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Synthesis of Bis(imidazole-2-thion-4-yl)phosphanes

Susanne Sauerbrey,[1] Paresh Kumar Majhi,[1] Sebastian Schwieger,[1] Anthony J. Arduengo III,[2] and Rainer Streubel[1]

[1]*Institut für Anorganische Chemie, Rheinische Friedrich-Wilhelms-Universität Bonn, D-53121 Bonn, Germany*

[2]*Department of Chemistry, University of Alabama, Tuscaloosa, AL 35487*

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ABSTRACT: *Novel bis(imidazole-2-thion-4-yl)-phosphanes (***2a–d***) were synthesized via lithiation of the precursor imidazole-2-thiones followed by the phosphanylation reaction. Oxidation of bis(imidazole-2-thion-4-yl)phosphane* **2b–d** *with elemental sulfur and selenium led selectively and in good yields to the P-thio (***3b–d***) and P-seleno (***4c***) derivatives of bis(imidazole-2-thion-4-yl)phosphanes, respectively. The treatment of* **2a,c** *with phosphorus trichloride gives the corresponding P-chloro derivatives* **5a,c**. *These compounds were unambiguously characterized by elemental analyses, spectroscopic and spectrometric methods, in addition by single-crystal X-ray structure analysis in the case of* **2d**.
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INTRODUCTION

The importance of imidazole **I** and imidazole-2-thione **II** derivatives (see Fig. 1) both in the field of biologically active compounds such as antibacterial [1], anti-inflammatory [2,3], analgesic [3], antitumor [4,5], anticancer activities [6] etc., and in organic synthesis is well documented [7–10]. The synthetic access to various *C*-phosphorylated five-membered N-heterocycles via electrophilic phosphorylation with P(III) halides is known [10–13]. The coordination of phosphanes to metals and the spectroscopic properties of phosphorus are two important aspects of this chemistry [14]. Furthermore, it has been demonstrated that 1-methyl-imidazoles substituted at the C^2 carbon center can be functionalized at position five (C^5) with a phosphorus-containing group **IV** [15,16]. Recently, we showed that imidazole-2-thiones can also be functionalized at the C^4 position with phosphorus-containing groups **V** in a similar fashion [17]. Kuhn demonstrated an efficient synthetic route to N-heterocyclic carbene (NHCs) **III** by the reduction of imidazole-2-thione **II** with potassium in boiling tetrahydrofuran [18]. Recently, Gates and colleagues [19] and Bertrand and coworkers [20] reported the first examples of C^4-phosphanyl substituted NHCs **VI**. Two (1-methyl-2-R-imidazoles) were also added on the phosphorus center, resulting in structures **VII** and **VIII** [16]. The compounds of type **VIII** could be used to synthesize tripodal ligands [21], which shows interesting coordination properties and can act as a model ligand for enzymatic activities. Herein, we present the synthesis of a series of bis(imidazole-2-thion-4-yl) phosphanes.

Correspondence to: Anthony J. Arduengo III; e-mail: aj@ajarduengo.net. Rainer Streubel; e-mail: r.streubel@uni-bonn.de.
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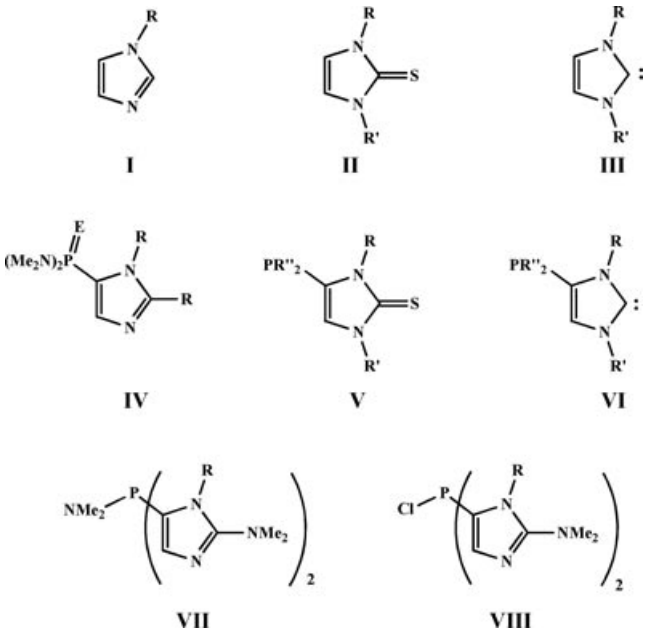
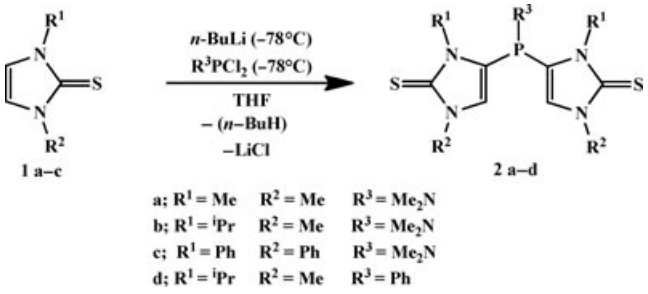


