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PAPER

Synthesis, structure and reactivity of 4-phosphanylated 1,3-dialkyl-imidazole-2-thiones†

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Selective formation of 4-phosphanylated 1,2-dialkyl imidazole-2-thiones **3a–f** has been obtained *via* a lithiation followed by phosphanylation reaction. The reactivity of **3a–f** was examined towards oxidation and complexation reactions. All products were unambiguously characterized by elemental analyses, spectroscopic and spectrometric methods including X-ray analysis (**3a**, **3b**, **4b**, **4d**, **5b**, **6a** and **6d**).

Introduction

Imidazole-2-thiones are a long known class of heterocyclic compounds,[1] which are of importance for chemical and pharmaceutical industry. Some of their applications include drugs treating hyperthyroidism like Methimazol or Carbimazol,[2,3] or catalyst in cross-linking of polymers,[4] complexation agents[5] and precursors of halogen-free ionic liquids[6] as well as stable *N*-heterocyclic carbenes.[7] Backbone-substituted imidazole-2-thiones include ring-anellated compounds,[8–10] those with nitrogen-containing substituents (amino,[11] azo,[12] imino[13]), oxygen-containing substituents (hydroxy,[14] methoxy[15]), and halogen-substituted compounds.[16] However, the access to a large library of imidazol-2-thione substituted phosphanes has not achieved considerable attention.

Results and discussion

In this paper we present the synthesis, structural characterization and reactivity of a series of 4-phosphanylated imidazole-2-thiones. Different imidazole-2-thiones, namely 1,3-dimethylimidazole-2-thione (**2a**),[19–23] 1,3-diphenylimidazole-2-thione (**2b**),[6] 1,3-diisopropylimidazole-2-thione (**2c**),[19] 1-isopropyl-3-methylimidazole-2-thione (**2d**),[25] 1-n-butyl-3-methylimidazole-2-thione (**2e**)[6] and 1-*tert*-butyl-3-methylimidazole-2-thione (**2f**),[26] were used as starting materials. Except for 1,3-diphenylimidazole-2-thione (**2b**), which was prepared following a literature protocol,[6] all imidazole-2-thiones **2a–f** were synthesized *via* the reaction of the corresponding imidazolium salts **1a–f**[19] with sodium hydride and elemental sulphur in the presence of catalytic amount of potassium *tert*-butoxide in tetrahydrofuran in good to very good yields (Scheme 1).[22] The obtained yields were increased in comparison to those reported in the literature, where the imidazole-2-thiones have been prepared using different bases[19,20,25] or different methodologies.[6,26]

Commonly used synthetic routes to the phosphorylated heterocycles[28,29] in pyridine–triethylamine mixtures proved to be unsuitable in the case of imidazole-2-thiones. Therefore another synthetic methodology to the imidazole-2-thione was followed by reacting **2a–f** with n-butyl lithium and then subsequently with diphenylchlorophosphane to yield the 4-phosphanylated imidazole-2-thiones **3a–f** (Scheme 1).[27] The completion of the reaction was monitored by ^{31}P NMR spectroscopy. After removal of the formed lithium chloride, the crude product were purified and isolated *via* recrystallization from hot toluene or diethyl ether–n-pentane mixtures as colorless to yellow solids (**3a–f**). The final products were unequivocally established by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy (see Experimental section). Analysis of the phosphanylated compounds by ^{31}P NMR spectroscopy confirms that only a single product is formed, which resonates in the chemical shift range of −31 ppm to −35 ppm with a coupling constant ($^{3}J_{P,H}$) range of 5 to 9 Hz depending upon the substituent at the both nitrogen centre of the imidazole-2-thione. The selective phosphanylation at the 4-position, might be due to steric reasons in the asymmetric substituted imidazole-2-thiones **2d** and **2f**. Only in the case of **2e**, a positional isomer, namely 1-n-butyl-3-methyl-5-diphenylphosphino-imidazol-2-thione **3e′**, was observed (ratio **3e** : **3e′** 2.3 : 1). In this case, the steric demand of the n-butyl group was probably not bulky enough to prevent the lithiation followed by phosphanylation at C^{5} position.

X-ray single-crystal structure analysis was performed for the compounds **3a** and **3b**. The crystals were obtained from toluene at low temperature. These two compounds crystallized isostructurally in the monoclinic crystal system, with different space group $P2_1/c$ for **3a** and $P2_1/n$ for **3b**. The selected bond parameters were given in the figure caption of the corresponding

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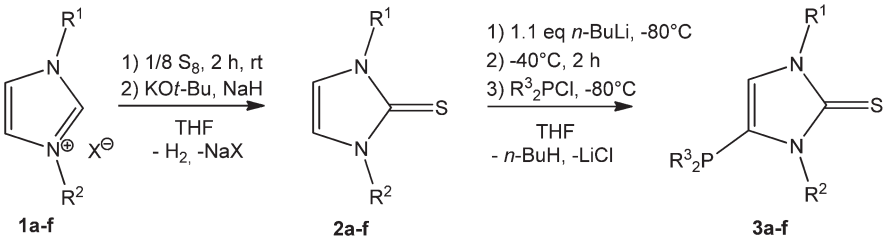
†Electronic supplementary information (ESI) available: CCDC 859623 (**3a**), 859624 (**3b**), 859625 (**4b**), 859626 (**4d**), 859627 (**5b**), 859628 (**6d**) and 859812 (**6a**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt12483a



a: R^1 = Me, R^2 = Me, R^3 = Ph
b: R^1 = Ph, R^2 = Ph, R^3 = Ph
c: R^1 = *i*-Pr, R^2 = *i*-Pr, R^3 = Ph
d: R^1 = *i*-Pr, R^2 = Me, R^3 = Ph
e: R^1 = *n*-Bu, R^2 = Me, R^3 = Ph
f: R^1 = *t*-Bu, R^2 = Me, R^3 = Ph

Scheme 1 Synthesis of P-functional imidazole-2-thiones.

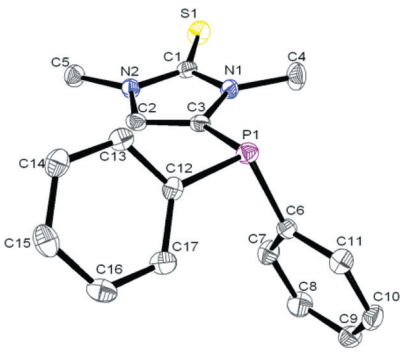


Fig. 1 Molecular structure of compound **3a**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): C(1)–N(1) 1.360(2), C(1)–N(2) 1.363(2), C(2)–C(3) 1.349(2), C(4)–N(1) 1.452(2), C(1)–S(1) 1.6821(18), P(1)–C(3) 1.8185(18), P(1)–C(6) 1.8368(18), P(1)–C(12) 1.8287(19); C(3)–P(1)–C(6) 102.23(8), C(3)–P(1)–C(12) 98.22(8), N(1)–C(3)–P(1) 121.81(13), C(6)–P(1)–C(12) 103.40(8).

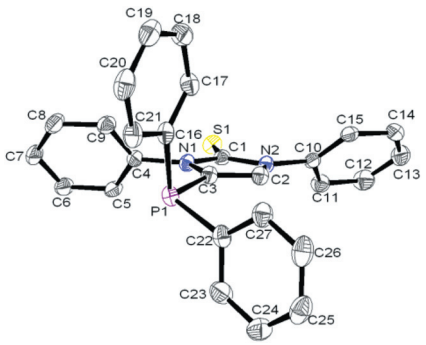


Fig. 2 Molecular structure of compound **3b**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): C(1)–N(1) 1.373(2), C(1)–N(2) 1.3773(19), C(2)–C(3) 1.352(2), C(4)–N(1) 1.4419(19), C(1)–S(1) 1.6683(16), P(1)–C(3) 1.8190(5), P(1)–C(6) 1.8318(16), P(1)–C(22) 1.8337(17); C(3)–P(1)–C(16) 102.53(7), C(3)–P(1)–C(22) 99.42(7), N(1)–C(3)–P(1) 122.42(11), C(16)–P(1)–C(22) 102.26(7).

