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Abstract: The facile regioselective synthesis of the P(III) substituted thiazol-2-thione **2** is presented. Reaction of **2** with hydrogenperoxide-urea, elemental sulfur and selenium resulted in P(V) chalcogenide thiazol-2-thiones **3**-**5**. All compounds were characterized using ^{31}P, ^{1}H, ^{13}C NMR, IR and elemental analyses and, additionally, by single-crystal X-ray diffraction technique. Oxidative desulfurization of the 5-phosphinoylated thiazol-2-thione **3** using hydrogenperoxide led to the first *C*-phosphanoyl substituted thiazolium salt (**6**). Deprotonation of **6** and in *situ* reaction with cyclooctadiene rhodium(I) chloride dimer yielded thiazol-2-ylidene rhodium(I) complex **7** which was confirmed by NMR spectroscopy and ESI-MS spectrometry.

Introduction

The chemistry of 1,3-thiazoles started in the late nineteenth century[1] and since then they have become an important class of heterocycles being of great interest due to their broad spectrum of remarkable industrial biological and pharmaceutical applications.[2-5] 1,3-Thiazol-2-thiones in particular emerged to have valuable applications in photography, radiochemistry, agrochemistry and polymer chemistry[6-8] but their potential as precursors for thiazolium salts and in turn N-heterocyclic carbenes (NHC)[9, 10] made them subject of high interest in organometallic, coordination[10] and catalytic chemistry.[11, 12] Despite the fact that the isolation of free thiazol-2-ylidenes remained a difficult target for decades, Breslow explained their presence and usage in nature by showing their role in the catalysis of benzoin condensation.[13] Since then thiazol-2-thiones and thiazolium salts have been preferentially explored as unique precursors for designing NHCs and considerable amount of research can be attributed to these thiazole-based isolobal, divalent and neutral carbon species and their complexes.[10-12, 14] The backbone functionalization of NHCs with different groups *e.g.* halo[15, 16], cyano and nitro[17, 18] received enormous interest due the impact of these moieties upon the overall reactivity and catalytic properties of NHC metal complexes.[19, 20] These investigations then recently led to the decoration of NHC backbones with heteroatoms.[21-27] C^4-Phosphanylated imidazol-2-ylidene **I** (Figure 1) represent the first example,[28] which was obtained via treatment of 1,3-dimesityl-imidazol-2-ylidene with a phosphaalkene. This reaction was described as "abnormal" because the outcome in the form of a 4-substituted NHC derivative **XII,** having the unprotected C^2 position intact, was quite unexpected. A C^2-C^4 rearrangement was used to gain access to C^4- and/or $C^{4,5}$-functionalized imidazol-2-ylidenes**,**[29] and hetero- and/or homo-bimetallic Au and Pd[30] complex, e.g. **II** were reported. In a different approach, $C^{4,5}$-bis-phosphanylated imidazol-2-ylidene complexes were obtained from imidazolium salt[31] serving as the NHC precursor.

I,3-Thiazol-2-ylidenes have been used in organo catalysis for years and are subject of high interest for chemists,[32,33] even before their isolation by Arduengo in 1997 (**III**).[9] Based on earlier investigations on imidazoles, it is known that heteroatoms at the backbone (can) have a considerable effect on the reactivity and catalytic properties of NHC-metal compounds,[34, 35] as a consequence of synthetic challenges, NHCs (type **VI**) backbone is (mostly) restricted to the presence of alkyl or aryl groups.[9, 14] Based on our recent investigations in this area, *i.e.* synthesis of mono- and bis(phosphanoylation) of imidazol-2-thiones and their conversion into mono- and bimetallic complexes,[36] we became interested to extend this synthetic strategy using thiazol-2-thiones. We envisioned that backbone substitution of thiazol-2-thione with electron withdrawing phosphanoyl group could enable not only to design mono and bimetallic complexes, but will also enable to further knowledge about the chemistry of thiazol-2-thiones,[37-39] thiazol-2-ylidenes and their complexes currently accessible.[40-43]

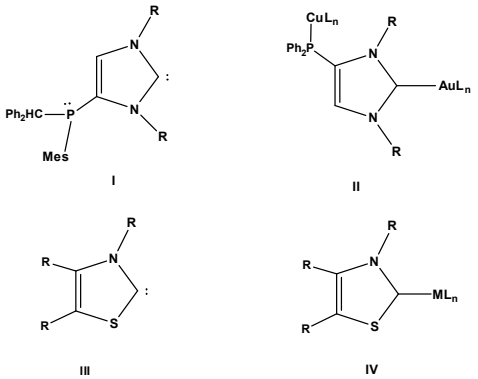

Figure 1. Examples of backbone P-substituted NHCs **I**, dinuclear complexes **II**, thiazole-based NHC **III** and NHC-metal complex **IV** (R denotes an alkyl or aryl group)**.**

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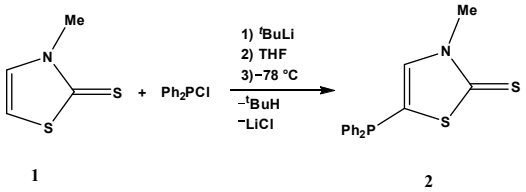
Results and discussion