FIGURE 1 Imidazoles (**I**), imidazole-2-thiones (**II**), imidazol-2-ylidenes (**III**), and selected phosphorus derivatives **IV–VIII.**

RESULTS AND DISCUSSION

The imidazole-2-thione derivatives **1a–c,** used in this study, were synthesized according to the reported procedures [22]. The imidazole-2-thiones were deprotonated in tetrahydrofuran with ^{n}BuLi at –78°C and allowed to react with 0.5 equiv of dichloro(organo)phosphane to afford bis(imidazole-2-thione) phosphanes **2a–d** (Scheme 1) selectively. The ^{31}P NMR chemical shifts and $^{3}J_{PH}$ coupling constants to the NMe_2 and *ortho*-phenyl protons for **2a–d** are provided in Table 1. ^{1}H NMR spectra revealed small couplings to the C^5H and none to the N^3-Me protons.

Single-crystal X-ray diffraction structure analysis was performed for compound **2d**. The crystal was obtained from a saturated toluene solution at low temperature (–20°C). Compound **2d** crystallizes



SCHEME 1 Synthesis of compounds **2a–d**.

TABLE 1 $^{31}P\{^{1}H\}$ NMR Chemical Shifts and Coupling Constants for Compounds **2a–d**

	2a	*2b*	*2c*	*2d*
^{31}P NMR ($CDCl_3$)				
δ (ppm)	14.4	16.1	16.8	–57.2
$^{3}J_{PH}$ (Hz)	10.2	10.0	9.3	8.4

in a triclinic lattice with space group *P*ī. Selected structural parameters are given in Table 2. Crystallographic data are presented in Table 3. The structure and numbering scheme for **2d** is shown in Fig. 2 (the disordered toluene solvate unit is omitted for clarity).

Compounds **2a–d** can be converted into P(V) derivatives **3b–d**, **4c** by using classical oxidation methods (Scheme 2). The reactions of compounds **2b–d** with elemental sulfur and selenium appeared quantitative according to ^{31}P NMR spectroscopic monitoring. The *P*-thio (**3b–d**) and *P*-seleno (**4c**) phosphorylated bis(imidazole-2-thiones) crystallized from the reaction mixtures and thus could easily be obtained in a pure form. The analytical data of phosphane sulfides and selenides are given in the Experimental section. For all P(V) derivatives described herein, the ^{31}P NMR signal of **3b–d** and **4c** was shifted to lower field compared to the parent phosphanes **2b–d**. The same tendencies were observed before in the series of imidazole-substituted phosphane chalcogens [16,23].

TABLE 2 Selected Bond Lengths and Angles for **2d**

Property	*Value*
Bond lengths (Å)	
C(1)–P(1)	1.817(2)
C(8)–P(1)	1.814(2)
C(15)–P(1)	1.834(2)
C(2)–S(1)	1.680(2)
C(9)–S(2)	1.688(2)
C(1)–N(1)	1.396(2)
C(8)–N(3)	1.398(2)
C(1)–C(3)	1.352(3)
C(8)–C(10)	1.351(3)
Bond angles (deg)	
C(8)-P(1)-C(1)	101.05(8)
C(8)-P(1)-C(15)	98.58(9)
C(1)-P(1)-C(15)	102.45(9)
C(3)-C(1)-P(1)	133.3(2)
C(10)-C(8)-P(1)	128.5(1)
N(1)-C(2)-N(2)	105.0(2)
N(3)-C(9)-N(4)	106.1(2)
C(1)-C(3)-N(2)	108.4(2)
C(8)-C(10)-N(4)	108.4(2)