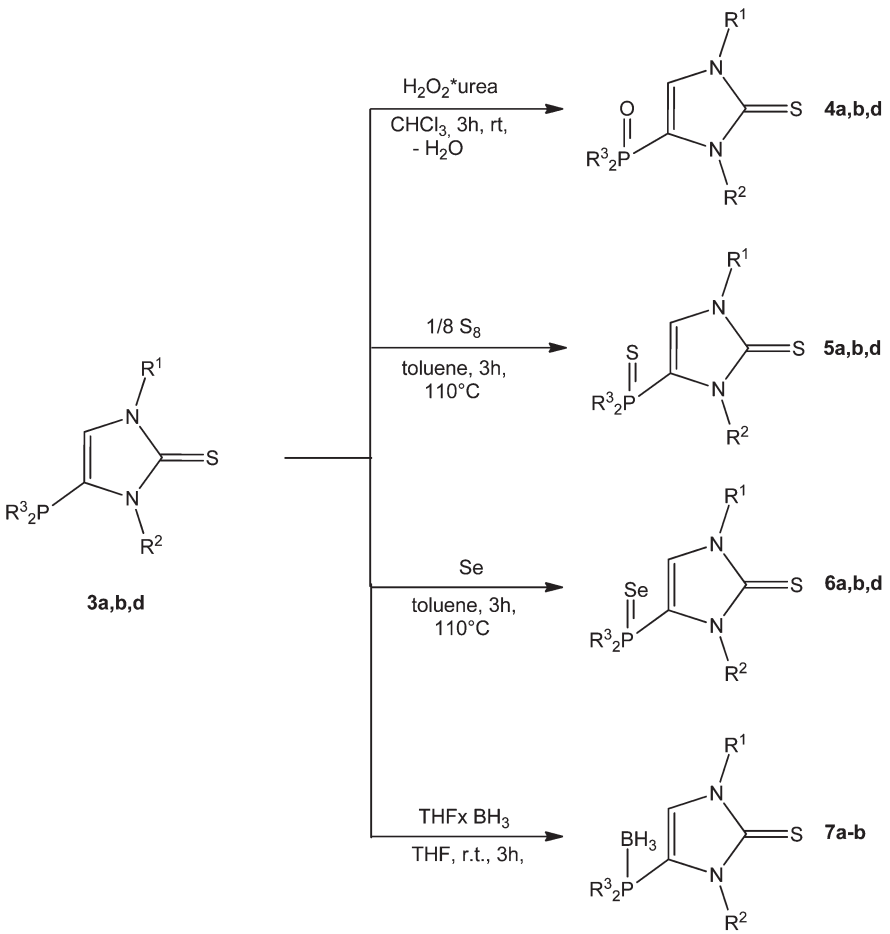
compounds. For crystallographic data see Table S1 (ESI†). The structure and numbering scheme for **3a** and **3b** are shown in Fig. 1 and 2 respectively. Despite that, the structure of **3a** and **3b** are the first report of a diphenylphosphino substituted imidazole-2-thione derivative, structural parameters shall not be discussed further as bond lengths and angles are in the common range for diphenylphosphino substituted heterocycles.[31]

To study the reactivity of **3a,b,d**, various oxidation and complexation reactions were performed as described in Scheme 2. The reactions of compound **3a,b,d** with H_2O_2–urea adduct, elemental sulphur and selenium were quantitative according to ^{31}P NMR spectroscopy. However elemental tellurium did not react with **3a,b,d** under the same condition as of **5a,b,d**. All phosphane oxides **4a,b,d** were recrystallized from hot toluene and obtained as white solid. The thio (**5a,b,d**) and seleno (**6a,b,d**) phosphorylated imidazole-2-thione were crystallized out of the reaction mixtures and thus could easily be obtained in pure form. The analytical data of phosphane oxides, sulfides and selenides are given in the Experimental section. As expected for P^V derivatives the ^{31}P NMR signal of **4a,b,d–6a,b,d** was shifted to lower field compared to phosphane **3a,b,d**, whereby the greatest shift was observed for the phosphane sulfide **5a,b,d**. The same tendencies were observed before in the series of imidazole phosphane chalcogens.[30]

IR spectra of phosphorylated derivatives are summarized in the Experimental section. A strong absorption band in the region 1305–1230 cm^{-1} in **4a,b,d** has been ascribed to P═O stretching vibrations. Another absorption bands in the region 660–640 cm^{-1} in derivatives **5a,b,d** were assigned for P═S vibrations.

X-ray single-crystal structure analysis was performed for compounds **4b**, **4d**, **5b**, **6a** and **6d**. The selected bond parameters are given in the figure caption of the corresponding compounds (Fig. 3–7, respectively). For crystallographic data see Tables S1 and S2 (ESI†). Despite the structure, these are the first report of a diphenyl(thio, seleno)phosphoryl substituted imidazole-2-thione derivatives, structural parameters shall not be discussed further as bond lengths and angles are in the common range for P^V chalcogenide derivatives.[32–34]

As an extension of this work, we also examined the reactivity of phosphanylated 1,2-dialkylimidazole-2-thiones towards borane. For this **3a,b** were reacted with the BH_3–THF complex at room temperature. The completion of the reaction was monitored by ^{31}P{^{1}H}-NMR spectroscopy. After the removal of solvent, colorless solid was obtained; this was then washed with n-pentane and then dried. The product **7a,b** were characterized by ^{31}P, ^{11}B, ^{1}H and ^{13}C-NMR spectroscopy. The ^{31}P{^{1}H}-NMR spectra of **7a,b** showed a downfield shift around 9 ppm as of corresponding phosphanes. The ^{11}B{^{1}H}-NMR spectra of **7a,b**



Scheme 2 Reactions of P-functional imidazole-2-thiones.

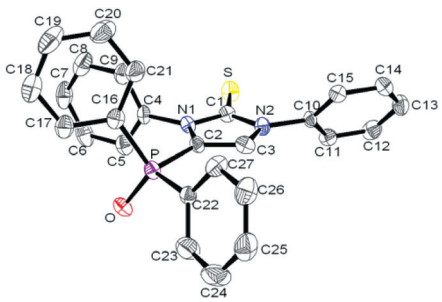


Fig. 3 Molecular crystal structure of compound **4b**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): C(1)–N(1) 1.370(3), C(1)–N(2) 1.375(3), C(2)–C(3) 1.349(3), C(4)–N(1) 1.446(3), C(1)–S1 1.670(3), P–O 1.4875(17), P–C(2) 1.785(3), P–C(16) 1.796(3), P–C(22) 1.799(3); C(2)–P–C(16) 102.23(8), C(2)–P–C(22) 102.83(12), N(1)–C(2)–P 124.96(18), C(16)–P–C(22) 108.45(12), C(2)–P–O 113.79(11), C(16)–P–O 112.32(12), C(22)–P–O 112.70(22).

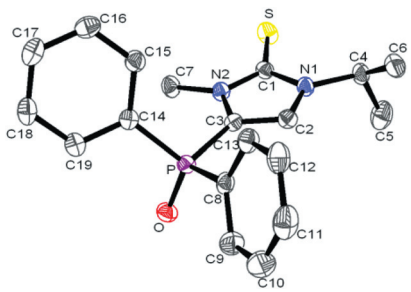


Fig. 4 Molecular structure of compound **4d**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): C(1)–N(1) 1.363(2), C(1)–N(2) 1.362(2), C(2)–C(3) 1.348(2), C(4)–N(1) 1.477(2), C(1)–S 1.6831(19), P–O 1.4858(13), P–C(3) 1.7857(18), P–C(8) 1.798(2), P–C(14) 1.7966(18); C(3)–P–C(8) 102.82(8), C(3)–P–C(14) 106.96(8), N(2)–C(3)–P 126.48(13), C(8)–P–C(14) 106.21(8), C(3)–P–O 115.02(8), C(8)–P–O 113.14(8), C(14)–P–O 111.90(8).

resonates in the chemical shift range of −40 ppm to −42 ppm. Electron-impact mass spectrometry was a useful tool in proving the structure of phosphane boranes **7a,b**. In these cases, intense loss of BH_3 could be seen. To the best of our knowledge, no examples of phosphane borane complexes of phosphorus substituted imidazole-2-thione derivatives are known so far.

Conclusions

A synthetic methodology has been developed to synthesize a series of phosphanyl substituted 1,3-dialkyl imidazole-2-thione. The oxidation of phosphanyl substituted 1,3-dialkyl imidazole-2-thione occurred selectively to yield the corresponding P^V–E products (E = O, S, Se) **4a,b,d–6a,b,d**, firmly established by

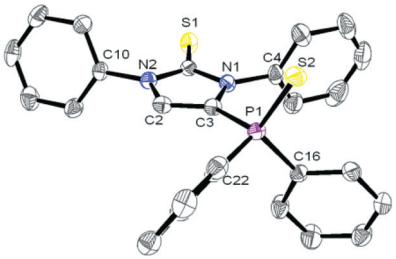


Fig. 5 Molecular structure of compound **5b**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): C(1)–N(1) 1.368(3), C(1)–N(2) 1.379(3), C(2)–C(3) 1.352(3), C(4)–N(1) 1.444(3), C(1)–S(1) 1.666(2), P(1)–S(2) 1.9526(8), P(1)–C(3) 1.801(2), P(1)–C(16) 1.822(2), P(1)–C(22) 1.820(2); C(3)–P(1)–C(16) 106.42(10), C(3)–P(1)–C(22) 103.22(10), N(1)–C(3)–P(1) 124.78(16), C(16)–P(1)–C(22) 107.50(10), C(3)–P(1)–S(2) 114.17(8), C(16)–P(1)–S(2) 112.32(8), C(22)–P(1)–S(2) 112.54(8).

