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Synthesis and spectroscopic study of new substituted phosphoramidates and 1,3,2-diazaphospholidine-2,5-diones

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ABSTRACT

A new series of substituted 1, 3, 2-diazaphospholidine-2,5-diones was synthesized by an efficient method, starting from a primary amines and amino esters. We have established that phenyl phosphonic dichloride is a suitable reagent allowing the introduction a phosphoryl group. We have prepared the phosphoramidates in two steps. These compounds provide access to 1, 3, 2- diazaphospholidine-2,5-diones by intramolecular cyclization using potassium carbonate.

Keywords: phenyl phosphonic dichloride, amino-esters, phosphoramidates, intramolecular cyclization.

INTRODUCTION

Chiral organophosphorus compounds found broad applications in asymmetric catalysis as ligands of transition metals [1] or as catalysts [2]. The Chiral ligands with three P–O and/or P–N bonds have become increasingly important during the last decade [3-5]. In this area, hemilabile P-O ligands have been extensively studied in coordination chemistry [6] and have found applications in important catalytic processes such as oligomerization of olefins [7-8], carbonylation [9] and carbon dioxide activation [10], hydrogenation [11] or dehydrogenation [12].

The synthesis of heterocyclic organophosphorus compounds containing N- and pentavalent P atoms (phospholidines) as well as carbonyl groups (**Fig.1**) were conducted by Becke-Goehring and Wolf [13] reacting oxamide with PCl_5.

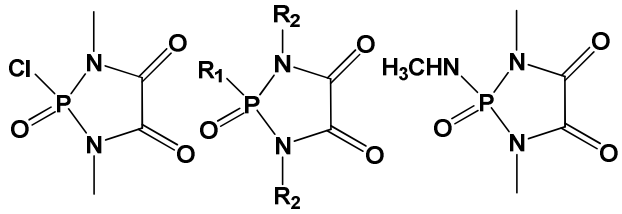


Fig.1

In the present study, One of the main objectives of our organophosphorus research programme [14-18] is the synthesis a new series of modified 1,3,2-diazaphospholidine-2,5-diones (**Fig.2)** starting from phenyl phosphonic dichloride, by adding a coordinating nitrogen atom to these structures (using amine and aminoester), we obtained hybrid bidentate and unsymmetrical P, N ligands, interesting because of the different electronic properties of phosphorus and nitrogen atom which might enhance both the catalyst activity and the enantioselectivity [19].

MATERIALS AND METHODS

Experimental section

IR spectra were recorded on a Perkine Elmer FT-600 spectrometer. ^{1}H, ^{13}C, and ^{31}P nuclear magnetic resonance was determined with a 360 WB or AC 250-MHz Brüker spectrometer using $CDCl_3$ as a solvent. Chemical shifts are referred to TMS (^{1}H, ^{13}C) as internal standard and to 85% H_3PO_4 (^{31}P) as external standard. All coupling constants *J* are reported in hertz. Multiplicity is indicated as s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet) and combination of these signals. Electron ionization mass spectra (30 eV) were recorded in positive or negative mode on a Water MicroMass ZQ. High-resolution mass HRMS were measured on a Joel SX 102 mass spectrometer and recorded in FAB positive mode. All reactions were monitored by TLC on silica Merck h60 F254 (Art. 5554) precoated aluminum plates and were developed by spraying with ninhydrin solution. Visualization was made with ultraviolet light. Column chromatography was performed on Merck silica gel 60H (Art. 9385).

General procedure for the synthesis of phosphoramidates 1a-g.

To a stirred solution of phenylphosphonic dichloride (1.393g, 1mL, 0.0071 mmol) in dry THF (40 mL) a solution of primary or secondary amine (1 equiv, 0.0071 mmol) and triethylamine (1 equiv, 0.98 mL) in the same solvent was added dropwise while cooling at 0°C. Then a mixture of amino ester or 2-chloroacetamide and 1.1 equiv of TEA in THF were added at 0°C. After stirring for 1 hour, the solvent was evaporated under vacuum and the oily product was dissolved in CH_2Cl_2 and washed with 5% NaOH, 5% HCl and water. The organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuum to give the crude product. The residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH: 9/1) to give a phosphoramidates in good yields.