TABLE 3 Crystallographic data for **2d**·1/2C_7H_8

Crystal system	Triclinic
Space group	*P* -1
A (Å)	10.5360(7)
b (Å)	11.0711(7)
c (Å)	11.7759(7)
α (°)	65.072(5)
β (°)	81.417(5)
γ (°)	87.247(5)
V (Å^3)	1231.5(1)
Z	1
d_c (g cm^{-3})	1.253
μ(mm^{-1})	0.299
F(000)	494
Crystal size (mm)	0.35 × 0.15 × 0.09
Reflections collected	12465
Reflections unique	5930
Mo Kα radiation (λ, Å)	0.71073
Final *R* indices (R1)	0.0409
*wR*2	0.0867
R indices (all data) *R*1	0.0722
*wR*2	0.0932
GOF	0.856
Parameters	314

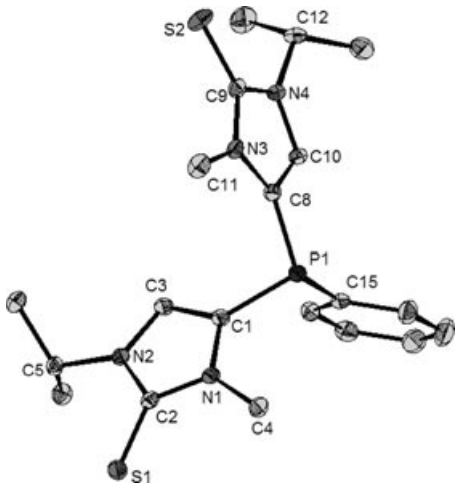
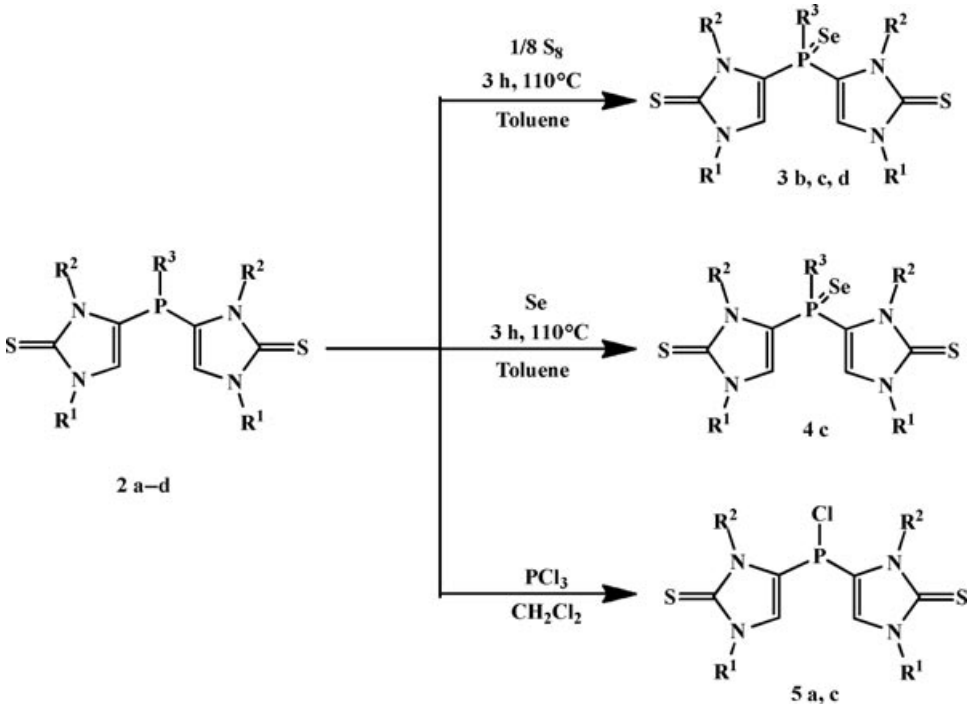


FIGURE 2 Molecular structure of **2d** (at a 30% probability level).

Attempted preparation of the bis(imidazole-2-thion-4-yl)phosphinous chloride analogous to **5a,c** by phosphorylation of imidazole-2-thiones **1a,c** with phosphorus trichloride in a 2:1 ratio resulted in a mixture of mono-, bis-, and tris(imidazole)-substituted phosphane derivatives. Therefore, another synthetic methodology was followed by reacting **2a,c** with a stoichiometric amount of phosphorus trichloride to yield **5a,c** as yellow solids (Scheme 2). The analytical data of **5a,c** are given in the Experimental section. Compounds **5a,c** have ^{31}P NMR chemical shifts similar to their **2a,c** analogs, i.e., 22.6 (**5a**) and 19.9 (**5c**).



SCHEME 2 Synthesis of P(V) and *P*-chloro derivatives (for abbreviation of **a–d** (see Scheme 1).