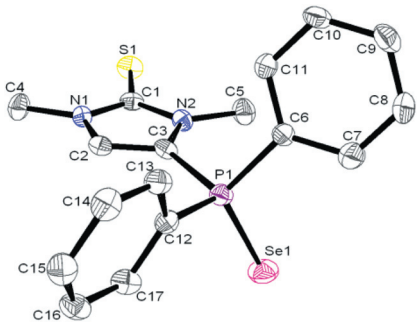


Fig. 6 Molecular structure of compound **6a**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): C(1)–N(1) 1.360(3), C(1)–N(2) 1.357(5), C(2)–C(3) 1.356(4), C(4)–N(1) 1.461(4), C(1)–S(1) 1.679(3), P(1)–Se(1) 2.1008(9), P(1)–C(3) 1.782(3), P(1)–C(6) 1.811(3), P(1)–C(12) 1.811(3); C(3)–P(1)–C(6) 105.17(14), C(3)–P(1)–C(12) 101.78(14), N(2)–C(3)–P(1) 125.3(2), C(6)–P(1)–C(12) 107.83(13), C(3)–P(1)–Se(1) 113.91(10), C(6)–P(1)–Se(1) 113.16(10), C(12)–P(1)–Se(1) 114.00(10).

their X-ray crystal structures; derivatives **4b**, **4d**, **5b**, **6a** and **6d** represent the first examples within the series of *P*-substituted imidazole-2-thione derivatives. New examples of phosphane borane complexes of phosphorus substituted imidazole-2-thione derivatives were reported. This synthetic route is amenable to the preparation of multigram quantities of product in a linear fashion. Current studies aim at the synthesis of new backbone functionalized *N*-heterocyclic carbenes (NHCs) starting from phosphanyl and phosphoryl substituted imidazol-2-thiones described herein.

Experimental section

General

The synthesis of the imidazole-2-thiones and the lithiation reactions were performed under an argon atmosphere, using common Schlenk techniques and dry solvents. Tetrahydrofuran was dried over sodium wire–benzophenone, dichloromethane over calcium hydride and further purified by subsequent distillation.

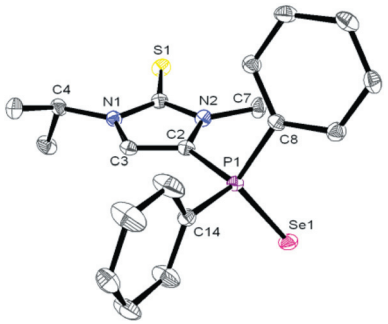


Fig. 7 Molecular structure of compound **6d**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): C(1)–N(1) 1.372(3), C(1)–N(2) 1.364(3), C(2)–C(3) 1.355(3), C(4)–N(1) 1.485(3), C(1)–S(1) 1.680(2), P(1)–Se(1) 2.1083(6), P(1)–C(2) 1.791(2), P(1)–C(8) 1.815(2), P(1)–C(14) 1.812(3); C(2)–P(1)–C(8) 104.04(10), C(2)–P(1)–C(14) 103.90(11), N(2)–C(2)–P(1) 124.04(18), C(8)–P(1)–C(14) 107.05(11), C(2)–P(1)–Se(1) 113.56(8), C(8)–P(1)–Se(1) 113.42(8), C(14)–P(1)–Se(1) 113.92(8).

Diphenylchlorophosphane was distilled prior to use and stored under an argon atmosphere. All other chemicals were used as received. 1,3-Dimethylimidazolium iodide (**1a**),[19] 1,3-diisopropylimidazolium chloride (**1c**),[20] 1-isopropyl-3-methylimidazolium bromide (**1d**),[16] 1-n-butyl-3-methylimidazolium iodide (**1e**),[17] 1-*tert*-butyl-3-methylimidazolium iodide (**1f**)[18] and 1,3-diphenylimidazole-2-thione (**2b**)[6] were synthesized following literature protocols. All NMR spectra were recorded on a Bruker AX-300 spectrometer, with a frequency of 300.1 MHz for ^{1}H. The ^{1}H and ^{13}C spectra were referenced to the residual protons and the ^{13}C signals of the deuterated solvents, the ^{11}B to BF_3*OEt_2 and ^{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, they are uncorrected. Elemental analyses were carried out on a Vario EL gas chromatograph. Mass spectrometric data were collected on a Kratos MS 50 spectrometer using EI, 70 eV. The infrared spectra were recorded on a Nicolet 80 FT-IR spectrometer using KBr plates or Nujol. The UV/Vis spectra were recorded in solution on a Shimadzu UV-1950 PC spectrometer. The X-ray analyses were performed on a Nonius Kappa CCD or a Bruker X8-KappaApex TT type diffractometer at 123(2) or 100(2) K, respectively. The structures were solved by direct methods refined by full-matrix least-squares technique in anisotropic approximation for non-hydrogen atoms using SHELXS97 and SHELXL97[35] program packages. Hydrogen atoms were located from Fourier synthesis and refined isotropically.

General protocol for the synthesis of imidazole-2-thiones 2a–f

The imidazolium salts (0.1 mol) were suspended in 125 mL of tetrahydrofuran in a Schlenk flask. Sublimed elemental sulphur (3.21 g, 0.1 mol) was added and the mixture was stirred for 2 h at ambient temperature. Upon addition of potassium *tert*-butoxide (112 mg, 0.001 mol) the reaction mixture turned reddish brown. The flask was cooled in a water bath. Sodium hydride (60–80% in oil, 0.1 mol) was added in small portions. After each portion it was waited for the end of gas evolution before the next portion

of sodium hydride was added. During the reaction, the color changed from reddish brown to light orange. After complete addition the reaction mixture was stirred overnight. The whole work-up should be done under a well-ventilated fume hood, due to the formation of smelly by-products. The imidazole-2-thiones themselves are odourless. It was filtrated from the precipitated sodium salts using a g3-frit equipped with a celite pad. The light-yellow colored filtrate was collected and concentrated *in vacuo* (8×10^{-3} mbar). The obtained residue was washed multiple times with n-pentane to remove traces of the oil and then recrystallized from hot water. The obtained crystal needles were collected, washed with cold water and dried. 1-n-Butyl-3-methylimidazole-2-thione (**2e**) was purified using column chromatography with silica gel as stationary phase and petrol ether–diethyl ether mixtures as eluents. The yellow product fraction was collected and concentrated *in vacuo* (8×10^{-3} mbar) to give a very viscous yellow liquid. The analytical data of 1,3-dimethylimidazole-2-thione (**2a**),[19–23] 1,3-diphenylimidazole-2-thione (**2b**),[6,24] 1,3-diisopropylimidazole-2-thione (**2c**),[19] 1-isopropyl-3-methylimidazole-2-thione (**2d**),[25] 1-n-butyl-3-methylimidazole-2-thione (**2e**)[6] and 1-*tert*-butyl-3-methylimidazole-2-thione (**2f**)[26] were consistent with those reported in the literature.

Typical lithiation and phosphanylation protocol for the synthesis of 3a–f

In a Schlenk flask, the imidazole-2-thiones **2a–f** (10 mmol) were dissolved in 100 mL of tetrahydrofuran and cooled to −80 °C. n-Butyllithium (1.6 M in n-hexane, 17 mL, 11 mmol) was added and the reaction mixture was slowly warmed up to −40 °C. It was stirred for 2 h at this temperature. The reaction mixture was cooled again to −80 °C. The diorganochlorophosphane (Ph_2PCl) (11 mmol) was added and the reaction mixture was stirred overnight and warmed up to ambient temperature. It was concentrated *in vacuo* (8×10^{-3} mbar) and the residue was taken up in dichloromethane and filtered to remove the formed lithium chloride. The filtrate was collected and the solvent was removed *in vacuo* (8×10^{-3} mbar). The crude product was purified *via* recrystallization from hot toluene or a n-pentane–diethyl ether mixture (**3a–f**, **7a–d**). Colorless to light yellow crystals were obtained.

1,3-Dimethyl-4-diphenylphosphino-imidazole-2-thione (3a)

Yield: (2.47 g, 79%), colorless solid, mp. 187 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.43 (s br, 3H, N^3–CH_3), 3.48 (s br, 3H, N^1–CH_3), 6.02 (s br, 1H, C^5–H), 7.24–7.35 (m, 10H, C_6H_5–H). ^{13}C{^{1}H} NMR (75.0 MHz, $CDCl_3$): δ = 33.4 (d, $^3J_{P,C}$ = 9.5 Hz, N^3–CH_3), 35.9 (s, N^1–CH_3), 124.0 (d, $^2J_{P,C}$ = 4.8 Hz, C^5), 126.1 (d, $^1J_{P,C}$ = 10.7 Hz, C^4), 128.6 (d, $J_{P,C}$ = 7.3 Hz, C_6H_5), 129.4 (s, C_6H_5), 132.6 (d, $^1J_{P,C}$ = 7.2 Hz, *ipso*-C_6H_5), 133.0 (d, $J_{P,C}$ = 20.3 Hz, C_6H_5), 165.1 (s, C═S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = −31.5 (quint, $^3J_{P,H}$ = 6.4 Hz). MS (EI, 70 eV): *m*/*z* = 312 ($\dot{M}^+$, 100%), 235 ($\dot{M}^+ - C_6H_5$, 5%), 221 ($\dot{M}^+ - C_6H_5$–CH_3, 44%), 183 ($P(C_6H_5)_2^+$, 8%). Exact mass: found: 312.0846, calc.: 312.0850. IR (KBr, cm^{-1}): $\tilde{\nu}$ 3155 and 3042 (w, ν(C–H)), 1570 (m, ν(C═C)), 1476 (m, ν(P–C═C)), 1435 (s, ν(P–C_6H_5)), 1389 (s, ν(C═N)), 1190 (s, ν(C═S)), 755, 743 and 700 (s, δ(C_6H_5)). UV/Vis (Et_2O): λ_{max}: 209 nm. EA: calc. C 65.37, H 5.49, N 8.97, S 10.27, found: C 65.32, H 5.51, N 8.95, S 10.32.