First attempts to synthesize **2** from *N*-methyl thiazol-2-thione **1**[44] via the lithiation phosphanylation sequence[45,46] using ^{n}BuLi as base was met with limited success. But using ^{t}BuLi at low temperature achieved the synthesis of compound **2** via regioselective lithiation of **1** followed by the addition of chloro(diphenyl)phosphane (Scheme 1). As revealed by the $^{31}P\{^{1}H\}$ NMR spectrum, **2** was obtained selectively in good yields (72%), having a resonance at −23 ppm, thus being close to the value of the related imidazol-2-thione derivative (-31 ppm[45]). The ^{1}H NMR spectrum of **2** displayed a singlet (3.59 ppm), a doublet (7.14 ppm) and a multiplet (7.24–7.36 ppm) which were assigned to the CH_3, CH and C_6H_5 protons, respectively: all of which are in the expected range for heterocycles having a diphenylphosphanyl substituent at the backbone. Filtration over silica gel, followed by recrystallization from hot toluene and washing with *n*-pentane (3×5 mL) afforded pure **2** as white powder; crystals suitable for X-ray diffraction study were obtained via slow solvent evaporation.



Scheme 1. Synthesis of C^5-phosphanyl substituted thiazol-2-thione **2**.

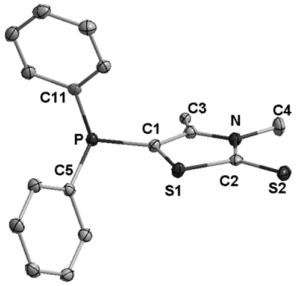
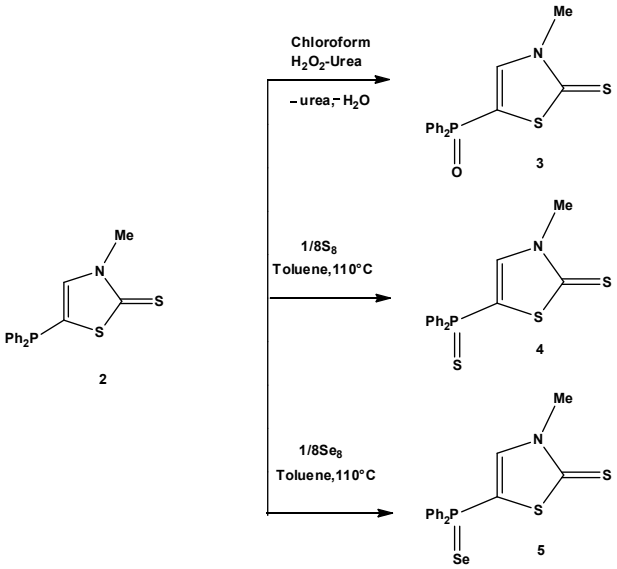


Fig. 2. Molecular structure of compound **2** (thermal ellipsoids are drawn at a 50 % probability level, hydrogen atoms have been omitted for clarity).Selected bond distances (Å) and angles (°): C(2)-S(2)1.6674(14), C(1)-P1.8098(13), N-C(2)-S(1)108.54(10), S(1)-C(1)-P 125.46(8), C(3)-C(1)-P 125.60(11).

Compound **2** (figure 2) crystallized in the monoclinic system (space group P c), and the molecular structure confirms the regiochemistry of the phosphanyl substituent (C^5position). Selected parameters are given in the caption of figure 2, but will be discussed together with other derivatives later.

In order to study the reactivity of phosphanyl-thiazol-2-thione **2**, various oxidation reactions were carried out (Scheme 2) using our established protocols.[45,46] The reaction of **2** with the H_2O_2-urea adduct proceeded in a clean manner, as revealed by $^{31}P\{^{1}H\}$ NMR spectroscopic monitoring. The ^{31}P NMR resonance of **3**(18.7 ppm) is similar to literature known values.[45-47] The ^{31}P NMR resonances of compound **4** (30.7 ppm) and **5** (19.2 ppm), which were obtained via reaction of **2** with elemental sulfur or selenium, obtained in very high yield (89 %) (Scheme2), are also in the expected shift range.[45-47] The ^{1}H NMR spectra of **3-5** displayed similar, characteristic signals being assigned to N–CH_3, *m*-, *p*-C_6H_5, C^4–H and the *o*-C_6H_5 protons in a straightforward manner.



Scheme 2. Synthesis of P(V) substituted thiazol-2-thiones.

Single crystal diffraction studies were performed for **3**, crystals were obtained via slow evaporation of concentrated chloroform solution of **3** (monoclinic, space group: P21/c). Compound **3** followed the same pattern of differences in the thiazole ring bond angles and bond distances as observed for **2**. However, the C(1)-C(2) and S(2)-C(3) bonds of **3** appeared to be slightly shorter than those of **2**; similarly, slight decrease in the C(1)-P bond distance occurs, *i.e.* **2:** 1.8098(13) Å and 1.7917(17) Å in **3**.

