

This article was downloaded by:

On: 28 January 2011

Access details: Access Details: Free Access

Publisher Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

THE SYNTHESIS AND REACTION OF HETEROCYCLIC THIOPHOSPHORYL CHLORIDES WITH $AlCl_3$ OR CF_3SO_3Ag . AN ATTEMPT TO OBTAIN $\delta^5\delta^3$ -THIOPHOSPHORYL CATIONS

Tian-Bao Huang^{ab}; Xiao-Ming Yu^{ab}; Lingfei Liu^{ab}; Ke Wang^{ab}

^a Institute of Pesticides and Pharmaceuticals, East China University of Science and Technology, Shanghai ^b Institute of Organic Synthesis, Central China Normal University, Wuhan

To cite this Article Huang, Tian-Bao, Yu, Xiao-Ming, Liu, Lingfei and Wang, Ke (2000) 'THE SYNTHESIS AND REACTION OF HETEROCYCLIC THIOPHOSPHORYL CHLORIDES WITH $AlCl_3$ OR CF_3SO_3Ag . AN ATTEMPT TO OBTAIN $\delta^5\delta^3$ -THIOPHOSPHORYL CATIONS', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 156: 1, 9 – 20

To link to this Article: DOI: 10.1080/10426500008044990

URL: <http://dx.doi.org/10.1080/10426500008044990>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

THE SYNTHESIS AND REACTION OF HETEROCYCLIC THIOPHOSPHORYL CHLORIDES WITH AlCl_3 OR $\text{CF}_3\text{SO}_3\text{Ag}$. AN ATTEMPT TO OBTAIN $\lambda^5\sigma^3$ -THIOPHOSPHORYL CATIONS

TIAN-BAO HUANG*, XIAO-MING YU, LINGFEI LIU and KE WANG

Institute of Pesticides and Pharmaceuticals, East China University of Science and Technology, P. O. Box 544, Shanghai 200237; Institute of Organic Synthesis, Central China Normal University, Wuhan 430079

(Received November 13, 1998; In final form March 17, 1999)

Two new heterocyclic thiophosphoryl chlorides (**2**), derivatives of 1,3,2-benzodiazaphosphole, are synthesized. The reaction of respective thiophosphoryl chlorides (**1**) and (**2**) with AlCl_3 affords dimeric heterocyclic diphosphonium dications **3** and **4**. The reaction of **2a** with $\text{CF}_3\text{SO}_3\text{Ag}$ gives rise to dimeric anhydride **5** instead of the expected $\lambda^5\sigma^3$ -thiophosphoryl cations. The results show that $\lambda^5\sigma^3$ -thiophosphonium cations incorporated into a thiadiazaphospholic system (**1**) or benzodiazaphospholic system (**2**) are not stable, and undergo a structural rearrangement to give a $\lambda^4\sigma^4$ -phosphorus-centre products.

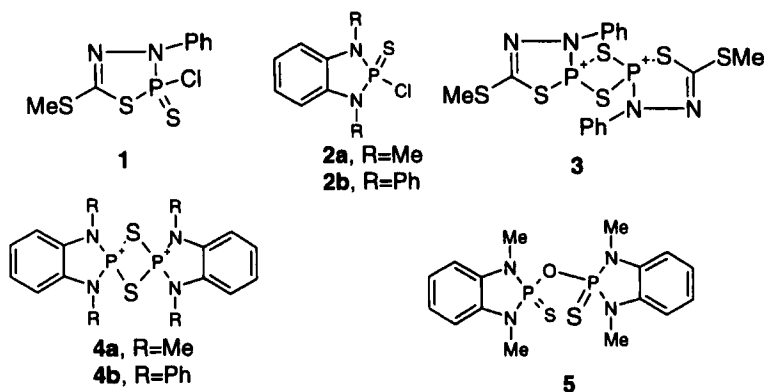
Keywords: $\lambda^5\sigma^3$ -Phosphonium cation; phosphoryl cation; **1**; **3**; **4**; 2-thiadiazaphosphole; **1**; **3**; 2-benzodiazaphosphole

INTRODUCTION

$\lambda^5\sigma^3$ -Phosphonium cations include oxo-, thio- or seleno-phosphoryl cation, imino-phosphonium cations and methylene-phosphonium cations. Phosphoryl cations have been invoked as reactive intermediates for thirty years,¹ but only one selenophosphoryl cation has been fully characterized.² The formation of iminophosphonium cation was still in debate.^{3,4} The first identification of alkenic $\lambda^5\sigma^3$ -methylenephosphonium salts were reported by

* Correspondence Author.