Methyl 2-((3,4dihydroisoquinolin-2(1H)-yl)(phenyl)phosphoryl amino)-4-methylpentanoate 1a:

Oil. **Yield:** 89%. **R_f** = 0.80 (CH_2Cl_2/MeOH: 9/1).**^{1}H NMR ($CDCl_3$, δ ppm):** 7.85 (m, 2**H**, **H**-Ar); 7.50 (m, 3**H**, **H**-Ar); 7.27-7.15 (m, 4**H**, **H**-Ar); 3.60 (s, 2**H**, C**H**$_2$-N), 3.55 (s, 3**H**, C**H**$_3$-O); 3.50 (m, 1**H**, *C**H**); 3.30 (m, 2**H**, C**H**$_2$ cycle); 3.10 (m, 2**H**, C**H**$_2$ cycle); 2.80 (d, 1**H**, N**H**); 1.75 (m, 1**H**, *C**H**i-But*); 1.55 (m,2**H**, C**H**$_2$*i-But*); 0.90(2d, 6**H**, 2(C**H**$_3$) *i-But*). **^{13}C NMR ($CDCl_3$, δ ppm):** 171.6; 134.1; 134.0; 132.4; 128.8; 127.5; 126.8; 126.4; 125.6; 51.7; 51.1; 42.3; 28.0; 24.9; 22.8;.**^{31}P NMR ($CDCl_3$, δ ppm):** 16.5379. **IR (CCl_4, ν cm^{-1}):** 2854 (NH); 1739 (C=O); 1433 (C=C); 1274 (P=O). **MS ESI$^+$ 30 eV m/z:** 401 $[M+H]^+$ 100% calcd for $[C_{22}H_{29}N_2O_3P]$. 400.

Methyl 2-((3,4dihydroisoquinolin-2(1H)yl)(phenyl)phosphorylamino)-3methylbutanoate 1b:

Oil. **Yield:** 90%. **R_f** = 0.79 (CH_2Cl_2/MeOH: 9/1).**^{1}H NMR ($CDCl_3$, δ ppm):** 7.80 (m, 2**H**, **H**-Ar); 7.50 (m, 3**H**, **H**-Ar); 7.20-7.10 (m, 4**H**, **H**-Ar); 3.60 (s, 2**H**, C**H**$_2$-N), 3.65 (s, 3**H**, C**H**$_3$-O); 3.40 (m, 1**H**, *C**H**); 3.35 (m, 2**H**, C**H**$_2$ cycle); 3.15 (m, 2**H**, C**H**$_2$ cycle); 2.60 (s, 1**H**, N**H**); 2.00 (m, 1**H**, *C**H**i-Pro*); 0.91(2d, 6**H**, 2(C**H**$_3$)*i-Pro*)**. ^{13}C NMR ($CDCl_3$, δ ppm):** 171.5; 134.3; 134.1; 132.2; 128.8; 127.5; 126.8; 126.5; 125.7; 61.2; 51.8; 51.0; 50.4; 32.0; 28.1; 18.7;. **^{31}P NMR ($CDCl_3$, δ ppm):** 16.3533 . **IR (CCl_4, ν cm^{-1}):** 2906 (NH); 1740 (C=O); 1429 (C=C); 1275 (P=O). **MS ESI$^+$ 30 eV m/z:** 387 $[M+H]^+$ 100% calcd for $[C_{21}H_{27}N_2O_3P]$ 386.

Methyl 2-((3,4dihydroisoquinolin-2(1H)-yl)(phenyl)phosphorylamino)-3-phenyl propanoate 1c:

