{25}H_{20}N_3PSe$ (472.39) calcd.: C, 63.57; H, 4.27; N, 8.90. Found: C, 63.82; H, 4.38; N, 8.84. IR (KBr), ν (cm^{-1}): 3227, 3051, 2918, 2849, 1583.

*Dimethyl-(5-[bis(dimethylamino)thiophosphinoyl]-5,6a,11-triaza-6-phosphabenzo[a]fluoren-6-yl)-amine (***16***)*

To a $CDCl_3$ solution of 60 mg (0.15 mmol) of **3** in a NMR tube, 5.0 mg (0.16 mmol) of sulfur was added followed by vigorous stirring. ^{31}P NMR spectra registered immediately showed quantitative formation of **16**, which was not isolated. ^{13}C NMR ($CDCl_3$): δ 149.3 (dd, $^2J_{PC}$ 4.4 and $^4J_{PC}$ 1.3 Hz, C2), 119.7 (C4), 123.5 (C5), 123.0 (C6), 111.1 (d, $^3J_{PC}$ 10.9 Hz, C7), 135.9 (d, $^2J_{PC}$ 22.0 Hz, C8), 144.5 (d, $^3J_{PC}$ 4.1 Hz, C9), 121.6 (d, $^3J_{PC}$ 6.3 Hz, C10), 138.4 (dd, $^2J_{PC}$ 2.9 and $^2J_{PC}$ 2.0 Hz, C11), 123.5 (dd, $^3J_{PC}$ 4.7 and $^3J_{PC}$ 1.3 Hz, C12), 130.9 (C13), 124.5 (C14), 127.1 (C15), 39.2 (d, $^2J_{PC}$ 20.7 Hz, P─N($\underline{C}H_3)_2$), 38.7 (d, $^2J_{PC}$ 8.6 Hz, P[N($\underline{C}H_3)_2]_2$), 38.7 (d, $^2J_{PC}$ 7.8 Hz, P[N($\underline{C}H_3)_2]_2$). ^{1}H NMR ($CDCl_3$): δ 7.87 (d, J_{HH} 7.63 Hz, H4), 7.36 (dd, J_{HH} 7.36 and 7.59 Hz, H5), 7.32 (dd, J_{HH} 7.36 and 7.50 Hz, H6), 7.71 (d, J_{HH} 7.50 Hz, H7), 8.09 (d, J_{HH} 8.35 Hz, H12), 7.45 (dd, J_{HH} 8.23 and 7.40 Hz, H13), 7.29 (dd, J_{HH} 7.70 and 7.40 Hz, H14), 8.41 (d, J_{HH} 7.70 Hz, H15), 2.40 (d, $^3J_{PH}$ 10.75 Hz, P─N($C\underline{H}_3)_2$), 2.83 (d, $^3J_{PH}$ 10.56 Hz, P[N($C\underline{H}_3)_2]_2$), 2.54 (d, $^3J_{PH}$ 10.84 Hz, P[N($C\underline{H}_3)_2]_2$). MS: *m/z* (%): 432.25 (6) $[M]^+$, 388.20 (10), 314.15 (7), 238.15 (19), 237.15 (12), 151.15 (97), 119.15 (100).

*Dimethyl-(5-[bis(dimethylamino)selenophosphinoyl]-5,6a,11-triaza-6-phosphabenzo[a]fluoren-6-yl)-amine (***17***)*

It was obtained in the same way as **16** using 60 mg (0.15 mmol) of **3** and 12 mg (0.15 mmol) of selenium in $CDCl_3$. According to the ^{31}P NMR spectra the reaction was quantitative. Compound **17** was not isolated. ^{13}C NMR ($CDCl_3$): δ 149.1 (dd, $^2J_{PC}$ 4.3 and $^4J_{PC}$ 1.4 Hz, C2), 119.6 (C4), 123.4 (C5), 123.0 (C6),