The structures of compounds **4** and **5** were also confirmed by single-crystal X-ray diffraction studies; molecular structures of **4** (monoclinic, P21/c) and **5** (triclinic, P-1) are shown in figure 4 and 5. While single crystals of **4** were obtained by slow evaporation of its chloroform solution, compound **5** crystallized upon slow cooling of the reaction solution. Whereas the unit cell of compound **5** exhibits two independent molecules (Figure 5), there was only one in case of **4**. As the bond lengths of both molecules of **5** are within the margins of the experimental error, only one data set will be given here. The P-S bond distance of **4** (1.9442(16) Å) and P-Se bond distance (2.1098(8) Å) of **5** are within the expected range and can be compared with literature known values of similar compounds, *i.e. the* P-S distance of 1.9526(8) Å in 4-diphenylthiophosphoryl-imidazol-2-thione) and the P-Se distance of 2.1083(6) 4-diphenylselenophosphoryl-imidazol-2-thione) respectively.[45] The C=S bond distance of **4** (1.663(4) Å) did not show much variation in comparison to **2** (1.6674(14) Å) while the bond in **5** (1.658(3) Å) appeared to be slightly shorter than in **2** and **4**. Interestingly, a significant narrow-wing of the S(1)-C(1)-P angle (121.48(9)° was observed for **3** as compared to those angles in **2**,**4** and **5** which lie in the range 125.4-126.1°. The opposite angle (C(2)-C(1)-P) in **3** appeared to be widened (129.08(12)°) compared to those of compounds **2**, **4** and **5** (124.0-125.8°).

Attempts were made to synthesize the corresponding *P*-telluride derivative. Despite being selective, the reaction of **2** with elemental tellurium (110°C in toluene) did not lead to completion (only 18% conversion of **2**). The $^{31}P\{^{1}H\}$ NMR spectrum showed a new signal at

14.7 ppm, but Te satellites were not observed due to the low content of the product.[47,48] As all attempts to purify this compound and, hence, to establish its constitution failed, this proposal remains tentative.

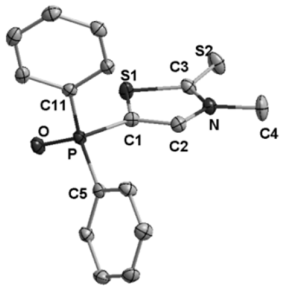


Fig. 3 Molecular structure of compound **3** (thermal ellipsoids are drawn at a 50 % probability level; hydrogen atoms have been omitted for clarity).Selected bond distances (Å) and angles (°): S(2)-C(3) 1.6552(17), P-C(1) 1.7914(17), P-O 1.4895(11), N-C(3)-S(1) 108.01(12), S(1)-C(1)-P 121.48(9), C(2)-C(1)-P 129.08(12).

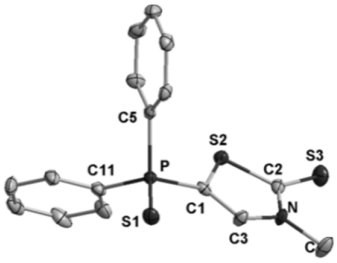


Fig. 4. Molecular structure of **4** (thermal ellipsoids are drawn at a 50 % probability level; hydrogen atoms have been omitted for clarity). Selected bond distances (Å) and angles (°): C(2)-S(3) 1.663(4), C(1)-P 1.800(4), P-S(1) 1.9442(16), N-C(2)-S(2) 108.5(3), S(2)-C(1)-P 126.1(3), C(3)-C(1)-P(1) 125.8(2).

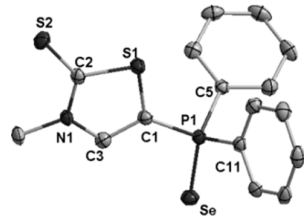
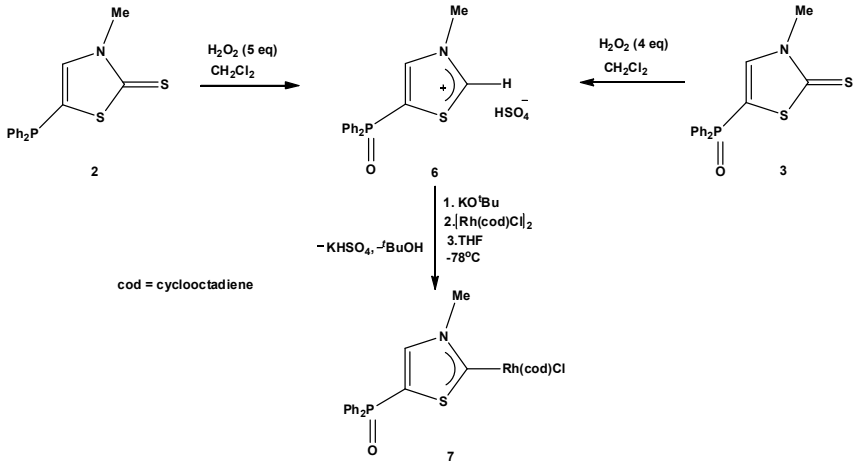


Fig. 5 Molecular structure of 5(thermal ellipsoids are drawn at a 50 % probability level; hydrogen atoms have been omitted for clarity).Selected bond distances (Å) and angles (°): C(2)-S(2) 1.658(3), C(1)-P(1) 1.789(3), P(1)-Se(1) 2.1098(8), N(1)-C(2)-S(1) 108.58(19), S(1)-C(1)-P(1) 125.27(13), C(3)-C(1)-P 124.0(3).