CONCLUSIONS

A synthetic methodology was developed to synthesize a series of bis(imidazole-2-thion-4-yl)-phosphanes. The oxidation of bis(imidazole-2-thion-4-yl)phosphanes occurred selectively to yield the corresponding P^V-E products (E = S, Se) **3b–d** and **4c** was firmly established by spectroscopic and spectrometric methods. The treatment of **2a,c** with phosphorus trichloride leads to corresponding *P*-chloro derivatives **5a,c**. This synthetic route is amenable to the preparation of multigram quantities of product in a linear fashion. The new phosphanyl- and phosphoryl-substituted bis(imidazole-2-thione) could be of interest in the synthesis of backbone functionalized imidazol-2-ylidenes.

EXPERIMENTAL

General Considerations

The synthesis of the imidazole-2-thiones and the lithiation reactions were performed under argon, using common Schlenk techniques and dry solvents. Tetrahydrofuran was dried over sodium wire/benzophenone, dichloromethane over calcium hydride, and further purified by subsequent distillation. All used phosphanes were distilled prior to use and stored under argon. All other chemicals were used as received. 1,3-Dimethylimidazole-2-thione (**1a**) [22a], 1-isopropyl-3-methyl-imidazole-2-thione (**1b**) [22b], and 1,3-diphenylimidazole-2-thione (**1c**) [22c] were synthesized following literature protocols. All NMR spectra were recorded on a Bruker (Germany) AX-300 spectrometer (300.1 MHz for ^{1}H, 75.5 MHz for ^{13}C, 121.5 MHz for ^{31}P). The ^{1}H and ^{13}C spectra were referenced to the residual proton resonance and the ^{13}C signals of the deuterated solvents, ^{31}P to 85% H_3PO_4 as external standard, respectively. Melting points were determined in one-side melted off capillaries using a Büchi type S or a Carl Roth type MPM-2 apparatus (Germany), and they are uncorrected. Elemental analyses were carried out on a Vario EL gas chromatograph (Germany). Mass spectrometric data were collected on a Kratos MS 50 spectrometer (Germany) using EI, 70 eV. The infrared spectra were recorded on a Nicolet 380 FT-IR spectrometer (Germany) using KBr pellets. The single-crystal X-ray analysis was performed on a STOE IPDS2T diffractometer (Germany) (Mo Kα radiation, graphite monochromator) at 123(2) K. The structure was solved by direct methods and refined by full-matrix least-squares technique in an anisotropic approximation for non-hydrogen atoms using SHELXS97 and SHELXL97 [24] program packages. Hydrogen atoms were calculated on idealized positions and refined isotropically by using a riding model.

Typical Lithiation and Phosphanylation Protocol for the Synthesis of **2a-d**

In a Schlenk flask, the imidazole-2-thiones **1a–c** (10 mmol) were dissolved in tetrahydrofuran (100 mL) and cooled to –78°C, *n*-butyl lithium (1.6 M in *n*-hexane, 17 mL, 11 mmol) was then added, and the reaction mixture was slowly warmed to –40°C; it was stirred for 2 h at this temperature. The reaction mixture was cooled again to –78°C, the dichlorophosphane (Me_2NPCl_2 or $PhPCl_2$) (5 mmol) was then added, and the reaction mixture was stirred for about 18 h while warming to ambient temperature. It was then concentrated in vacuo (8×10^{-3} mbar), and the residue was taken up in dichloromethane and filtered over celite to remove lithium chloride. The filtrate was collected, and the solvent was removed in vacuo (8×10^{-3} mbar). The crude product was then purified via crystallization from hot toluene (**2a–d**). Colorless to light yellow crystals were obtained.

*Bis(1,3-dimethyl-imidazole-2-thion-4-yl)-dimethylaminophosphane (**2a**).* Yield: 2.42 g (62%), white solid, mp 179°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.60 (d, $J_{P,H}$ = 0.8 Hz, 2H, C^5-H), 3.55 (s br, 6H, N^3-CH_3), 3.52 (s br, 6H, N^1-CH_3), 2.65 (d, $J_{P,H}$ = 10.2 Hz, 6H, P-N-CH_3). ^{13}C{^{1}H} NMR (75.0 MHz, $CDCl_3$): δ 165.5 (s, C=S), 125.3 (d, $J_{P,C}$ = 8.0 Hz, C^4), 122.8 (d, $J_{P,C}$ = 0.8 Hz, C^5), 40.8 (d, $J_{P,C}$ = 16.0 Hz, P-N-CH_3), 35.2 (s, N^1-CH_3), 33.5 (d, $J_{P,C}$ = 9.6 Hz, N^3-CH_3). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 14.4. MS (EI, 70 eV): *m/z* (%) 329 (100) $[M]^{\bullet+}$, 285 (72) $[M - N(CH_3)_2]^+$, 212 (4) $[M - N(CH_3)_2\text{-}2S\text{-}CH_3]^+$. HR-ESI-MS: found: 352.0790, calcd 352.0790 as $C_{12}H_{20}N_5PS_2Na^+$. IR (KBr, cm^{-1}): ν = 3154, 3065, 1574, 1492, 1389, 1181, 664. EA: calcd C 43.75, H 6.12, N 21.26, S 19.47; found: C 43.98, H 6.16, N 20.93, S 19.68.