111.0 (d, $^3J_{PC}$ 10.9 Hz, C7), 135.8 (d, $^2J_{PC}$ 22.1 Hz, C8), 144.4 (d, $^3J_{PC}$ 4.1 Hz, C9), 121.8 (d, $^3J_{PC}$ 5.9 Hz, C10), 138.1 (t, $^2J_{PC}$ 2.5 Hz, C11), 123.5 (dd, $^3J_{PC}$ 4.7 and $^3J_{PC}$ 1.3 Hz, C12), 130.7 (C13), 124.6 (C14), 127.0 (C15), 39.4 (d, $^2J_{PC}$ 20.9 Hz, P—N($\underline{C}H_3)_2$), 38.9 (d, $^2J_{PC}$ 8.7 Hz, P[N($\underline{C}H_3)_2]_2$), 38.9 (d, $^2J_{PC}$ 8.3 Hz, P[N($\underline{C}H_3)_2]_2$). ^{1}H NMR ($CDCl_3$): δ 7.85 (d, J_{HH} 7.41 Hz, H4), 7.33 (dd, J_{HH} 7.41 and 7.30 Hz, H5), 7.30 (dd, J_{HH} 7.30 and 7.69 Hz, H6), 7.69 (d, J_{HH} 7.40 Hz, H7), 8.04 (d, J_{HH} 8.32 Hz, H12), 7.43 (dd, J_{HH} 7.34 and 8.32 Hz, H13), 7.28 (dd, J_{HH} 7.77 and 7.32 Hz, H14), 8.39 (d, J_{HH} 7.77 Hz, H15), 2.38 (d, $^3J_{PC}$ 10.73 Hz, P—N($C\underline{H}_3)_2$), 2.82 (d, $^3J_{PH}$ 10.92 Hz, P[N($C\underline{H}_3)_2]_2$), 2.54 (d, $^3J_{PH}$ 11.37 Hz, P[N($C\underline{H}_3)_2]_2$). ^{77}Se NMR: −207.8 (dd, $^1J_{PSe}$ 829.7 and $^3J_{PSe}$ 8.6 Hz). MS: *m/z* (%): 480.20 (3) $[M]^+$, 362.15 (4), 298.20 (3), 238.15 (28), 237.15 (15), 199.15 (12), 119.15 (100).

*5-Diphenylthiophosphinoyl-6-phenyl-5,6a,11-triaza-6-phospha-benzo[a]fluorene (**18**)*

It was obtained from reaction of 480 mg (0.96 mmol) of **11** in toluene and 31 mg (0.96 mmol) of sulfur, and stirring overnight at rt. ^{31}P NMR showed quantitative formation of **18**. It was not isolated due to its great fragility and it was immediately used to prepare compound **20**. ^{13}C NMR ($CDCl_3$): δ 49.7 (C2), 120.1 (C4), 123.8 (C5), 124.1 (C6), 111.1 (d, $^3J_{PC}$ 6.9 Hz, C7), 136.8 (d, $^2J_{PC}$ 19.4 Hz, C8), 144.3 (C9), 123.0 (C10), 136.2 (dd, $^2J_{PC}$ 15.8 and 5.7 Hz, C11), 125.1 (d, $^3J_{PC}$ 4.2 Hz, C12), 130.3 (C13), 125.4 (C14), 127.5 (C15), 138.0 (C*i*), 132.6 (d, $^4J_{PC}$ 2.7 Hz, C*o*), 132.1 (d, $^4J_{PC}$ 2.7 Hz, C*o*), 128.9 (C*m*), 128.5 (C*m*), 129.9 (C*p*) (P—$\underline{Ph}$), 133.8 (d, $^1J_{PC}$ 6.0 Hz, C*i*), 132.8 (d, $^2J_{PC}$ 10.6 Hz, C*o*), 132.4 (dd, $^2J_{PC}$ 11.0 and $^4J_{PC}$ 3.3 Hz, C*o*), 128.7 (d, $^3J_{PC}$ 3.5 Hz, C*m*), 128.7 (d, $^3J_{PC}$ 4.3 Hz, C*m*), 129.5 (C*p*), 129.3 (C*p*) (P—$\underline{Ph}_2$). ^{1}H NMR ($CDCl_3$): δ 7.98–8.05 (m, H4), 7.44 (dd, J_{HH} 6.41 and 6.70 Hz, H5), 7.30–7.42 (m, H6, H7), 7.65 (d, J_{HH} 7.94 Hz, H12), 6.95 (dd, J_{HH} 7.50 and 7.97 Hz, H13), 7.03 (dd, J_{HH} 7.44 and 7.60 Hz, H14), 8.22 (d, J_{HH} 7.47 Hz, H15), 7.50–7.54 (m, H*o*), 7.30–7.42 (m, H*o*, H*m*), 7.18–7.28 (m, H*m*), 7.08–7.14 (m, H*p*) (P—$\underline{Ph}$), 7.98–8.05 (m, H*o*), 7.75–7.82 (m, H*o*), 7.30–7.42 (m, H*m*), 7.08–7.14 (m, H*m*, H*p*, H*p*) (P—$\underline{Ph}_2$). MS: *m/z* (%): 531.20 (14) $[M]^+$, 392.20 (35), 391.20 (100), 347.20 (12), 314.25 (17), 238.25 (10), 217.25 (43), 139.15 (14).

