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Synthesis and first complexes of $C^{4/5}$ P-bifunctional imidazole-2-thiones†

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A synthetic route to $C^{4/5}$-bis(phosphinoyl)imidazole-2-thiones (**7d,e**) (d: R^1 = ^{n}Bu, R^2 = Me; e: R^1 = *n*-dodecyl, R^2 = Me) and $C^{4/5}$-bis(thio/selenophosphinoyl)imidazole-2-thiones (**8b,c**), (**9a,b,e**) and **10a** (a: R^1 = R^2 = Me; b: R^1 = R^2 = Ph, c: R^1 = ^{i}Pr, R^2 = Me) is presented that employs initial C^5 lithiation of mono-phosphinoyl/thiophosphinoyl substituted imidazole-2-thiones (**3c–e**)/(**4a–c,e**) followed by reaction with chlorodiphenylphosphane, leading to mixed phosphinoyl and phosphanyl substituted imidazole-2-thiones (**5c–e**) or mixed thiophosphinoyl and phosphanyl substituted imidazole-2-thiones (**6a–c,e**). Subsequent oxidation of mixed phosphinoyl and phosphanyl substituted imidazole-2-thione (**5d,e**) with H_2O_2–urea gives the bis(phosphinoyl) substituted imidazole-2-thiones (**7d,e**), and the oxidation of mixed thiophosphinoyl and phosphanyl substituted imidazole-2-thione (**6a–c,e**) using H_2O_2–urea, elemental sulfur or elemental selenium gives a set of mixed P(v)-chalcogenide substituted imidazole-2-thiones (**8b, c**), (**9a,b,e**) and **10a**, respectively. P(v,v) substituted imidazole-2-thiones **7d** and **9a** reacted with tellurium tetrachloride, titanium tetrachloride or palladium dichloride to give complexes **11d**, (**12d** and **12d'**) and **14a**, respectively, having a bidentate chelate (**11d** and **14a**) or a monodentate bonding motif (**12d,d'**). The titanium complexes **12d,d'** slowly and selectively converted into the mono-ethoxy substituted product **13** possessing a seven membered chelate motif being unprecedented in the titanium chemistry of phosphine oxide donor ligands. The compounds were characterized by elemental analyses, spectroscopic and spectrometric methods and, in addition, X-ray diffraction studies in the case of **5c**, **7d**, **8b**, **9a** and **13**.

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Introduction

Imidazole-2-thiones, which are cyclic analogs of thiourea, are of particular interest because of their wide range of applications,[1–3] *e.g.* as precursors to unusual thion-ylides,[4] tri-coordinate sulfuranes,[5] desulfurizing agents for a thiirane,[6] in catalyzing cross-linking of polymers,[7] complexating agents,[8] halogen free ionic liquids,[9] stable N-heterocyclic carbenes (NHCs)[10] as well as in the field of biologically[11] active compounds.

The electronic properties of NHCs can be influenced by electron withdrawing groups such as CN, Cl, NO_2 positioned in the backbone (C^4 and C^5);[12] recently, $^{13}C^2$ labelled NHCs with broken symmetry were investigated with respect to the scalar couplings between the metal centre or C^2 and the other ring atoms.[13] We envisioned that backbone substitution of imidazole-2-thiones and, ultimately, NHCs by electron withdrawing groups such as phosphinoyl groups not only will help to "tune" electronic properties and understand NMR features, but also to synthesize homo- and hetero-bimetallic complexes, hence enabling a new catalyst design.[14] Therefore, backbone functionalization of imidazole-2-thiones is a promising prospect, that includes ring-annellated[15] and amino[16] group substituted imidazole-2-thiones. On the other hand, organophosphorus compounds such as tertiary phosphine oxides, sulfides, or selenides **I**, **II** (Fig. 1) bearing O, S, or Se donor atoms have been the subject of numerous investigations because of their coordination chemistry, extractive metallurgy, catalytic properties, and structural chemistry.[17] Among them, the *carbon* bridged bisphosphanes **II**, **III** have been extensively used in coordination chemistry because of their chelation to metals, and their metal complexes have been employed in catalysis.[18] The combination of good σ-donor properties, and minimal steric demands in combination with the rigidity offered by *ortho*-phenylene-type backbones that increases

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†Electronic supplementary information (ESI) available. CCDC 888238–888241 and 934725. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt51557e

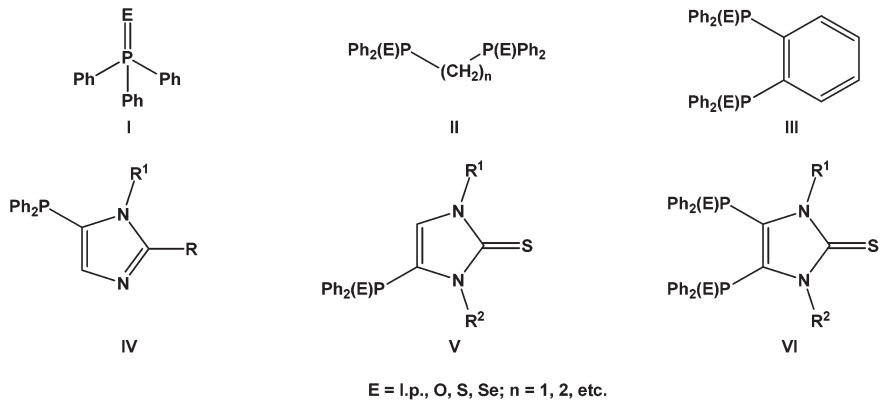


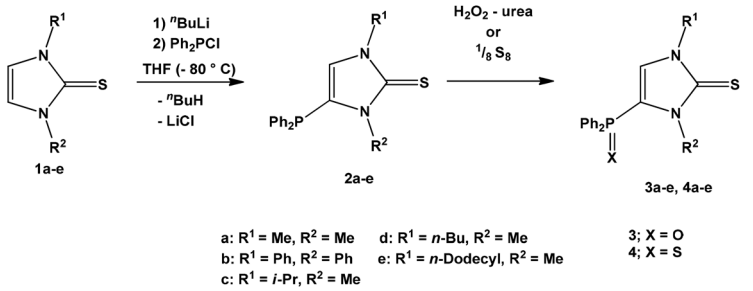
Fig. 1 Various types of organophosphorus ligands **I–VI**.

resistance of the ligand against dissociation from the metal makes chelates of the structural type **III** especially interesting. Recently, phosphane substituted imidazoles **IV** have been synthesized and their reactivity and spectroscopic properties studied.[19] However, flexible access to a library of imidazole-2-thione substituted phosphanes has not achieved considerable attention, until reports on 4-phosphanylated 1,2-dialkyl imidazole-2-thiones **V**, their oxidation and complexation reactions appeared.[20] From this perspective it is particularly useful to synthesize compounds of type **VI** having P(III) and/or P(V) centres and imidazole-2-thiones as rigid spacers, thus being able to start studying their coordination properties. Additionally, synthesis of homo- and hetero-bimetallic complexes using imidazole-2-thiones as precursors to imidazole-2-ylidenes[21] and novel P-functional ionic liquids[9] may prove realistic. Herein, the first synthesis of backbone-bifunctional imidazole-2-thiones (type **VI**) having pairs of P(V/III) and P(V/V) phosphorus substituents is presented. Furthermore, a preliminary study on the coordination abilities of P(V/V) systems using tellurium tetrachloride, titanium tetrachloride and palladium dichloride suggests that this ligand design may prove generally useful for both transition metals and main-group elements.

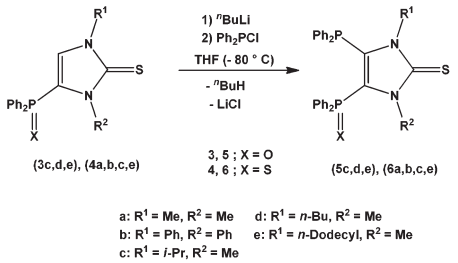
Results and discussion

Recently, a facile protocol to access *C*-phosphinoyl substituted imidazole-2-thiones has been reported.[20] It was observed that the steric demand of one *n*-butyl group (at one nitrogen centre) is not sufficient to selectively direct the lithiation and the following phosphanylation and, hence, the C^4 and C^5 (positional) isomers were obtained. Following this protocol,[20] **2a–e** were synthesized and used for P-oxidation to obtain the *C*-phosphinoyl derivatives **3** and the *C*-thiophosphinoyl derivatives **4** as starting materials (Scheme 1). In the case of **3d,e** and **4e** mixtures of both $C^{4/5}$ positional isomers (denoted hereafter as **3d′,e′** and **4e′**) (ratio 2.3 : 1 (**3d** : **3d′**), 2 : 1 (**3e** : **3e′**), 2 : 1 (**4e** : **4e′**)) were used as such for further transformations without any purification or separation. Deprotonation of **3c–e** and **4a–c,e** was achieved in THF using ^{n}BuLi (−78 °C). Subsequent addition of 1 equivalent of chlorodiphenylphosphane afforded imidazole-2-thiones **5c–e** and **6a–c,e** having mixed-valence P(V/III) substituents (Scheme 2); completion of the reactions was monitored by ^{31}P NMR spectroscopy. In the case of **4c–e** (X = O) the reaction did not proceed selectively to **5c–e** and yielded a mixture of products that could not be identified; nevertheless, small amounts of **5c** were obtained through crystallization, sufficient to perform an X-ray diffraction analysis.

In contrast to the *P*-oxide derivatives, selective reactions were observed for *P*-sulfides to yield **6a–c,e** (X = S); the reaction of **4e** yielded two $C^{4/5}$ positional isomers of **6e,e′** in a 1.7 : 1 ratio. After removal of lithium chloride, the crude products were purified by crystallization from toluene, followed by washing with *n*-pentane, thus giving **6a–c** as colourless solids. In contrast, **5c** precipitated from a methylene chloride solution of the crude product mixture on standing at ambient



Scheme 1 Synthesis of phosphinoyl and thiophosphinoyl substituted imidazole-2-thiones.



Scheme 2 Synthesis of mixed-valence P(v/iii) imidazole-2-thiones.

