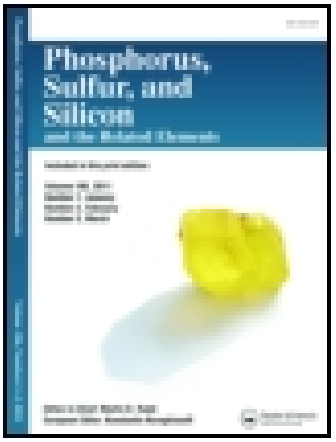

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
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Improved Synthesis of Asymmetrical Substituted 1H-1,2,4-Diazaphospholes

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Accepted author version posted online: 07 May 2014.Published online: 25 Sep 2014.

To cite this article: Qiaoyun Liu, Jing Wu, Junfei Li, Junwen Wang, Wenjun Zheng & Herbert W. Roesky (2014): Improved Synthesis of Asymmetrical Substituted 1H-1,2,4-Diazaphospholes, Phosphorus, Sulfur, and Silicon and the Related Elements, DOI: 10.1080/10426507.2014.919580

To link to this article: http://dx.doi.org/10.1080/10426507.2014.919580

Phosphorus, Sulfur, and Silicon, 189:1–12, 2014

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426507.2014.919580

IMPROVED SYNTHESIS OF ASYMMETRICAL SUBSTITUTED 1*H*-1,2,4-DIAZAPHOSPHOLES

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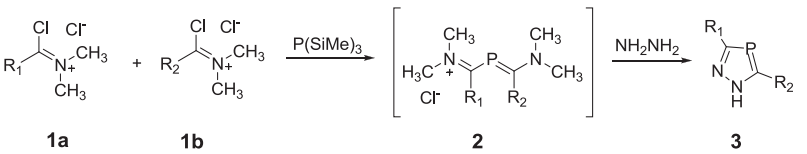
GRAPHICAL ABSTRACT



1a **1b** **2** **3**

R_1 = *t*Bu, R_2 = H(**3a**), Me(**3b**), *i*Pr(**3c**), Ph(**3e**), 2-furanyl(**3f**), 2-thienyl(**3g**)
R_1 = Ph, R_2 = H(**3d**)

Abstract *The reaction of tris(trimethylsilyl)phosphine and a mixture of two different* N,N*-dimethylalkylamides (**1a**,**b**), followed by the treatment with dry hydrazine in situ, resulted in seven asymmetrical 3,5-disubstituted 1H-1,2,4-diazaphospholes (**3a**-**g**). Compounds **3a**-**g** are characterized by single crystal X-ray structural analysis. The present protocol provides a general route to this class of molecules without using phosphaalkynes or phosphaalkenes.*

Keywords Asymmetrical 1*H*-1,2,4-diazaphosphole; hydrogen bonding; X-ray structure; synthesis

INTRODUCTION

Heterocycles containing a low-coordinate phosphorus center[1] have found widespread applications ranging from ligands in metal complexes,[2] devices in materials science[3] to fundamental importance in theoretical and experimental research.[4–7] 1*H*-1,2,4-diazaphosphole (**A**) (H[3,5-R_2dp]) (Figure 1) exhibits electrochemical and coordinating properties due to the low-coordinate P and N atoms. Moreover, it represents a class of a unique aromatic

Received 4 December 2013; accepted 27 April 2014.
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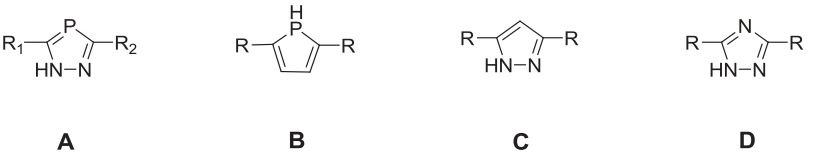


Figure 1 Various five-membered rings with the hetero atoms nitrogen and phosphorus.

five-membered heterocyclic system,[6,8] and may be viewed as a hybrid molecule of the corresponding phosphole (**B**)[9] and pyrazole (**C**)[10] (P-doped pyrazole),[5] or as 1*H*-1,2,4-trizole analogue in which the 4-nitrogen atom is replaced by a $\sigma^2\lambda^3$-phosphorus atom (**D**).