*5-Diphenylselenophosphinoyl-6-phenyl-5,6a,11-triaza-6-phospha-benzo[a]fluorene (**19**)*

It was prepared using the same procedure as for **18** from 480 mg (0.96 mmol) of **11** and 76 mg (0.96 mmol) of selenium. The reaction was quantitative. Compound **19** was not isolated. ^{13}C NMR ($CDCl_3$): δ 149.6 (C2), 120.0 (C4), 123.7 (C5), 124.0 (C6), 110.0 (d, $^3J_{PC}$ 6.2 Hz, C7), 136.6 (d, $^2J_{PC}$ 20.0 Hz, C8), 144.3 (C9), 123.4 (C10), 135.9 (dd, $^2J_{PC}$ 16.9 and 6.7 Hz, C11), 124.8 (d, $^3J_{PC}$ 4.6 Hz, C12), 130.0 (C13), 125.4 (C14), 127.4 (C15), 137.9 (C*i*), 132.7 (d, $^4J_{PC}$ 3.1 Hz, C*o*), 132.1 (d, $^4J_{PC}$ 3.1 Hz, C*o*), 128.7 (C*m*), 128.4 (C*m*), 129.9 (C*p*) (P—$\underline{Ph}$), 135.4 (d, $^1J_{PC}$ 7.7 Hz, C*i*), 135.2 (d, $^1J_{PC}$ 7.7 Hz, C*i*), 133.0 (d, $^2J_{PC}$ 12.3 Hz, C*o*), 132.5 (d, $^2J_{PC}$ 10.0 Hz, C*o*), 128.6 (d, $^3J_{PC}$ 3.1 Hz, C*m*), 128.5 (C*m*), 129.6 (C*p*), 129.4 (C*p*) (P—$\underline{Ph}_2$). ^{1}H NMR ($CDCl_3$): δ 8.00 (d, J_{HH} 7.32 Hz, H4), 7.43 (dd, J_{HH} 7.16 and 6.60 Hz, H5), 7.31–7.38 (m, H6, H7), 7.63 (d, J_{HH} 8.04 Hz, H12), 6.94 (dd, J_{HH} 8.04 and 7.32 Hz, H13), 7.03 (dd, J_{HH} 7.72 and 7.32 Hz, H14), 8.22 (d, J_{HH} 7.68 Hz, H15), 7.47–7.51 (m, H*o*), 7.31–7.38 (m, H*o*, H*m*), 7.16–7.27 (m, H*m*), 7.08–7.14 (m, H*p*) (P—$\underline{Ph}$), 8.00 (dd, $^3J_{PH}$ 14.27 and J_{HH} 6.96 Hz, H*o*), 7.82 (dd, $^3J_{PH}$ 13.91 and J_{HH} 7.32 Hz, H*o*), 7.31–7.38 (m, H*m*), 7.08–7.14 (H*m*, H*p*, H*p*). ^{77}Se NMR: −181.8 (dd, $^1J_{PSe}$ 792.6 and $^3J_{PSe}$ 6.1 Hz). MS: *m/z* (%): 579.10 (1) $[M]^+$, 395.00 (39), 393.05 (22), 391.05 (23), 315.20 (22), 314.10 (39), 269.20 (16), 238.15 (100), 186.15 (24), 108.05 (30).

*5-Diphenylthiophosphinoyl-6-thioxo-6-phenyl-5,6a,11-triaza-6-phospha-benzo[a]fluorene (**20**)*