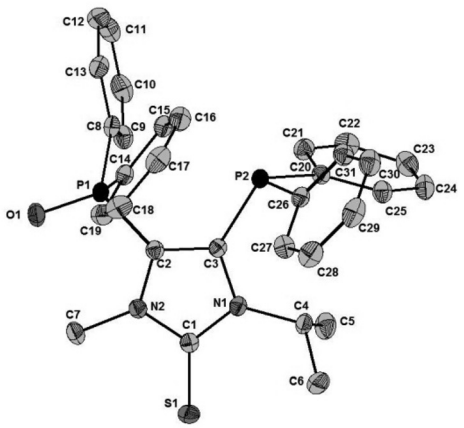
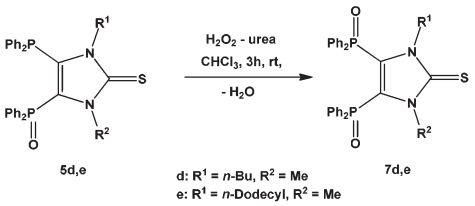


Fig. 2 Molecular structure of compound **5c**; hydrogen atoms have been omitted for clarity (50% probability level). Selected bond distances (Å) and angles (°): C(1)–N(1) 1.371(2), C(1)–N(2) 1.3372(2), C(2)–C(3) 1.3737(1), C(1)–S(1) 1.6844(16), P(1)–O(1) 1.4832(12), P(1)–C(2) 1.8279(16), P(1)–C(8) 1.7958(16), P(1)–C(14) 1.8045(16); C(2)–P(1)–C(8) 105.75(7), C(2)–P(1)–C(14) 104.89(7), C(3)–P(2)–C(26) 104.25(7), C(8)–P(1)–O(1) 112.17(7), C(14)–P(1)–O(1) 111.61(7).

temperature. The constitution of compounds **5c** and **6a–c,e** was established by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. Based on previous observations on mono-substituted imidazole-2-thiones,[20] the assignments of resonances in the ^{31}P{^{1}H} NMR spectra of **5c–e** were straightforward: doublets at about 20 to 22 ppm are typical for P(v) environments ($P(O)Ph_2$) and those at −35 to −33 ppm for P(iii) (PPh_2); the resonances displayed $^{3}J_{P,P}$ couplings of 7–11 Hz. Similarly, **6a–c,e** showed doublets at about 29 to 31 ppm ($(S)PPh_2$) and −33 to −28 ppm (PPh_2) with $^{3}J_{P,P}$ couplings of 11–19 Hz.

For compound **5c** a single-crystal X-ray diffraction study was performed using a crystal obtained from a super-saturated methylene chloride solution at ambient temperature. Compound **5c** crystallizes in a monoclinic lattice with space group *P*21/*n*; the molecular structure is shown in Fig. 2 and selected structural parameters are given in the figure caption of the corresponding compound; for crystallographic data see Table S1 (ESI† section).

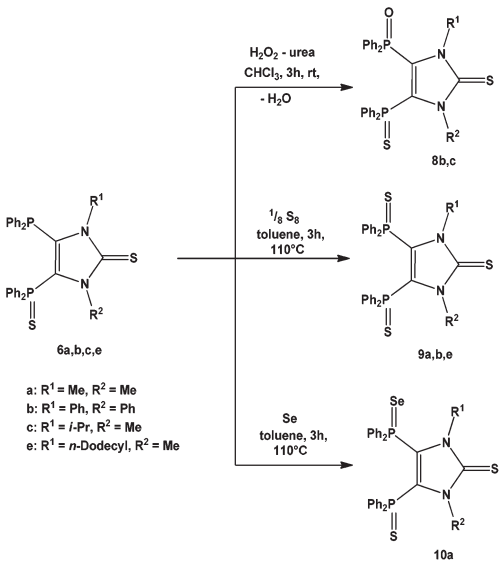
The determined bond lengths and angles of **5c** are within the typical ranges observed for diphenylphosphanyl and diphenylphosphinoyl substituted imidazoles[21] and imidazole-2-thiones.[20] The atoms P(1) and P(2) are staggered slightly out



Scheme 3 Synthesis of *C*,*C*′-bis(phosphinoyl) imidazole-2-thiones.

of the plane of the imidazole-2-thione ring. The folding angle of the P(1)–C(2)–C(3) plane and the imidazole best plane is 4.29(19)° while that for the P(2)–C(3)–C(2) and imidazole planes is 5.19(18)°. Hence, the torsion angle between the P(1)–C(2)–C(3) and P(2)–C(3)–C(2) planes is 9.5(2)°. The P(1)–O(1) bond vector is directed away from P(2) with a tilt angle of 5.73(11)° with respect to the imidazole ring plane.

Various oxidation reactions displayed in Schemes 3 and 4 are possible for these bis(phosphorus) adducts. Reaction of a mixture of **5d,d′** (ratio 1.6 : 1) and **5e,e′** (ratio 1.7 : 1) with H_2O_2–urea led to the P(v,v) substituted imidazole-2-thiones **7d,e**. Since **5d** and **5d′** and/or **5e** and **5e′** are two positional isomers, upon oxidation both of the isomers gave single products **7d,e** and no further isomerization is observed for **7d,e**. These products were purified by column chromatography using silica as the stationary phase and diethyl ether–petrol ether as the eluent. The ^{31}P{H} NMR spectra of **7d,e** each showed two distinguishable signals at 22.2 and 24.4 ppm (**7d**) and 22.3 and 24.4 ppm (**7e**), which can be assigned to the two magnetically (and chemically) inequivalent phosphinoyl groups. Upon oxidation, both phosphorus nuclei appeared as singlets indicating that the $^{3}J_{P,P}$ coupling between the phosphorus nuclei was significantly diminished, so that no coupling was observed. Compound **7e** showed a remarkably low melting point (128 °C) compared to the other *C*,*C*′-bis(phosphanyl/phosphinoyl) substituted imidazole-2-thione



Scheme 4 Synthesis of mixed P(v/v) substituted imidazole-2-thiones.

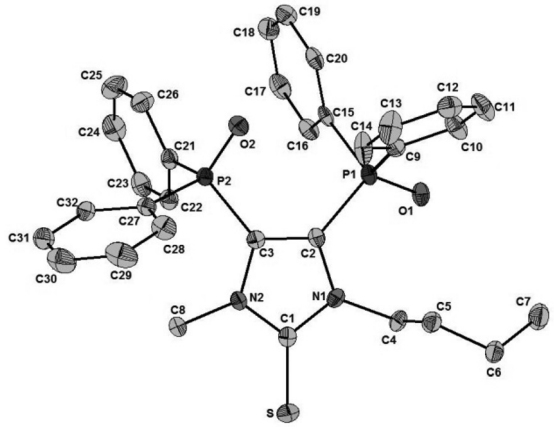


Fig. 3 Molecular structure of compound **7d**; hydrogen atoms have been omitted for clarity (50% probability level). Selected bond distances (Å) and angles (°): C(1)–N(1) 1.367(3), C(1)–N(2) 1.371(3), C(2)–C(3) 1.367(3), C(1)–S(1) 1.6777(1), P(1)–O(1) 1.4857(1), P(1)–C(2) 1.832(2), P(1)–C(9) 1.8007(2), P(1)–C(15) 1.8046(2); N(1)–C(1)–N(2) 105.42(19), C(3)–C(2)–N(1) 106.8(2), C(3)–C(2)–P(1) 31.95(18), N(1)–C(2)–P(1) 120.85(17), C(9)–P(1)–C(2) 108.38(11), C(2)–C(3)–P(2) 127.71(18).

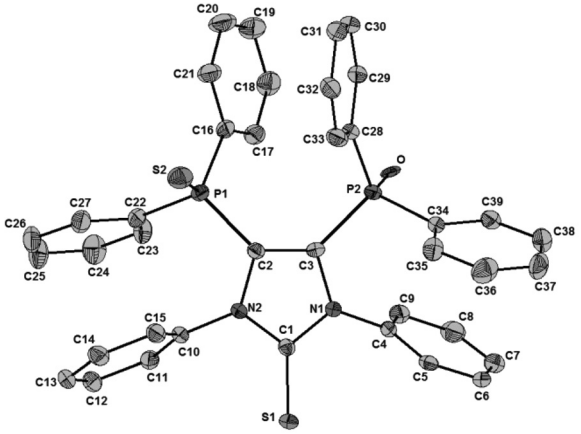


Fig. 4 Molecular structure of compound **8b**; hydrogen atoms have been omitted for clarity (50% probability level). Selected bond distances (Å) and angles (°): C(1)–N(1) 1.376(3), C(1)–N(2) 1.369(3), C(2)–C(3) 1.375(3), C(4)–N(1) 1.453(3), C(1)–S(1) 1.665(2), P(1)–S(2) 1.9169(10), P(2)–O(1) 1.604(2), P(1)–C(16) 1.808(2); C(2)–P(1)–C(16) 107.22(11), C(2)–P(1)–C(22) 104.55(11), C(2)–P(1)–S(2) 113.22(10), C(3)–P(2)–C(28) 108.94(11), C(3)–P(2)–O(1) 114.32(10), C(22)–P(1)–S(2) 112.89(9).

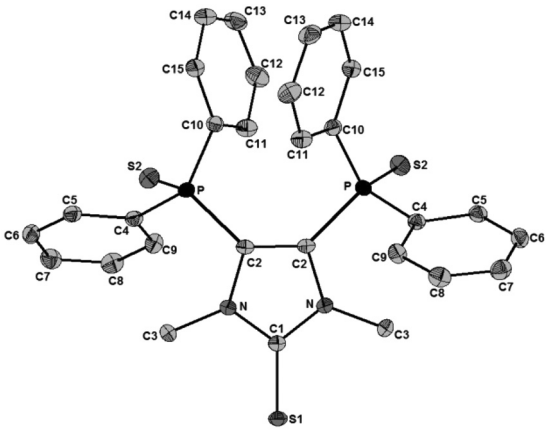


Fig. 5 Molecular structure of compound **9a**; hydrogen atoms have been omitted for clarity (50% probability level). Selected bond distances (Å) and angles (°): C(1)–N 1.3648(15), C(1)–N#1 1.3649(15), C(2)–C(2)#1 1.377(3), C(3)–N 1.4679(16), C(1)–S(1) 1.6768(19), P–S(2) 1.9501(5), P–C(2) 1.8223(13), P–C(4) 1.8259(14); C(2)–P–C(4) 101.64(6), C(10)–P–C(2) 108.49(6), N–C(2)–P 118.77(9), C(10)–P–S(2) 116.34(5), C(2)–P–S(2) 114.04(5), C(5)–C(4)–P 118.28(10), C(9)–C(4)–P 121.90(10).

derivatives described in this paper and, hence, could serve as a precursor to P-bifunctional ionic liquids.