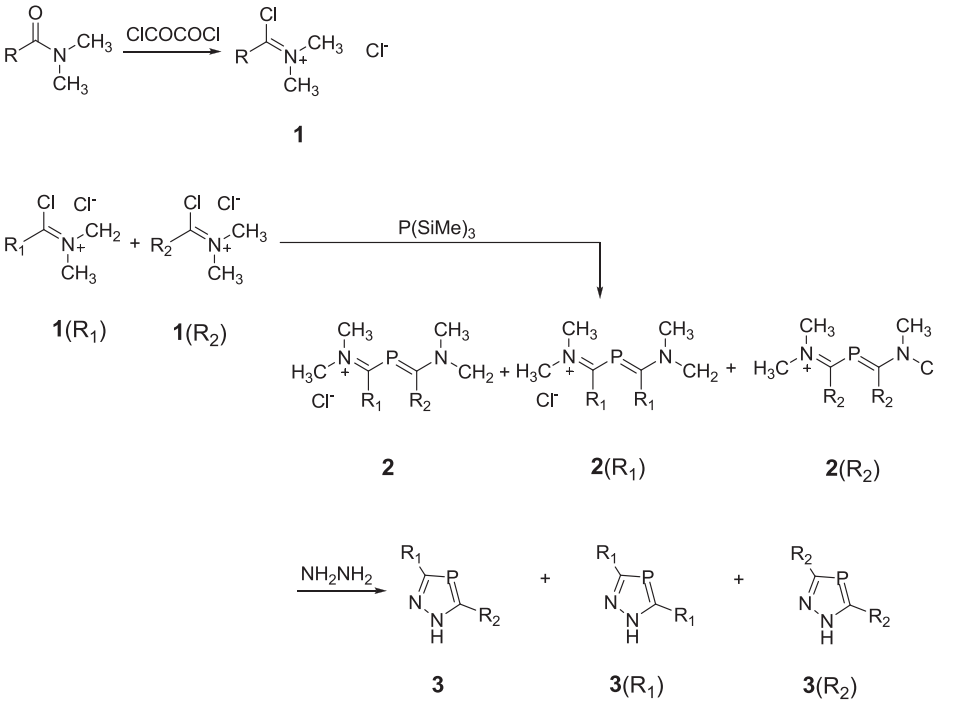
Recently, we reported on two pseudoruthenocenes containing symmetric 1,2,4-diazaphospholide ligands,[11] which play an important role as ligands in efficient palladium catalyzed Heck reactions, where phosphorus-palladium π-backbonding is possible.[12] This is consistent with the results that palladium complexes incorporating phospha- and diphosphaferrocenes with a metallocene backbone and a sp^2-hybridized phosphorus atom[13] were found to be highly efficient ligands in palladium-catalyzed Suzuki cross-coupling reactions.[14] We became interested in planar-chiral pseudo-1,2,4-diazaphospholide metallocenes[11,12] due to their properties as potential planar-chiral catalysts with low-valent late transition metals in asymmetric organic transformations.[15–18] Therefore, we set out to develop a facile and general route to asymmetric 1*H*-1,2,4-diazaphopholes (Figure 1, **A**).[19] Herein, we report on an alternative synthesis to a number of asymmetric 1*H*-1,2,4-diazaphopholes.

RESULTS AND DISCUSSION

Synthesis of Compounds 3

As shown in Scheme 1, *N*,*N*-dimethylimidoyl chlorides **1** were prepared by the reaction of the corresponding acyl chlorides RCOCl with Me_2NH, followed by reaction with oxalylchloride in anhydrous ether. In the case of commercially available amides $RCONMe_2$ these were used for the reaction with oxalyl chloride in anhydrous ether.[20,21] The reactions of $P(SiMe_3)_3$[22] with the mixture of **1**(R_1) and **1**(R_2) in a ratio of 1:1 in anhydrous acetonitrile afforded the corresponding 1,3-bis(dimethylamino)-2-phospha- allyl chloride (**2**) and two additional known symmetric 1,3-bis(dimethylamino)-2-phospha- allyl chlorides (**2**(R_1) and **2**(R_2)) as byproducts (Scheme 1).[8,23] Compound **2** was used without further purification.

Compounds **3a-g** were prepared by the reaction of anhydrous hydrazine at ambient temperature with a mixture of **2**, **2**(R_1) and **2**(R_2) (Scheme 1), which gives after workup the target compound **3** and the two byproducts **3**(R_1) and **3**(R_2). **3** was isolated by column chromatography in pretty good yields based on the starting material **1**.[24] To avoid the hydrolysis of **2**, anhydrous hydrazine was used. Compounds **3** are very soluble in $CHCl_3$ and CH_2Cl_2 and well soluble in THF and ether, but they are not soluble in *n*-hexane. They can also be purified by sublimation in high vacuum. The yield of compounds **3** depends on the content of **2** in the mixture of the asymmetrical and symmetrical phosphaallylic salts as well as on the nature of the substituents R_1 and R_2. To improve the yield of **2** and lower the quantities of **2**(R_1) and **2**(R_2) we alternatively added a solution of **1**(R_1) in acetonitrile



R_1 = *t*Bu, R_2 = H(**3a**), Me(**3b**), *i*Pr(**3c**), Ph(**3e**), 2-furanyl(**3f**), 2-thienyl(**3g**)
R_1 = Ph, R_2 = H(**3d**)

Scheme 1

and $P(SiMe_3)_3$ simultaneously to **1**(R_2) in acetonitrile to produce **2** in 50–70% yield based on the ^{1}H NMR spectra.