Oil. **Yield:** 85%. **R_f** = 0.77 (CH_2Cl_2/MeOH: 9/1).**^{1}H NMR ($CDCl_3$, δ ppm):** 7.75 (m, 2**H**, **H**-Ar); 7.45 (m, 3**H**, **H**-Ar); 7.15 (m, 6**H**, **H**-Ar); 7.10 (m, 3**H**, **H**-Ar); 3.85 (m, 1**H**, *C**H**); 3.81 (s, 2**H**, C**H**$_2$-N), 3.67 (s,3**H**, C**H**$_3$-O); 3.50 (m, 2**H**, *C**H**$_2$Bn*); 3.30 (m, 2**H**, C**H**$_2$ cycle); 2.90 (m, 2**H**, C**H**$_2$ cycle); 2.85 (s, 1**H**, N**H**). **^{13}C NMR ($CDCl_3$, δ ppm):** 171.8; 136.7; 134.2; 134.1; 132.1; 128.8; 128.5; 127.5; 127.4; 126.9; 126.2; 125.9; 125.6; 56.6; 51.8; 51.4; 50.0; 38.0; 28.2;. **^{31}P NMR ($CDCl_3$, δ ppm):** 16.5434. **IR (CCl_4, ν cm^{-1}):** 2896 (NH); 1730 (C=O); 1432 (C=C); 1270 (P=O). **MS ESI$^+$ 30 eV m/z:** 435 $[M+H]^+$ 100% calcd for $[C_{25}H_{27}N_2O_3P]$ 434.

Methyl 2-((benzylamino)(phenyl)phosphorylamino)-4-methylpentanoate 1d:

Oil. **Yield:** 93%. **R_f** = 0.80 (CH_2Cl_2/MeOH: 9/1).**^{1}H NMR ($CDCl_3$, δ ppm):** 7.80 (m, 2**H**, **H**-Ar); 7.50 (m, 3**H**, **H**-Ar); 7.25 (m, 5**H**, **H**-Ar); 4.10 (ddd System ABX, 2**H**, C**H**$_2$-*Bn*); 3.70 (s, 3**H**, C**H**$_3$-O); 3.45 (m,1H, *C**H**); 3.15 (d, 1**H**, N**H**); 1.70 (m, 2**H**, C**H**$_2$*i-But*); 1.50 (m,1**H**, C**H***i-But*); 0.90 (d, 6**H**, 2(C**H**$_3$) *i-But*). **^{13}C NMR ($CDCl_3$, δ ppm):** 171.3; 141.6; 134.2; 134.1; 132.2; 128.9; 128.6; 126.8; 126.7; 51.8; 51.5; 44.3; 42.0; 24.9; 22.8;.**^{31}P NMR ($CDCl_3$, δ ppm):** 16.3333 . **IR (CCl_4, ν cm^{-1}):** 3159 and 2873 (2NH); 1678 (C=O); 1454 (C=C); 1265 (P=O). **MS ESI$^+$ 30 eV m/z:** 375 $[M+H]^+$ 100% calcd for $[C_{20}H_{27}N_2O_3P]$37 4.

Methyl 2-((benzylamino)(phenyl)phosphorylamino)-3-methylbutanoate 1e:

Oil. **Yield:** 83%. **R_f** = 0.78 (CH_2Cl_2/MeOH: 9/1).**^{1}H NMR ($CDCl_3$, δ ppm):** 7.90 (m, 2**H**, **H**-Ar); 7.75 (m, 3**H**, **H**-Ar); 7.25 (m, 5**H**, **H**-Ar); 4.10 (ddd System ABX, 2**H**, C**H**$_2$-*Bn*); 3.70 (s, 3**H**, C**H**$_3$-O); 3.25 (m,1H, *C**H**); 2.4 (s, 2**H**, N**H**); 2.00 (m,1**H**, C**H***i*-Pr); 0.90 (d, 6**H**, 2(C**H**$_3$) *i*-Pr). **^{13}C NMR ($CDCl_3$, δ ppm):** 171.5; 141.5; 134.2; 134.0; 132.3; 128.9; 128.4; 126.9; 126.6; 61.0; 51.8; 44.0; 32.1; 18.9;.**^{31}P NMR ($CDCl_3$, δ ppm):** 16.3340. **IR (CCl_4, ν cm^{-1}):**

3163 and 2896 (2NH); 1735 (C=O); 1461 (C=C); 1250 (P=O). **MS ESI$^+$ 30 eV m/z:** 361 $[M+H]^+$ 100% calcd for $[C_{19}H_{25}N_2O_3P]$ 360.