Reactions of compounds **6a–c,e** with H_2O_2–urea, elemental sulfur or selenium allowed synthesis of a set of mixed P(v/v)-chalcogenide substituted imidazole-2-thiones. The reaction of **6b,c** with H_2O_2–urea gave C^4-thiophosphinoyl, C^5-phosphinoyl imidazole-2-thiones **8b,c**. The reaction of **6a,b,e(e′)** with elemental sulfur or selenium led quantitatively and selectively to **9a,b,e** and **10a**, respectively. As previously mentioned, the reaction of **6e,e′** with elemental sulfur provided the single product **9e**. Compounds **8b,c** were recrystallized from hot toluene and obtained as white solids. Compounds **9a,b,e** and **10a** were crystallized directly from the reaction mixtures. Analytical data on these new compounds are presented in the Experimental section. As mentioned previously, upon oxidation both P(v) phosphorus nuclei appeared as singlets in the $^{31}P\{H\}$ NMR spectra and no $^3J_{P,P}$ couplings were observed.

Single-crystal X-ray diffraction analysis was performed for **7d**, **8b** and **9a**. Selected bond parameters are given in the figure caption of the corresponding compounds, and for crystallographic data see Tables S1 and S2 (ESI† section). The molecular structures of **7d**, **8b** and **9a** are shown in Fig. 3–5, respectively, and provide unambiguous constitutional proof.

Irrespective of the substitution pattern in the backbone of the imidazole-2-thione moiety, it was observed that the C=S bond length of **5c**, **7d**, **8b** and **9a** remained constant. It is noteworthy that atoms P(1) and P(2) for **7d** are found slightly out of the plane of the imidazole-2-thione ring: the folding angle of the P(1)–C(2)–C(3) plane and the C(1)–N(2)–C(2)–C(3)–N(1) plane is 8.0(3)° and that of the P(2)–C(3)–C(2) plane and the C(1)–N(2)–C(2)–C(3)–N(1) plane is 0.7(3)°. The torsion angle between the P(1)–C(2)–C(3) plane and the P(2)–C(3)–C(2) plane is 8.6(3)°. Furthermore, two different dihedral angles were found for the O–P–C units and the imidazole-2-thione ring plane: 23.54(15)° for the O(1)–P(1)–C(2) plane and 28.69(16)° for the O(2)–P(2)–C(3) plane, respectively.

As observed above for **7d**, atoms P(1) and P(2) in compound **8b** are slightly out of the imidazole ring plane: the folding angle of the P(1)–C(2)–C(3) plane and the C(1)–N(2)–C(2)–C(3)–N(1) plane is 1.8(3)° and that of the P(2)–C(3)–C(2) plane and the C(1)–N(2)–C(2)–C(3)–N(1) plane is 6.5(3)°. The torsion angle between the P(1)–C(2)–C(3) plane and the P(2)–C(3)–C(2) plane is 8.0(4)°. Two different dihedral angles were found for the E–P–C units and the imidazole-2-thione ring plane: 79.49(13)° for the S(2)–P(1)–C(2) plane and 83.14(14)° for the

O–P(2)–C(3) plane, respectively. The PO and the PS units are located on opposite sides of the imidazole-2-thione plane.

Also in the structure of compound **9a**, both P atoms are slightly out of the plane of the imidazole-2-thione ring having two PS units on opposite sides of the imidazole-2-thione plane and are connected by a C2 axis.

Coordination chemistry studies

A methylene chloride solution of **7d** was treated with tellurium tetrachloride at ambient temperature to obtain **11d**; similarly, reaction of **7d** with titanium tetrachloride afforded **12d** and **12d′** (Scheme 5). The products were obtained as red (**11d**) and yellow (**12d**, **12d′**) solids after removal of the solvent *in vacuo* and repeated washing with *n*-pentane followed by drying of the residue. The coordination of **7d** to the tellurium and titanium centres was confirmed by NMR spectroscopy, *e.g.* the $^{31}P\{^{1}H\}$ NMR spectrum of **11d** showed two signals having slightly different chemical shifts compared to the starting material (24.6 and 23.3 ppm (**11d**) *vs.* 24.4 and 22.2 ppm (**7d**)), whereas two sets of two signals downfield of the later resonances were observed for the titanium complexes (29.8, 27.1 ppm and 29.2, 27.6 ppm, ratio 1.3 : 1) which were attributed to the two mono-coordinated phosphinoyl titanium adducts **12d** and **12d′**.

Single-crystal X-ray diffraction analysis was performed using a crystal obtained from a saturated methylene chloride–diethyl ether (1 : 1) solution of **12d** and **12d′** at low temperature (−20 °C, 4 weeks). The result showed the molecular structure of complex **13** (Fig. 6), revealing a new 7-membered chelate motif and that one of the chloride ligands was replaced by an ethoxy group.

Albeit the pathway of product formation is unclear, cleavage of diethyl ether upon coordination to titanium tetrachloride with elimination of ethyl chloride and ethoxy substitution of a chloride has been reported by Mutin and coworkers.[22] For crystallographic data of **13** see Table S2 (see ESI† section); selected structural parameters are given in the figure caption. The unit cell of **13** contains three methylene chloride molecules. Since there is no strong interaction between these (solvent) molecules and **13**, they were omitted for clarity in Fig. 6. The structure of **13** shows a distorted octahedral geometry of the Ti(IV) centre having a chelating bis(phosphinoyl) substituted imidazole-2-thione ligand. Although coordination of phosphine oxides to a titanium centre is known,[23] in general, formation of a seven-membered metallacyclic ring consisting of a bisphosphine oxide ligand has not yet been reported in the Cambridge Crystallographic Data Base. It should be noted that synthesis of a related seven-membered metallacyclic ring of $TiCl_4$ with diester ligands of the type *cis* RO(O)C–C=C–C(O)OR and their use in Ziegler–Natta catalysis has been reported by Iiskola and coworkers.[24] The titanium coordination environment has a distorted octahedral geometry as revealed by the bond angles at the Ti centre: all *trans* angles are equal to 172°, whereas most of the *cis* angles deviate much from 90°, *e.g.* O(2)–Ti–Cl 85.3(1)°. The titanium–oxygen bond lengths are significantly different (Ti–O(3) 1.74(0), Ti–O(2) 2.04(0) and Ti–O(1) 2.06(0) [Å]), thus revealing the covalent and coordinative bonding nature. Only slight bond elongation was observed for both P=O bonds upon coordination to the titanium centre

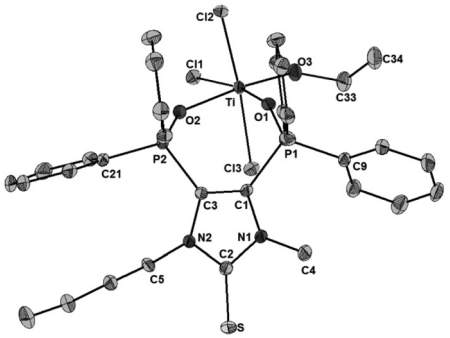
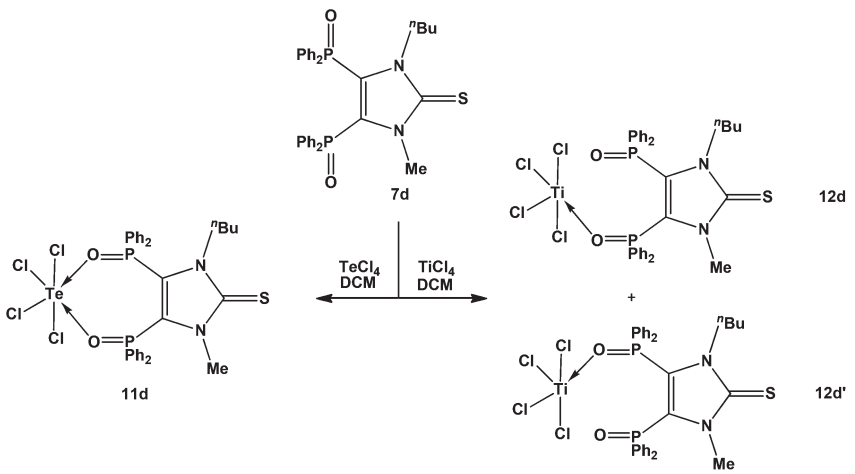
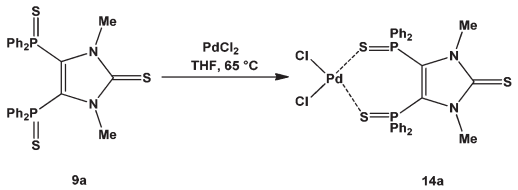


Fig. 6 Molecular structure of complex **13**; hydrogen atoms have been omitted for clarity (50% probability level). Selected bond distances (Å) and angles (°): C(2)–N(1) 1.363(3), C(2)–N(2) 1.368(3), C(1)–C(3) 1.374(3), C(2)–S 1.672(2), Ti–O(1) 2.0662(16), Ti–O(3) 1.7474(16), Ti–Cl(3) 2.3930(7), P(1)–O(1) 1.5052(16); C(3)–P(2)–O(2) 113.12(10), C(1)–P(1)–O(1) 109.70(8), O(2)–Ti–O(1) 80.82(6), O(3)–Ti–O(2) 172.01(7).



Scheme 5 Synthesis of the first P(V/V) imidazole-2-thione Te(IV) (**11d**) and Ti(IV) (**12d**, **12d′**) complexes.