1,3-Diphenyl-4-diphenylphosphino-imidazol-2-thione (3b)

Yield: (3.58 g, 82%), light yellow solid, mp. 213 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.32 (s br, 1H, C^5–H), 7.12 (dd, $^3J_{H,H}$ = 7.7 Hz, $^4J_{H,H}$ = 1.5 Hz, 2H, N–C_6H_5–H), 7.22–7.33 (m, 12H, C_6H_5–H), 7.39 (t br, $^3J_{H,H}$ = 7.7 Hz, 4H, P–C_6H_5–H), 7.53 (dd, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.5 Hz, 4H, *P*–C_6H_5–H). ^{13}C{^{1}H} NMR (75.0 MHz, $CDCl_3$): δ = 124.5 (s br, C^5), 128.5 (s, N–C_6H_5), 128.8 (d, $J_{P,C}$ = 7.2 Hz, P–C_6H_5), 128.9 (d, $J_{P,C}$ = 2.4 Hz, P–C_6H_5), 129.1 (s, N–C_6H_5), 129.6 (d, $^1J_{P,C}$ = 12.8 Hz, C^4), 129.8 (s, N–C_6H_5), 133.1 (d, $^1J_{P,C}$ = 8.0 Hz, P–*ipso*-C_6H_5), 133.7 (d, $J_{P,C}$ = 20.8 Hz, P–C_6H_5), 136.3 (s, N–*ipso*-C_6H_5), 138.1 (s, N–*ipso*-C_6H_5), 167.3 (s, C═S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = −31.7 (quint br, $^3J_{P,H}$ = 9.2 Hz). MS (EI, 70 eV): *m*/*z* = 436 ($\dot{M}^+$, 100%), 403 ($\dot{M}^+ - S$, 24%), 359 ($\dot{M}^+ - C_6H_5$, 28%), 328 ($\dot{M}^{+-}C_6H_5$–S, 4%), 183 ($P(C_6H_5)_2^+$, 10%), 77 ($C_6H_5^+$, 14%). Exact mass: found: 436.1165, calc.: 436.1163. IR (KBr, cm^{-1}): $\tilde{\nu}$ 3064 and 3011 (w, ν(C–H)), 1593 (m, ν(C═C)), 1496 (vs, ν(P–C═C)), 1434 (s, ν(P–C_6H_5)), 1380 (s, ν (C═N)), 1152 (m, ν (C═S)), 771, 764 and 699 (s, δ(C_6H_5)). UV/Vis (Et_2O): λ_{max}: 209 nm. EA: calc. C 74.29, H 4.85, N 6.42, found: C 73.97, H 4.83, N 6.32.

1,3-Diisopropyl-4-diphenylphosphino-imidazole-2-thione (3c)

Yield: (53 mg, 1.43%), colorless solid, mp. 186 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29 (d, $^3J_{H,H}$ = 6.8 Hz, 6H, C_3H_7–CH_3), 5.09 (hept, $^3J_{H,H}$ = 6.8 Hz, 1H, C_3H_7–CH), 6.03 (s, 1H, C^5–H), 7.02–7.75 (m, 10H, C_6H_5–H). ^{13}C{^{1}H} NMR (75.0 MHz, $CDCl_3$): δ = 20.9 (s, C_3H_7–CH_3), 47.4 (s, C_3H_7–CH), 127.2 (d, $^2J_{P,C}$ = 7.1 Hz, C^5), 127.8 (d, $J_{P,C}$ = 7.8 Hz, C_6H_5), 128.5 (s, C_6H_5), 129.7 (d, $^1J_{P,C}$ = 12.8 Hz, C^4), 131.6 (d, $^1J_{P,C}$ = 2.7 Hz, *ipso*-C_6H_5), 132.3 (d, $J_{P,C}$ = 20.7 Hz, C_6H_5), 164.4 (s br, C═S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = −31.2 (quint, $^3J_{P,H}$ = 5.1 Hz). MS (EI, 70 eV): *m*/*z* = 368 ($\dot{M}^+$, 100%), 335 ($\dot{M}^+ - S$, 30%), 326 ($\dot{M}^+ - C_3H_6$, 68%), 291 ($\dot{M}^+ - C_6H_5$, 23%), 284 ($\dot{M}^+ - 2C_3H_6$, 34%), 183 ($P(C_6H_5)_2^+$, 26%), 77 ($C_6H_5^+$, 8%), 43 ($C_3H_6^+$, 4%). Exact mass: found: 368.1481, calc.: 368.1476. IR (KBr, cm^{-1}): $\tilde{\nu}$ 3143 and 3079 (w, ν(C–H)), 1433 (s, ν(P–C_6H_5)), 1410 (s, ν(C═N)), 1171 (m, ν(C═S)), 752 and 691 (s, δ(C_6H_5)). UV/Vis (Et_2O): λ_{max}: 268 nm.

1-Isopropyl-3-methyl-4-diphenylphosphino-imidazole-2-thione (3d)

Yield: (2.89 g, 85%), colorless solid, mp. 132 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.28 (d, $^3J_{H,H}$ = 6.8 Hz, 6H, C_3H_7–CH_3), 3.50 (s, 3H, N^3–CH_3), 5.09 (hept, $^3J_{H,H}$ = 6.8 Hz, 1H, C_3H_7–CH), 6.19 (s, 1H, C^5–H), 7.30–7.42 (m, 10H, C_6H_5–H). ^{13}C{^{1}H} NMR (75.0 MHz, $CDCl_3$): δ = 21.8 (s, C_3H_7–CH_3), 33.4 (d, $^3J_{P,H}$ = 9.3 Hz, N^3–CH_3), 49.1 (s, C_3H_7–CH), 119.8 (d, $^2J_{P,C}$ = 7.3 Hz, C^5), 126.7 (d, $^1J_{P,C}$ = 12.0 Hz, C^4), 129.0 (d, $J_{P,C}$ = 7.4 Hz, C_6H_5), 129.7 (s, C_6H_5), 133.1 (d, $^1J_{P,C}$ = 7.3 Hz, *ipso*-C_6H_5), 133.2 (d, $J_{P,C}$ = 20.1 Hz, C_6H_5), 164.4 (s br,

C═S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = −31.6 (quint, $^3J_{P,H}$ = 8.1 Hz). MS (EI, 70 eV): *m/z* = 340 ($M^{\cdot+}$, 100%), 298 ($\dot{M}^+$ − C_3H_6, 20%), 249 ($\dot{M}^+$ − C_6H_5–CH_3, 9%), 221 ($\dot{M}^+$ − C_3H_6–C_6H_5, 6%), 215 ($\dot{M}^+$ − C_6H_5–CH_3–S, 24%), 207 ($\dot{M}^+$ − C_3H_6–C_6H_5–CH_3, 41%), 183 ($P(C_6H_5)_2^+$, 20%), 44 ($C_3H_7^+$, 16%). Exact mass: found: 340.1160, calc.: 340.1163. IR (KBr, cm^{-1}): $\tilde{\nu}$ 3143, 3051 and 2974 (w, ν(C–H)), 1584 (w, ν(C═C)), 1436 (s, ν(P–C_6H_5)), 1404 (s, ν(C═N)), 1179 (vs, ν(C═S)), 751, 745 and 698 (s, δ(C_6H_5)). UV/Vis (Et_2O): λ_{max}: 208 nm. EA: calc. C 67.04, H 6.22, N 8.23, found: C 67.60, H 5.91, N 6.59.

1-n-Butyl-3-methyl-4-diphenylphosphino-imidazole-2-thione (3e)