Methyl 2-((benzylamino)(phenyl)phosphorylamino)-3-phenylpropanoate 1f:
Oil. **Yield:** 80%. **R_f** = 0.80 (CH_2Cl_2/MeOH: 9/1). **^{1}H NMR ($CDCl_3$, δ ppm):** 8.00-7.00 (m, 15**H**, **H**-Ar); 4.15 (s, 2**H**, C**H**$_2$-*Bn*); 3.70 (s, 3**H**, C**H**$_3$-O); 3.80-3.50 (ddd System ABX, 2**H**, C**H**$_2$-*Bn*); 3.40 (m,1H,*C**H**); 3.00 (m, 1**H**, N**H**). **^{13}C NMR ($CDCl_3$, δ ppm):** 175.0; 142.6; 137.8; 134.2; 134.1; 133.3; 128.8; 128.6; 128.3; 127.7; 126.9; 126.6; 125.8; 55.3; 50.9; 43.1; 39.3;.**^{31}P NMR ($CDCl_3$, δ ppm):** 16.3345. **IR (CCl_4, ν cm^{-1}):** 3120 and 2900 (2NH); 1735 (C=O); 1450 (C=C); 1200 (P=O). **MS ESI$^+$ 30 eV m/z:** 409 $[M+H]^+$ 100% calcd for $[C_{23}H_{25}N_2O_3P]$ 408.

N-((benzylamino)(phenyl) phosphoryl)-2-chloroacetamide 1g:
Oil. **Yield:** 92%. **R_f** = 0.79 (CH_2Cl_2/MeOH: 9/1).**^{1}H NMR ($CDCl_3$, δ ppm):** 7.90 (m, 2**H**, **H**-Ar); 7.50 (m, 3**H**, **H**-Ar); 7.25 (m, 5**H**, **H**-Ar); 4.10 (ddd System ABX, 2**H**, C**H**$_2$-*Bn*); 4.00 (s, 2**H**, C**H**$_2$-CO); 3.05 (dd, **H**, N**H**). 2.30 (s, **H**, N**H**). **^{13}C NMR ($CDCl_3$, δ ppm):** 167.0; 142.8; 134.2; 134.0; 132.6; 129.8; 128.9; 126.8; 126.6; 44.0;. **^{31}P NMR ($CDCl_3$, δ ppm):** 16.5379. **IR (CCl_4, ν cm^{-1}):** 3150 and 2869 (2NH); 1655 (C=O); 1450 (C=C); 1256 (P=O). **MS ESI$^+$ 30 eV m/z:** 375 $[M+H]^+$ 100% calcd for $[C_{15}H_{16}ClN_2O_2P]$ 322 .

General procedure for the synthesis of 1,3,2-diazaphospholidine-2,5-diones 2d-f.
A solution of phosphoramidate (0.47 g, 1.28 mmol) in dry CH_3CN (20 mL) or acetone was added a K_2CO_3 (0.17 g, 1.23 mmol) a one fraction. The reaction mixture was stirred at room temperature under inert atmosphere. Progress of the reaction is monitored by TLC, which indicates complete disappearance of phosphoramidate within 1.5 h. Then the reaction mixture was filtered and concentrated under vacuum to give the 1,3,2 diazaphospholidine-2,5-diones in god yield.