Scheme 6 Synthesis of the first Pd(II) complex of a P(V/V) imidazole-2-thione.

(P(1)–O(1) 1.50(0) and P(2)–O(2) 1.49(0) Å *vs.* P(1)–O(1) 1.48(1) and P(2)–O(2) 1.47(1) Å in **7d**).

Finally, the reactivity of **9a** towards a cationic metal(II) centre was investigated, using palladium(II) as a case in point. When a solution of **9a** was treated with palladium dichloride (Scheme 6) at ambient temperature no reaction occurred after several days. Then the suspension was heated to 65 °C for a longer period of time (16 h) through which an orange solution was formed. Complex **14a** was obtained as an orange solid after removal of the solvent *in vacuo* and repeated washing with *n*-pentane and drying of the residue. The $^{31}P\{^{1}H\}$ NMR spectrum of complex **14a** showed a similar chemical shift compared to the starting material (29.6 ppm (**14a**) *vs.* 29.8 ppm (**9a**)); low solubility of **14a** prevented the acquisition of good quality ^{13}C NMR data. Taking the previous results into consideration, the chelating κS,κS-coordination of the ligand **9a** to the palladium centre can be deduced from the appearance of a singlet in the $^{31}P\{^{1}H\}$ NMR spectrum. The presence of two chloride ligands in **14a** was confirmed *via* pos. ESI-MS experiments which showed the *m*/*z* value 760.90 for the cation $Na[C_{29}H_{26}Cl_2N_2P_2PdS_3]^+$ (Na-**14a**) and the *m*/*z* value 702.94 of a cationic fragment (after loss of chloride from the molecule ion) that possessed one chloride ligand $[C_{29}H_{26}ClN_2P_2PdS_3]^+$.

Conclusions

A facile and effective protocol was presented that enables synthesis of $C^{4/5}$ disubstituted imidazole-2-thiones bearing diphenylphosphinoyl and diphenylphosphanyl groups or diphenylthiophosphinoyl and diphenylphosphanyl groups. It was observed that the directional abilities of *P*-sulfides are superior to *P*-oxides in the *C*-lithiation step. Subsequent oxidation of the diphosphanyl group using H_2O_2–urea, elemental sulfur or selenium selectively led to homo/hetero-chalcogenide P(V/V)-substituted imidazole-2-thiones. First investigations on the ligand properties of bisphosphine oxide and sulphide derivatives towards cationic metal(IV) and metal(II) centres revealed a preferred chelating mode in the case of the system tellurium tetrachloride/bisphosphine oxide and palladium dichloride/bisphosphine sulphide, whereas titanium tetrachloride/bisphosphine oxide preferred a κO-mono coordination. Upon chloride substitution the resulting ethoxy trichlorotitanium complex preferred the chelating bonding mode of the bisphosphine oxide ligand; the latter also represent the first example of such a titanium complex. Currently, studies on catalytic reactions using new titanium complexes are underway.

Experimental section

General considerations

The lithiation/phosphanylation reactions were performed under an argon atmosphere, using common Schlenk techniques and dry solvents. Tetrahydrofuran, diethyl ether, pentane, and toluene were dried over sodium wire/benzophenone, methylene chloride over calcium hydride and further purified by subsequent distillation. Chlorodiphenylphosphane was distilled prior to use and stored under an argon atmosphere; other chemicals were used as received. All NMR spectra were recorded on a Bruker 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 resonances and the ^{13}C signals of the deuterated solvents and ^{31}P to 85% H_3PO_4 as the 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 380 FT-IR spectrometer using KBr pellets or *via* total reflection (diamond ATR). The UV/Vis spectra were recorded in solution on a Shimadzu UV-1950 PC spectrometer. The X-ray diffraction 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 the full-matrix least-squares technique in anisotropic approximation for non-hydrogen atoms using the SHELXS97 and SHELXL97[25] program packages. Hydrogen atoms were located from Fourier synthesis and refined isotropically. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-888238 (**5c**), CCDC-888239 (**7d**), 888240 (**8b**), CCDC-888241 (**9a**), CCDC-934725 (**13**).

Typical lithiation and phosphanylation procedure for the synthesis of 5c–e and 6a–c,e

In a Schlenk flask, the P(V)-substituted imidazole-2-thiones **3c–e** or **4a–c,e** (10 mmol each) were dissolved in 50 mL of THF and cooled to −78 °C. 6.9 mL *n*-butyllithium (1.6 M in *n*-hexane, 11 mmol) was added and the reaction mixture was slowly warmed to −40 °C and stirred for 2 h at this temperature. The reaction mixture was cooled again to −78 °C and 1.98 mL (11 mmol) of chlorodiphenylphosphane (Ph_2PCl) was added and the reaction mixture stirred overnight while warming to ambient temperature. The solution was then concentrated *in vacuo* (8×10^{-3} mbar), the dry residue taken up in methylene chloride (50 mL) and filtered over a G3 frit equipped with a layer of Celite® to remove lithium chloride. The filtrate was collected and the solvent was removed *in vacuo*

(8×10^{-3} mbar). The crude product was purified *via* crystallization from hot toluene (20 mL) followed by washing with *n*-pentane (2×15 mL). In doing so colourless to light yellowish crystals of **5c** and **6a–c** were obtained. **5d,e** were not selectively obtained and, therefore, were used for further transformations without separation or purification. In the case of **6e**, two positional (C^4 (**6e**)- and C^5 (**6e′**) substituted) isomers were obtained in a 1.7 : 1 ratio (**6e** : **6e′**).

1-Isopropyl-3-methyl-4-diphenylphosphinoyl-5-diphenylphosphanyl-imidazole-2-thione (5c). Colourless crystals, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.23 (d, $^3J_{H,H}$ = 7.1 Hz, 6H, C_3H_7–CH_3), 3.57 (s, 3H, N^3–CH_3), 4.31 (hept, $^3J_{H,H}$ = 7.1 Hz, 1H, C_3H_7–C*H*), 7.21 (dd, $J_{P,H}$ = 8.2 Hz, $J_{H,H}$ = 7.1 Hz, 4H, C_6H_5–H), 7.27–7.39 (m, 12H, C_6H_5–H), 7.96 (dd, $J_{P,H}$ = 14.0 Hz, $J_{H,H}$ = 8.1 Hz, 4H, C_6H_5–H). ^{31}P {^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = −33.2 (d, $^3J_{P,P}$ = 10.2 Hz, Ph_2P-Imz), 21.4 (d, $^3J_{P,P}$ = 10.2 Hz, Ph_2P=O). Adduct **5c** precipitated in small amounts only after keeping the crude mixture in dichloromethane over two weeks at room temperature; the crystals thus obtained were used for the X-ray diffraction study.

1-*n*-Butyl-3-methyl-4(5)-diphenylphosphinoyl-5(4)-diphenylphosphanyl-imidazole-2-thione (5d(d′)). ^{31}P {^{1}H} NMR (121.5 MHz, THF): δ = −35.3 (d, $^3J_{P,P}$ = 7.8 Hz) and 20.2 (d, $^3J_{P,P}$ = 7.8 Hz) (**5d**), −31.9 (d, $^3J_{P,P}$ = 6.8 Hz) and 19.8 (d, $^3J_{P,P}$ = 6.8 Hz) (**5d′**) (**5d** : **5d′** 1.6 : 1 ratio) and unidentified products (37%); oily product.

1-*n*-Dodecyl-3-methyl-4(5)-diphenylphosphinoyl-5(4)-diphenylphosphanyl-imidazole-2-thione (5e(e′)). ^{31}P {^{1}H} NMR (121.5 MHz, THF): δ = −35.3 (d, $^3J_{P,P}$ = 7.9 Hz) and 20.0 (d, $^3J_{P,P}$ = 7.9 Hz) (**5e**), −31.9 (d, $^3J_{P,P}$ = 6.7 Hz) and 19.6 (d, $^3J_{P,P}$ = 6.7 Hz) (**5e′**) (**5e** : **5e′** 1.7 : 1 ratio) and unidentified products (45%); oily product.

1,3-Dimethyl-4-diphenylthiophosphinoyl-5-diphenylphosphanyl-imidazole-2-thione (6a). Yield: 4.10 g (7.80 mmol, 78%), colourless solid, m.p. 245 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.93 (s, 3H, N^3–CH_3), 3.56 (s, 3H, N^1–CH_3), 7.01–7.42 (m, 16H, C_6H_5–*H*), 7.48–7.83 (m, C_6H_5-*H*). ^{13}C{^{1}H} NMR (75.0 MHz, $CDCl_3$): δ = 36.0 (s br, N^1–CH_3), 36.3 (s, N^3–CH_3), 128.7 (d, $^1J_{P,C}$ = 60.8 Hz, P^{III}-*ipso*-C_6H_5), 128.9 (d, $J_{P,C}$ = 16.9 Hz, C_6H_5), 129.0 (d, $J_{P,C}$ = 13.6 Hz, C_6H_5), 130.3 (dd, $^1J_{P,C}$ = 50.9 Hz, $^2J_{P,C}$ = 15.6 Hz, C^5), 131.0 (d, $J_{P,C}$ = 18.8 Hz, C_6H_5), 131.6 (d, $^1J_{P,C}$ = 87.6 Hz, P^V-*ipso*-C_6H_5), 132.0 (d, $J_{P,C}$ = 3.1 Hz, C_6H_5), 132.2 (d, $J_{P,C}$ = 3.1 Hz, C_6H_5), 132.9 (d, $J_{P,C}$ = 14.9 Hz, C_6H_5), 133.5 (dd, $^1J_{P,C}$ = 102.2 Hz, $^2J_{P,C}$ = 38.5 Hz, C^4), 169.8 (dd, $J_{P,C}$ = 4.9 Hz, C=S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = −32.9 (m, $^3J_{P,H}$ = 6.4 Hz, $^3J_{P,P}$ = 10.5 Hz), 29.9 (m, $^3J_{P,H}$ = 14.3 Hz, $^3J_{P,P}$ = 10.5 Hz). MS (EI, 70 eV): *m*/*z* (%) 528 (68) $[M]^+$, 496 (52) $[M - S]^+$, 451 (100) $[M - C_6H_5]^+$, 419 (30) $[M - C_6H_5 - S]^+$, 405 (8) $[M - C_6H_5 - S - CH_3]^+$, 344 (8) $[M - P(C_6H_5)_2]^+$, 329 (5) $[M - P(C_6H_5)_2 - CH_3]^+$, 312 (5) $[M - P(C_6H_5)_2 - S]^+$, 183 (21) $[P(C_6H_5)_2]^+$. HR-MS ($C_{29}H_{26}N_2P_2S_2$): found: 528.1018, calc.: 528.1013. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3052 (w, ν(C–H)), 1582 (w, ν(C=C)), 1431 (s), 1372 (vs) 1163 (s, ν(C=S)), 644 (s, ν(P=S)). UV/Vis (Et_2O): λ_{max}: 271 nm. EA: calc. C, 65.89, H, 4.96, N, 5.30, S, 12.13; found: C, 64.79, H, 5.02, N, 5.12, S, 11.82.