*Bis(1-isopropyl-3-methyl-imidazole-2-thion-4-yl)-dimethylaminophosphane (**2b**).* Yield: 5.65 g (92%), white solid, mp 135°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.05 (s, 2H, C^5-H), 5.05 (hept, $J_{H,H}$ = 6.8 Hz, 2H, C_3H_7-C*H*), 3.54 (s, 6H, N^3-CH_3), 2.63 (d, $J_{H,H}$ = 10.0 Hz, 6H, P-N-CH_3), 1.31 (d, $J_{H,H}$ = 6.8 Hz, 12H, C_3H_7-CH_3). ^{13}C{^{1}H} NMR (75.0 MHz, $CDCl_3$): δ 165.5 (d, $J_{P,C}$ = 1.1 Hz, C=S), 126.1 (d, $J_{P,C}$ =

8.4 Hz, C^4), 125.6 (d, $J_{P,C}$ = 1.9 Hz, C^5), 49.6 (s, C_3H_7-CH), 41.3 (d, $J_{P,C}$ = 16.3 Hz, P-N-CH_3), 33.6 (d, $J_{P,C}$ = 10.2 Hz, N^3-CH_3), 22.2 (d, $J_{P,C}$ = 8.5 Hz, N^1-$C_3H_7-CH_3$). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ16.1. MS (EI, 70 eV): *m/z* (%) 385 (100) $[M]^{\bullet+}$, 341 (88) $[M - N(CH_3)_2]^+$, 299 (37) $[M - 2(C_3H_7)]^+$, 257 (16) $[C_8H_{14}N_3PS]^+$, 230 (10) $[C_9H_{17}N_3PS]^+$, 91 (100) $[C_5H_5N_2]^+$, 65 (14) $[C_3HN_2]^+$. HR-MS: found: 385.1522, calcd 385.1535. IR (KBr, cm^{-1}): ν = 3107, 3055, 2970, 1555, 1434, 1406, 1189, 673. EA: calcd C 49.85, H 7.32, N 18.17, S 16.63; found: C 49.93, H 7.47, N 18.33, S 16.70.

*Bis(1,3-diphenyl-imidazole-2-thion-4-yl) dimethylamino-phosphane (**2c**)*

Yield: 3.85 g (78%), white solid, mp 217°C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.54–7.16 (m, 20H, C_6H_5), 6.84 (s 2H, C^5-H), 2.38 (d, $J_{P,H}$ = 9.3 Hz, 6H, P-N-CH_3). $^{13}C\{^1H\}$ NMR (75.0 MHz, $CDCl_3$): δ 166.9 (s, C=S), 137.6 (s, N-*ipso*-Ph), 136.6 (s, N-*ipso*-Ph), 129.0 (s, N-Ph), 128.4 (s, N-Ph), 127.0 (d, $J_{P,C}$ = 12.5 Hz, C^4), 125.8 (s, N-Ph), 123.4 (s, C^5), 40.8 (d, $J_{P,C}$ = 19.1 Hz, P-N-CH_3). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ16.8. MS (EI, 70 eV): *m/z* (%) 577 (100) $[M]^{\bullet+}$, 533 (88) $[M - N(CH_3)_2]^+$, 326 (5) $[C_{17}H_{16}N_3PS]^+$, 251 (20) $[C_{15}H_{11}N_2S]^+$, 77(15) $[C_2H_7NP]^+$. HR-ESI-MS: found: 577.1519, calcd 577.1524. IR (KBr, cm^{-1}): ν = 3148, 3065, 1594, 1497, 1384, 1151, 691. EA: calcd C 66.53, H 4.89, N 12.12, S 11.10; found: C 66.24, H 4.73, N 12.02, S 11.01.