This compound was prepared by adding 12 mg (0.38 mmol) of sulfur to a toluene solution of 200 mg (0.38 mmol) of **18** prepared freshly. After heating at reflux for 1 h, the reaction mixture was filtered and the solvent evaporated in vacuum to afford 198 mg (93%) of a yellow solid. mp 130–134°C. Compound **20** was also obtained reacting compound **11** with an excess of sulfur for 1 h in refluxing toluene. ^{13}C NMR ($CDCl_3$): δ 150.6 (C2), 120.3 (C4), (C5), (C6), 114.2 (C7), 136.6 (d, $^2J_{PC}$ 5.7, C8), 144.6 (d, $^3J_{PC}$ 11.1 Hz, C9), 124.8 (C10), (d, $^2J_{PC}$ 2.9 Hz, C11), 128.0 (dd, $^3J_{PC}$ 5.4 and 4.5 Hz, C12), 130.1 (C13), 127.0 (C14), 127.5 (C15), 134.3 (d, $^1J_{PC}$ 42.3 Hz, C*i*), 132.1 (dd, $^2J_{PC}$ 12.2 and $^4J_{PC}$ 2.8 Hz, C*o*), 128.9 (d, $^3J_{PC}$ 15.8 Hz, C*m*), 131.8 (C*p*) (P—$\underline{Ph}$), 135.8 (d, $^1J_{PC}$ 12.2 Hz, C*i*), 132.6 (d, $^2J_{PC}$ 10.7 Hz, C*o*), 131.7 (d, $^2J_{PC}$ 11.5 Hz, C*o*), 128.5 (d, $^3J_{PC}$ 8.4 Hz, C*m*), 128.3 (d, $^3J_{PC}$ 8.1 Hz, C*m*), 129.3 (C*p*), 129.2 (C*p*) (P$\underline{Ph}_2$). ^{1}H NMR ($CDCl_3$): δ 7.99 (d, J_{HH} 8.34 Hz, H4), 7.48 (dd, J_{HH} 8.16 and 7.38 Hz, H5), 7.39 (dd, J_{HH} 7.32 and 8.18 Hz, H6), 8.33 (d, J_{HH} 8.07 Hz, H7), 7.00 (d, J_{HH} 8.30 Hz, H12), 6.78 (dd, J_{HH} 7.27 and 7.42 Hz, H13), 7.05 (dd, J_{HH} 7.35 and 7.90 Hz, H14), 8.15 (d, J_{HH} 7.66 Hz, H15), 7.16–7.36 [m, H(*o*), H(*m*), H(*p*)] (P—$\underline{Ph}$), 7.87–7.94 [m, H(*o*)], 7.16–7.36 [m, H(*m*), H(*p*)] (P—$\underline{Ph}_2$). MS: *m/z* (%): 563.20 (22) $[M]^+$, 454.15 (11), 423.20 (7), 391.20 (6), 347.20 (16), 314.20 (8), 218.20 (17), 217.20 (100), 139.15 (22).

Compounds **21–24**

They were prepared following the same procedure as described for **20**, using 256 mg (0.44 mmol) of **19** and 45 mg (0.57 mmol) of selenium. ^{31}P NMR spectrum showed a mixture of the compounds **21** (30%), **22** (50%), and **23** (15%).