1,3-Diphenyl-4-diphenylthiophosphinoyl-5-diphenylphosphanyl-imidazole-2-thione (6b). Yield: 5.21 g (8.0 mmol, 80%), colourless solid, m.p. 260 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.66 (dd, $J_{H,H}$ = 8.3 Hz, $J_{H,H}$ = 1.3 Hz, 2H, C_6H_5–H), 6.92 (t, $J_{H,H}$ = 7.5 Hz, 2H, C_6H_5–H), 7.00 (td, $J_{P,H}$ = 7.7 Hz, $J_{H,H}$ = 7.1 Hz, $J_{H,H}$ = 1.3 Hz, 4H, C_6H_5–H), 7.10–7.36 (m, 18H, C_6H_5–H), 7.93 (ddd, $J_{P,H}$ = 14.3 Hz, $J_{H,H}$ = 7.2 Hz, $J_{H,H}$ = 1.3 Hz, 4H, C_6H_5–H). ^{13}C {^{1}H} NMR (75.0 MHz, $CDCl_3$): δ = 128.2 (d, $J_{P,C}$ = 6.1 Hz, C_6H_5), 128.4 (d, $J_{P,C}$ = 18.4 Hz, C_6H_5), 128.4 (s, C_6H_5), 128.6 (s, C_6H_5), 128.6 (s, C_6H_5), 129.0 (s, C_6H_5), 129.3 (s, C_6H_5), 130.1 (s, C_6H_5), 131.5 (d, $J_{P,C}$ = 2.9 Hz, C_6H_5), 132.9 (dd, $^1J_{P,C}$ = 53.2 Hz, $^2J_{P,C}$ = 17.2 Hz, C^5), 131.9 (d, $J_{P,C}$ = 2.5 Hz, C_6H_5), 132.1 (d, $J_{P,C}$ = 19.7 Hz, C_6H_5), 132.1 (d, $J_{P,C}$ = 2.4 Hz, C_6H_5), 132.2 (d, $J_{P,C}$ = 2.6 Hz, C_6H_5), 132.6 (d, $J_{P,C}$ = 2.1 Hz, C_6H_5), 135.3 (dd, $^1J_{P,C}$ = 87.3 Hz, $^2J_{P,C}$ = 33.4 Hz, C^4), 136.0 (d, $^1J_{P,C}$ = 56.8 Hz, P^{III}-*ipso*-C_6H_5), 137.0 (d, $^1J_{P,C}$ = 78.8 Hz, P^V-*ipso*-C_6H_5), 173.6 (dd, $J_{P,C}$ = 5.0 Hz, C=S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = −28.4 (m, $^3J_{P,H}$ = 7.7 Hz, $^3J_{P,P}$ = 18.6 Hz), 30.3 (m, $^3J_{P,H}$ = 14.3 Hz, $^3J_{P,P}$ = 18.6 Hz). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3052 (w, ν(C–H)), 1596 (m, ν(C=C)), 1437 (vs) 1156 (m, ν(C=S)), 634 (s, ν(P=S)). UV/Vis (Et_2O): λ_{max}: 209 nm. EA: calc. for $C_{39}H_{30}N_2P_2S_2$: C, 71.76, H, 4.63, N, 4.29, S, 9.82; found: C, 71.96, H, 4.89, N, 4.16, S, 9.88.

1-Isopropyl-3-methyl-4-diphenylthiophosphinoyl-5-diphenylphosphanyl-imidazole-2-thione (6c). Yield: 4.0 g (7.20 mmol 72%), colourless solid, m.p. 232 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.13 (d, $^3J_{H,H}$ = 7.1 Hz, 6H, C_3H_7–CH_3), 3.50 (s, 3H, N^3–CH_3), 4.11 (hept, $^3J_{H,H}$ = 7.1 Hz, 1H, C_3H_7–C*H*), 7.25 (dd, $J_{P,H}$ = 8.2 Hz, $J_{H,H}$ = 7.1 Hz, 4H, C_6H_5–H), 7.29–7.41 (m, 12H, C_6H_5–H), 7.93 (dd, $J_{P,H}$ = 14.0 Hz, $J_{H,H}$ = 8.1 Hz, 4H, C_6H_5–H). ^{13}C{^{1}H} NMR (75.0 MHz, $CDCl_3$): δ = 17.6 (s, C_3H_7–*C*H_3), 35.4 (s, N^3–CH_3), 52.7 (s, C_3H_7–*C*H), 128.7 (d, $J_{P,C}$ = 13.2 Hz, C_6H_5), 128.7 (dd, $^1J_{P,C}$ = 117.3 Hz, $^2J_{P,C}$ = 49.4 Hz, C^4), 129.0 (d, $J_{P,C}$ = 19.1 Hz, C_6H_5), 131.3 (d, $J_{P,C}$ = 19.1 Hz, C_6H_5), 131.8 (d, $J_{P,C}$ = 2.5 Hz, C_6H_5), 131.8 (d, $J_{P,C}$ = 11.0 Hz, C_6H_5), 132.2 (s, C_6H_5), 132.9 (dd, $^1J_{P,C}$ = 52.2 Hz, $^2J_{P,C}$ = 20.3 Hz, C^5), 133.9 (d, $^1J_{P,C}$ = 63.7 Hz, P^{III}-*ipso*-C_6H_5), 134.4 (d, $^1J_{P,C}$ = 102.6 Hz, P^V-*ipso*-C_6H_5), 167.5 (d, $J_{P,C}$ = 5.1 Hz, C=S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = −34.3 (m, $^3J_{P,H}$ = 8.2 Hz, $^3J_{P,P}$ = 16.5 Hz), 30.2 (m, $^3J_{P,H}$ = 14.0 Hz, $^3J_{P,P}$ = 16.5 Hz). MS (EI, 70 eV): *m*/*z* (%) 556 (75) $[M]^+$, 524 (30) $[M - S]^+$, 479 (100) $[M - S - C_3H_7]^+$, 437 (100) $[M - 2S - C_3H_7 - CH_3]^+$, 183 (50) $[P(C_6H_5)_2]^+$. HR-MS: 556.1326, calc.: 556.1326. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3049 (w, ν(C–H)), 1584 (m, ν(C=C)), 1436 (vs), 1385 (m) 1176 (s, ν(C=S)), 644 (s, ν(P=S)). UV/Vis (Et_2O): λ_{max}: 270 nm. EA: calc. for $C_{31}H_{30}N_2P_2S_2$: C, 66.89, H, 5.43, N, 5.03, S, 11.52; found: C, 66.41, H, 5.43, N, 4.91, S, 11.68.

1-*n*-Dodecyl-3-methyl-4(5)-diphenylthiophosphinoyl-5(4)-diphenylphosphanyl-imidazole-2-thione (6e(e′)). Yield of the **6e** : **6e′** mixture (both isomers): 6.41 g (9.3 mmol, 93%), yellow dense liquid, ^{31}P {^{1}H} NMR (121.5 MHz, THF): δ = −32.3 (d, $^3J_{P,P}$ = 11.0 Hz) and 30.3 (d, $^3J_{P,P}$ = 11.0 Hz) (**6e**), {−31.9 (d, $^3J_{P,P}$ = 10.8 Hz) and 29.0 (d, $^3J_{P,P}$ = 10.8 Hz) (**6e′**)} (**6e** : **6e′** 1.7 : 1 ratio).

Procedure for the generation of *C*-phosphinoyl derivatives

To 1 mmol of the phosphane derivatives **6b,c**, dissolved in 15 mL of chloroform, 0.094 g (1 mmol) of the

hydrogenperoxide–urea adduct was added into a round bottom flask and the reaction mixture was stirred until ^{31}P NMR showed complete conversion of the starting material (*ca.* 3 h). The reaction mixture was then filtered over a funnel equipped with filter paper to remove the urea, and the filtrate was collected and concentrated *in vacuo* (8×10^{-3} mbar). The crude product was purified *via* crystallization from hot toluene and the obtained crystalline material was washed with *n*-pentane (2×5 mL) and dried *in vacuo* (8×10^{-3} mbar).

7d,e were synthesized by taking the crude reaction mixtures (ratios 1.6 : 1 (**5d** : **5d′**) and 1.7 : 1 (**5e** : **5e′**)) obtained from **5d,e** (coming from **3e**) and subsequent reaction with 0.94 g (10 mmol) of the H_2O_2–urea adduct. The products were isolated after purification by column chromatography at room temperature using silica as the stationary phase and diethyl ether as the eluent.