Yield: (2.98 g, 84%), colorless solid, mp. 45 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.82 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, C_4H_9–CH_3), 1.21 (q, $^3J_{H,H}$ = 7.6 Hz, 2H, C_4H_9–CH_2), 1.60 (q, $^3J_{H,H}$ = 7.7 Hz, 2H, C_4H_9–CH_2), 3.50 (s, 3H, N^3–CH_3), 3.92 (m, 2H, C_4H_9–CH_2), 6.03 (s, 1H, C^5–H), 7.22–7.30 (m, 10H, C_6H_5–H). $^{13}C\{^1H\}$ NMR (75.0 MHz, $CDCl_3$): δ = 13.3 (s, C_4H_9–CH_3), 19.4 (s, C_4H_9–CH_2), 30.5 (s, C_4H_9–CH_2), 33.4 (d, $^3J_{P,H}$ = 9.5 Hz, N^3–CH_3), 47.4 (s, C_4H_9–CH_2), 123.1 (d, $^2J_{P,C}$ = 6.0 Hz, C^5), 126.0 (d, $^1J_{P,C}$ = 11.3 Hz, C^4), 128.6 (d, $J_{P,C}$ = 7.2 Hz, C_6H_5), 129.4 (s, C_6H_5), 132.7 (d, $^1J_{P,C}$ = 7.2 Hz, *ipso*-C_6H_5), 132.9 (d, $J_{P,C}$ = 20.3 Hz, C_6H_5), 164.4 (s br, C═S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = −31.6 (quint br, $^3J_{P,H}$ = 6.4 Hz). MS (EI, 70 eV): *m/z* = 354 ($\dot{M}^+$, 39%), 321 ($\dot{M}^+$ − S, 22%), 298 ($\dot{M}^+$ − C_4H_8, 8%), 203 ($\dot{M}^+$ − $2C_6H_5$, 100%), 183 ($P(C_6H_5)_2^+$, 14%), 170 ($\dot{M}^+$ − $2C_6H_5$–P, 65%), 137 ($\dot{M}^+$ − $2C_6H_5$–P–S, 36%), 114 ($\dot{M}^+$ − $2C_6H_5$ − P − C_4H_8, 36%), 84 ($\dot{M}^+$ − $2C_6H_5$ − P − C_4H_8 − S, 17%), 57 ($C_4H_9^+$, 9%). Exact mass: found: 354.1320, calc.: 354.1320. IR (Nujol, cm^{-1}): $\tilde{\nu}$ 3158 and 3050 (w, ν(C–H)), 1552 (m, ν(C═C)), 1439 (vs, ν(P–C_6H_5)), 1408 (s, ν(C═N)), 1179 (m, ν(C═S)), 751 and 695 (s, δ(C_6H_5)). UV/Vis (CH_2Cl_2): λ_{max}: 271 nm. EA: calc. C 67.77, H 6.54, N 7.90, found: C 67.76, H 6.30, N 7.29.

1-n-Butyl-3-methyl-5-diphenylphosphino-imidazole-2-thione (3e′)

Colorless dense liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.72 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, C_4H_9–CH_3), 3.43 (s, 3H, N^3–CH_3), 6.02 (s, 1H, C^5–H). The other signals were masked by the major isomer **3e**. $^{13}C\{^1H\}$ NMR (75.0 MHz, $CDCl_3$): δ = 13.3 (s, C_4H_9–CH_3), 19.5 (s, C_4H_9–CH_2), 30.1 (d, $^4J_{P,C}$ = 3.0 Hz, C_4H_9–CH_2), 34.7 (s, N^3–CH_3), 46.5 (d, $^3J_{P,C}$ = 8.4 Hz, C_4H_9–CH_2), 124.3 (d, $^2J_{P,C}$ = 7.2 Hz, C^4), 125.9 (d, $^1J_{P,C}$ = 10.7 Hz, C^5), 128.5 (d, $J_{P,C}$ = 7.8 Hz, C_6H_5), 129.3 (s, C_6H_5), 133.1 (d, $J_{P,C}$ = 20.9 Hz, C_6H_5), 134.8 (d, $^1J_{P,C}$ = 7.2 Hz, *ipso*-C_6H_5), 164.4 (s br, C═S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = −35.3 (s br).

1-*tert*-Butyl-3-methyl-4-diphenylphosphino-imidazole-2-thione (3f)

Yield: (2.09 g, 59%), light yellow solid, mp. 163 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.65 (s br, 9H, C_4H_9), 3.39 (s br, 3H, N^3–CH_3), 6.21 (s, 1H, C^5–H), 7.18–7.32 (m, 10H, C_6H_5–H). $^{13}C\{^1H\}$ NMR (75.0 MHz, $CDCl_3$): δ = 27.0 (s, C_4H_9–CH_3), 32.4 (d, $^3J_{P,H}$ = 9.1 Hz, N^3–CH_3), 58.4 (s, C_4H_9–C), 120.5 (d, $^2J_{P,C}$ = 8.4 Hz, C^5), 123.9 (d, $^1J_{P,C}$ = 11.6 Hz, C^4), 127.9 (d, $J_{P,C}$ = 7.8 Hz, C_6H_5), 128.6 (s, C_6H_5), 132.2 (d, $^1J_{P,C}$ = 7.1 Hz, *ipso*-C_6H_5), 132.2 (d, $J_{P,C}$ = 20.0 Hz, C_6H_5), 163.1 (s br, C═S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = −30.3 (quint br, $^3J_{P,H}$ = 8.9 Hz). MS (EI, 70 eV): *m/z* = 354 ($\dot{M}^+$, 48%), 298 ($\dot{M}^+$ − C_4H_8, 100%), 207 ($\dot{M}^+$ − C_4H_9–C_6H_5–CH_3, 66%), 183 ($P(C_6H_5)_2^+$, 16%), 170 ($\dot{M}^+$ − $2C_6H_5$–P, 65%). Exact mass: found: 354.1323, calc.: 354.1320. IR (KBr, cm^{-1}): $\tilde{\nu}$ 3178, 3066, 2984 and 2966 (w, ν(C–H)), 1549 (w, ν(C═C)), 1475 (m, ν(P–C═C)), 1434 (s, ν(P–C_6H_5)), 1397 (s, ν(C═N)), 1362 (vs, ν(C–C)), 1173 (vs, ν(C═S)), 756, 741 and 698 (s, δ(C_6H_5)). UV/Vis (Et_2O): λ_{max}: 209 nm. EA: calc. C 67.77, H 6.54, N 7.90, found: C 67.57, H 6.39, N 7.97.

Typical procedure for the generation of phosphane oxides

The phosphanes **3a,b,d** (3 mmol), 10 mL of chloroform and H_2O_2–urea adduct (3 mmol) was stirred for 24 h. The reaction mixture was then filtered off to remove unreacted urea. Then the solvent was removed *in vacuo* (8×10^{-3} mbar). The product was recrystallized from hot toluene followed by washing with n-pentane and then dried *in vacuo* (8×10^{-3} mbar) to form white solid.

1,3-Dimethyl-4-diphenylphosphoryl-imidazole-2-thione (4a)

Yield: (309 mg, 94%), colorless solid, mp. 156 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.50 (s, 3H, N^3–CH_3), 3.52 (s, 3H, N^1–CH_3), 6.34 (d, $^3J_{P,H}$ = 2.8 Hz, 1H, C^5–H), 7.25–7.58 (m, 6H, C_6H_5–H), 7.64 (ddd, $^3J_{P,H}$ = 12.8 Hz, $^3J_{H,H}$ = 7.0 Hz, $^4J_{H,H}$ = 1.3 Hz, *ortho*-C_6H_5–H). $^{13}C\{^1H\}$ NMR (75.0 MHz, $CDCl_3$): δ = 34.5 (s, N^3–CH_3), 35.5 (s, N^1–CH_3), 122.4 (d, $^1J_{P,C}$ = 124.2 Hz, C^4), 127.7 (d, $^2J_{P,C}$ = 19.2 Hz, C^5), 129.0 (d, $J_{P,C}$ = 12.8 Hz, C_6H_5), 130.0 (d, $^1J_{P,C}$ = 112.9 Hz, *ipso*-C_6H_5), 131.8 (d, $J_{P,C}$ = 10.4 Hz, C_6H_5), 133.0 (d, $J_{P,C}$ = 3.2 Hz, C_6H_5), 167.6 (d, $^{3+4}J_{P,C}$ = 4.8 Hz, C═S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 15.8 (quint br, $^3J_{P,H}$ = 12.8 Hz). MS (EI, 70 eV): *m/z* = 328 ($\dot{M}^+$, 8%), 312 ($\dot{M}^+$ − O, 100%), 279 ($\dot{M}^+$ − O − S, 3%), 235 ($\dot{M}^+$ − O − C_6H_5, 6%), 221 ($\dot{M}^+$ − O − C_6H_5 − CH_3, 49%), 183 ($P(C_6H_5)_2^+$, 5%). HR-ESI-MS: found: 351.0692, calc.: 351.0691, as $C_{17}H_{17}N_2OPSNa^+$. IR (KBr, cm^{-1}): $\tilde{\nu}$ 3129 and 3075 (w, ν(C–H)), 1589 (w, ν(C═C)), 1479 (s, ν(P–C═C)), 1439 (s, ν(P–C_6H_5)), 1398 (s, ν(C═N)), 1304 (m, ν(P═O)), 1189 (vs, ν(C═S)), 751, 723 and 695 (s, δ(C_6H_5)). UV/Vis (n-pentane): λ_{max}: 272 nm. EA: calc. C 62.18, H 5.22, N 8.53, S 9.76, found: C 62.37, H 5.27, N 8.56, S 9.87.