Grutzmacher^{5a} in 1989, and near a dozen of them were known.⁵ These $\lambda^5\sigma^3$ -Phosphonium cations are thought to be stabilized by the steric shielding from the very much sterically hindered substitutes, such as $(\text{Ph}_3\text{P}=\text{C}^2(\text{Ph}))$, $i\text{-Pr}_2\text{N}^5$ $t\text{-Bu}$,^{4,5} and Me_3Si ,^{4,5} etc. group. In principle, Huckel (6π - and 10π) delocalization should also afford a stabilization to allow $\lambda^3\sigma^5$ -phosphonium cation to be persistent in solution. The principal objective of our work was to explore the possibility of the stabilization of $\lambda^5\sigma^3$ -phosphonium cations when phosphonium unit is incorporated into a heterobenzenic system (1) or heteronaphthalenic system (2). We have shown that 2,3-dihydro-1,3,4,2-thiadiazaphosphole ring as well as N-phenyl group can afford a sufficient stabilization for an $\lambda^3\sigma^2$ -phosphonium ($\text{N-P}^+\text{-S}$) cation.⁶ Furthermore, in the view of the structure, 2,3-dihydro-benzodiazaphosphole-2-thion skeleton, whose di-, tri, quadra- and penta- coordinated derivatives were known,⁷ should be suited for a $\lambda^5\sigma^3$ -Phosphonium cation. Therefore we synthesized the known 2-chloro-2-thiono-3-N-phenyl-5-methylthio-2,3-dihydro-1,3,4,2-thiadiazaphosphole (1)⁸ and two new compounds, 2-chloro-2-thiono-2,3-dihydro-1,3,2-benzodiazaphosphole-1,3-bis-methyl (2a) and -1,3-bisphenyl (2b), and performed the reaction of these thiophosphoryl chlorides (1 and 2) with AlCl_3 , and the reaction of 2a with $\text{CF}_3\text{SO}_3\text{Ag}$. Unexpectedly, none of them afforded an $\lambda^5\sigma^3$ -thiophosphoryl cationic product, the former resulted in dimeric heterocyclic diphosphonium dicationic 3 and 4, the latter gave rise to dimeric anhydride 5. These demonstrated that the heterobenzenic and heteronaphthalenic $\lambda^5\sigma^3$ -phosphoryl cations are not persistent at room temperature.



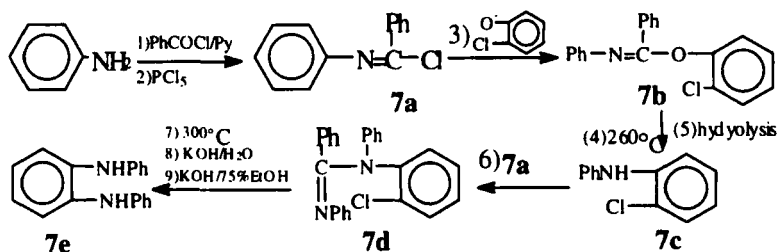
SCHEME 1

RESULTS AND DISCUSSION

Preparation of Precursor Heterocyclic Thiophosphoryl Chloride 1 and 2

2-chloro-2-thiono-3-N-phenyl-5-methylthio-2,3-2(H)-1,3,4,2-thiadiazaphosphole (**1**)⁸ was synthesized according to a procedure by Huang *et al.*, Jennings^{7a} and Gloede^{7c} found that 2-chloro-2,3-dihydro-1,3,2-benzodiazaphosphole-1,3-dimethyl and -1,3-diethyl could be prepared by refluxing the mixture of *o*-phenylenediamine-N,N'-dimethyl or -N,N'-diethyl with PCl_3 . We treated the respective *o*-phenylenediamine-N,N'-dimethyl (**6**) and -N,N'-diphenyl (**7e**) with PSCl_3 in toluene at 110 °C to give 84% yield of 2-chloro-2-thiono-1,3-bismethyl-2,3-dihydro-1,3,2-benzodiazaphosphole (**2a**) and 45.8% yield of 2-chloro-2-thiono-1,3-bisphenyl-2,3-dihydro-1,3,2-benzodiazaphosphole (**2b**). The structures of **1** and **2** were confirmed by MS, IR, ^1H , ^{13}C , ^{31}P NMR and microanalyses. The data is listed in the experimental part.

o-Phenylenediamine-N,N'-dimethyl (**6**) was prepared according to reported method.⁹ We failed to obtain N,N'-diphenyl-*o*-phenylenediamine (**7e**) from *o*-phenylenediamine and *o*-chlorobenzoic acid according to procedure by Clemo.^{10a} We synthesized **7e** by 9 steps (SCHEME II) from aniline and *o*-chlorophenol on basis of the modifying Chapman's method.^{10b-c} The data were described in details in the experimental part.