1-*n*-Butyl-3-methyl-4,5-bis(diphenylphosphinoyl)imidazole-2-thione (7d). Yield: 2.28 g (4.0 mmol, 40%) (the given yield is with reference to the starting material **3d** used), colourless solid, m.p. 198 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.71 (t, $^3J_{H,H}$ = 7.3 Hz, 3H, C_4H_9–CH_3), 1.03–1.16 (m, 2H, C_4H_9–CH_2), 1.31–1.45 (m, 2H, C_4H_9–CH_2), 3.34 (s, 3H, N^3–CH_3), 4.44 (t, $^3J_{H,H}$ = 8.2 Hz, 2H, C_4H_9–CH_2), 7.22–7.50 (m, 16H, C_6H_5–H), 7.61–7.72 (m, 4H, C_6H_5–H). ^{13}C{^{1}H} NMR (75.0 MHz, $CDCl_3$): δ = 13.5 (C_4H_9–CH_3), 19.8 (C_4H_9–CH_2), 30.2 (C_4H_9–CH_2), 36.7 (N^3–CH_3), 49.0 (C_4H_9–CH_2), 128.0 (d, $J_{P,C}$ = 13.4 Hz, C_6H_5), 128.6 (d, $J_{P,C}$ = 13.2 Hz, C_6H_5), 130.4 (dd, $^1J_{P,C}$ = 112.8 Hz, $^2J_{P,C}$ = 15.7 Hz, C^4/C^5), 131.2 (d, $^1J_{P,C}$ = 113.7 Hz, *ipso*-C_6H_5), 131.6 (d, $^1J_{P,C}$ = 112.6 Hz, *ipso*-C_6H_5), 131.6 (d, $J_{P,C}$ = 10.9 Hz, C_6H_5), 131.7 (dd, $^1J_{P,C}$ = 110.8 Hz, $^2J_{P,C}$ = 15.4 Hz, C^5/C^4), 132.3 (d, $J_{P,C}$ = 11.1 Hz, C_6H_5), 132.4 (d, $J_{P,C}$ = 2.4 Hz, C_6H_5), 132.6 (d, $^1J_{P,C}$ = 2.9 Hz, C_6H_5), 167.5 (dd, $J_{P,C}$ = 5.5 Hz, C═S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 22.2 (quint br, $^3J_{P,H}$ = 13.0 Hz), 24.4 (quint br, $^3J_{P,H}$ = 13.1 Hz). MS (EI, 70 eV): *m*/*z* (%) 570 (83) [M]$^+$, 537 (38) [M − S]$^+$, 514 (10) [M − C_4H_8]$^+$, 493 (21) [M − C_6H_5]$^+$, 437 (100) [M − C_4H_8 − C_6H_5]$^+$, 201 (47) [Ph_2PO]$^+$, 77 (12) [Ph]$^+$. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2961 and 2910 (w, ν(C–H)), 1589 (m, ν(C═C)), 1437 (s), 1395 (s), 1337 (s), 1270 (s), 1187 (vs, ν(C═S)). UV/Vis (CH_2Cl_2): λ_{max}: 268 nm. EA: calc. for $C_{32}H_{32}N_2O_2P_2S$: C, 67.36, H, 5.65, N, 4.91, S, 5.62; found: C, 67.35, H, 5.40, N, 4.93, S, 5.96.

1-*n*-Dodecyl-3-methyl-4,5-bis(diphenylphosphinoyl)imidazole-2-thione (7e). Yield: 2.04 g (3.0 mmol, 30%) (the given yield is with reference to the starting material **3e**), colourless solid, m.p. 128 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.80 (t, $^3J_{H,H}$ = 6.9 Hz, 3H, $C_{12}H_{25}$–CH_3), 0.97–1.38 (m, 20H, $C_{12}H_{25}$–CH_2), 3.30 (s, 3H, N^3–CH_3), 4.38 (t, $^3J_{H,H}$ = 8.3 Hz, 2H, $C_{12}H_{25}$–CH_2), 7.17–7.46 (m, 16H, C_6H_5–H), 7.56–7.65 (m, 4H, C_6H_5–H). ^{13}C{^{1}H} NMR (75.0 MHz, $CDCl_3$): δ = 14.1 ($C_{12}H_{25}$–CH_3), 22.7 ($C_{12}H_{25}$–CH_2), 26.6 ($C_{12}H_{25}$–CH_2), 28.2 ($C_{12}H_{25}$–CH_2), 29.0 ($C_{12}H_{25}$–CH_2), 29.3 ($C_{12}H_{25}$–CH_2), 29.4 ($C_{12}H_{25}$–CH_2), 29.5 ($C_{12}H_{25}$–CH_2), 29.6 ($C_{12}H_{25}$–CH_2), 31.9 ($C_{12}H_{25}$–CH_2), 36.7 (N^3–CH_3), 49.3 ($C_{12}H_{25}$–CH_2), 128.0 (d, $J_{P,C}$ = 13.3 Hz, C_6H_5), 128.6 (d, $J_{P,C}$ = 13.3 Hz, C_6H_5), 130.2 (dd, $^1J_{P,C}$ = 103.8 Hz, $^2J_{P,C}$ = 15.9 Hz, C^4/C^5), 131.1 (d, $^1J_{P,C}$ = 113.7 Hz, *ipso*-C_6H_5), 131.6 (dd, $^1J_{P,C}$ = 100.7 Hz, $^2J_{P,C}$ = 15.4 Hz, C^5/C^4), 131.7 (d, $^1J_{P,C}$ = 115.1 Hz, *ipso*-C_6H_5), 131.7 (d, $J_{P,C}$ = 10.5 Hz, C_6H_5), 132.3 (d, $J_{P,C}$ = 10.5 Hz, C_6H_5), 132.6 (d, $J_{P,C}$ = 3.1 Hz, C_6H_5), 169.6 (dd, $J_{P,C}$ = 5.5 Hz, C═S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 22.3 (quint br, $^3J_{P,H}$ = 12.9 Hz), 24.4 (quint br, $^3J_{P,H}$ = 13.2 Hz). MS (EI, 70 eV): *m*/*z* (%) 682 (55) [M]$^+$, 649 (47) [M − S]$^+$, 498 (11) [M − CH_3 − $C_{12}H_{25}$]$^+$, 482 (46) [M − S − $C_{12}H_{24}$]$^+$, 465 (21) [M − O − Ph_2PO]$^+$, 449 (100) [M − S − Ph_2PO]$^+$, 281 (11) [M − S − Ph_2PO − $C_{12}H_{24}$]$^+$, 201 (61) [Ph_2PO]$^+$, 77 (12) [Ph]$^+$. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3061 and 2010 (w, ν(C–H)), 1512 (m, ν(C═C)), 1438 (s), 1375 (s), 1339 (s), 1265 (s), 1182 (vs, ν(C═S)). UV/Vis (CH_2Cl_2): λ_{max}: 269 nm. EA: calc. for $C_{40}H_{48}N_2O_2P_2S$: C, 70.36, H, 7.09, N, 4.10, S, 4.69; found: C, 70.06, H, 6.35, N, 4.13, S, 4.76.

1,3-Diphenyl-4-diphenylthiophosphinoyl-5-diphenylphosphinoyl-imidazole-2-thione (8b). Yield: 0.55 g (0.83 mmol, 83%), colourless solid, m.p. 307 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.06–7.36 (m, 26 H, C_6H_5–*H*), 7.64–7.74 (dd, $^3J_{H,H}$ = 14.3 Hz, $^4J_{H,H}$ = 7.1 Hz, 4H, C_6H_5–*H*). ^{13}C{^{1}H} NMR (75.0 MHz, $CDCl_3$): δ = 124.3 (s, C_6H_5), 127.1 (d, $J_{P,C}$ = 1.4 Hz, C_6H_5), 127.4 (d, $J_{P,C}$ = 13.3 Hz, C_6H_5), 127.4 (d, $^1J_{P,C}$ = 90.5 Hz, *P*(*O*)-*ipso*-C_6H_5), 127.5 (d, $J_{P,C}$ = 13.2 Hz, C_6H_5), 127.6 (d, $J_{P,C}$ = 4.2 Hz, C_6H_5), 129.1 (d, $^1J_{P,C}$ = 66.5 Hz, *P*(*S*)-*ipso*-C_6H_5), 129.5 (d, $J_{P,C}$ = 4.4 Hz, C_6H_5), 129.9 (dd, $^1J_{P,C}$ = 109.5 Hz, $^2J_{P,C}$ = 13.7 Hz, C^5), 130.1 (d, $J_{P,C}$ = 11.7 Hz, C_6H_5), 130.2 (d, $J_{P,C}$ = 3.0 Hz, C_6H_5), 130.4 (d, $J_{P,C}$ = 11.6 Hz, C_6H_5), 131.4 (d, $J_{P,C}$ = 34.0 Hz, C_6H_5), 131.6 (dd, $^1J_{P,C}$ = 91.3 Hz, $^2J_{P,C}$ = 15.7 Hz, C^4), 135.1 (d, $J_{P,C}$ = 43.0 Hz, C_6H_5), 136.8 (s, C_6H_5), 171.8 (dd, $J_{P,C}$ = 3.8 Hz, C═S). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 14.1 (s, P═O), 30.8 (s, P═S). MS (EI, 70 eV): *m*/*z* (%) 668 (18) [M]$^+$, 636 (15) [M − S]$^+$, 559 (100) [M − S − Ph]$^+$, 452 (8) [M − Ph_2PS]$^+$, 434 (12) [M − S − Ph_2PO]$^+$, 217 (10) [Ph_2PS]$^+$, 201 (19) [Ph_2PO]$^+$. HR-MS: found: 668.1260, calc.: 668.1260. EA: calc. for $C_{39}H_{30}N_2OP_2S_2$: C, 70.04, H, 4.52, N, 4.19, S, 9.59, found: C, 68.92, H, 4.67, N, 4.32, S, 9.36.