NMR Spectroscopy

The ^{31}P NMR data of symmetrical phosphaallylic salts as well as of symmetrical 1*H*-1,2,4-diazaphospholes have already been reported in literature.[8a,25] The ^{31}P NMR resonance of the asymmetric phosphaallylic salts **2** is close to those of the corresponding two symmetrical phosphaallylic salts **2**(R_1) and **2**(R_2).[24a] Compounds **3** were characterized by spectral and analytical methods.[26] The results of elemental analysis are in complete agreement with the formula of compounds **3**. The ^{31}P NMR chemical shifts of **3** range from $\delta = 66.7$ to 80.4 ppm (Table 1) and are consistent with the electron donor capacity of the substituents. The physical and spectroscopic data of compounds **3a**,**b** and **3d**,**e** are identical to those reported previously.[19a,b,27] They were prepared by [2+3]-cycloaddition of hydrocarbon-substituted phosphaalkynes (phosphaalkenes) such as *t*BuC≡P (ClP=C($SiMe_3$)Ph) with diazomethanes RCH=N_2. Our synthetic protocol easily allows tuning the properties of the 3,5-substitutents attached to the 1,2,4-diazaphosphole ring and a variety of asymmetrical 1*H*-1,2,4-diazaphospholes are now accessible.

Table 1 ^{31}P NMR chemical shifts and yields of compounds **3**

Entry	**3**	R_1	R_2	^{31}P NMR, δ (ppm)	Yield (%) based on **1**
1	**a**	*t*Bu	H	76.7 (d, $^2J_{PH} = 42.5$ Hz)	24
2	**b**	*t*Bu	Me	74.5 (d, $^3J_{PH} = 9.5$ Hz)	37
3	**c**	*t*Bu	*i*Pr	66.7 (d, $^3J_{PH} = 5.4$ Hz)	42
4	**d**	Ph	H	80.4 (d, $^2J_{PH} = 41.3$ Hz)	20
5	**e**	*t*Bu	Ph	71.3 (s)	44
6	**f**	*t*Bu	2-furanyl	70.7 (s)	35
7	**g**	*t*Bu	2-thienyl	70.6 (s)	30

Structure Conformations in the Solid State

The crystal structures of **3a**,**b** and **3d** feature cyclic tetramers that present a pseudo-42*m* (D_{2h}) internal symmetry, of which only a two-fold axis remains as a crystallographic element, while those of **3e** and **3g** form cyclic dimers with a pseudo-two-fold axis (Table 2).[26,28] All structures exhibit NH···N bridges in the solid state and are linked to oligomers. The intermolecular hydrogen bonds of **3** are shown by the special molecular orientation in the packing diagram.[25,28] No formation of a P−H tautomeric structure was observed. This is consistent with the recently published theoretical calculations.[29] The small difference between the two nitrogen internal angles of **3** is likely attributable to the disordered NH protons (Figures 2–4).

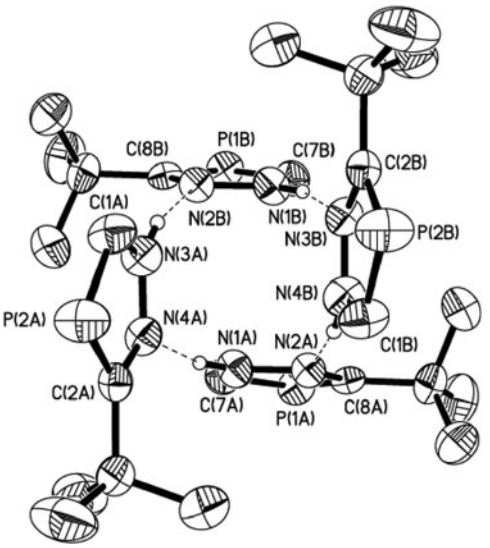


Figure 2 Molecular structure of **3a** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P(1A)−C(7A) 1.719(6), N(1A)−N(2A) 1.342(6), N(1A)−C(7A) 1.317(6); C(7A)−P(1A)−C(8A) 86.6(6), C(7A)−N(1A)−N(2A) 113.0(4), N(1A)−N(2A)−C(8A) 112.8(4). Structure of **3b** is analogous with methyl group in place of hydrogen atom: P(1A)−C(1A) 1.760(4), C(1A)−N(1A) 1.336(4), N(1A)−N(2A) 1.363(4); C(1A)−P(1A)−C(6A) 87.42(17), C(6A)−N(2A)−N(1A) 111.0(3), N(2A)−N(1A)−C(1A) 115.6(3).

Table 2 Crystal data and data collection parameters of compounds **3a**,**b**,**d**,**e**,**g**