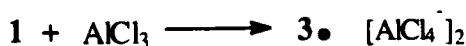


SCHEME 2

Reaction of 1 with AlCl_3

Chloride abstraction from a phosphoryl chloride system has been proved to be a useful approach toward tricoordinate phosphonium cations.

Burford^{4a} showed that the reactions of diaminothiophosphinic chlorides and AlCl_3 have at least two modes of reactivity, either to form Lewis acid-base complexes or to produce dimeric $\lambda^4\sigma^4$ -diphosphonium compounds. Here, the reaction of 2-chloro-2-thiono-3-N-phenyl-5-methylthio-2,3-dihydro-1,3,4,2-thiadiazaphosphole (**1**)⁷ with AlCl_3 at -20°C for 1–2 hr produce exclusively dimeric cation **3** (SCHEME III) in solution and in solid state, as indicated by IR, ^1H , ^{27}Al , ^{31}P NMR, the equivalent conductivity, ESCA and FAB-MS data, which were listed in experimental part and Table I.



SCHEME 3

The IR (487cm^{-1}) and ^{27}Al NMR (102.4 ppm) confirmed the formation of anion $[\text{AlCl}_4]^-$. The phosphorus nucleus of **3** give rise to a signal at 60.4 ppm, slightly shielded from that in **1** ($\delta_{\text{P}}=82.0$ ppm), indicative of absence of low coordinate phosphorus species. The ^1H NMR exhibits peaks at 2.98 ppm (s, 3H, MeS) and 7.65 to 7.85 ppm (m, 5H, Ph) which are downfield from those of **1** (2.60 ppm, MeS; 7.01–7.60 ppm, Ph). The equivalent conductivity for **1**, $\mathbf{3} \cdot [\text{AlCl}_4]^-$ and $\text{Ph}_3\text{P}^+\text{CH}_2\text{Ph} \cdot \text{Br}^-$ are 46.7, 6177.6 and $1270 \text{ uScm}^2\text{M}^{-1}$, respectively. These data disclose the ionic character of **3**.

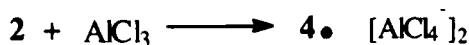
Since ESCA is capable of telling charged compounds from neutral, we performed ESCA spectra of **1** and **3**, the Cl (2p) binding energy in **3** are 199.30 and 199.21 eV, P (2p) binding energy are 133.78 and 134.1 eV, respectively, these imply that phosphorus in **3** has partial positive charge. FAB-MS spectrum of **3** give M^+ peak at 518 (16%) confirming of dimeric diphosphonium dicationic structure.

The expected thiophosphoryl cation is observed as dicationic phosphetane dimer **3**. While it is tempting to assign a monomeric cation as an intermediate in the reaction, there is no evidence for such a species.

The reaction of **2** with AlCl_3

The reactions of **2** with AlCl_3 afforded $4 \cdot [\text{AlCl}_4]^-$, shown in the SCHEME IV. The mode of the reaction was similar to those of **1**. No sig-

nal for $\lambda^5\sigma^3$ -phosphoryl cation could be found in ^{31}P NMR spectroscopy of the solution of the reaction of respective 2-chloro-2-thiono-1, 3-bis-methyl-2, 3-dihydro-1,3,2-benzodiazaphosphole (**2a**) and 2-chloro-2-thiono-1,3-bisphenyl-2,3-dihydro-1,3,2-benzodiazaphosphole (**2b**) with AlCl_3 . The structures of **4** were supported by IR, ^{27}Al and ^{31}P NMR, the equivalent conductivity and FAB-MS, which were listed in experimental part and Table I.



SCHEME 4

The reaction of **2a** with Silver Trifluoromethanesulfonate ($\text{CF}_3\text{SO}_3\text{Ag}$)

The dimeric anhydride **5**, not a monomeric cation, was observed in the reaction of **2a** with $\text{CF}_3\text{SO}_3\text{Ag}$. The $\text{CF}_3\text{SO}_3\text{Ag}$ was selected as the chloride scavenger because of the low nucleophilicity of its anion. We allow a mixture of **5** and a stoichiometric quantity of dry $\text{CF}_3\text{SO}_3\text{Ag}$ in CH_2Cl_2 to stir in a dry evacuated dual compartment vessel shielded from light at 0°C . A white precipitate, found to be AgCl , was isolated in nearly quantitative yield. The ^{31}P NMR spectrum of the reaction mixture showed after 24 hours two signals at 69.0 ppm (**2a**) and 58.7 ppm, after 48 hours a sole peak at 59.1 ppm. Product **5** was isolated in yield of 87.3% by chromatography on silica gel with centrifugal TLC using petroleum ether/ether (8:1) as the eluent. The MS show M^+ peak at 418 (30.2%). The ^{31}P NMR give a single signal at 59.2 ppm, the absence of $^2\text{J}_{\text{P-X-P}}$ implies that **5** has a symmetric structure.