*Bis(1-isopropyl-3-methyl-imidazole-2-thion-4-yl)-phenylphosphane (**2d**)*

Yield: 5.90 g (88%), white solid, mp 108°C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.42–7.32 (m, 5H, C_6H_5), 6.26 (s, 2H, C^5-H), 5.03 (hept, $J_{H,H}$ = 6.8 Hz, 2H, C_3H_7-C*H*), 3.48 (s, 6H, N^3-CH_3), 1.26 (dd, $J_{H,H}$ = 6.8 Hz, $J_{P,H}$ = 5.3 Hz, 12H, C_3H_7-CH_3). $^{13}C\{^1H\}$ NMR (75.0 MHz, $CDCl_3$): δ 165.3 (s, C=S), 133.0 (d, $J_{P,C}$ = 21.2 Hz, C_6H_5), 130.8 (s, C_6H_5), 129.5 (d, $J_{P,C}$ = 7.9 Hz, C_6H_5), 129.2 (d, $J_{P,C}$ = 34.9 Hz, *ipso*-C_6H_5), 128.9 (d, $J_{P,C}$ = 6.7 Hz, C^4), 120.1 (d, $J_{P,C}$ = 5.2 Hz, C^5), 49.4 (s, C_3H_7-CH), 33.4 (d, $J_{P,C}$ = 9.5 Hz, N^3-CH_3), 21.7 (d, $J_{P,C}$ = 5.0 Hz, N^1-$C_3H_7-CH_3$). ^{31}P NMR$\{^1H\}$ (121.5 MHz, $CDCl_3$): δ –55.0. MS (EI, 70 eV): *m/z* (%) 418 (8) $[M]^{\bullet+}$, 320 (70) $[C_{15}H_{16}N_4PS_3]^+$, 263 (17) $[C_{13}H_{16}N_2PS]^+$, 221 (30) $[C_{10}H_9N_2PS]^+$, 91 (100) $[C_5H_5N_2]^+$. HR-MS: found: 418.1419, calcd 418.1414. IR (KBr, cm^{-1}): ν = 3140, 3052, 1548, 1434, 1371, 1182. EA: calcd C 57.39, H 6.50, N 13.39, S 15.32; found: C 57.21, H 6.43, N 13.25, S 15.22.

*Typical Procedure for the Generation of Phosphane Sulfides (**3b–d**) and Phosphane Selenide (**4c**)*

A solution of phosphanes **2b–d** (3 mmol) in toluene (10 mL) containing elemental sulfur or selenium (3 mmol) was heated for 3 h at 110°C. The reaction mixture was cooled down to ambient temperature. The product precipitated in the form of colorless crystals. The obtained crystals were washed with *n*-pentane and dried in vacuo (8×10^{-3} mbar).

*Bis(1-isopropyl-3-methyl-imidazole-2-thion-4-yl)-dimethyl-aminophosphane Sulfide (**3b**).* Yield: 4.4 g (95%), white solid, mp 205°C. ^1H NMR (300 MHz, $CDCl_3$): δ 6.94 (d,$J_{P,H}$ = 3.4 Hz, 2H, C^5-H), 5.05 (hept, $J_{H,H}$ = 6.8 Hz, 2H, C_3H_7-C*H*), 3.71 (s, 6H, N^3-CH_3), 2.74 (d, $J_{P,H}$ = 13.9 Hz, 6H, P-N-CH_3), 1.32 (dd, $J_{H,H}$ = 6.8 Hz, $J_{P,H}$ = 3,7 Hz, 12H, C_3H_7-CH_3). $^{13}C\{^1H\}$ NMR (75.0 MHz, $CDCl_3$): δ 166.2 (d, $J_{P,C}$ = 5.8 Hz, C=S), 122.0 (d, $J_{P,C}$ = 20.7 Hz, C^5), 120.8 (d, $J_{P,C}$ = 139.2 Hz, C^4), 48.7 (s, C_3H_7-CH), 36.2 (d, $J_{P,C}$ = 4.5 Hz, P-N-CH_3), 32.9 (d, $J_{P,C}$ = 9.5 Hz, N^3-CH_3), 20.9 (s, N^1-$C_3H_7-CH_3$). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 33.9. MS (EI, 70 eV): *m/z* (%) 417 (100) $[M]^{\bullet+}$, 341 (10) $[M - N(CH_3)_2]^+$, 299 (37) $[M^{\bullet+} - 2(C_3H_7]^+$, 257 (16) $[C_8H_{14}N_3PS]^+$, 248 (18) $[C_8H_{14}N_3PS_2]^+$. HR-MS: found: 417.1247, calcd 417.1239. IR (KBr, cm^{-1}): ν = 3119, 3064, 1546, 1438, 1409, 1187, 647. EA: calcd C 46.02, H 6.76, N 16.77, S 23.04; found: C 45.94, H 6.67, N 16.68, S 23.00.