Compounds	**3a**	**3b**	**3d**	**3e**	**3g**
Formula	$C_6H_{11}N_2P$	$C_7H_{13}N_2P$	$C_8H_7N_2P_1$	$C_{12}H_{15}N_2P$	$C_{10}H_{13}N_2PS$
fw	142.14	156.16	162.13	218.23	224.25
Cryst. size (mm)	0.30 × 0.20 × 0.20	0.30 × 0.20 × 0.20	0.30 × 0.20 × 0.20	0.30 × 0.20 × 0.20	0.21 × 0.16 × 0.12
Cryst. Syst.	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*	*P*2(1)/*n*	*P*2(1)	*P*2(1)/*c*
a (Å)	20.785(6)	12.260(17)	15.1257(8)	11.8190(14)	11.9543(2)
b (Å)	9.875(3)	22.05(3)	11.5748(6)	8.5829(9)	8.8572(2)
c (Å)	18.310(5)	14.10(2)	19.0517(10)	24.840(3)	12.5222(2)
α(deg)	90	90	90	90	90
β(deg)	117.922(4)	94.24(2)	93.5880(10)	103.238(2)	115.9730(10)
γ(deg)	90	90	90	90	90
V (Å$^{3)}$	3320.5(16)	3802(9)	3329.0(3)	2452.8(5)	1191.96(4)
Z	16	16	4	8	4
Dc (g cm^{-3})	1.137	1.091	1.294	1.182	1.250
Absorption coefficient (mm^{-1})	0.253	0.226	0.262	0.195	0.371
F (000)	1216	1344	1344	928	472
T (K)	296(2)	296(2)	296(2)	296(2)	296(2)
Range (deg)	2.22–25.04	1.85–24.99	1.67–25.05	1.77–25.05	1.89–25.99
reflns measured	16631	9803	34623	13876	16465
Unique reflns	2946	3336	5885	8157	2340
θ_{max} (deg)	25.04	24.99	25.05	25.05	25.99
R_{int}	0.0509	0.0346	0.0360	0.0653	0.0203
Max and min Transmn	0.9511 and 0.9280	0.9561 and 0.9352	0.9494 and 0.9255	0.9621 and 0.9439	0.9565 and 0.9256
*R*1, *wR*2 [$I > 2\sigma(I)$][a]	0.0801, 0.2310	0.0567, 0.1489	0.0409, 0.0998	0.0656, 0.1105	0.0512, 0.1494
*R*1, *wR*2 (all data)[b]	0.1077, 0.2633	0.0835, 0.1687	0.0630, 0.1149	0.1643, 0.1411	0.0596, 0.1601
GOF	1.057	1.075	1.029	0.981	1.022
$\Delta\rho$(max) (e·Å^{-3})	0.563	0.435	0.238	0.185	0.567
$\Delta\rho$(min) (e·Å^{-3})	−0.525	−0.255	−0.243	−0.195	−0.304

[a] $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] $wR2 = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{0.5}$.

In spite of the tendency of compounds **3a**,**b** to show proton disorder, the molecular structure of **3a** exclusively exhibits a conformation with two-fold symmetry in the solid state (Figure 1), connected by N−H···N hydrogen bonds.[25] There are two independent molecules in the asymmetric unit and the *tert*-butyl groups show large amplitudes of internal rotational motion. The bond lengths are slightly longer in **3a**,**b** and the bond angles are less acute than those found in H[dp] (P(1)−C(3) 1.710(3) Å, N(1)−C(2) 1.305(3) Å, N(1)−N(2) 1.323(3) Å, C(3)−P(1)−C(2), 85.1(1)°).[23a]

As illustrated in Figure 3, the 1*H*-1,2,4-diazaphosphole rings of four **3d** molecules in the asymmetric unit are connected by N−H···N hydrogen bonds to form cyclic four-membered oligomers in the solid state. In two of the 1,2,4-diazaphosphole rings it is the N atom in position 1 that carries the H atom, whereas in the other two rings the N atom

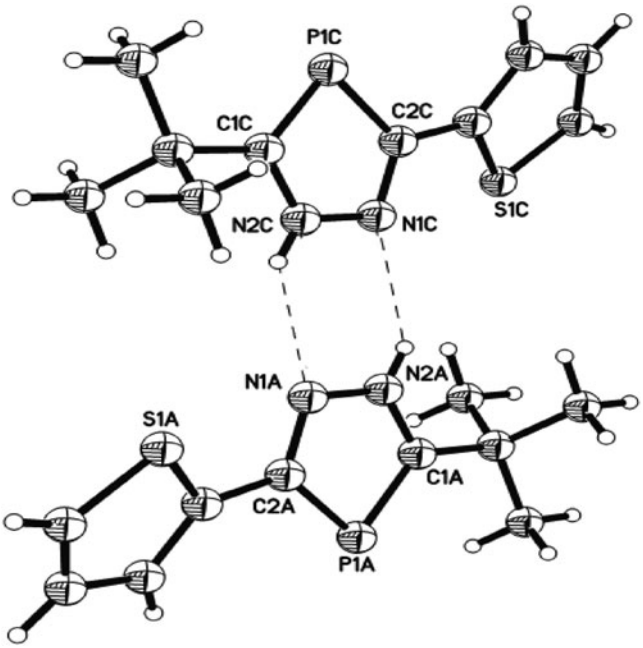


Figure 3 Molecular structure of **3g** with thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg): P(1A)−C(2A) 1.728(2), C(1A)−N(2A) 1.335(3), N(2A)−N(1A) 1.358(3); C(1A)−P(1A)−C(2A) 87.08(12), C(1A)−N(2A)−N(1A) 118.5(2), N(2A)−N(1A)−C(2A) 108.1(2). Structure of **3e** is analogous with phenyl group in place of 2-thienyl group, **3e**: P(2)−C(13) 1.725(6), C(13)−N(3) 1.340(6), N(3)−N(4) 1.345(6); C(13)−P(2)−C(20) 87.3(3), C(13)−N(3)−N(4) 109.2(5), N(3)−N(4)−C(20) 117.0(5).