SCHEME 5

From above discussion it is concluded that $\lambda^5\sigma^3$ -thiophosphonium cations incorporated into a Huckel thiadiazaphospholic system (**1**) or benzodiazaphospholic system (**2**) are not stable, and undergo a structural rearrangement to give a $\lambda^4\sigma^4$ -phosphorus-centre products.

TABLE I Data of ^{31}P NMR, the equivalent conductivity and ESCA

Compound		$\delta^{31}\text{P}$ (ppm)	Λ_{eq} ($\mu\text{S}\cdot\text{cm}^2\cdot\text{M}^{-1}$)	ESCA (ev)	
No	R			Cl (2p)	P (2p)
1		82.0	46.7	199.30	133.78
2a	Me	68.8	131.1	199.31	133.74
2b	Ph	59.0	286.3	199.31	133.73
3		60.4	7177.6	199.21	134.10
4a	Me	59.3	7954.4	199.27	134.07
4b	Ph	54.5	6821.3	199.25	134.00
5		58.7	547.5		
$\text{Ph}_3\text{P}^+\text{CH}_2\text{Ph}\cdot\text{Br}^-$			1270.0		

Considering that thiazaphosphenium^{6,11} and diazaphosphenium¹² cations are stable for hours and even are somewhat aromatic, it is tempting to conclude that the $\lambda^5\sigma^3$ -thiophosponium cation is more active than the corresponding $\lambda^3\sigma^2$ -phosphenium cation.

EXPERIMENTAL

Elemental analyses were obtained with a Carlo Erba 1106 elementary analyzer for C, H and N or with the chemical method for P and Cl. Mass spectra were recorded with a HP 5988A spectrometer at 20 eV ionization energy and with VG-7070-HF spectrometer in *glycerol medium*. The ^1H , ^{27}Al , ^{13}C and ^{31}P NMR were recorded with Bruker AM 300 MHz spectrometer. The chemical shifts were reported in ppm relative to the internal standard TMS for ^1H and ^{13}C NMR, and external standard $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ $[(\text{NO}_3)_3]^{3-}$ and 85% H_3PO_4 for ^{27}Al and ^{31}P NMR. IR were recorded on PE-983G spectrometer. ESCA (xps) was obtained on XSAM 800 at 1253.6 eV ($\text{MgK}\alpha$). The equivalent conductivity was measured on DDS-11 conductor at 0.01M, 0°C under dry N_2 , reported in $\mu\text{S}\cdot\text{cm}^2\cdot\text{M}^{-1}$. Toluene were dried with sodium. CH_2Cl_2 , CD_2Cl_2 (Aldrich) and CDCl_3 were dried over P_2O_5 and stored over CaH_2 . All manipulations were carried out under an atmosphere of dry nitrogen. Standard Schlenk technology was applied.

2-Chloro-2-thiono-3-n-phenyl-5-methylthio-2,3-2(H)-1,3,4,2-thiadiazaphospholes (1)

Were synthesized according to the reported procedure.⁸ The equivalent conductivity and ESCA data were listed in Table I.

2-Chloro-2-thiono-1,3-bismethyl-2,3-dihydro-1,3,2-benzodiazaphosphole (2a)

The mixture of **6** (14.9 g, 0.11 mol) in 300 ml of toluene and PSCl_3 (11.0 ml, 0.12 mol) were refluxed for 10 hrs. Completion was indicated by the disappearance of **6** on silica gel TLC. The clear filtrate was concentrated at reduced pressure. The residue was purified on a flash silica gel column using petroleum ether/ether (8:1) as the eluent to give **2a**, white crystal, m.p. 84.5–86.0 °C (ether), 27.25 g (84.3%). IR (KBr, cm^{-1}): 639, 739, 920, 1047, 1116, 1201, 1216, 1276, 1446, 1465, 1484, 1599, 2853, 2924, 3059. δ ^1H (CDCl_3 , ppm): 3.26 (d, 6H, $J=14$ Hz, 2Me), 6.82–7.05 (m, 4H, C_6H_4). δ ^{13}C (CDCl_3 , ppm): 27.57 (d, $^2J_{\text{PNC}}=14.5$ Hz, Me), 109.1 (d, $^2J_{\text{PNC}}=8.8$ Hz), 122.0 and 134.2 (Ph). δ ^{31}P (CDCl_3 , ppm): 68.8. MS (20ev, m/e, %): 232 (M^+ , 67.5), 197 (M-Cl, 27.4), 165 (100, M-Cl-S), 15 (Me, 41.7). Anal. Calcd. For $\text{C}_8\text{H}_{10}\text{ClN}_2\text{PS}$: C, 41.30; H, 4.30; N, 12.05; Cl, 15.25; P, 13.33. Found: C, 41.41; H, 4.50; N, 12.03; Cl, 14.96; P, 12.89.