Having achieved a facile and high yield access to *P*(III) and *P*(V) substituted thiazol-2-thione, interest arose to convert them into thiazolium salts and to explore their chemistry and properties. As the conversion into free NHCs and/or NHC metal complexes are of particular interest, we decided to aim first at a deprotonation of a thiazolium salt using the established protocol.[49] The widely used method for the conversion of imidazol-2-thiones and/or thiazol-2-thiones into their corresponding hetazolium salts is the oxidative desulfurization using benzoyl peroxide and sodium bicarbonate,[50] nitric acid,[51] iron(III) chloride[52] and or hydrogen peroxide.[10,53, 54] Synthesis of P(V) functional thiazolium derivative **6** was achieved via oxidative desulfurization, treating a dichloromethane solution of **2** with five eq. of H_2O_2 at 0 °C (Scheme 3). Derivative **6** could be also prepared by treating **3** in dichloromethane with four equivalents of H_2O_2 at 0°C, and warming to ambient temperature. After several steps (see experimental part), **6** was obtained as hygroscopic yellowish semi solid, which was washed (3x10mL) with *n*-pentane and finally isolated as white powder.



Scheme 3. Synthesis of the first P-functional thiazolium salt **6** and thiazol-2-ylidene metal complex (**7**)

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The conversion of the *P*(III) functionality into the corresponding *P*(V) was clearly demonstrated by the $^{31}P\{^{1}H\}$ spectral data of **6** (17.9 ppm), as revealed by the downfield shift (compared to **2**) being typical for *P*(V) environments. Noteworthy is that the ^{31}P NMR resonance of **6** is solvent dependent: in dichloromethane it is at 17.9 ppm, while in D_2O it appears at 26.4 ppm. Strong evidence for the desulfurization came from the ^{1}H NMR spectrum of **6** as a new signal appeared at 10.23 ppm, assigned to the C^2 proton. A similar value of 9.56 ppm was reported earlier for the corresponding imidazolium salt;[49] a similar value was reported also for the 3-mesityl-4,5-dimethylthiazol-2-ium perchlorate[10] (10.26 ppm).

In further accordance with a desulfurization was the $^{13}C\{^{1}H\}$NMR resonance of the C^2carbon of **6** (144.9 ppm) which lies in the typical range for thiazolium[10] and imidazolium salt[49] resonances, while the signal for the C=S carbon atom (191.7 ppm in **2**) had disappeared. The positive and negative ESI-MS spectra also confirmed the composition of **6** as to have the cation m/z 300.1 (found), 300.0 (calc.)$[C_{16}H_{15}NOPS]^+$ and the anion m/z 97.0 (found), 96.9 (calc.) $[HSO_4]^-$.

Single-crystal X-ray diffraction studies were performed for **6** (Fig. 6), using crystals obtained via slow evaporation of a concentrated solution in isopropanol. **6** crystallized in orthorhombic system (space group Pbca). The bond lengths and bond angles (given in the figure caption of **6**) are within the expected range for known thiazolium salts[55] and are close to the data of *P*(V)-substituted imidazolium salts[49]. However, the ring angle (N-C(2)-S(1)) became significantly reduced (112.49(17)°) compared to compounds **2**-**5**, while the exocyclic angle C(3) C(1)P 134.05(17) was significantly enlarged.

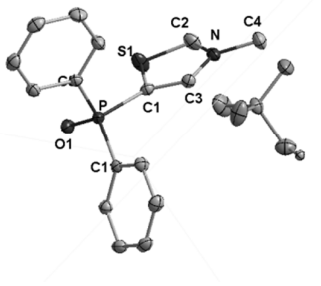

Fig. 6. Molecular structure of salt **6** (thermal ellipsoids are drawn at a 50 % probability level; hydrogen atoms have been omitted for clarity)except the anion (HSO_4^-). Selected bond distances (Å) and angles (°):C(1)-P1.814(2), P-O 1.4863(15), N-C(2)-S(1)112.49(17), S(1)C(1)P 115.50(12),C(3) C(1)P 134.05(17).

Because it is well established that thiazolium salts are good precursors for NHCs, given a sterically demanding substituent is present at the nitrogen atom,[40, 41, 56] [40,41] **6** was then treated with potassium *tert*-butoxide in THF at -78 °C in the presence of 0.5 eq. of cyclooctadiene rhodium(I) chloride dimer in order to achieve complexation (Scheme 4). The $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture (after stirring overnight -78 °C to r.t) showed moderate selectivity of the reaction (79 % conversion), and small amounts of other products were observed.

After filtration and removing of all volatile components at reduced pressure, **7** was isolated in 63% yield by recrystallization from THF and subsequent washing with diethylether and *n*-pentane, respectively. However, some small impurities remained which could not be removed by subsequent column chromatography. Therefore, single-crystals of **7** suitable for X-ray analysis could not be obtained. Nevertheless, the ^{1}H NMR spectrum of **7** exhibited the characteristic signals for the COD ligand along with the expected signals for the *P*-substituted thiazol-2-ylidene ligand: 4.40 (s, 3H, N–CH_3), 7.23-7.90 (m, 11H, C_6H_5, C^4-H). Since the C^2–H signal, as being the structurally characteristic signal for the thiazolium cation **6,** had disappeared, coordination to the Rh(I) center via the C^2 carbon was indicated. In comparison with reported imidazol-2-ylidene Rh(I) complexes,[36, 42, 57] the $^{13}C\{^{1}H\}$ NMR signal for the C^2 carbon atom of **7** appeared in the expected range (dd, 225.7 ppm) having a $^{1}J_{C,Rh}$ coupling of 48.5 Hz and a $^{3}J_{P,C}$ coupling of 1.3 Hz; it should be noted that the C^2 resonance could only be observed if a highly concentrated solution of **7** was used. Based on these findings, the possibility of an abnormal[31] NHC Rh(I) complex can be ruled out. Further support for the composition of compound **7** was obtained by ESI mass spec-trometry: m/z586.01 (found), 586.01 (calc.) which corresponds to the molecular ion $[C_{24}H_{26}ClNOPRhSNa]^+$

Experimental

General

The common Schlenk technique was used for all the lithiation and phosphanylation reactions. The reactions, except for the oxidation and the oxidative desulfurization using H_2O_2, were performed under argon atmosphere, using dry solvents. Tetrahydrofuran, diethyl ether and *n*-pentane were dried over sodium wire/benzophenone. Dichloromethane was dried over calcium hydride and further purification was done by distillation. Chloro(diphenyl)phosphane was distilled before use and was stored under argon atmosphere. All other chemicals were used as received.