1,3-Diphenyl-4-diphenylphosphoryl-imidazole-2-thione (4b)

Yield: (421 mg, 93%), light yellow solid, mp. 266 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.84 (d, $^3J_{P,H}$ = 3.8 Hz, 1H, C^5–H), 7.07–7.73 (m, 20H, C_6H_5–H). $^{13}C\{^1H\}$ NMR (75.0 MHz, $CDCl_3$): δ = 121.1 (d, $^1J_{P,C}$ = 119.6 Hz, C^4), 124.9 (s, N–C_6H_5), 125.2 (s, N–C_6H_5), 125.3 (d, $^2J_{P,C}$ = 3.3 Hz, C^5), 125.4 (s, N–C_6H_5), 125.8 (d, $J_{P,C}$ = 20.0 Hz, P–C_6H_5), 126.9 (d, $^1J_{P,C}$ = 112.5 Hz, P–*ipso*-C_6H_5), 128.2 (d, $J_{P,C}$ = 9.7 Hz, P–C_6H_5), 129.1 (d, $J_{P,C}$ = 2.6 Hz, P–C_6H_5), 133.1 (s, N–C_6H_5), 134.3

(s, N–C_6H_5), 165.2 (d, $^{3+4}J_{P,C}$ = 3.9 Hz, C═S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 9.0 (quint, $^3J_{P,H}$ = 12.7 Hz, 3.8 Hz). MS (EI, 70 eV): *m/z* = 452 ($\dot{M}^+$, 100%), 375 ($\dot{M}^+$ − C_6H_5, 10%), 183 ($P(C_6H_5)_2^+$, 3%). HR-ESI-MS: found: 475.1008, calc.: 475.1004, as $C_{27}H_{21}N_2OPSNa^+$. IR (KBr, cm^{-1}): $\tilde{\nu}$ 3061 (w, ν(C–H)), 1594 (w, ν(C═C)), 1498 (s, ν(P–C═C)), 1437 (s, ν(P–C_6H_5)), 1386 (s, ν(C═N)), 1234 (m, ν(P═O)), 1196 (vs, ν(C═S)), 760, 726 and 693 (s, δ(C_6H_5)). UV/Vis (n-pentane): λ_{max}: 272 nm. EA: calc. C 71.66, H 4.68, N 6.19, found: C 69.64, H 4.76, N 5.72.

1-Isopropyl-3-methyl-4-diphenylphosphoryl-imidazole-2-thione (4d)

Yield: (342 mg, 96%), colorless solid, mp. 157 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.21 (d, $^3J_{H,H}$ = 6.8 Hz, 6H, C_3H_7–CH_3), 3.51 (s, 3H, N^3–CH_3), 4.99 (hept, $^3J_{H,H}$ = 6.8 Hz, 1H, C_3H_7–CH), 6.38 (d, $^3J_{P,H}$ = 2.8 Hz, 1H, C^5–H), 7.44–7.56 (m, 6H, C_6H_5–H), 7.64 (ddd, $^3J_{P,H}$ = 12.8 Hz, $^3J_{H,H}$ = 7.1 Hz, $^4J_{H,H}$ = 1.3 Hz, 4H, *ortho*-C_6H_5–H). ^{13}C{^{1}H} NMR (75.0 MHz, $CDCl_3$): δ = 21.7 (s, C_3H_7–CH_3), 34.1 (s, N^3–CH_3), 49.5 (s, C_3H_7–CH), 122.8 (d, $^1J_{P,C}$ = 124.2 Hz, C^4), 123.2 (d, $^2J_{P,C}$ = 19.2 Hz, C^5), 129.0 (d, $J_{P,C}$ = 12.8 Hz, C_6H_5), 130.1 (d, $^1J_{P,C}$ = 112.9 Hz, *ipso*-C_6H_5), 131.6 (d, $J_{P,C}$ = 10.4 Hz, C_6H_5), 133.0 (d, $J_{P,C}$ = 3.2 Hz, C_6H_5), 166.5 (d, $^{3+4}J_{P,C}$ = 4.8 Hz, C═S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 15.9 (quint br, $^3J_{P,H}$ = 12.8 Hz). MS (EI, 70 eV): *m/z* = 356 ($\dot{M}^+$, 100%), 323 ($\dot{M}^+$ − S, 4%), 314 ($\dot{M}^+$ − C_3H_6, 17%), 281 ($\dot{M}^+$ − C_3H_7 − S, 2%), 265 ($\dot{M}^+$ − C_6H_5 − CH_3, 10%), 223 ($\dot{M}^+$ − C_3H_6 − C_6H_5 − CH_3, 6%), 183 ($P(C_6H_5)_2^+$, 7%). HR-ESI-MS: found: 357.1187, calc.: 357.1190, as $C_{19}H_{21}N_2OPSH^+$. IR (KBr, cm^{-1}): $\tilde{\nu}$ 3140, 3077 and 2961 (w, ν(C–H)), 1590 (w, ν(C═C)), 1483 (w, ν(P–C═C)), 1437 (s, ν(P–C_6H_5)), 1413 (s, ν(C═N)), 1276 (s, ν(P═O)), 1195 (vs, ν(C═S)), 750, 723 and 699 (s, δ(C_6H_5)). UV/Vis (Et_2O): λ_{max}: 273 nm. EA: calc. C 64.03, H 5.94, N 7.86, S 9.00, found: C 63.79, H 5.97, N 7.85, S 9.10.

Typical procedure for the generation of phosphane sulfides and selenides

The phosphanes **3a,b,d** (3 mmol), 10 mL of toluene and elemental sulphur or selenium (3 mmol) were 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).

1,3-Dimethyl-4-diphenylthiophosphoryl-imidazole-2-thione (5a)

Yield: (940 mg, 91%), colorless solid, mp. 227 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.47 (s, 3H, N^3–CH_3), 3.53 (s, 3H, N^1–CH_3), 6.21 (d, $^3J_{P,H}$ = 2.5 Hz, 1H, C^5–H), 7.42–7.56 (m, 6H, C_6H_5–H), 7.70–7.78 (m, $^3J_{P,H}$ = 14.0 Hz, *ortho*-C_6H_5–H). ^{13}C{^{1}H} NMR (75.0 MHz, $CDCl_3$): δ = 34.2 (s, N^3–CH_3), 35.1 (s, N^1–CH_3), 121.3 (d, $^1J_{P,C}$ = 107.3 Hz, C^4), 126.3 (d, $^2J_{P,C}$ = 17.3 Hz, C^5), 128.7 (d, $J_{P,C}$ = 13.1 Hz, C_6H_5), 129.6 (d, $^1J_{P,C}$ = 91.2 Hz, *ipso*-C_6H_5), 131.6 (d, $J_{P,C}$ = 11.3 Hz, C_6H_5), 132.3 (d, $J_{P,C}$ = 3.0 Hz, C_6H_5), 167.4 (d, $^{3+4}J_{P,C}$ = 5.4 Hz, C═S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 27.2 (qqd, $^3J_{P,H}$ = 14.0 Hz, $^3J_{P,H}$ = 3.8 Hz, $^3J_{P,H}$ = 2.5 Hz). MS (EI, 70 eV): *m/z* = 344 ($\dot{M}^+$, 10%), 312 ($\dot{M}^+$ − S, 2%), 279 ($\dot{M}^+$ − S − CH_3, 3%), 256 ($\dot{M}^+$ − 88, 100%), 224 ($\dot{M}^+$ − 88 − S, 8%), 192 ($\dot{M}^+$ − 88 − 2S, 38%), 127 ($C_5H_7N_2S^+$, 42%). HR-ESI-MS: found: 345.0645, calc.: 344.0571, as $C_{17}H_{18}N_2PS_2^+$. IR (KBr, cm^{-1}): $\tilde{\nu}$ 3147 (w, ν(C–H)), 1438 (s, ν(P–C_6H_5)), 1394 (s, ν(C═N)), 1189 (vs, ν(C═S)), 717 and 696 (s, δ(C_6H_5)), 648 (s, ν(P═S)). UV/Vis (Et_2O): λ_{max}: 209 nm. EA: calc. C 59.28, H 4.97, N 8.13, S 18.62, found: C 58.53, H 5.00, N 8.06, S 18.23.

1,3-Diphenyl-4-diphenylthiophosphoryl-imidazole-2-thione (5b)

Yield: (1.307 g, 93%), light yellow solid, mp. 234 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.74 (d, $^3J_{P,H}$ = 3.3 Hz, 1H, C^5–H), 6.96–7.51 (m, 16H, C_6H_5–H), 7.69–7.74 (dd, $^3J_{P,H}$ = 13.7 Hz, $^3J_{H,H}$ = 7.6 Hz, 4H, *ortho*-C_6H_5–H). ^{13}C{^{1}H} NMR (75.0 MHz, $CDCl_3$): δ = 124.1 (d, $^1J_{P,C}$ = 102.5 Hz, C^4), 124.9 (s, N–C_6H_5), 125.2 (s, N–C_6H_5), 128.0 (d, $^2J_{P,C}$ = 17.6 Hz, C^5), 128.5 (s, N–C_6H_5), 128.8 (d, $J_{P,C}$ = 12.8 Hz, P–C_6H_5), 129.9 (d, $^1J_{P,C}$ = 92.1 Hz, P–*ipso*-C_6H_5), 132.2 (d, $J_{P,C}$ = 11.2 Hz, P–C_6H_5), 132.4 (d, $J_{P,C}$ = 2.4 Hz, P–C_6H_5), 135.9 (s, N–*ipso*-C_6H_5), 137.6 (s, N–*ipso*-C_6H_5), 169.9 (d, $^{3+4}J_{P,C}$ = 3.2 Hz, C═S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 27.5 (quint br, $^3J_{P,H}$ = 13.7 Hz). MS (EI, 70 eV): *m/z* = 468 ($\dot{M}^+$, 15%), 436 ($\dot{M}^+$ − S, 3%), 375 ($\dot{M}^+$ − S − C_6H_5, 5%), 283 ($\dot{M}^+$ − 2S − C_6H_5, 2%), 183 ($P(C_6H_5)_2^+$, 3%). HR-EI-MS: found: 468.0889, calc.: 468.0884. IR (KBr, cm^{-1}): $\tilde{\nu}$ 3142 and 3058 (w, ν(C–H)), 1591 (m, ν(C═C)), 1496 (s, ν(P–C═C)), 1438 (s, ν(P–C_6H_5)), 1383 (s, ν(C═N)), 1168 (vs, ν(C═S)), 763, 720 and 690 (s, δ(C_6H_5)), 660 (s, ν(P═S)). UV/Vis (CH_2Cl_2): λ_{max}: 230 nm. EA: calc. C 69.21, H 4.52, N 5.98, S 13.69, found: C 70.43, H 4.88, N 5.71, S 13.00.