*Spirophosphoranes (***24***)*

To a $CDCl_3$ solution of 40 mg (0.14 mmol) of **2** in a NMR tube was added 31 mg (0.14 mmol) of 3,5-di-*tert*-butyl-1,2-benzoquinone at rt. The phosphorane **24** was formed quantitatively after stirring for 30 min at rt, according to ^{31}P NMR spectrum and it was not isolated. ^{13}C NMR ($CDCl_3$): δ Major isomer 151.8 (C2), 119.2 (C4), 122.6 (C5), 122.5 (C6), 115.1 (C7), 136.8 (d, $^2J_{PC}$ 2.0 Hz, C8), 144.1 (C9), 140.7 (d, $^2J_{PC}$ 3.0 Hz, C11), 117.8 (d, $^3J_{PC}$ 14.9 Hz, C12), 130.8 (C13), 123.0 (C14), 126.7 (C15), 142.7 (C16), 138.7 (C17), 106.5 (d, $^3J_{PC}$ 17.4 Hz, C18), 145.6 (C19), 114.2 (C20), 132.1 (d, $^3J_{PC}$ 9.2 Hz, C21), 35.0 (C22), 31.8 (C23), 34.6 (C24), 29.9 (C25), 40.2 (d, $^2J_{PC}$ 7.4 Hz, N-CH_3); minor isomer 151.6 (C2), 118.9 (C4), 122.3 (C5), 122.3 (C6), 115.4 (C7), 136.4 (d, $^2J_{PC}$ 2.3 Hz, C8), 144.3 (C9), 138.1 (d, $^2J_{PC}$ 2.3 Hz, C11), 116.8 (C12), 130.8 (C13), 123.0 (C14), 126.6 (C15), 142.4 (d, $^2J_{PC}$ 3.0 Hz, C16), 139.0 (C17), 105.1 (d, $^3J_{PC}$ 11.9 Hz, C18), 145.3 (d, $^4J_{PC}$ 3.5 Hz, C19), 114.4 (C20), 134.0 (d, $^3J_{PC}$ 14.1 Hz, C21), 34.7 (C22), 31.8 (C23), 34.3 (C24), 30.1 (C25), 40.2 (d, $^2J_{PC}$ 7.4 Hz, N-CH_3). ^{1}H NMR ($CDCl_3$): δ major isomer 7.86 (d, J_{HH} 7.61 Hz, H4), 7.27–7.38 (m, H5, H6, H13), 7.68 (d, J_{HH} 8.48 Hz, H7), 6.83–7.00 (m, H12, H18, H20), 7.14 (t, J_{HH} 7.71 Hz, H14), 8.47 (d, J_{HH} 7.82 Hz, H15), 1.29 (s, H23), 1.52 (s, H25), 2.48 (d, $^3J_{PH}$ 12.75 Hz, N-CH_3), 5.84 (d, $^2J_{PH}$ 4.52 Hz, N—H); minor isomer 7.85 (d, J_{HH} 7.28 Hz, H4), 7.27–7.38 (m, H5, H13), 7.22 (dd, J_{HH} 8.24 and 7.94 Hz, H6), 7.64 (d, J_{HH} 8.21 Hz, H7), 6.83–7.00 (m, H12, H18, H20), 7.14 (t, J_{HH} 7.71 Hz, H14), 8.47 (d, J_{HH} 7.82 Hz, H15), 1.35 (s, H23), 1.16 (s, H25), 2.50 (d, $^3J_{PH}$ 12.06 Hz, N—CH_3), 6.13 (d, $^2J_{PH}$ 4.74 Hz, N—H).

REFERENCES

[1] Otaki, K.; Inoue, J.; Yamazaki, Z.; Itaya, M.; Takai, Y.; Yasue, M.; Mizuno, D. Yakugaku Zasshi 1965, 85, 926 (Chem Abstr 1966, 64, 2434f).

[2] Kolosova, M. O.; Ozeretskovskaya, N. N.; Gein, O. Med Parazitol Parazit Bolez 1970, 39, 528 (Chem Abstr 1971, 74, 86172v).

[3] Shinohara, A.; Kusano, S.; Matsui, S.; Muramatsu, N.; Kawada, S. Japan Kokai 1978, 29, 934 (Chem Abstr 1978, 89, 101871c).

[4] (a) Reddy, R. K. V.; Reddy, P. S. N.; Ratnam, C. V. Synth Commun 1991, 21, 49; (b) Inaba, S.; Yamamoto, M.; Ishzumi, K.; Mori, K.; Koshiba, M.; Yamamoto, H. German Patent 2 141 616, 1972 (Chem Abstr 1972, 76, 140859f); (c) Bell, S. C. US Patent 3 505 333, 1970; American Home Products Corp. (Chem Abstr 1970, 73, 25507r).

[5] Khajavi, M. S.; Rad-Moghadam, K.; Hazarkhani, H. Synth Commun 1999, 29, 2617.

[6] Brana, M. F.; Castellano, J. M.; Keilhauer, G.; Machuca, A.; Martin, Y.; Redondo, C.; Schlick, E.; Walker, N. Anti-Cancer Drug Res 1994, 9, 527 (Chem Abstr 1995, 122, 204569q).

[7] Vyas, P. C.; Kaur, N.; Vyas, P.; Kaushal, A. K. Asian J Chem 1995, 7, 571 (Chem Abstr 1995, 123, 256877d).

[8] Mansingh, P. S.; Dash, K. C. NUCAR 95: Proc Nucl Radiochem Symp 1995, 204 (Chem Abstr 1998, 128, 109942w).

[9] Mendiola, M. A.; Masaguer, J. R.; Molleda, C. Synth React Inorg Met-Org Chem 1992, 22, 955 (Chem Abstr 1992, 117, 225182v).

[10] Tamayo, P.; Mendiola, M. A.; Masaguer, J. R.; Molleda, C. Transition Met Chem 1989, 14, 283 (Chem Abstr 1990, 112, 29819r).

[11] Marcos, M. L.; García-Vazquez, J. A.; Masaguer, J. R.; Molleda, C. Transition Met Chem 1987, 12, 352 (Chem Abstr 1988, 108, 230861j).