All NMR spectra were recorded on a BrukerAvance DMX–300 spectrometer, with a frequency of 300.1 MHz for ^{1}H, 75.5 MHz for ^{13}C and 121.5 MHz for ^{31}P. 85% H_3PO_4 was used as external standard for ^{31}P spectra while ^{1}H and ^{13}C spectra were referenced to the residual protons of the deuterated solvents. Melting points were determined in one-sided melted off capillaries using Büchi Type apparatus. The infrared Spectra were recorded on a Nicolet 80 FT-IR spectrometer, using a diamond ATR. The UV/vis spectra were collected in solution on a Shimadzu UV-1950 PC spectrometer. Mass Spectrometric data were collected on a Kratos MS 50 spectrometer using EI 70 eV. Elemental analyses were done using a Vario EL gas chromatograph. The X-ray analyses were performed on a Nonius Kappa CCD or a Bruker X8-KappaApex. The structures were solved by direct methods refined by full-matrix least-squares

technique in anisotropic approximation for non-hydrogen atoms using SHELXS97[54] and other program packages. Monoisotopic masses and isotope patterns were calcu-lated using Mass5.1.0.[55]
Note: The numbering of the thiazole ring (for NMR data) is given according to the IUPAC system.

3-Methyl-5-diphenyl phosphanyl-thiazol-2-thione (2)
3-Methyl-1,3-thiazol-2-thione (1.48 g, 11.27mmol) was dissolved in 27 mL of dry THF in a Schlenk flask and cooled to −78 °C. *tert*-butyl-lithium (1.7 M in *n*-hexane, 6.60 mL, 11.30mmol) was added dropwise and the reaction mixture was slowly warmed to −70 °C and stirred for 3 h at this temperature. The reaction mixture was cooled again to −78 °C and the phosphine (Ph_2PCl) (2.03 mL, 11.30mmol) was added dropwise, the reaction mixture was stirred overnight and warmed to ambient temperature. The orange solution was concentrated in *vacuo* (8×10^{-3} mbar) and the residue was taken up in dry dichloromethane and filtered over a 3G-frit having a celite® pad to remove the formed lithium chloride. The filtrate was collected and the solvent was removed *in vacuo* (8×10^{-3} mbar) and then dried. The residue was recrystallized twice from toluene, the crystals washed twice with *n*-pentane (10 mL, 7 mL) and then dried *in vacuo* (8×10^{-3} mbar).

Yield: 2.57 g (8.14mmol), 72 %, white solid, m.p. 157°C. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ= 3.59 (s, 3H, N–CH_3), 7.14 (d, 1H, $^3J_{P,H}$ = 4.8 Hz, C^4–*H*), 7.24-7.36 (m, 10H, C_6H_5); ^{13}C NMR (75 MHz, $CDCl_3$): δ= 37.4 (s, N–CH_3), 123.0 (d, $J_{P,C}$ = 36.7 Hz, C^5), 128.8 (d, $J_{P,C}$ = 7.2 Hz, C_6H_5), 129.5 (s, C_6H_5), 132.8 (d, $J_{P,C}$ = 19.7 Hz, C_6H_5), 135.3 (d, $J_{P,C}$ = 6.7 Hz,i-C_6H_5), 139.0 (d $^2J_{P,C}$ = 42.8 Hz C^4), 191.7 (d, $J_{P,C}$ = 1.21 Hz, *C*=S);^{31}P NMR (121.5MHz, $CDCl_3$): δ= −23.0 (s). MS (EI,70 eV): m/z (%) = 315.0 (100) $[M]^+$, 237.9 (37) $[M-C_6H_5]^+$, 185.0 (8) $[P(C_6H_5)_2]^+$, 77.0 (6) $[C_6H_5]^+$; HR-MS: found = 315.0305, calc. = 315.0305; IR (ATR, ũ {cm^{-1}}): ũ = 3046 (w), 1480 (m), 1432 (m), 1207 (s), 692 (s), 754 (s) 739 (s);UV/Vis (CH_2Cl_2): λ_{max} [nm] (abs.): 331.00(0.674), 230.00(0.735), 211.00(0.250), 206.50(0.295). Elemental analysis for $C_{16}H_{14}NPS_2$: found: C 60.51, H 4.56, N 4.47, S 20.87 Calc.: C 60.93, H 4.47, N 4.44, S 20.33.