in position 2 carries the H atom. There are no further short contacts between symmetry-equivalent oligomers. The average planes formed by phenyl groups and the heterocyclic ring are not coplanar in **3d**. The dihedral angles (25.56°) are likely caused by an intramolecular interaction of adjacent groups due to a repulsive interaction between the CH of phenyl groups and the NH.[23b] This observation of the two twisted conformations is similar to those found in H[3,5-Ph_2dp].[23b] The bond lengths and angles of **3d** are comparable with those found in H[3,5-Ph_2dp] (P(1)−C(1) 1.7404(18) Å, N(1)−C(1) 1.329(2) Å, N(1)−N(2) 1.341(2) Å, C(3)−P(1)−C(2), 87.16(9)°).[23b]

Compounds **3e** and **3g** crystallize in the monoclinic space group *P*21/*c*. Molecular dimensions are shown in Figure 4. As illustrated in these figures, the planes formed by the phenyl (thienyl) groups and the heterocycle ring show that they are not coplanar (the dihedral angle is 27.2° for **3e** and 24.8(3)° for **3g**), which is likely caused by an intramolecular interaction of adjacent groups due to a repulsive interaction between the CH of phenyl groups and the NH,[23b] or by steric effects between the thienyl groups and the heterocycles. Hydrogen bridging has been previously observed in 1,2,4-diazaphosphole structures in which there are similar H-bond patterns.[25] The dimers are held together by four symmetry related hydrogen bonds. Interestingly, one phenyl ring is at the same orientation to the other in **3e**, while one thienyl group is at the opposite position of the other in **3g**. The bond lengths and angles of **3e** and **3g** are comparable with those found in H[3,5-*t*Bu_2dp] (P(1)−C(1) 1.737(5) Å, N(1)−C(1) 1.330(5) Å, N(1)−N(2) 1.360(5) Å, C(3)−P(1)−C(2), 87.3(2)°).[23a]

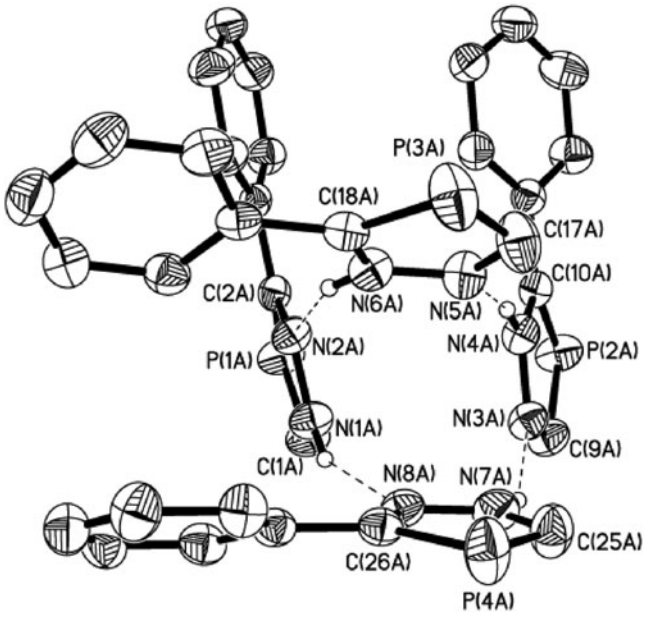


Figure 4 Molecular structure of **3d** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P(1A)−C(1A) 1.722(2), P(1A)−C(2A) 1.746(2), N(1A)−N(2A) 1.340(2), N(1A)−C(1A) 1.318(3); C(1A)−P(1A)−C(2A) 86.22(10), C(1A)−N(1A)−N(2A) 113.65(18), N(1A)−N(2A)−C(2A) 112.10(17).

CONCLUSIONS

In summary, we report an improved and general route to asymmetrical 3,5-substituted 1*H*-1,2,4-diazaphospholes by condensation reaction of hydrazine and two different substituted 1,3-bis(amino)-2-phosphaallyl chlorides. The products have been structurally characterized. Successful preparation of asymmetrically 3,5-substituted 1*H*-1,2,4-diazaphospholes as ligands is an important step for the preparation of planar-chiral pseudo-1,2,4-diazaphospholide complexes. The chemistry is in progress in our laboratory.