1-Isopropyl-3-methyl-4-diphenylthiophosphoryl-imidazole-2-thione (5d)

Yield: (1.062 g, 95%), colorless solid, mp. 178 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.44 (d, $^3J_{H,H}$ = 6.9 Hz, 6H, C_3H_7–CH_3), 3.93 (s, 3H, N^3–CH_3), 5.35 (hept, $^3J_{H,H}$ = 6.9 Hz, 1H, C_3H_7–CH), 6.60 (d, $^3J_{P,H}$ = 2.9 Hz, 1H, C^5–H), 7.42–7.30 (m, 6H, C_6H_5–H), 8.12 (ddd, $^3J_{P,H}$ = 14.6 Hz, $^3J_{H,H}$ = 7.3 Hz, $^4J_{H,H}$ = 1.3 Hz, 4H, *ortho*-C_6H_5–H). ^{13}C{^{1}H} NMR (75.0 MHz, $CDCl_3$): δ = 21.7 (s, C_3H_7–CH_3), 34.3 (s, N^3–CH_3), 49.8 (s, C_3H_7–CH), 122.4 (d, $^1J_{P,C}$ = 107.0 Hz, C^4), 122.5 (d, $^2J_{P,C}$ = 18.1 Hz, C^5), 129.2 (d, $J_{P,C}$ = 12.9 Hz, C_6H_5), 130.8 (d, $^1J_{P,C}$ = 88.6 Hz, *ipso*-C_6H_5), 132.2 (d, $J_{P,C}$ = 11.8 Hz, C_6H_5), 132.8 (d, $J_{P,C}$ = 3.3 Hz, C_6H_5), 167.5 (d, $^{3+4}J_{P,C}$ = 5.2 Hz, C═S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 26.9 (quint, $^3J_{P,H}$ = 14.6 Hz, $^3J_{P,H}$ = 2.9 Hz). MS (EI, 70 eV): *m/z* = 372 ($\dot{M}^+$, 100%), 340 ($\dot{M}^+$ − S, 20%), 326 ($\dot{M}^+$ − S − CH_3, 8%), 298 ($\dot{M}^+$ − C_3H_7 − S, 5%), 183 ($P(C_6H_5)_2^+$, 60%), 77 ($C_6H_5^+$, 5%), 42 ($C_3H_6^+$, 5%). HR-EI-MS: found: 352.0878, calc.: 372.0884. IR (KBr, cm^{-1}): $\tilde{\nu}$ 3054 and 2972 (w, ν(C–H)), 1437 (s, ν(P–C_6H_5)), 1381 (m, ν(C═N)), 1184 (s, ν(C═S)), 754, 716 and 696 (s, δ(C_6H_5)), 644 (s, ν(P═S)). UV/Vis (Et_2O): λ_{max}: 209 nm. EA: calc. C 61.26, H 5.68, N 7.52, S 17.22, found: C 61.25, H 5.70, N 7.52, S 16.97.

1,3-Dimethyl-4-diphenylselenophosphoryl-imidazole-2-thione (6a)

Yield: (1.151 g, 97%), colorless solid, mp. 206 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.48 (s, 3H, N^3–CH_3), 3.53 (s, 3H, N^1–CH_3), 6.18 (d, $^{3}J_{P,H}$ = 2.5 Hz, 1H, C^5–H), 7.41–7.56 (m, 6H, C_6H_5–H), 7.71–7.79 (m, $^{3}J_{P,H}$ = 14.0 Hz, *ortho*-C_6H_5–H). ^{13}C{^{1}H} NMR (75.0 MHz, $CDCl_3$): δ = 33.6 (s, N^3–CH_3), 34.5 (s, N^1–CH_3), 118.9 (d, $^{1}J_{P,C}$ = 98.9 Hz, C^4), 125.6 (d, $^{2}J_{P,C}$ = 16.8 Hz, C^5), 127.6 (d, $^{1}J_{P,C}$ = 82.1 Hz, *ipso*-C_6H_5), 128.0 (d, $J_{P,C}$ = 12.9 Hz, C_6H_5), 131.5 (d, $J_{P,C}$ = 11.6 Hz, C_6H_5), 131.7 (d, $J_{P,C}$ = 3.2 Hz, C_6H_5), 167.0 (s, C=S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 15.3 $^{1}J_{Se,P}$ = 754.0 Hz (qqd, $^{3}J_{P,H}$ = 14.0 Hz, $^{3}J_{P,H}$ = 3.8 Hz, $^{3}J_{P,H}$ = 2.5 Hz). MS (EI, 70 eV): *m*/*z* = 392 ($\dot{M}^+$, 13%), 344 ($\dot{M}^+$ − S − CH_3, 18%), 312 ($\dot{M}^+$ − Se, 100%), 225 ($\dot{M}^+$ − Se − C_6H_5, 10%), 221 ($\dot{M}^+$ − Se − C_6H_5 − CH_3, 36%), 183 $(P(C_6H_5)_2)^+$, 42%). HR-ESI-MS: found: 393.0091, calc.: 392.0015, as $C_{17}H_{18}N_2PSSe^+$. IR (KBr, cm^{-1}): $\tilde{\nu}$ 3146 (w, ν(C–H)), 1436 (vs, ν(P–C_6H_5)), 1393 (vs, ν(C=N)), 1198 (s, ν(C=S)), 760, 715 and 691 (s, δ(C_6H_5)). UV/Vis (Et_2O): λ_{max}: 208 nm. EA: calc. C 52.18, H 4.38, N 7.16, S 8.19, found: C 52.04, H 4.39, N 7.13, S 8.25.

1,3-Diphenyl-4-diphenylselenophosphoryl-imidazole-2-thione (6b)

Yield: (1.515 g, 98%), light yellow solid, mp. 244 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.74 (d, $^{3}J_{P,H}$ = 3.5 Hz, 1H, C^5–H), 6.94–7.51 (m, 16H, C_6H_5–H), 7.68–7.74 (ddd, $^{3}J_{P,H}$ = 13.7 Hz, $^{3}J_{H,H}$ = 7.1 Hz, $^{4}J_{H,H}$ = 1.3 Hz, 4H, *ortho*-C_6H_5–H). ^{13}C{^{1}H} NMR (75.0 MHz, $CDCl_3$): δ = 122.0 (d, $^{1}J_{P,C}$ = 92.9 Hz, C^4), 124.9 (s, N–C_6H_5), 125.2 (s, N–C_6H_5), 128.4 (d, $^{2}J_{P,C}$ = 16.8 Hz, C^5), 128.5 (s, N–C_6H_5), 128.6 (d, $J_{P,C}$ = 12.8 Hz, P–C_6H_5), 132.7 (d, $^{1}J_{P,C}$ = 82.4 Hz, P–*ipso*-C_6H_5), 132.4 (d, $J_{P,C}$ = 3.2 Hz, P–C_6H_5), 132.7 (d, $J_{P,C}$ = 12.0 Hz, P–C_6H_5), 135.8 (s, N–*ipso*-C_6H_5), 137.5 (s, N–*ipso*-C_6H_5), 170.1 (d, $^{3+4}J_{P,C}$ = 3.2 Hz, C=S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 16.9 $^{1}J_{Se,P}$ = 764.5 Hz (quint, $^{3}J_{P,H}$ = 13.7 Hz, $^{3}J_{P,H}$ = 3.1 Hz). MS (EI, 70 eV): *m*/*z* = 516 ($\dot{M}^+$, 10%), 436 ($\dot{M}^+$ − Se, 48%), 403 ($\dot{M}^+$ − Se − S, 14%), 359 ($\dot{M}^+$ − Se − C_6H_5, 18%), 218 ($\dot{M}^+$ − Se − 2S − $2C_6H_5$, 6%), 183 $(P(C_6H_5)_2)^+$, 8%). HR-EI-MS: found: 512.0350, calc.: 516.0328. IR (KBr, cm^{-1}): $\tilde{\nu}$ 3052 (w, ν(C–H)), 1592 (m, ν(C=C)), 1495 (s, ν(P–C=C)), 1439 (s, ν(P–C_6H_5)), 1380 (s, ν(C=N)), 1168 (m, ν(C=S)), 750, 731 and 693 (s, δ(C_6H_5)). UV/Vis (CH_2Cl_2): λ_{max}: 209 nm. EA: calc. C 62.91, H 4.11, N 5.43, S 6.22, found: C 62.79, H 4.15, N 5.34, S 6.19.