*Bis(1,3-diphenyl-imidazole-2-thion-yl)-dimethylamino-phosphane Sulfide (**3c**).* Yield: 1.65 g (90%), white solid, mp 195°C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.49–7.09 (m, 20H, C_6H_5), 6.94 (d, $J_{P,H}$ = 3.5 Hz, 2H, C^5-H), 2.45 (d, $J_{P,H}$ = 15.1 Hz, 6H, P-N-CH_3). $^{13}C\{^1H\}$ NMR (75.0 MHz, $CDCl_3$): δ 169.8 (s, C=S), 136.9 (s, N-*ipso*-Ph), 136.2 (s, N-*ipso*-Ph), 129.5 (s, N-Ph), 129.0 (s, N-Ph), 127.9 (s, C^5), 125.6 (s, N-Ph), 120.8 (d, $J_{P,C}$ = 141.3 Hz, C^4), 37.3 (d, $J_{P,C}$ = 2.4 Hz, P-N-CH_3). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 35.9. HR-ESI-MS: found: 632.1149, calcd 632.1137 as $C_{32}H_{28}N_5PS_3Na^+$. IR (KBr, cm^{-1}): ν = 3132, 3057, 1595, 1403, 1169, 663. EA: calcd. C 63.03, H 4.63, N 11.49, S 15.78; found: C 62.81, H 4.49, N 11.21, S 15.62.

*Bis(1-isopropyl-3-methyl-imidazole-2-thion-4-yl)-phenyl-phosphane Sulfide (**3d**).* Yield: 6.5 g (81%), white solid, mp 198°C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.76–7.09 (m, 5H, C_6H_5), 6.53 (d, $J_{P,H}$ = 3.9 Hz, 2H, C^5-H), 5.04 (hept, $J_{H,H}$ = 6.4 Hz, 2H, C_3H_7-C*H*), 3.62 (s, 6H, N^3-CH_3), 1.27 (m br, 12H, C_3H_7-CH_3). $^{13}C\{^1H\}$ NMR (75.0 MHz, $CDCl_3$): δ 167.2

(d, $J_{P,C}$ = 5.3 Hz, C=S), 133.3 (d, $J_{P,C}$ = 3.3 Hz, C_6H_5), 131.6 (d, $J_{P,C}$ = 12.6 Hz, C_6H_5), 129.1 (d, $J_{P,C}$ = 13.9 Hz, Ph), 127.8 (d, $J_{P,C}$ = 97.4 Hz, *ipso*-C_6H_5), 122.4 (d, $J_{P,C}$ = 19.3 Hz, C^5), 119.4 (d, $J_{P,C}$ = 117.0 Hz, C^4), 49.5 (s, $C_3H_7 - CH$), 34.1 (s, N^3-CH_3), 21.4 (s, N^1-$C_3H_7 - CH$). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 10.5. MS (EI, 70 eV): *m/z* 450 (100) $[M]^{\bullet+}$, 418 (10) $[M - S]^+$, 352 (15) $[C_{15}H_{16}N_4PS_3]^+$, 250 (5) $[C_{10}H_9N_2PS_2]^+$, 221 (30) $[C_{10}H_9N_2PS]^+$. HR-MS: found: 450.1139, calcd 450.1127. IR (KBr, cm^{-1}): ν = 3121, 3068, 1548, 1436, 1378, 1186. EA: calcd C 53.31, H 6.04, N 12.43, S 21.35; found: C 53.20, H 6.13, N 12.38, S 21.37.