3-Methyl-5-diphenylphosphanoyl-thiazol-2-thione (3)
3-Methyl-5-diphenylphosphinyl-thiazole-2-thione (**2**) (1.00 g, 3.17 mmol) was dissolved in 20 mL of chloroform, then H_2O_2/urea (0.29 g, 3.17 mmol) added at ambient temperature and the reaction mixture stirred for 24 h. Then the reaction mixture was filtered to remove unreacted urea. The solvent was removed *in vacuo* (8×10^{-3} mbar) and the obtained product was recrystallized from toluene. Then it was washed twice (7mL, 5mL) with *n*-pentane and dried *in vacuo* (8×10^{-3} mbar), slightly yellow to white powder was obtained.

Yield: 0.89 g (2.68 mmol), 89 % m.p. 224 °C. ^{1}H-NMR (300.1 MHz, $CDCl_3$): = 3.59 (s br, 3H, N–CH_3), 7.33-7.58 (m, 7H, C_6H_5, C^4–*H*), 7.58-7.70 (m, 4H *ortho*-C_6H_5); ^{13}C-NMR (75MHz, $CDCl_3$): = 37.8 (s, N–CH_3), 117.5 (d, $J_{P,C}$ = 107 Hz, C^5), 128.9 (d, $J_{P,C}$ = 13.0 Hz, C_6H_5), 130.9 (d, $J_{P,C}$ = 105 Hz, *ipso*-C_6H_5), 131.5 (d, $J_{P,C}$ = 10.6 Hz, C_6H_5), 132.9 (d, $J_{P,C}$ = 3.0 Hz, C_6H_5), 140.5 (d, $^2J_{P,C}$ = 12.6 Hz, C^4), 191.3 (d, $J_{P,C}$ = 3.8 Hz, *C*=S); ^{31}P-NMR (121.5 MHz, $CDCl_3$): = 18.7(s). MS (EI, 70 eV): m/z (%): 331.0 (100) $[M]^+$, 316.0 (7) $[M-CH_3]^+$, 254.0 (17) $[M-C_6H_5]^+$, 178.0 (6) $[M-2C_6H_5]^+$; HR-MS: found = 331.0250, calc. = 331.0254; IR (ATR, ũ {cm^{-1}}): ũ = 3048 (w), 1557 (w), 1439 (m), 1329 (s), 1185 (s), 701(s), 726(s), 755 (s); UV/Vis (CH_2Cl_2): λ_{max} [nm] (abs.): 418.20(0.009),330.40(0.797),273.60(0.163), 267.00(0.171);Elemental Analysis for $C_{16}H_{14}NOPS_2$: found: C 57.03, H 4.79, N 4.13, S 19.28 Calc.: C 57.99, H 4.26, N 4.23, S 19.35.

Procedure for the synthesis of thiophosphanoyl-thiazol-2-thione (4) and selenophosphanoyl-thiazole-2-thione (5)
In two separate Schlenk tubes, **2** (1.00 g, 3.17 mmol each), 20 mL of toluene and elemental sulfur (0.11 g, 3.43mmol), and elemental selenium (0.25 g, 3.17 mmol) were heated for three hours at 110 °C. The solvent was removed *in vacuo*(8×10^{-3} mbar), the product was washed twice with *n*-pentane (5mL,3mL) and dried *in vacuo* (8×10^{-3} mbar); a white powder was thus obtained.

3-Methyl-5-diphenylthiophosphanoyl-thiazol-2-thione (4)

Yield: 0.98 g (2.82 mmol), 89 %, m.p. 160 °C, ^{1}H-NMR (300.1 MHz, $CDCl_3$): δ = 3.59 (s br, 3H, N–CH_3), 7.33-7.51 (m, 6H, C_6H_5), 7.53(d, $^3J_{P,H}$ = 7.5 Hz, C^4–*H*), 7.59-7.76 (m, 4H, *ortho*-C_6H_5);^{13}C-NMR ((75MHz, $CDCl_3$): δ = 37.4 (s, N–CH_3), 117.9 (d, $J_{P,C}$ = 87.7 Hz, C^5), 128.5 (d, $J_{P,C}$ = 13.27 Hz, C_6H_5), 131.1 (d, $J_{P,C}$ = 11.5 Hz, C_6H_5), 131.3 (d, $J_{P,C}$ = 90.7 Hz, *ipso*-C_6H_5), 132.7 (d, $J_{P,C}$ = 3.2 Hz, C_6H_5), 141.3 (d, $^2J_{P,C}$ = 15.3Hz, C^4), 191.7 (d, $J_{P,C}$ = 3.27 Hz, *C*=S);^{31}P-NMR (121.5 MHz, $CDCl_3$): δ= 30.7 (s); MS (EI, 70 eV): m/z (%): 347.0 (16) $[M]^{\cdot+}$, 161.8 (17) $[M-P(C_6H_5)]^+$, 192.9 (23) $[M-2C_6H_5]^+$, 237.9(10) $[M-S-C_6H_5]^+$ HR-MS: found = 347.0025,calc. = 347.0026; IR (ATR, ũ {cm^{-1}}):ũ = 1134(s), 688(s), 713(s), 724(s), 746(s);UV/Vis (CH_2Cl_2): λ_{max} [nm] (abs.): 334.20(0.933), 229.00(0.955), 214.90(0.294), 210.70(0.269), 206.60(0.288), 200.20(0.276); Elemental Analysis for $C_{16}H_{14}NPS_3$: found: C 54.94, H 4.143, N 4.07, S 28.18 calc.: C 55.31, H 4.06, N 4.03, S 27.69.