1-Isopropyl-3-methyl-4-diphenylthiophosphinoyl-5-diphenylphosphinoyl-imidazole-2-thione (8c). Yield: 0.43 g (0.75 mmol, 75%), colourless solid, m.p. 215 °C. ^{1}H NMR (300 MHz, DMSO(d_6)): δ = 1.26 (d, $^3J_{H,H}$ = 6.7 Hz, 6H, C_3H_7–CH_3), 3.23(s, 3H, *N*^{3}–CH_3), 4.14 (sept, 1H, C_3H_7–C*H*), 7.67–7.23 (m, 16 H, C_6H_5–*H*), 8.03 (dd, 4H, C_6H_5–H). ^{13}C{^{1}H} NMR (75.0 MHz, DMSO(d_6)): δ = 17.2 (s, C_3H_7–CH_3), 30.6 (s, *N*^{3}–CH_3), 54.1 (s, C_3H_7–*C*H), 128.2 (d, $J_{P,C}$ = 11.0 Hz, C_6H_5), 128.9 (d, $J_{P,C}$ = 10.6 Hz), 130.0 (dd, $^1J_{P,C}$ = 112.6 Hz, $^2J_{P,C}$ = 11.0 Hz, C^5), 130.5(d, $J_{P,C}$ = 11.5 Hz, C_6H_5), 131.2 (d, $J_{P,C}$ = 3.1 Hz, C_6H_5), 131.4 (d, $J_{P,C}$ = 11.7 Hz, C_6H_5), 131.4 (d, $J_{P,C}$ = 56.8 Hz, *P*(*S*)-*ipso*-C_6H_5), 133.2 (d, $J_{P,C}$ = 2.8 Hz, C_6H_5), 133.4 (d, $J_{P,C}$ = 91.0 Hz, *P*(*O*)-*ipso*-C_6H_5), 133.7 (dd, $^1J_{P,C}$ = 112.6 Hz, $^2J_{P,C}$ = 11.0 Hz, C^4), 166.7 (dd, $J_{P,C}$ = 4.7 Hz, C═S). ^{31}P{^{1}H} NMR (121.5 MHz, DMSO(d_6)): δ = 21.1 (s, P═O), 31.9 (s, P═S). MS (EI, 70 eV): *m*/*z* (%) 572 (12) [M]$^+$, 540 (12) [M − S]$^+$, 526 (12) [M − S − CH_3]$^+$, 463 (28) [M − S − Ph]$^+$, 417 (100) [M − 2Ph]$^+$, 201 (70) [Ph_2PO]$^+$. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3055, 2986 (w, ν(C–H)), 1438 (m, ν(C═C)), 1374 (vs), 1426 (s), 1278 (s), 1162 (s, ν(C═S)). UV/Vis (CH_2Cl_2): λ_{max}: 254 nm. HR-MS: found: 572.1275, calc.: 572.1275. EA: calc. for $C_{31}H_{30}N_2OP_2S_2$: C, 65.02, H, 5.28, N, 4.89, S, 11.20; found: C, 64.28, H, 5.49, N, 5.01, S, 11.22.

Procedure for the generation of *C*-thio- and *C*-selenophosphinoyl derivatives

To a solution of phosphane derivatives **6a,b,e** (1 mmol) in 15 mL of toluene, 0.032 g (1 mmol) of elemental sulfur or 0.078 g (1 mmol) of selenium was added into a 50 mL Schlenk tube and heated for 3 h at 110 °C. The reaction mixture was cooled down to ambient temperature, whereby the product precipitated in the form of colourless crystals. The obtained crystals were washed with *n*-pentane (2 × 5 mL) and dried *in vacuo* (8×10^{-3} mbar).

1,3-Dimethyl-4,5-bis(diphenylthiophosphinoyl)imidazole-2-thione (9a). Yield: 0.50 g (0.9 mmol, 90%) colourless solid, m.p. 318 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.35(s, 6H, CH_3), 7.71–7.11 (m, 20H, C_6H_5–*H*). $^{13}C\{^1H\}$ NMR (75.0 MHz, $CDCl_3$): δ = 34.9 (s, CH_3), 127.2 (dd, $^1J_{P,C}$ = 71.3 Hz, $^2J_{P,C}$ = 14.7 Hz, C^4&C^5), 127.7 (d, $^1J_{P,C}$ = 66.7 Hz, *ipso*-Ph), 128.2 (d, $J_{P,C}$ = 13.5 Hz, C_6H_5), 129.5 (d, $J_{P,C}$ = 10.9 Hz, C_6H_5), 130.4 (d, $J_{P,C}$ = 3.2 Hz, C_6H_5), 164.3 (s br, C═S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 29.8 (bq, $^3J_{P,H}$ = 14.0 Hz). MS (EI, 70 eV): *m*/*z* (%) 560 (12) $[M]^{+}$, 529 (20) $[M - 2CH_3]^+$, 528 (60) $[M - S]^+$, 497 (19) $[M - 2\ CH_3 - S]^+$, 496 (56) $[M - 2S]^+$, 452 (27) $[M - 2CH_3 - Ph]^+$, 451 (100) $[M - S - Ph]^+$, 420 (10) $[M - 2CH_3 - S - Ph]^+$, 419 (40) $[M - 2S - Ph]^+$, 310 (10) $[M - Ph_2P(S) - S]^+$, 217 (25) $[Ph_2PS]^+$, 185 (19) $[Ph_2P]^+$. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3054, 2982 (w, ν(C–H)), 1435 (m, ν(C═C)), 1373 (vs), 1356 (s), 1158 (s, ν(C═S)). UV/Vis (CH_2Cl_2): λ_{max}: 265 nm. EA: calc. for $C_{29}H_{26}N_2P_2S_3$: C, 62.12, H, 4.67, N, 5.06, S, 17.16; found: C, 60.50, H, 4.77, N, 4.55, S, 15.40.

1,3-Diphenyl-4,5-bis(diphenylthiophosphinoyl)imidazole-2-thione (9b). Yield: 0.56 g (0.82, 82%), colourless solid, m.p. 315 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.22–6.91 (m, 22H, C_6H_5–*H*), 7.57–7.46 (dd, 8H, C_6H_5–*H*). $^{13}C\{^1H\}$ NMR (75.0 MHz, CD_2Cl_2): δ = 127.5 (s, C_6H_5), 128.5 (s, C_6H_5), 128.7 (d, $J_{P,C}$ = 13.8 Hz, C_6H_5), 129.9 (dd, $^1J_{P,C}$ = 93.2 Hz, $^2J_{P,C}$ = 13.5 Hz, C^4&C^5), 130.2 (d, $^1J_{P,C}$ = 85.4 Hz, P^V-*ipso*-C_6H_5), 131.1 (d, $J_{P,C}$ = 5.1 Hz, C_6H_5), 131.2 (s, C_6H_5), 136.0 (s, *N*-*ipso*-C_6H_5), 163.3 (s br, C═S). ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ = 30.4 (bq, $^3J_{P,H}$ = 13.7 Hz). MS (EI, 70 eV): *m*/*z* (%) 684 (20) $[M]^+$, 652 (29) $[M - S]^+$, 620 (15) $[M - 2S]^+$, 575 (100) $[M - S - Ph]^+$, 468 (40) $[M - Ph_2PS]^+$, 435 (12) $[M - S - Ph_2PS]^+$, 217 (25) $[Ph_2PS]^+$. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3138 and 3052 (w, ν(C–H)), 1590 (m, ν(C═C)), 1492 (s, ν(P–C═C)), 1438 (s), 1413 (s), 1168 (vs, ν(C═S)). UV/Vis (CH_2Cl_2): λ_{max}: 270 nm. HR-MS ($C_{39}H_{30}N_2P_2S_3$): found: 684.1046, calc.: 684.1040.

1-*n*-Dodecyl-3-methyl-4,5-bis(diphenylthiophosphinoyl)imidazole-2-thione (9e). Yield: 0.60 g (0.84 mmol, 84%), colourless solid, m.p. 191 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.81 (t, $^3J_{H,H}$ = 6.8 Hz, 3H, $C_{12}H_{25}$–CH_3), 1.19 (m, 18H, $C_{12}H_{25}$–CH_2), 1.70 (m, 2H, $C_{12}H_{25}$–CH_2), 3.35 (s, 3H, N^3–CH_3), 3.85 (t, $^3J_{H,H}$ = 8.3 Hz, 2H, $C_{12}H_{25}$–CH_2), 7.11–7.29 (m, 12H, C_6H_5–H), 7.46–7.60 (m, 8H, C_6H_5–H). $^{13}C\{^1H\}$ NMR (75.0 MHz, $CDCl_3$): δ = 14.1 ($C_{12}H_{25}$–CH_3), 22.7 ($C_{12}H_{25}$–CH_2), 26.6 ($C_{12}H_{25}$–CH_2), 27.2 ($C_{12}H_{25}$–CH_2), 29.0 ($C_{12}H_{25}$–CH_2), 29.4 ($C_{12}H_{25}$–CH_2), 29.6 ($C_{12}H_{25}$–CH_2), 29.7 ($C_{12}H_{25}$–CH_2), 31.9 ($C_{12}H_{25}$–CH_2), 36.9 (N^3–CH_3), 49.6 ($C_{12}H_{25}$–CH_2), 127.8 (d, $^1J_{P,C}$ = 99.4 Hz, *ipso*-C_6H_5), 128.5 (dd, $^1J_{P,C}$ = 98.8 Hz, $^2J_{P,C}$ = 28.9 Hz, C^4/C^5), 129.1 (d, $J_{P,C}$ = 13.4 Hz, C_6H_5), 129.1 (d, $J_{P,C}$ = 13.4 Hz, C_6H_5), 130.3 (d, $^1J_{P,C}$ = 10.4 Hz, C_6H_5), 130.5 (d, $J_{P,C}$ = 10.4 Hz, C_6H_5), 131.3 (d, $J_{P,C}$ = 1.8 Hz, C_6H_5), 170.0 (dd, $J_{P,C}$ = 5.0 Hz, C═S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 29.1 (quint br, $^3J_{P,H}$ = 14.5 Hz), 30.2 (quint br, $^3J_{P,H}$ = 14.5 Hz). MS (EI, 70 eV): *m*/*z* (%) 714 (20) $[M]^+$, 682 (10) $[M - S]^+$, 650 (12) $[M - 2S]^+$, 605 (70) $[M - S - CH_3]^+$, 497 (10) $[M - Ph_2P(S)]^+$, 217 (68) $[Ph_2PS]^+$, 185 (48) $[Ph_2P]^+$, 77 (12) $[Ph]^+$. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3054 and 2922 (w, ν(C–H)), 1594 (m, ν(C═C)), 1460 (s), 1436 (s), 1390 (s), 1158 (vs, ν(C═S)). UV/Vis (CH_2Cl_2): λ_{max}: 271 nm. EA: calc. for $C_{40}H_{48}N_2P_2S_3$: C, 67.20, H, 6.77, N, 3.92, S, 13.45; found: C, 66.54, H, 6.05, N, 3.68, S, 12.88.