1-Isopropyl-3-methyl-4-diphenylselenophosphoryl-imidazole-2-thione (6d)

Yield: (1.22 g, 97%), colorless solid, mp. 199 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 (d, $^{3}J_{H,H}$ = 6.9 Hz, 6H, C_3H_7–CH_3), 3.53 (s, 3H, N^3–CH_3), 5.00 (hept, $^{3}J_{H,H}$ = 6.9 Hz, 1H, C_3H_7–CH), 6.21 (d, $^{3}J_{P,H}$ = 2.5 Hz, 1H, C^5–H), 7.41–7.55 (m, 6H, C_6H_5–H), 7.73 (ddd, $^{3}J_{P,H}$ = 14.0 Hz, $^{3}J_{H,H}$ = 6.8 Hz, $^{4}J_{H,H}$ = 1.5 Hz, 4H, *ortho*-C_6H_5–H). ^{13}C{^{1}H} NMR (75.0 MHz, $CDCl_3$): δ = 21.7 (s, C_3H_7–CH_3), 34.3 (s, N^3–CH_3), 49.6 (s, C_3H_7–CH), 120.2 (d, $^{1}J_{P,C}$ = 98.9 Hz, C^4), 122.4 (d, $^{2}J_{P,C}$ = 17.5 Hz, C^5), 128.8 (d, $^{1}J_{P,C}$ = 81.5 Hz, *ipso*-C_6H_5), 129.1 (d, $J_{P,C}$ = 12.9 Hz, C_6H_5), 132.4 (d, $J_{P,C}$ = 11.6 Hz, C_6H_5), 132.7 (d, $J_{P,C}$ = 3.2 Hz, C_6H_5), 167.0 (d, $^{3+4}J_{P,C}$ = 4.5 Hz, C=S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 16.0 $^{1}J_{Se,P}$ = 751.5 Hz (quint, $^{3}J_{P,H}$ = 14.0 Hz, $^{3}J_{P,H}$ = 2.5 Hz). MS (EI, 70 eV): *m*/*z* = 420 ($\dot{M}^+$, 30%), 372 ($\dot{M}^+$ − S − CH_3, 8%), 340 ($\dot{M}^+$ − Se, 100%), 326 ($\dot{M}^+$ − Se − CH_3, 5%), 298 ($\dot{M}^+$ − C_3H_7 − S, 20%), 249 ($\dot{M}^+$ − Se − CH_3 − C_6H_5, 9%), 207 ($\dot{M}^+$ − Se − CH_3 − C_6H_5 − C_3H_7, 38%), 183 $(P(C_6H_5)_2)^+$, 22%). HR-EI-MS: found: 416.0348, calc: 420.0328. IR (KBr, cm^{-1}): $\tilde{\nu}$ 3154, 3052 and 2970 (w, ν(C–H)), 1571 (m, ν(C=C)), 1435 (vs, ν(P–C_6H_5)), 1381 (s, ν(C=N)), 1182 (s, ν(C=S)), 753, 714 and 701 (s, δ(C_6H_5)). UV/Vis (CH_2Cl_2): λ_{max}: 281 nm. EA: calc. C 54.41, H 5.05, N 6.68, S 7.65, found: C 54.48, H 5.06, N 6.70, S 7.78.

Procedure for the synthesis of phosphane borane complexes

In a Schlenk flask, the phosphanes **3a,b** (500 mg, 1.6 to 1.1 mmol) were dissolved in 20 mL of tetrahydrofuran. Borane tetrahydrofuran complex (1 M solution in tetrahydrofuran, 1 equivalent) was added and the reaction mixture was stirred for 3 h at ambient temperature. The solvent was removed *in vacuo* (8×10^{-3} mbar), and the crude product was washed with n-pentane and dried *in vacuo* (8×10^{-3} mbar).

1,3-Dimethyl-4-diphenylphosphino-κP-borane-imidazole-2-thione (7a)

Yield: (470 mg, 90%), colorless solid, mp. 184 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.17 (d vbr, $^{2}J_{P,H}$ = 15.7 Hz, 3H, BH_3), 3.37 (s, 3H, N^3–CH_3), 3.51 (s, 3H, N^1–CH_3), 6.47 (d, $^{3}J_{P,H}$ = 2.6 Hz, 1H, C^5–H), 7.40–7.60 (m, 10H, C_6H_5–H). ^{13}C{^{1}H} NMR (75.0 MHz, $CDCl_3$): δ = 35.1 (s, N^3–CH_3), 35.6 (s, N^1–CH_3), 118.3 (d, $^{1}J_{P,C}$ = 70.5 Hz, C^4), 126.2 (d, $^{1}J_{P,C}$ = 60.1 Hz, *ipso*-C_6H_5), 128.2 (d, $^{2}J_{P,C}$ = 14.2 Hz, C^5),129.4 (d, $J_{P,C}$ = 10.3 Hz, C_6H_5), 132.4 (d, $J_{P,C}$ = 2.6 Hz, C_6H_5), 132.8 (d, $J_{P,C}$ = 10.3 Hz, C_6H_5), 167.9 (d, $^{3+4}J_{P,C}$ = 3.2 Hz, C=S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 8.3 (s vbr). ^{11}B{^{1}H} NMR (96.3 MHz, $CDCl_3$): δ = −41.2 (s br). MS (EI, 70 eV): *m*/*z* = 326 ($\dot{M}^+$, 3%), 312 ($\dot{M}^+$ − BH_3, 92%), 279 ($\dot{M}^+$ − BH_3 − S, 3%), 221 ($\dot{M}^+$ − BH_3 − S − C_6H_5 − CH_3, 49%), 199 ($C_{12}H_{13}BP^+$, 6%), 183 $(P(C_6H_5)_2)^+$, 8%). HR-ESI-MS: found: 349.1073, calc.: 349.1070, as $C_{17}H_{20}BN_2PSNa^+$. IR (KBr, cm^{-1}): $\tilde{\nu}$ 3150 (w, ν(C–H)), 2389 (vs, ν(B–H), E), 2347 (s, ν(B–H), A′), 1437 (vs, ν(P–C_6H_5)), 1393 (vs, ν(C=N)), 1154 (vs, ν(C=S)), 694 (s, δ(C_6H_5)). UV/Vis (Et_2O): λ_{max}: 209 nm.

1,3-Diphenyl-4-diphenylphosphino-κP-borane-imidazole-2-thione (7b)

Yield: (466 mg, 94%), colorless solid, mp. 186 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.10 (s vbr, 3H, BH_3), 6.92 (d, $^{3}J_{P,H}$ = 7.9 Hz, 1H, C^5–H), 7.15–7.68 (m, 20H, C_6H_5–H). ^{13}C{^{1}H} NMR (75.0 MHz, $CDCl_3$): δ = 120.2 (d, $^{1}J_{P,C}$ = 63.4 Hz, C^4), 125.2 (s, N–C_6H_5), 126.0 (d, $^{1}J_{P,C}$ = 61.4 Hz, P–*ipso*-C_6H_5), 128.4 (d, $^{2}J_{P,C}$ = 16.8 Hz, C^5), 128.9 (s, *N*–C_6H_5), 129.0 (d, $J_{P,C}$ = 7.1 Hz, P–C_6H_5), 129.5 (s, N–C_6H_5), 132.0 (d, $J_{P,C}$ = 2.6 Hz,

P–C_6H_5), 133.0 (d, $J_{P,C}$ = 10.3 Hz, P–C_6H_5), 136.0 (s, N–*ipso*-C_6H_5), 137.6 (s, N–*ipso*-C_6H_5), 170.0 (s, C═S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 8.7 (s vbr). $^{11}B\{^1H\}$ NMR (96.3 MHz, $CDCl_3$): δ = −40.5 (s br). MS (EI, 70 eV): *m*/*z* = 450 ($\dot{M}^+$, 10%), 436 ($\dot{M}^+ - BH_3$, 100%), 403 ($\dot{M}^+ - BH_3 - S$, 34%), 359 ($\dot{M}^+ - BH_3 - C_6H_5$, 30%), 327 ($\dot{M}^+ - BH_3 - C_6H_5 - S$, 2%), 281 ($\dot{M}^+ - BH_3 - 2C_6H_5$, 2%), 251 ($C_{15}H_{11}N_2S^+$, 20%), 199 ($C_{12}H_{13}BP^+$, 10%), 183 ($P(C_6H_5)_2^+$, 20%). HR-ESI-MS: found: 473.1391, calc.: 473.1383, as $C_{27}H_{24}N_2PSNa^+$. IR (KBr, cm^{-1}): $\tilde{\nu}$ 3058 (w, ν(C–H)), 2363 (vs, ν(B–H), E), 2341 (vs, ν(B–H), A′), 1438 (vs, ν(P–C_6H_5)), 1381 (s, ν(C═N)), 1167 (m, ν(C═S)), 755 and 694 (s, δ(C_6H_5)). UV/Vis (Et_2O): λ_{max}: 209 nm. EA: calc. C 72.01, H 5.37, N 6.22, S 7.12, found: C 71.04, H 5.39, N 6.06, S 7.04.

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