EXPERIMENTAL

General Experimental and Physical Measurements

All manipulations were carried out in an argon atmosphere under anaerobic conditions using standard Schlenk, vacuum line and glove box techniques. The solvents were thoroughly dried, deoxygenated, and distilled in an argon atmosphere prior to use. The ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra were recorded with a Bruker DRX-600 spectrometer. IR measurements were carried out with a NICOLET 360 FT-IR spectrometer from Nujol mulls prepared in a dry box. Melting points were measured in sealed argon-filled capillaries without temperature correction with an apparatus XT4-100A (Electronic and Optical Instruments, Beijing). Elemental analyses were performed on an Elemental Vario EL3 (J&K Chemicals and Sigma-Aldrich, Germany) elemental analyzer by the Analytical Laboratory at Shanxi Normal University. Diffraction data of compounds **3a**,**b**,**d**,**e**,**g** were collected

on a Stoe-Siemens four-circle diffractometer. Tris(trimethylsilyl)phosphine $P(SiMe_3)_3$ was prepared according to the literature.[22]

Syntheses

Preparation of Imidoyl Chlorides (1)[8a,25,30]. To a solution of the corresponding *N*,*N*-dimethylamide (125 mmol) in anhydrous ether (350 mL), oxalyl chloride (32 mL, 375 mmol) was slowly added by a syringe at room temperature under stirring. After gas evolution ceased the suspension was stirred for further 12 h and then filtered. The white solid was washed with anhydrous ether (3 × 100 mL) and dried in vacuo to afford *N*,*N*-dimethylimidoyl chloride **1** as pure solid.

Preparation of Asymmetrical 1,3-Bis(amino)-2-phosphaallyl Chlorides (2)[8a,25]. To a solution of mixed **1(R$_1$)** (15 mmol) and **1(R$_2$)** (15 mmol) in anhydrous acetonitrile (120 mL), tris(trimethylsilyl)phosphine $P(SiMe_3)_3$ (11 mL, 35 mmol)[22] was slowly added by a syringe within 1 h. After the solution was stirred for 10 h, the volatile components were removed in high vacuum (0.01 mm Hg). The resulting residue was washed with anhydrous ether (3 × 20 mL) to give **2** as dark orange solid, which was used without further purification.

Synthesis of Asymmetrical 1H-1,2,4-diazaphospholes (3)[8a,25]. To a solution of **2** (30.0 mmol) in trichloromethane (90 mL), anhydrous hydrazine (5.5 mL, 165 mmol) was slowly added. The color changed immediately from orange to gray. The reaction mixture was stirred for 24 h at room temperature, and then heated to reflux for 12 h. After the volatile components were removed under reduced pressure, the residue was extracted with ether (5 × 30 mL). The combined organic layers were washed with water (2 × 100 mL), dried with $MgSO_4$, and filtered. The solvent of the filtrate was removed under reduced pressure and the resulting white solid was purified by column chromatography on silica-gel using ethylacetate / petroleum ether (6:9) as an eluent to afford **3** as pure white solid. The physical and spectroscopic data of compounds **3a**,**b**,[19a,b] **3d**,[27] and **3e**[19a,b] are identical to those reported previously.

1*H*-3-tert-Butyl-1,2,4-diazaphosphole (3a). The crude product was purified on silica-gel using ethylacetate/petroleum (10:1) as eluent. Yield: 1.05 g (24.0%). M.p. 75−76°C. ^{1}H NMR (600 MHz, $CDCl_3$, 23°C): δ = 11.0 (s, br., 1H, N*H*), 8.52 (d, $^2J_{PH}$ = 43.2 Hz, 1H, C*H*), 1.43 (d, $^3J_{PH}$ = 6.0 Hz, 9H, *t*-Bu); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 23°C): δ = 189.8 (d, $^1J_{PC}$ = 63.0 Hz, N=*C*Bu), 159.8 (d, $^1J_{PC}$ = 73.5 Hz, P=*C*H), 35.1 (d, $^2J_{PC}$ = 15.0 Hz, *C*(CH_3)$_3$), 31.93 (d, $^3J_{PC}$ = 6.0 Hz, *C*H_3); ^{31}P NMR (243 MHz, $CDCl_3$, 23°C): δ = 76.7 (d, $^2J_{PH}$ = 42.5 Hz); anal. calcd for $C_6H_{11}N_2P$: C, 50.70; H, 7.80; N, 19.71. Found: C, 50.81; H, 7.83; N, 19.65%. Single crystals suitable for X-ray diffraction analysis were obtained by sublimation of the crude product at 40°C under high vacuum.

1*H*-3-tert-Butyl-5-methyl-1,2,4-diazaphosphole (3b). The crude product was purified through column chromatography (ethylacetate/petroleum, 1:6) as eluent. Yield: 1.74 g (37.0%). M.p. 115−118°C. ^{1}H NMR (600 MHz, $CDCl_3$, 23°C): δ = 10.4 (s, br., 1H, N*H*), 2.59 (d, $^3J_{PH}$ = 9.6 Hz, 3H, C*H*$_3$), 1.41 (d, $^4J_{PH}$ = 1.2 Hz, 9H, *t*-Bu); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 23°C): δ = 191.2 (d, $^1J_{PC}$ = 60.0 Hz, N=*C*Bu), 173.2 (d, $^1J_{PC}$ = 55.5 Hz, P=*C*CH_3), 35.3 (d, $^2J_{PC}$ = 13.5 Hz, PC*C*HCH_3), 31.8 (d, $^3J_{PC}$ = 6.0 Hz, C(*C*H_3)$_3$), 29.7 (s, *C*(CH_3)$_3$), 15.9 (d, $^2J_{PC}$ = 22.5 Hz, PC*C*H_3); ^{31}P NMR (243 MHz, $CDCl_3$, 23°C): δ = 74.5 (q, $^3J_{PH}$ = 9.5 Hz); anal. calcd for $C_7H_{13}N_2P$: C,

53.84; H, 8.39; N, 17.94. Found: C, 53.89; H, 8.30; N, 17.99 %. Single crystals suitable for X-ray diffraction analysis were obtained by sublimation at 70°C under high vacuum.