[12] Shashikala, N.; Gowda, N.; Nanje, M.; Reddy, G. K. N. J Indian Chem Soc 1985, 62, 928 (Chem Abstr 1987, 106, 187817u).

[13] Bielawski, J.; Niedenzu, K. Synth React Inorg Met-Org Chem 1980, 10, 479 (Chem Abstr 1981, 94, 103455x).

[14] Hernández-Díaz, J.; Flores-Parra, A.; Contreras, R. Heteroatom Chem 2004, 15(4), 307.

[15] Barendt, J. M.; Haltiwanger, R. C.; Norman, A. D. J Am Chem Soc 1986, 108, 3127.

[16] Barendt, J. M.; Bent, E. G.; Haltiwanger, R. C.; Norman, A. D. Inorg Chem 1989, 28, 2334.

[17] Moskva, V. V.; Kuliev, A. K.; Akhmedzade, D. A.; Pudovik, M. A.; Sakhnovskaya, J. Gen Chem USSR (Engl Transl) 1985, 55, 834.

[18] Barendt, J. M.; Haltiwanger, R. C.; Squier, C. A.; Norman, A. D. Inorg Chem 1991, 30, 2342.

[19] Barendt, J. M.; Haltiwanger, R. C.; Norman, A. D. Inorg Chem 1986, 25, 4323.

[20] Garrigues, B. Ph D thesis No. 920, Paul Sabatier University, Toulouse, France, 1980.

[21] Schmutzler, R. J Chem Soc 1965, 5630.

[22] Ramos-Organillo, A. PhD thesis, Chemistry Department, Cinvestav-IPN.

[23] Eichhorn, B.; Nöth, H.; Seifert, T. Eur J Inorg Chem 1999, 2355.

[24] Crutchfield, M. M.; Dungan, C. H.; Letcher, J. H.; Mark, V.; Van Wazer, J. R. (Eds.). ^{31}P NMR, Topics in Phosphorus Chemistry; Wiley: New York, 1967; Vol. 5.

[25] PC Spartan Plus 1.5, Wavefuntion Inc., Irvine C. A., 1996-1998.

[26] Contreras, R.; Grevy, J.-M.; García-Hernández, Z.; Güizado-Rodríguez, M.; Wrackmeyer, B. Heteroat Chem 2001, 12, 542.

[27] Cross, R. J.; Green, T. H.; Keat, R. J Chem Soc, Dalton Trans 1976, 1424.

[28] Neda, I.; Fischer, A.; Jones, P. G.; Schmutzler, R. Phosphorus, Sulfur, and Silicon 1993, 78, 271.

[29] Balakrishna, M. S.; Klein, R.; Uhlenbroche, S.; Pinkerton, A. A.; Cavell, R. G. Inorg Chem 1993, 32, 5676; for others examples, Faller, J. W.; Lloret-Fillol, J.; Parr, J. New J Chem 2002, 26, 883.

[30] Tebby, J. C. (Ed.) CRC Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data; CRC Press: Boca Raton, FL, 1991.
[31] Fluck, E.; Binder, H. Z Anorg Allg Chem 1969, 354, 139.
[32] Garrigues, B.; Muñoz, A.; Koenig, M.; Sanchez, M.; Wolf, R. Tetrahedron 1977, 33, 635.
[33] Muñoz, A.; Koenig, M.; Garrigues, B.; Wolf, R. Compt Rend Acad Sci 1972, 274C, 1413.
[34] Farkens, M.; Neda, I.; Fischer, A.; Jones, P. G.; Schmutzler, R. Z Natursforsch 1993, 48b, 853.
[35] (a) Kommana, P.; Kumaraswamy, S.; Vittal, J. J.; Swamy, K. C. K. Inorg Chem 2002, 41, 2356; (b) Kumaraswamy, S.; Muthiah, C.; Swamy, K. C. K. J Am Chem Soc 2000, 122, 964 and references cited therein.
[36] Hernández-Díaz, J.; Contreras, R.; Wrackmeyer, B. Heteroat Chem 2000, 11, 11.
[37] Perrin, D. D.; Armarego W. L. F.; Perrin, D. R. Purification of Laboratory Chemicals, 3th ed.; Pergamon Press; 1988.
[38] Hein, D. W.; Alheim R. J.; Leavitt, J. J. J Am Chem Soc 1957, 79, 427.