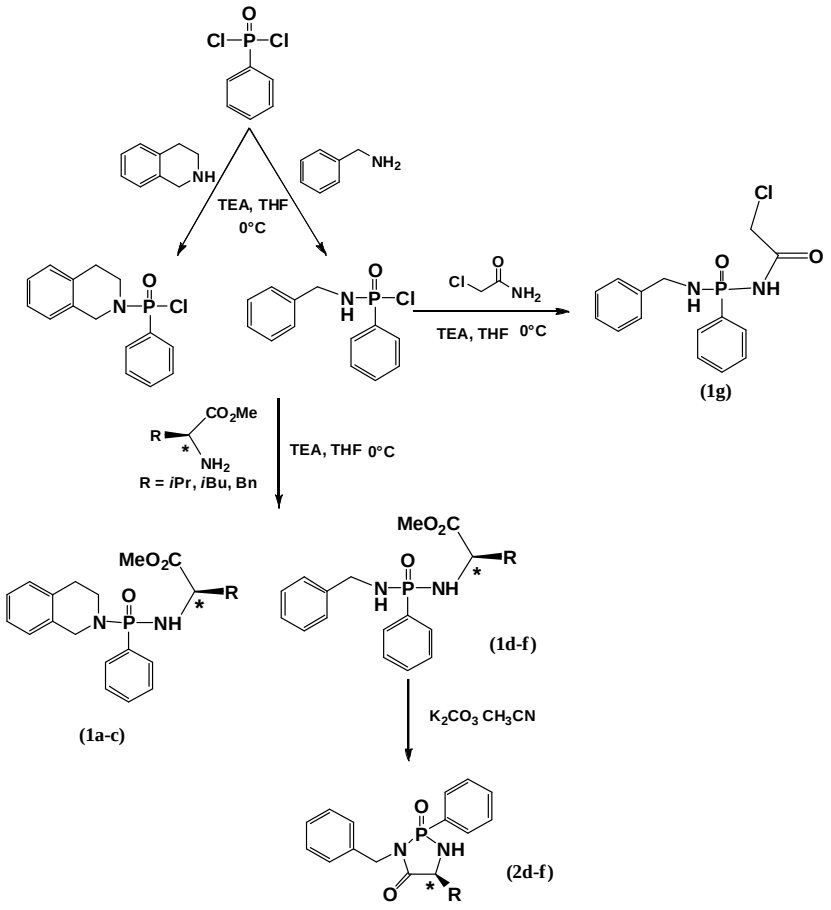
1-Benzyl 4-isobutyl 2-phenyl* 1,3,2-diazaphospholidine-2,5-diones *2d:
Oil. **Yield:** 75 % . **R_f** = 0.41 (CH_2Cl_2/MeOH: 9/1).**^{1}H NMR ($CDCl_3$, δ ppm):** 8.25 (s, 1H, N**H**); 7.80 (m, 2**H**, **H**-Ar); 7.50 (m, 3**H**, **H**-Ar); 7.25 (m, 5**H**, **H**-Ar); 5.15 (m, 1**H**, *C**H**); 4.00 (ddd System ABX, 2**H**, C**H**$_2$-*Bn*); 1.80 (m, 1**H**, C**H** *i-But*); 1. 50(m, 2**H**, C**H**$_2$*i-But*); 0.90 (d, 6**H**, 2(C**H**$_3$)*i-But*). **^{13}C NMR ($CDCl_3$, δ ppm):** 177.9; 142.6; 134.3; 134.2; 132.0; 128.8; 128.6; 126.8; 126.6; 60.0; 43.6; 43.7; 24.0; 21.5;.**^{31}P NMR ($CDCl_3$, δ ppm):** 16.3000 . **IR (CCl_4, ν cm^{-1}):** 2872 (NH); 1675 (C=O); 1449 (C=C); 1248 (P=O). **MS ESI$^+$ 30 eV m/z:** 343. $[M+H]^+$ 100% calcd for $[C_{19}H_{23}N_2O_2P]$ 342.

1-Benzyl 4-isopropyl 2-phenyl 1,3,2-diazaphospholidine-2,5-diones 2e:
Oil. **Yield:**70 %. **R_f** = 0.40 (CH_2Cl_2/MeOH: 9/1).**^{1}H NMR ($CDCl_3$, δ ppm):** 8.00 (s, 1H, N**H**); 7.75 (m, 2**H**, **H**-Ar); 7.50 (m, 3**H**, **H**-Ar); 7.20 (m, 5**H**, **H**-Ar); 5.10 (m, 1**H**, *C**H**); 4.00 (ddd System ABX, 2**H**, C**H**$_2$-*Bn*); 1.95 (m, 1**H**, C**H***i-Pro*); 0.91 (d, 6**H**, 2(C**H**$_3$) *i-Pro*). **^{13}C NMR ($CDCl_3$, δ ppm):** 177.0; 142.6; 134.2; 134.1; 132.3; 128.8; 128.6; 126.8; 126.7; 68.2; 43.6; 33.6; 19.5;. **^{31}P NMR ($CDCl_3$, δ ppm):** 16.0000 . **IR (CCl_4, ν cm^{-1}):** 2922 (NH); 1670 (C=O); 1455 (C=C); 1250 (P=O). **MS ESI$^+$ 30 eV m/z:** 329 $[M+H]^+$ 100% calcd for **[**$C_{18}H_{21}N_2O_2P$**]** 328.