1*H*-3-tert-Butyl-5-isopropyl-1,2,4-diazaphosphole (3c). The crude product was purified through column chromatography (petroleum/ethylacetate 16:1) as eluent. Yield: 2.34 g (42 %). M.p. 138−139°C. ^{1}H NMR (600 MHz, $CDCl_3$, 23°C): $\delta = 11.0$ (br., 1H, N*H*), 3.20 (m, 1H, C*H*CH_3), 1.42 (d, $^{4}J_{PH} = 3.0$ Hz, 9H, *t*-Bu), 1.37 (d, $^{3}J_{HH} = 6.6$ Hz, 6H, CHC*H*$_3$); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, 23°C): $\delta = 189.5$ (d, $^{1}J_{PC} = 60.0$ Hz, N=*C*Bu), 182.3 (d, $^{1}J_{PC} = 57.0$ Hz, *C*CH), 31.81 (d, $^{2}J_{PC} = 6.0$ Hz, *C*$(CH_3)_3$), 24.4 (d, $^{2}J_{PC} = 6.0$ Hz, *C*H); ^{31}P NMR (243 MHz, $CDCl_3$, 23°C): $\delta = 66.7$ (d, $^{3}J_{PH} = 5.4$ Hz); anal. calcd for $C_9H_{17}N_2P$: C, 58.68; H, 9.30; N, 15.21; P, 16.81. Found: C, 58.84; H, 9.26; N, 15.31%.

1*H*-3-Phenyl-1,2,4-diazaphosphole (3d). The residue was purified by column chromatography (petroleum/ethylacetate 6:1) to yield **3d** as white solid (0.98 g, 20 %). M.p. 70−71°C. ^{1}H NMR (600 MHz, $CDCl_3$, 23°C): $\delta = 8.74$ (d, $^{2}J_{PH} = 40.2$ Hz, 1H, P=C*H*), 7.86 (d, $^{3}J_{HH} = 8.4$ Hz, 2H, *o*-H), 7.38−7.43 (m, 3H, *m*,*p*-H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, 23°C): $\delta = 207.3$ (d, $^{1}J_{PC} = 60.0$ Hz, P=*C*Ph), 177.5 (d, $^{1}J_{PC} = 56.0$ Hz, P=*C*H), 158.5 (s, *C*Ph), 136.6 (s, Ph), 129.4 (s, Ph), 128.4 (s, Ph), 126.4 (s, Ph); ^{31}P NMR (243 MHz, $CDCl_3$, 23°C): $\delta = 80.3$ (d, $^{2}J_{PH} = 41.3$ Hz); anal. calcd for $C_8H_7N_2P$: C, 59.27; H, 4.35; N, 17.28. Found: C, 59.18; H, 4.28; N, 17.34 %. Single crystals suitable for X-ray diffraction analysis were sublimed at 60°C under high vacuum.

1*H*-3-Phenyl-5-tert-butyl-1,2,4-diazaphosphole (3e). The crude product was purified by column chromatography (petroleum/ethyl acetate 20:1) as eluent. Yield: 2.87 g (44 %). M.p. 78−79°C. ^{1}H NMR (600 MHz, $CDCl_3$, 23°C): $\delta = 11.5$ (br., 1H, N*H*), 7.80 (d, $^{3}J_{HH} = 8.4$ Hz, 2H, *o*-H) 7.35−7.81 (m, 3H, *m*,*p*-H), 1.48 (d, $^{4}J_{PH} = 6.0$ Hz, 9H, *t*-Bu); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, 23°C): $\delta = 190.0$ (d, $^{1}J_{PC} = 61.0$ Hz, N=*C*Bu), 177.5 (d, $^{1}J_{PC} = 56.0$ Hz, P=*C*H), 126.2 (d, $^{3}J_{PC} = 9.0$ Hz, Ph), 128.9 (s, Ph), 31.8 (d, $^{2}J_{PC} = 6.0$ Hz, *C*$(CH_3)_3$), 29.4 (d, $^{3}J_{PC} = 1.5$ Hz, C(*C*$H_3)_3$); $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$, 23°C): $\delta = 71.3$; anal. calcd for $C_{12}H_{15}N_2P$: C, 66.04; H, 6.93; N, 12.84. Found: C, 65.88; H, 7.01; N, 12.95 %. Single crystals suitable for X-ray diffraction analysis were obtained by crystallization from ether.