*Bis (1 , 3 - diphenyl - imidazole - 2 - thion - 4 - yl) - dimethylamino-phosphane Selenide (***4c***).* Yield: 1.81 g (92%), white solid, mp 190°C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.48–7.05 (m, 20H, C_6H_5), 6.87 (d br, $J_{P,H}$ = 3.8 Hz, 2H, C^5-H), 2.37 (d, $J_{P,H}$ = 16.5 Hz, 6H, P-N-CH_3). $^{13}C\{^1H\}$ NMR (75.0 MHz, $CDCl_3$): δ 169.5 (d, $J_{P,C}$ = 4.2 Hz, C=S), 136.8 (s, N-*ipso*-Ph), 136.0 (s, N-*ipso*-Ph), 129.6 (s, N-Ph), 129.0 (s, N-Ph), 128.8 (d, $J_{P,C}$ = 10.7 Hz, C^5), 125.6 (s, N-Ph), 119.0 (d, $J_{P,C}$ = 126.4 Hz, C^4), 38.1 (d, $J_{P,C}$ = 3.0 Hz, P-N-CH_3). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 29.3 ($J_{Se,P}$ = 807.4 Hz). MS (EI, 70 eV): *m/z* (%) 657 (65) $[M]^{\bullet+}$, 577 (55) $[M - Se]^+$, 533 (100) $[M - Se\text{-}N(CH_3)_2]^+$, 281 (100) $[C_{15}H_{11}N_2PS]^+$, 251 (68) $[C_{15}H_{11}N_2S]^+$. EA: calcd C 58.53, H 4.30, N 10.67, Se 12.02; found: C 58.39, H 4.22, N 10.53, Se 11.88.

Typical Procedure for the Generation of Chlorophosphanes **5a,c**

In separate Schlenk flasks, the phosphanes **3a,c** (1 equiv) were dissolved in dichloromethane (10 mL) and cooled to –20°C, 1 equiv of phosphorus trichloride was added to each and the reaction mixtures were warmed up to ambient temperature. The solvent was removed from each reaction in vacuo (8×10^{-3} mbar), and the crude products obtained were each washed several times with *n*-pentane and then dried in vacuo (8×10^{-3} mbar).

*Bis(1,3-dimethyl-imidazole-2-thion-4-yl)-chlorophosphane (***5a***).* Yield: 1.05 g (91%), orange solid, mp 129°C. ^1H NMR (300 MHz, $CDCl_3$): δ 6.90 (s br, 2H, C^5-H), 3.63 (s, 6H, N^1-CH_3), 3.58 (s br, 6H, N^3-CH_3). $^{13}C\{^1H\}$ NMR (75.0 MHz, $CDCl_3$): δ 168.1 (s, C=S), 126.7 (d, $J_{P,C}$ = 23.3 Hz, C^4), 121.6 (s, C^5), 35.6 (s, N^1-CH_3), 34.6 (s, N^3-CH_3). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 22.6. IR (KBr, cm^{-1}): ν = 3115, 1466, 1394, 1182, 461. MS (EI, 70 eV, ^{35}Cl): *m/z* (%) 320 (100) $[M]^{\bullet+}$, 285 (67) $[M - Cl]^{\bullet+}$, 193 (28) $[M - C_5H_7N_2S]^+$, 158 (31) $[M - Cl\text{-}C_5H_7N_2S]^+$. EA: calcd C 37.44, H 4.40, N 17.46, S 19.99; found: C 37.69, H 4.56, N 17.21, S 19.76.

*Bis (1 , 3 - diphenyl - imidazole - 2 - thion - 4 - yl) - chlorophosphane (***5c***).* Yield: 1.70 g (92%), orange solid, mp 249°C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.54–7.24 (m, 20H, C_6H_5), 6.90 (s br, 2H, C^5-H). $^{13}C\{^1H\}$ NMR (75.0 MHz, $CDCl_3$): δ 168.3 (d, $J_{P,C}$ = 1.2 Hz, C=S), 137.0 (s, N-*ipso*-Ph), 135.8 (d, $J_{P,C}$ = 1.2 Hz, N-*ipso*-Ph), 129.4 (s, N-Ph), 129.1 (s, N-Ph), 129.0 (s, N-Ph), 128.7 (s, N-Ph), 127.0 (d, $J_{P,C}$ = 23.3 Hz, C^4), 125.6 (s, N-Ph), 122.3 (s, C^5). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 19.9. MS (EI, 70 eV, ^{35}Cl): *m/z* (%) 568 (100) $[M]^{\bullet+}$, 533 (62) $[M - Cl]^+$, 317 (8) $[C_{15}H_{11}ClN_2PS]^+$, 281 (25) $[C_{15}H_{11}N_2PS]^+$, 251 (30) $[C_{15}H_{11}N_2S]^+$, 77 (40) $[C_6H_5]^+$. HR-ESI-MS: found: 568.0716, calcd 568.0712. IR (KBr, cm^{-1}): ν = 3116, 3062, 1385, 1168, 773, 762, 693, 471. UV/vis (Et_2O): λ_{max}: 209 nm. EA: calcd C 63.32, H 3.90, N 9.85, S 11.27; found: C 63.19, H 3.80, N 9.77, S 11.19.

SUPPLEMENTARY MATERIAL

Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 858986 and can be obtained free of charge on application to CCDC, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk.

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