2-Chloro-2-thiono-1,3-bisphenyl-2,3-dihydro-1,3,2-benzodiazaphosphole (2b)

The mixture of **7e** (4.00 g, 0.015 mol) in 150 ml of toluene, 5.0 ml of Et_3N (0.036 mol) and PSCl_3 (2.50 ml, 0.28 mol) were refluxed for 32 hrs. Completion was indicated by the disappearance of **7e** on silica gel TLC. The clear filtrate was concentrated at reduced pressure. The residue was purified on a flash silica gel column using petroleum ether to give **2b**, white crystal, m.p. 98.0 °C (ether), 2.55 g (45.8%). IR (KBr, cm^{-1}): 661, 690, 739, 757, 899, 920, 927, 993, 1038, 1072, 1218, 1280, 1287, 1298, 1347, 1447, 1489, 1588, 3037. δ ^1H (CDCl_3 , ppm): 6.67–6.94 (m, 4H, C_6H_4), 7.49–7.65 (m, 10H, 2Ph). δ ^{13}C (CDCl_3 , ppm): 109.2–134.3 (m, 2Ph and C_6H_4). δ ^{31}P (CDCl_3 , ppm): 59.0. MS (20ev, m/e, %): 356 (M^+ , 100), 321 (M-Cl, 35.2), 289 (72.5, M-Cl-S), 212 (M-Ph-S-Cl, 5.2). Anal. Calcd. For $\text{C}_{18}\text{H}_{15}\text{ClN}_2\text{PS}$: C, 60.60; H, 4.21; N, 7.86; Cl, 9.94; P, 8.70. Found: C, 60.47; H, 4.26; N, 7.84; Cl, 9.61; P, 8.35.

Reaction of heterocyclic thiophosphoryl chloride **1**, **2a** and **2b** with AlCl_3 resulting in **3**, **4a** and **4b**

These reactions were performed in dual compartment vessels, which were flame-dried before used. Typically, a mixture of respective heterocyclic thiophosphoryl chloride (ca. 1 mmol) and AlCl_3 (ca. 3 mmol of each) in 10 ml of CH_2Cl_2 was stirred for 4–6 hr. at -20°C . A transparent solution was formed. In the cases of **1** and **2b**, the reaction solution is red. In the instances of **2a**, they were green. The solvent was removed slowly from the clear pale yellow solution to yield crystals. The supernatant liquid was decanted and the crystals were washed twice with small aliquots of cool CH_2Cl_2 , to characterize **3**, **4a** and **4b**.

For **3**: Red crystal, m.p. $143\text{--}145^\circ\text{C}$ (CH_2Cl_2 -Hexane), 86.5%. IR (KCl, cm^{-1}): 295, 487s, 686, 762, 963, 1099, 1423, 1491, 1596. $\delta^1\text{H}$ (CDCl_3 , ppm): 2.98 (s, 6H, 2MeS), 7.655–7.85 (m, 10H, $2\text{C}_6\text{H}_5$). $\delta^{13}\text{C}$ (CDCl_3 , ppm): 22.5 (MeS), 123.8, 125.4, 128.2, 132.9 (d, $^2J_{\text{PNC}}=13.5$ Hz) (Ph), 170.5 (d, $^2J_{\text{PNC}}=21.8$ Hz, C=N). $\delta^{27}\text{Al}$ (CDCl_3 , ppm): 102.23. $\delta^{27}\text{Al}$ (CDCl_3 , ppm): 102.43 ($\nu_{1/2}=12.5$ Hz). $\delta^{31}\text{P}$ (CDCl_3 , ppm): 60.42. FAB-MS (glycerol, m/e, %): M^+ 518 (M^+ , 16%), 259 (3%), 227 (83), 164 (11), 122 (6), 77 (100). Anal. Calcd. For $\text{C}_{16}\text{H}_{16}\text{N}_4\text{P}_2\text{S}_2\cdot[\text{AlCl}_4]_2$: C, 22.44; H, 1.87; N, 6.55; Cl, 33.15; P, 7.25. Found: C, 22.43; H, 1.85; N, 6.36; Cl, 33.33; P, 7.55. The equivalent conductivity and ESCA data were listed in Table I.