1*H*-3-tert-Butyl-5-furanyl-1,2,4-diazaphosphole (3f). The crude product was purified on silica-gel using a mixture of *n*-hexane and EtOAc (1:1) as eluent. Yield: 2.29 g (35.0 %). M.p. 161°C. ^{1}H NMR (600 MHz, $CDCl_3$, 23°C): $\delta = 11.5$ (s, br., 1H, N*H*), 7.47 (d, $^{3}J_{HH} = 3.6$ Hz, 1H, *C*H on the furanyl ring), 7.31 (d, $^{3}J_{HH} = 4.8$ Hz, 1H, *C*H on the furanyl ring), 7.08 (dd, $^{3}J_{HH} = 3.6$ Hz, $^{3}J_{HH} = 4.8$ Hz, 1H, *C*H on the furanyl ring), 1.51 (d, $^{4}J_{PH} = 0.6$ Hz, 9H, C(C$H_3)_3$); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, 23°C): $\delta = 142.3$ (d, $^{2}J_{PC} = 4.5$ Hz, P=C–*C*, furyl ring), 110.8 (s, furyl ring), 107.6 (s, furyl ring), 31.8 (s, *C*$(CH_3)_3$), 31.7 (s, C(*C*$H_3)_3$); $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$, 23°C): 70.7. Single crystals suitable for X-ray diffraction analysis were obtained by sublimation at 130°C under high vacuum.[31]

1*H*-3-tert-Butyl-5-thienyl-1,2,4-diazaphosphole (3g). The crude product was purified on silica-gel using a mixture of *n*-hexane and EtOAc (1:1) as eluent. Yield: 2.02 g (30 %). M.p. 154°C. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.44$ (d, $^{3}J_{HH} = 2.4$ Hz, 1H, on the thienyl ring), 7.26 (d, $^{3}J_{HH} = 4.2$ Hz, 1H, on the thienyl ring), 7.03 (dd, $^{3}J_{HH} = 4.0$ Hz, $^{3}J_{HH} = 2.4$ Hz, 1H, on the thienyl ring), 1.46 (d, $^{4}J_{PH} = 0.6$ Hz, 9H, C(C$H_3)_3$). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, 23°C): $\delta = 127.6$ (d, $^{3}J_{PC} = 1.5$ Hz, P=C–*C*, thienyl ring), 125.4 (s, thienyl ring), 125.3 (s, thienyl ring), 31.7 (s, *C*$(CH_3)_3$), 31.6 (s, C(*C*$H_3)_3$). $^{31}P\{^{1}H\}$ NMR

(243 MHz, $CDCl_3$, 23°C): $\delta = 70.6$. Single crystals suitable for X-ray diffraction analysis were obtained by sublimation at 120°C under high vacuum.

X-ray Crystallography. The single crystal X-ray diffraction data of **3** were collected using a Bruker SMART CCD diffractometer operating at 50 kV and 20 mA using Mo-Kα radiation ($\lambda = 0.71073$ Å). An empirical absorption correction was applied using the SADABS program. The structures were solved by direct methods, and all nonhydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using the SHELXTL package.[28]

CCDC 940090(**3a**), 940091(**3b**), 940094(**3d**), 940092(**3e**), and 940093(**3g**) contain the supplementary crystallographic data for compounds **3**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: data_request@ccdc.cam.ac.uk.

ACKNOWLEDGMENT

Liu thanks Dr. Hongbo Tong (Shanxi University) for the help with X-ray diffraction analysis.

FUNDING

We gratefully acknowledge financial support from the Program for the Top Young and Middle-Aged Innovative Talents of Higher Learning Institutions of Shanxi (TYMIT 2011), the Doctoral Foundation of Chinese Education Ministry (grant no. 20111404110001), National Natural Science Foundation of China (NSFC; grant no. 21272143), the Program for Changjiang Scholar and Innovative Research Team in University (IRT1156), State R&D Program of China (no. 2012BAE06B08), the State Key Laboratory of Advanced Technology for Comprehensive Utilization of Platinum Metals, Scientific and Technological Innovation Programs of Higher Education Institutions in Shanxi (STIP 20120016), Natural Science Foundation of Shanxi (grant no. 2013011011-2), and Natural Science Foundation of Shanxi Normal University (grant no. 872018).

SUPPLEMENTAL MATERIAL

Supplementary data for this article can be accessed on the publisher's website, www.tandfonline.com/gpss.

The X-ray crystallographic data, spectroscopic data, and the crystallographic plots of **3** are deposited in the Supporting Information.

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24. Note: The formation of two additional symmetric 1*H*-3,5-substituted 1,2,4-diazaphospholes H[3,5-R_1R_1dp] and H[3,5-R_2R_2dp] indicates moderate yields of **3** due to the presence of the two symmetric 1,3-bis(amino)-2-phosphaallyl chlorides in the system. The ^{31}P NMR data of the unsymmetrical phosphaallylic salts are not reliable for publication due to incomplete separation.
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31. Note: The quality of the crystallographic data of tetrameric **3f** is not warranted for publication due to the disorder of *t*Bu group, but the structural connections are reliable: $C_{10}H_{13}N_2OP$, $Mr = 208.19$, tetragonal, space group $I4(1)/a$, $a = 19.6212(4)$ Å, $b = 19.6212(4)$ Å, $c = 11.9224(5)$ Å, $\alpha = \beta = \gamma = 90^\circ$.