1,3-Dimethyl-4-diphenylthiophosphinoyl-5-diphenylselenophosphinoyl-imidazole-2-thione (10a). Yield: 0.52 g (0.86 mmol, 86%), colourless solid, m.p. more than 327 °C (limit of the apparatus). ^{1}H NMR (300 MHz,$CDCl_3$): δ = 2.28 (s br, 3H, N^1–CH_3), 4.72 (d, $^3J_{P,H}$ = 4.7 Hz, N^3–CH_3), 7.05–7.65 (m, 20H, C_6H_5–*H*). $^{13}C\{^1H\}$ NMR (75.0 MHz, $CDCl_3$): δ = 36.3 (s, N^1–CH_3), 36.4 (s, N^3–CH_3), 128.1 (d, $J_{P,C}$ = 1.4 Hz, C_6H_5), 128.3 (d, $J_{P,C}$ = 2.5 Hz, C_6H_5), 129.5 (d, $J_{P,C}$ = 20.0 Hz, C_6H_5), 130.5 (d, $J_{P,C}$ = 9.0 Hz, C_6H_5), 164.0 (s br, C═S) (other missing signals could not be resolved due to the low signal to noise ratio caused by poor solubility). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 22.3 (qq, $^3J_{P,H}$ = 15.3 Hz, $^1J_{Se,P}$ = 776 Hz, P═Se), 30.0 (qq, $^3J_{P,H}$ = 15.2 Hz, P═S). MS (EI, 70 eV): *m*/*z* = 608 (34) $[M]^+$, 576 (21) $[M - S]^+$, 544 (37) $[M - 2S]^+$ 217 (35) $[Ph_2PS]^+$. HR-MS ($C_{29}H_{26}N_2P_2S_2Se$): found: 608.018, calc.: 608.017.

General procedure for the synthesis of 11d and (12d and 12d′)

To 0.20 g (0.35 mmol) of derivative **7d**, dissolved in 10 mL of methylene chloride, 0.09 g (0.35 mmol) of tellurium tetrachloride for **11d** or 0.34 mL (0.35 mmol) of titanium tetrachloride (1 M solution in methylene chloride) for (**12d** and **12d′**) was added and stirred at ambient temperature until the starting material was consumed (^{31}P NMR control). The solvent was then removed *in vacuo* (8×10^{-3} mbar) and the yellowish-red colored solid was washed with *n*-pentane (2 × 5 mL) and dried *in vacuo* (8×10^{-3} mbar).

[Tetrachloro{[1-*n*-butyl-3-methyl-4,5-bis(diphenylphosphinoyl)-imidazol-2-thione]-κO^P,κO^P}tellurium(IV)] (11d). Yield: 0.27 g (0.32 mmol, 93%), red solid, m.p. 216 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.61 (t, $^3J_{H,H}$ = 7.2 Hz, 3H, C_4H_9–CH_3), 0.82–0.92 (m, 2H, C_4H_9–CH_2), 1.14–1.23 (m, 2H, C_4H_9–CH_2), 3.62 (s, 3H, N^3–CH_3), 4.40 (s br, 2H, C_4H_9–CH_2), 7.25–7.45 (m, 12H, C_6H_5–*H*), 7.54–7.66 (m, 8H, C_6H_5–*H*). $^{13}C\{^1H\}$ NMR (75.0 MHz, $CDCl_3$): δ = 12.3 (C_4H_9–CH_3), 18.8 (C_4H_9–CH_2), 30.4 (C_4H_9–CH_2), 38.6 (N^3–CH_3), 50.5 (C_4H_9–CH_2), 127.9 (d, $J_{P,C}$ = 13.7 Hz, C_6H_5), 128.0 (d, $J_{P,C}$ = 14.1 Hz, C_6H_5), 130.8 (d, $J_{P,C}$ = 11.3 Hz, C_6H_5), 131.2 (d, $J_{P,C}$ = 11.4 Hz, C_6H_5), 132.5 (s br); some signals were not observed. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 24.6 (quint br), 23.3 (quint br). Pos-ESI-MS: $(C_{32}H_{32}N_2O_2P_2S)TeCl_3^+$ calcd (found) 804.97 (804.98). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2960 (s), 1588 (s), 1436 (vs), 1394 (br), 1311 (br), 1260 (w), 1119 (s), 1025 (w), 818 (b), 728 (s), 686 (vs). UV/Vis (CH_2Cl_2): λ_{max}: 230 nm.

[Tetrachloro{[1-*n*-butyl-3-methyl-4,5-bis(diphenylphosphinoyl)-imidazol-2-thione]-κO^P,κO^P}titanium(IV)] (12d and 12d′). Yield of both isomers: 0.25 g (0.32 mmol, 94%), yellow solid, ^{1}H NMR of the major isomer (300 MHz, $CDCl_3$): δ = 0.52 (t, $^3J_{H,H}$ = 7.3 Hz, 3H, C_4H_9–CH_3), 1.24–1.32 (m, 2H, C_4H_9–CH_2), 3.06 (s, 3H, N^3–CH_3), 3.68 (m, 2H, C_4H_9–CH_2), 4.82 (s br, 2H, C_4H_9–CH_2), 7.27–7.37 (m, 12H, C_6H_5–H), 7.44–7.54 (m, 8H, C_6H_5–H). ^{13}C{^{1}H} NMR of the major isomer (75.0 MHz, $CDCl_3$): δ = 13.2 (C_4H_9–*C*H_3), 19.5 (C_4H_9–*C*H_2), 29.7 (C_4H_9–*C*H_2), 37.4 (N^3–CH_3), 49.0 (C_4H_9–*C*H_2), 126.3 (d, $^1J_{P,C}$ = 120.6 Hz, *ipso*-C_6H_5), 126.9 (d, $^1J_{P,C}$ = 119.4 Hz, *ipso*-C_6H_5), 129.2 (d, $J_{P,C}$ = 14.0 Hz, C_6H_5), 129.4 (d, $J_{P,C}$ = 14.6 Hz, C_6H_5), 132.7 (s br), 134.3 (s br); some signals were not observed. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 29.8 (quint br), 27.1 (quint br) and 29.2 (quint br) & 27.6 (quint br) in a 1.3 : 1 ratio. Pos-ESI-MS: ($C_{32}H_{32}N_2O_2P_2S$)$TiCl_2CH_2OH^+$ calcd (found) 719.069 (719.068). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3055 (w), 2961 (w), 1588 (s), 1438 (vs), 1398 (vs), 1353 (w), 1310 (s), 1202 (w), 1168 (s), 1117 (s), 1091 (s), 1061 (vs), 996 (s), 930 (s), 830 (vs), 726 (vs), 688 (vs). UV/Vis (CH_2Cl_2): λ_{max}: 232 nm.

After crystallization from a methylene chloride–diethyl ether mixture (2 : 1) over 4 weeks, single X-ray quality crystals were obtained and used for the X-ray analysis. **13**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.53 (t, $^3J_{H,H}$ = 7.2 Hz, 3H, C_4H_9–CH_3), 1.13 (t, $^3J_{H,H}$ = 7.0 Hz, 3H, OEt–CH_3), 1.19–1.36 (m, 2H, C_4H_9–CH_2), 3.07 (s, 3H, N^3–CH_3), 3.40 (q, *J* = 7.12 Hz and 21.0 Hz, OEt–CH_2), 3.66 (m, 2H, C_4H_9–CH_2), 4.84 (s br, 2H, C_4H_9–CH_2), 7.26–7.37 (m, 12H, C_6H_5–*H*), 7.43–7.55 (m, 8H, C_6H_5–*H*). ^{13}C{^{1}H} NMR (75.0 MHz, $CDCl_3$): δ = 13.2 (s, C_4H_9–*C*H_3), 15.3 (s, OEt–CH_3), 19.5 (s, C_4H_9–*C*H_2), 30.0 (s, C_4H_9–*C*H_2), 37.3 (s, N^3–CH_3), 49.0 (s, C_4H_9–*C*H_2), 65.8 (s,OEt–CH_2), 126.2 (d, $^1J_{P,C}$ = 119.8 Hz, *ipso*-C_6H_5), 126.9 (d, $^1J_{P,C}$ = 119.3 Hz, *ipso*-C_6H_5), 129.2 (d, $J_{P,C}$ = 14.2 Hz, C_6H_5), 129.4 (d, $J_{P,C}$ = 14.1 Hz, C_6H_5), 132.7 (s br), 134.4 (s br), 169.7 (dd, $J_{P,C}$ = 5.6 Hz, C═S); some signals were not observed. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 29.9 (quint br), 27.2 (quint br) and 29.4 (quint br) & 27.7 (quint br) in a 1.2 : 1 ratio.

Procedure for synthesis of 14a

To 0.28 g of bis(phosphane sulfide) **9a** (0.5 mmol), 10 mL of THF and 0.088 g of palladium dichloride (0.5 mmol) were added in a 50 mL Schlenk tube and heated for 10 h at 60 °C. The reaction mixture was cooled down to ambient temperature. Then solvent was removed *in vacuo* (8×10^{-3} mbar). The yellow colored solid was washed with *n*-pentane (2 × 5 mL) and dried *in vacuo* (8×10^{-3} mbar).

[Dichloro{1,3-dimethyl-4,5-bis(diphenylthiophosphinoyl)-imidazole-2-thione-κS^P,κS^P}palladium(II)] (14a). Yield: 0.33 g (0.45 mmol, 90%), orange solid, m.p. 312 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.98 (s, 3H, N^3–CH_3), 3.10 (s, 3H, N^1–CH_3), 7.48–7.78 (m, 20H, C_6H_5–*H*). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 29.6 (br q, $^3J_{P,H}$ = 13.9 Hz). Pos-ESI-MS: $C_{29}H_{26}ClN_2P_2PdS_3^+$ calcd (found) 702.9454 (702.9454), $C_{29}H_{26}Cl_2N_2NaP_2PdS_3^+$ calcd (found) 760.9039 (760.9039). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2962 (w, ν(C–H)), 1456 (s), 1377 (s), 1377 (s), 1304 (s, ν(C═S)). UV/Vis (CH_2Cl_2): λ_{max}: 278 nm.

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