For **4a**: Green crystal, m.p. $161\text{--}162^\circ\text{C}$ (CH_2Cl_2 -Hexane), 43%. IR (KCl, cm^{-1}): 294, 490s, 695, 742, 964, 1092, 1165, 1220, 1310, 1420, 1440, 1475, 1516, 1610, 2950, 3030. $\delta^1\text{H}$ (CDCl_3 , ppm): 3.38 (d, 15.8Hz, 12H, 4Me), 7.29–7.45 (m, 8H, $2\text{C}_6\text{H}_4$). $\delta^{27}\text{Al}$ (CDCl_3 , ppm): 102.71 ($\nu_{1/2}=12.0\text{Hz}$). $\delta^{31}\text{P}$ (CDCl_3 , ppm): 59.3. FAB-MS (glycerol, m/e, %): 394 (M^+ , 6%), 379 (3), 364 (6), 232 (16), 227 (13), 197 (11), 165 (100). Anal. Calcd. For $\text{C}_{16}\text{H}_{20}\text{N}_4\text{P}_2\text{S}_2\cdot[\text{AlCl}_4]_2$: C, 26.24; H, 2.74; N, 7.65; Cl, 38.76; P, 8.47. Found: C, 26.43; H, 2.57; N, 7.88; Cl, 38.27; P, 8.31. The equivalent conductivity datum was listed in Table I.

For **4b**: Purple crystal, m.p. $178\text{--}179^\circ\text{C}$ (CH_2Cl_2 -Hexane), 33%. IR (KCl, cm^{-1}): 295, 490s, 690, 736, 760, 896, 920, 995, 1040, 1290, 1350, 1480, 1491, 1588, 3030. $\delta^1\text{H}$ (CDCl_3 , ppm): 7.21–7.95 (m, Ar-H). $\delta^{27}\text{Al}$ (CDCl_3 , ppm): 102.36 ($\nu_{1/2}=11.4$ Hz). $\delta^{31}\text{P}$ (CDCl_3 , ppm): 54.5. FAB-MS (glycerol, m/e, %): M^+ 642 (21), 356 (25), 321 (7), 289 (100), 212 (3.5), 77 (90). Anal. Calcd. For $\text{C}_{36}\text{H}_{30}\text{N}_4\text{P}_2\text{S}_2\cdot[\text{AlCl}_4]_2$: C, 44.10; H,

3.06; N, 5.71; Cl, 28.95; P, 6.33. Found: C, 43.99; H, 2.97; N, 5.57; Cl, 28.66; P, 6.29. The equivalent conductivity datum was listed in Table I.

Reaction of 2-chloro-2-thiono-1,3-bismethyl-2,3-dihydro-1,3,2-benzodiazaphosphole (2a) with $\text{CF}_3\text{SO}_3\text{Ag}$ resulting in 5

A solution of 2-chloro-2-thiono-1,3-bismethyl-2,3-dihydro-1,3,2-benzodiazaphosphole (2a) (98.6 mg, 0.42 mmol) and dry $\text{CF}_3\text{SO}_3\text{Ag}$ (117.9 mg, 0.46 mmol) in 10 ml of CH_2Cl_2 is stirred at 0 °C for 48 hr from light. White AgCl is filtered off. The filtrate is evaporated and vacuum to remove the solvent. The residue is chromatographed on silica gel by centrifugal TLC using petroleum ether/ether (8:1) as the eluent to afford 5, 75.16 mg (87.3%), colorless crystal, m.p. 68–69 °C (ether). $\delta^1\text{H}$ (CDCl_3 , ppm): 3.24 (d, 12H, $J=12.4$ Hz, 4Me), 6.65–7.10 (m, 8H, $2\text{C}_6\text{H}_4$). $\delta^{31}\text{P}$ (CDCl_3 , ppm): 59.28 (single). MS (20ev, m/e, %): 418 (M^+ , 30.2%), 197 (76.6), 165 (100), 133 (29.4). Anal. Calcd. For $\text{C}_{16}\text{H}_{20}\text{N}_4\text{OP}_2\text{S}_2$: C, 46.83; H, 4.88; N, 27.30; P, 15.12. Found: C, 48.64; H, 4.76; N, 27.15; P, 15.11.

o-Phenylenediamine-N,N'-dimethyl (6)

Was prepared according to reported method.⁹

N,N'-Diphenyl-o-phenylenediamine (7e)