3-Methyl-5-diphenylselenophosphanoyl-thiazol-2-thione (5)
Yield: 1.11 g (2.81 mmol), 89 % white solid, m.p. 135 °C.^{1}H NMR (300.1 MHz, $CDCl_3$) δ = 3.59 (s br, 3H, N–CH_3), 7.32 –7.53 (m, 6H, C_6H_5), 7.58 (d, 1H, $^3J_{P,H}$ = 8.0 Hz,C^4–*H*), 7.61-7.76 (m, 4H, *ortho*-C_6H_5);^{13}C NMR ((75MHz, $CDCl_3$):δ = 37.8 (s, N–CH_3), 117.5 (d, $J_{P,C}$ = 107.1 Hz, C^5), 128.9 (d, $J_{P,C}$ =13.3 Hz, C_6H_5), 130.7 (d, $J_{P,C}$ = 83.0 Hz, *ipso*-C_6H_5), 131.9 (d, $J_{P,C}$ = 11.7 Hz, C_6H_5), 132.4 (d, $J_{P,C}$ = 3.3 Hz, C_6H_5), 143.0 (d, $^2J_{P,C}$ =16.8 Hz, C^4), 191.7 (d, $J_{P,C}$ =3.0 Hz, *C*=S);^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 19.2 (s, S_{sat} $^1J_{Se,P}$= 777.2 Hz); EI- MS (EI, 70 eV): m/z (%): 391.0 (10) $[M]^+$, 237.9 (50), $[M-Se-C_6H_5]^+$, 315.0 (100), $[M-Se]^+$, 207.0 (20) $[M-P(C_6H_5)_2]^+$, 282.0 (12) $[M-S-Se]^+$; HR-MS: found = 390.9499, calc. =394.9470; IR (ATR, ũ {cm^{-1}}):ũ = 2156(w), 1435(s), 1320(s), 1133(s), 707(s), 742(s);UV/Vis (CH_2Cl_2): λ_{max} [nm] (abs.): 337.00(0.754), 269.00(0.253), 229.50(0.992), 207.50(0.266). Elemental Analysis for $C_{16}H_{14}NPS_2Se$: Found: C 48.91, H 3.63, N 3.34, S 15.28. Calc.: C 48.73, H 3.58, N 3.58, S 16.26.

3-Methyl-5-diphenylphosphanoyl-thiazolium hydrogensulfate (6)
In a round bottom flask 5.57g (17.67 mmol) of **6** was dissolved in 70 mL of dichloromethane and cooled to 0°C. Then five eq. (88.38 mmol) of H_2O_2 solution (35 % in water) was added dropwise and the reaction mixture was stirred at this temperature for 30 min, then warmed to ambient temperature and stirred for 45 min. The solvent was removed and the product was dried *in vacuo* (8×10^{-3} mbar). The obtained yellow semi-solid was recrystallized from THF and washed thrice with ether (7 mL, 5 mL, 5mL) at ambient temperature, dried *in vacuo* (8×10^{-3} mbar). **6** wasobtained as white semi-solid, which was kept under argon because of its highly hygroscopic nature.

Yield:6.05 g (15.22 mmol), 86 % white solid, m.p. 188 °C.^{1}H NMR (300:1 MHz, D_2O): δ = 4.70 s, 3H, N–CH_3), 7.44-7.80 (m, 10H, C_6H_5),

8.42(d, 1H, $^{3}J_{P,H}$ = 4.51 Hz, C^{4}–*H*), 10.23 (s br, 1H, C^{2}–*H*);^{13}C NMR (75% MHz, D_2O): δ = 42.0 (s, N–CH_3), 126.9 (d, $^{1}J_{P,C}$ = 115.0 Hz, C^{5}), 129.5(d, $J_{P,C}$ = 13.7 Hz, C_6H_5), 130.7 (d, $^{2}J_{P,C}$ = 10.7 Hz, C^{4}), 131.6 (d, $J_{P,C}$ = 11.6 Hz, C_6H_5), 134.0 (d, $J_{P,C}$ = 3.0 Hz, C_6H_5), 134.2 (d, $J_{P,C}$ = 105 Hz, *ipso*-C_6H_5), 144.9 (d, $J_{P,C}$ = 14.7 Hz, C^{2});^{31}P NMR (121.5MHz, D_2O): δ = 25.9 (s br); MS: Pos. ESI-MS: Found = 300.1, calc. = 300.0 $[C_{16}H_{15}NOPS]^{+}$, neg. ESI-MS: Found = 97.0, calc. = 96.9 $[HSO_4]^{-}$;IR (ATR, ũ {cm^{-1}}):ũ =3054(w), 1436(m), 1157(s), 1120(s);UV/Vis (CH_2Cl_2): λ_{max} [nm] (abs.): 229.50(0.987), 206.50(0.238).Elemental Analysis for $C_{16}H_{16}NO_5PS_2.H_2O$: found: C 46.67, H 4.49, N 3.44, S 15.48calc.: C 46.26, H 4.37, N 3.37, S 15.44.

[Chloro(1,5-cyclooctadiene)(3-methyl-5-diphenylphosphanoyl-thiazol-2-ylidene)Rh(I)] (7)

To thiazolium salt **6** (0.50 g, 1.25 mmol), suspended in 20 mL of THF in a Schlenk tube, potassium *tert*-butoxide (162.35 mg, 1.44 mmol) and cyclooctadiene rhodium(I) chloride dimer (0.34g. 0.69 mmol) was added at 78°C and stirred (-78°C-rt) overnight. The formed potassium salt was then removed via filtration, the filtrate collected and the solvent removed *in vacuo* (8×10^{-3} mbar). The crude product was then recrystallized from 2mL of THF, washed thrice with diethyl ether (2 mL, 1 mL, 1 mL) and dried *in vacuo* (8×10^{-3} mbar). Complex **7** was thus obtained as a light brownish powder.