1-Benzyl 4- Benzyl 2-phenyl 1,3,2-diazaphospholidine-2,5-diones 2f:
Oil. **Yield:** 65%. **R_f** = 0.45 (CH_2Cl_2/MeOH: 9/1).**^{1}H NMR ($CDCl_3$, δ ppm):** 7.75 (m, 2**H**, **H**-Ar); 7.50 (m, 3**H**, **H**-Ar); 7.20 (m, 5**H**, **H**-Ar); 7.15 (m, 5**H**, **H**-Ar); 4.45 (ddd System ABX, 2**H**, C**H**$_2$-*Bn*); 4.00 (m, 1**H**, *C**H**); 3.95 (m, 2**H**, C**H**$_2$ *Bn*). **^{13}C NMR ($CDCl_3$, δ ppm):** 176.9; 141.6; 135.6; 134.2; 134.0; 132.3; 128.9; 128.7; 128.5;127.7; 126.7; 64.0; 43.6; 38.5;. **^{31}P NMR ($CDCl_3$, δ ppm):** 16.0032 . **IR (CCl_4, ν cm^{-1}):** 2901 (NH); 1760 (C=O); 1459 (C=C); 1241 (P=O). **MS ESI$^+$ 30 eV m/z:** 377 $[M+H]^+$ 100% calcd for **[**$C_{22}H_{21}N_2O_2P$**]** 376.

RESULTS AND DISCUSSION

The phosphoramidates derivatives (**1a-g**), **(Scheme 1)** were prepared in two synthetic routes [20-21], starting from corresponding amines and aminoester or 2-chloroacetamide with phenyl phosphonic dichloride in dry acetonitrile at 0°C. These compounds were obtained in good yields. The synthesis of 1,3,2 diazaphospholidine-2,5-diones (**2d-f**), was achieved by intramolecular cyclization of corresponding phosphoramidate in the presence of potassium carbonate. The heterocyclic compounds were obtained as yellow oil in 70 % yields. The characterization of the products was carried out by IR, ^{1}H, ^{13}C, ^{31}P NMR spectroscopy and also mass spectrometry.



Scheme 1. Preparation of phosphoramidates and 1,3,2-diazaphospholidine-2,5-diones

CONCLUSION

In summary, we have presented a new approach to the synthesis of new heterocyclic organophosphorus compounds, 1,3,2-diazaphospholidine-2,5-diones and phosphoramidates with good chemical yield. This synthesis has been performed easily starting from an amine, amino ester and phenyl phosphonic dichloride following with intramolecular cyclization to form 1,3,2- diazaphospholidine-2,5-diones derivatives.

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REFERENCES

[1] **(a)** H. Brunner, W. Zeittlmer, *Handbook of Enantioselective Catalysis with Transition Metals*; VCH: Weinheim, **1993**; Vol. I: Products and Catalysts and Vol. II: Ligands-References; **(b)** H. B. Kagan, M. Sasaki, In *The Chemistry of Organophosphorus Compounds*; F. R. Hartley, Ed.; John Wiley and Sons: New York, **1990**; pp. 51–102; **(c)** T. Ohkuma, M. Katamura, R. Noyori, In *Catalytic Asymmetric Synthesis*, 2nd ed.; I. Ojima, Ed.; Wiley-VCH: New York, **2000**; Chapter 1.
[2] **(a)** G. Buono, O. Chiodi, M. Wills, *Synlett.*, **1999**, 377– 388; **(b)** J. M. Brunel, G. Buono, In *New Aspects in Phosphorus Chemistry*, *Top. Curr. Chem.*; J.-P. Majoral, Ed.; Springer Verlag: Berlin, 2002; Vol. 220, pp. 79–105.
[3] J. Ansell, M. Wills, *Chem. Soc. Rev.*, **2002**, 31, 259.
[4] A. Alexakis, C. Benhaim, *Eur. J. Org. Chem.*, **2002**, 3221.
[5] O. Molt, T. Schrader, *Synthesis.*, **2002**, 2002, 2633.
[6] **(a)** A. Bader, E. Lindner, Coord, *Chem. Rev.*, **1991,** 108, 27; **(b)** K. R. Dunbar, J. H. Matonic, V. P. Saharan, *Inorg. Chem.*, **1994,** 33, 25; **(c)** E. T. Singewald, X. Shi, C. A. Mirkin, S. J. Shofer, C. L. Stern, *Organometallics.*, **1996,**15, 3062; **(d)** E. Lindner, K. Gierling, B. Keppeler, H. A. Mayer, *Organometallics.*, **1997**, 16, 3531; **(e)** R. G. Cavell, R.W. Hilts, H. Luo, R. McDonald, *Inorg. Chem.*, **1999,** 38, 897.