Was prepared from 7a on the basis of the modifying Chapman's method.^{10b-c}

(1) (N-Phenyl)(benzyliden)(chloro)imine (7a)

(1) Under vigorous agitation, to a solution of 91 ml of aniline in 300 ml of pyridine, 120 ml of PhCOCl was dropwise added. The mixture was refluxed for an hour, cooled to 60 °C, poured it into 1000 ml of vigorously stirring water, stirred for 1 hr. The solid collected by filtration was crystallized from 95 % EtOH to afford N-phenyl benzoyl amide (PhNHCOPh , 184 g, 93.4%, m.p. 161). (2) The solution of 40 g of N-phenyl benzoyl amide (0.2 mol) and 42.0 g of PCl_5 (0.2 mol) in 300 ml of toluene was refluxed until the disappearance of HCl for ca. 2 hrs. The POCl_3 and the solvent was removed off under vacuum. The residue was distilled under

vacuum to give pure **7a**, bp 150–158/1 mmHg, 38.0 g (88.0%), at room temperature oil becomes pale yellow-green crystal, m.p. 57.0–57.6 °C. Anal. Calcd. for $C_{13}H_{10}ClN$: Cl, 16.45. Found: Cl, 16.13.

(2) (N-Phenyl)(benzyliden)(o-chlorophenoxy)imine (7b)

The mixture of **7a** (8.5 g, 0.039 mol), Et_3N (5.5 ml, 0.04 mol) and *o*-chlorophenol (5.1 g, 0.04 mol) in 100 ml of ether was stirred at room temperature for 24 hours. Triethylamine hydrochloride is filtered off. The filtrate is evaporated under vacuum to remove the solvent. The residue is crystallized from 95 % EtOH to afford light yellow solid, (N-Phenyl)(benzyliden)(*o*-chlorophenoxy)imine (**7b**), 10.5 g, 85.4%, m.p. 161 °C. Anal. Calcd. For $C_{19}H_{14}ClNO$: Cl, 11.53. Found: Cl, 11.06.

(3) N-(o-Chlorophenyl)aniline (7c)

The 10.0 g of **7b** was heated at 260 for 1.5 hrs, cooled to room temperature. To it, 50 ml of 50 % KOH and 120 ml of 95 % EtOH was added, the mixture was refluxed for 2 hrs, and was concentrated to one third of the volume, then poured it into 500 ml of water. The water solution was extracted with 4×150 ml of ether. The ether solution was dried and evaporated to obtain oily residue which was distilled under vacuum to give pure **7c**, colorless oil, 5.0 g (67.6%), bp 138°C/10 mm Hg. Anal. Calcd. For $C_{12}H_{10}ClN$: Cl, 17.42. Found: Cl, 17.73.

(4) (N-Phenyl)(N'-phenyl)[N'-(o-chloro)phenyl]carboxamidine (7d)

The mixture of 5.0 g of **7c** (0.025 mol) and 5.5 g of **7a** (0.025 mol) was heated at 100 for 3 hrs, added 30 ml of pyridine and refluxed for half an hour. Poured the warm solution into 200 ml of water, the solid collected by filtration was crystallized from EtOH to obtain (N-Phenyl)(N'-phenyl)[N'-(*o*-chloro)phenyl]carboxamidine (**7d**), 2.34 g (24.5%), yellow crystal, m.p. 168 °C (benzene). Anal. Calcd. For $C_{25}H_{19}ClN_2$: Cl, 9.27. Found: Cl, 9.17.

(5) N,N'-Diphenyl-o-phenylenediamine (7e)

(1) The 2.0 g of **7d** was heated at 300 for 2 hrs, cooled to room temperature, added 60 ml of ice water, stirred and refluxed for a quarter of an hour. The pale green filtrate was adjusted to PH=13. The white solid obtained by filtration was crystallized from EtOH to afford N,N'-bisphenyl-N-ben-

zoyl-*o*-phenylenediamine (1.4 g, 73.5%, m.p. 151). (2) The mixture of 1.0 g of N,N'-bisphenyl-N-benzoyl-*o*-phenylenediamine in 15 ml of EtOH, and 5 ml of 50% KOH-H₂O was refluxed for 2.5 hrs, cooled to room temperature. The crystal obtained by filtration crystallized from petroleum ether (60–90°) to afford N,N'-diphenyl-*o*-phenylenediamine (7e), 4.0 g (70%), m.p. 105.5 °C (108°C^{10c}). IR (KBr, cm⁻¹): 690, 744, 759, 1074, 1155, 1172, 1184, 1226, 1243, 1257, 1280, 1301, 1316, 1408, 1420, 1455, 1465, 1494, 1513, 1590, 1601, 3039, 3047, 3388. δ ¹H (CDCl₃, ppm): 5.33–5.90 (br, 2NH), 6.78–7.32 (m, 14H, C₆H₄ and 2Ph). Anal. Calcd. For C₁₈H₁₆N₂: C, 83.08; H, 6.15; N, 10.77. Found: C, 83.44; H, 6.31; N, 10.52.

Acknowledgements

This project was supported by the National Natural Science Foundation of China (HTB-29602001) and Wuhan Chenguang Natural Science Foundation. We are pleased to thank Shanghai Institute of Organic Chemistry for NMR, IR, MS and microanalyses.

References

1. a) L. Maier, *Unorganische und Allgemeine Chemie*, **345** (1966); b) R. Chend, *J. Indian Chem Soc.*, **37**, 105 (1960).
2. A. Schmidpeter, G. Jochem, K. Karaghiosoff, and C. Robl, *Angew. Chem. Int. Ed. Engl.*, **31**, 1350 (1992).
3. a) M. R. Marre, M. Sanchez and R. Wolf, *Phos. Sulf. Silc.*, **13**, 327 (1982); b) M. R. Marre, M. Sanchez and R. Wolf, *Phos. Sulf. Silc.*, **14**, 453 (1983); c) M. R. Marre, M. Sanchez and R. Wolf, *J. Chem. Soc. Chem. Commun.*, 556 (1984), d) M. Sanchez, M. R. Mazieres, T. C. Kim, R. Wolf and J. Jaud, *Zeitsch. Fur Kristall*, **184**, 147 (1988).
4. a) N. Burford, R. E. Spence and R. D. Rogers, *J. Chem. Soc. Dalton Trans.*, 3611 (1990); b) N. Burford, P. Losier, S. Mason, B. W. Royan, R. E. Spence, P. K. Bahshi and T. S. Cameron, *Phos. Sulf. Silc.*, **76**, 17 (1993); c) N. Burford, R. E. Spence and J. F. Richardson, *J. Chem. Soc. Dalton Trans.*, 1617 (1991).
5. a) A. Igau, A. Baceiredo, H. Grutzmacher, H. Pritzkow, and G. Bertrand, *J. Am. Chem. Soc.*, **111**, 6853 (1989); b) H. Grutzmacher and H. Pritzkow, *Angew. Chem. Int. Ed. Engl.*, **30**, 709 (1991); c) H. Grutzmacher and H. Pritzkow, *Angew. Chem. Int. Ed. Engl.*, **31**, 99 (1992); d) H. Grutzmacher, U. Heim, H. Schonberg and H. Pritzkow, *Phos. Sulf. Silc.*, **76**, 21 (1993).
6. a) Tianbao Huang, Lingfei Liu, Jingling Zhang, Xuanlong Xu, Wenfang Huang, *Phos. Sulf. Silc.*, **140**, 183 (1998); b) Tianbao Huang, Jingling Zhang, Changguo Zhan, Youjie Zhang, *Science in China*, **36**, 641 (1993); c) T.-B. Huang, J.-L. Zhang, *Phos. Sulf. Silc.*, **76**, 79 (1993); d) Tianbao Huang, Jingling Zhang, Xuanlong Xu, Wenfang Huang, *Zh. Obshch Khim.*, **64**, 149 (1994).
7. a) W. Jennings, D. Randall, S. Worley, J. Hargis, *J. Chem. Soc. Perkin Trans. 2*, 1411 (1981); b) S. K. Nitchau, C. Malavand, *Tetrahedron*, **49**, 4651 (1993); c) J. Gloede, *Phos. Sulf. Silc.*, **82**, 211 (1993).
8. Tian-Bao Huang, Jing-Ling Zhang, *Phos. Sulf. Silc.*, **104**, 33 (1995).
9. G. W. H. Cheeseman, *J. Chem. Soc.*, 3308 (1955).

10. a) G. R. Clemo, W. H. Perkin and R. Robinson, *J. Chem. Soc.*, 1781 (1924); b) A. W. Chapman, *J. Chem. Soc.*, 2136 (1929); c) A. W. Chapman, and C. H. Perrott, *J. Chem. Soc.*, 1775 (1932).
11. N. Burford, A. I. Dipchand, B. W. Royan, P. S. White, *Inorg. Chem.*, **29**, 4938 (1992).
12. a) A. H. Cowley, R. A. Kemp, *Chem. Rev.*, **85**, 367 (1985); b) K. Denk, S. Gupta and R. Ramachandran, *Tetra. Lett.*, **37**, 9025 (1996).