[7] **(a)** W. Keim, *New J. Chem.*, **1987,** 11, 531; **(b)** W. Keim, *Angew. Chem. Int. Ed. Engl,*. **1990,** 29, 235.
[8] J. Skupinska, *Chem. Rev.*, **1991,** 91, 613.
[9] **(a)** E. Lindner, H.A. Mayer, P. Wegner, *Chem. Ber.*, **1986,** 119, 2616; **(b)** E. Lindner, A. Sickinger, P. Wegner, *J. Organomet. Chem,*. **1988,** 349, 75.
[10] P. Braunstein, D. Matt, D. Nobel, *J. Am. Chem. Soc.*, **1988,** 110, 3207.
[11] W. S. Knowles, *Acc. Chem. Res.*, **1983,** 16, 106.
[12] P. Braunstein, Y. Chauvin, J. Na¨hring, A. DeCian, J. Fischer, A. Tiripicchio, F. Ugozzoli, *Organometallics.*, **1996,** 15, 5551.
[13] M. Becke-Goehring, M. R. Wolf, Z. Anorg, *Allg. Chem.* **1970,** 373, 245.
[14] S. Hessainia, M. Berredjem, S .Ouarna, Z. Cheraiet, N. E. Aouf, *Phosphorus, Sulfur Silicon Relat. Elem.*, **2013,** 188, 719.
[15] A. Saib, H. Berrebbah, M. R. Djebar, M. Berredjem, *Toxicol. Res.*, **2014,** 3, 395.
[16] W. Boufas, H. Cheloufi, F. Bouchareb, M. Berredjem, N. E. Aouf, *Phosphorus, Sulfur Silicon Relat. Elem*., **2014,** 10, 1080.
[17] A. Bouzina, B. Belhani, N. E. Aouf, M. Berredjem, *RSC Adv.*, **2015,** 5, 46272.
[18] **(a)** B. Belhani, M. Berredjem, M. Le Borgne, Z. Bouaziz, J. Lebreton, N. E. Aouf, *RSC Adv.*, **2015,** 5, 39324.; **(b)** B. Belhani, A. Bouzina, M. Berredjem, N. E. Aouf, *Monatsh Chem*., **2015**, DOI 10.1007/s00706-015-1461-4.
[19] **(a)** A. C. Humphries, A. Pfaltz, In *Stimulating Concepts in Chemistry*; F. Vo¨ gtle, J. F. Stoddart, M. Shibasaki, Eds.; Wiley-VCH: New York, **2000**; pp. 89–103; **(b)** G. Helmchen, A. Pfaltz, *Acc. Chem. Res*., **2000**, 33, 336; **(c)** M. McCarthy, P. J. Guiry, *Tetrahedron.*, **2001**, 57, 3809. [20] H. M. Ali, A. A. Mostafa, M. F. El-zohry, *Heteroatom Chemistry*., **1999**, *10*, 455.
[21] F. Bouchareb, S. Hessainia, M. Berredjem, H. Benbouzid, H. Djebbar, N. E. Aouf, *American Journal of Organic Chemistry*., **2012**, *2* , 14.