Yield: 0.24 g, 0.44mmol, 63 % m.p. 188 °C. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 1.74 (m, 4H, cod), 2.40 (m, 4H, cod), 4.15 (m, 4H, cod), 4.40 (s, 3H, N–CH_3), 7.23-7.90 (m, 11H, C_6H_5, C^{4}-*H*);^{13}C-NMR (75MHz, $CDCl_3$): δ= 28.8 (s, cod), 32.9 (s, cod) 44.2 (s, N–CH_3),71.1 (d, $J_{Rh,C}$= 14.3Hz cod), 102.7 (d $J_{C,Rh}$= 6.5 Hz), 129.0 (d, $J_{P,C}$ = 13.0Hz, C_6H_5) 131.0 (d, $^{1}J_{P,C}$ = 111.8 Hz, *ipso*-C_6H_5), 131.5 (d,$J_{P,C}$ = 10.8 Hz, C_6H_5), 133 (d, $J_{P,C}$ = 2.9 HzHz, C_6H_5), 133.1 (dd, $J_{P,C}$ = 58.6 Hz,$^{3}J_{C,Rh}$ = 1.9 HzC^{5}), 143.7 (dd, $^{3}J_{P,C}$ = 16.0 Hz, $^{3}J_{C,Rh}$ = 1.9 Hz, C^{4}) 225.7 (dd, $^{1}J_{C,Rh}$ = 48.5 Hz,$^{3}J_{P,C}$ = 1.3HzC^{2}); ^{31}P-NMR (121.5 MHz, $CDCl_3$): δ = 17.9 (s br); MS: pos.-ESI: Found = 510.10, calc. = 510.05 $[C_{24}H_{26}NOPRhS]^{+}$,found =586.01, calc. = 586.01 $[C_{24}H_{26}ClNOPRhSNa]^{+}$; IR (ATR, ũ {$cm^{-1}$}):ũ = 2935, 2873 (w), 1436(m), 1191(s), 1118(s), 724(s);UV/Vis (CH_2Cl_2): λ_{max} [nm] (abs.): 230.50(0.959), 215.00(0.340), 206.50(0.304), 199.00(0.309).

X-ray crystallographic analyses of compounds 2-6

The crystallographic data for compounds **2**-**6** was collected on a NoniusKappaCCD or a STOE IPDS-2T diffractometer equipped with a low-temperature device at 123(2) K using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Using Olex2[13], the structure was solved with the XS structure solution program using Direct Methods and refined with the XL refinement package using Least Squares minimisation.

Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Centre having the corresponding numbers: 1423386(**2**),1423391(**3**), 1423389(**4**), 1423387(**5**) and 1423392(**6**). This data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for 2. $C_{16}H_{14}NPS_2$, M = 315.39, crystal size0.24 x 0.10 x 0.05 mm^3, monoclinic, space group P c, Z = 2, a = 8.7273(9) Å, b = 9.6573(10) Å, c = 9.3479(9) Å, α = 90.00°, β 106.287°,γ = 90.00°, V = 756.24(13)Å^3, d_c = 1.385 mgm^{-3}, μ = 0.446mm^{-1}, T = 100(2) K, 2θmax = 53.9°, no. of unique data 3073, R_{int} = 0.0247, R1 (for I>2σ(I)) = 0.0192, wR2 (for all data) = 0.0493, goodness of fit 1.048, ΔF(max/min) = 0.250/-0.159eÅ^{-3}.

Crystal data for 3. $C_{16}H_{14}NOPS_2$, M = 331.37, crystal dimensions 0.34 x 0.18 x 0.15mm^3, monoclinic, space group P 21/c Z = 4, a = 8.9328(4)Å, b = 16.3881(10) Å, c = 12.0195(6) Å, α = 90°, β = 119.457(3)°, γ = 90°, V = 1532.09(14) Å^3, d = 1.437 mgm^{-3}, μ = 0.449mm^{-1}, T = 123(2) K, 2θmax = 53.98°, no. of unique data 3307, R_{int} = 3307, R1 (for I > 2σ(I)) = 0.0297, wR2 (for all data) = 0.0781, goodness of fit 1.036, ΔF(max/min) = 0.268/-0.442 e Å^{-3}.

Crystal data for 4. $C_{16}H_{14}NPS_3$, M = 347.43, crystal dimensions 0.21 x 0.18 x 0.06 mm^3, monoclinic, space group P 21/c Z = 4, a = 14.358(3)Å, b = 8.8787(15) Å, c = 12.973(2) Å, α = 90°, β = 101.891(7)°, γ = 90°, V = 1618.3(5) Å^3, d = 1.426 mg m^{-3}, μ = 0.548 mm^{-1}, T = 123(2) K, 2θmax = 50.5°, no. of unique data 2810, R_{int} = 0.0542, R1 (for I > 2σ(I)) = 0.0385, wR2 (for all data) = 0.0970, goodness of fit 1.165, ΔF(max/min) = 0.412/-0.391 e Å^{-3}.

Crystal data for 5. $C_{16}H_{14}NPS_2Se$, M = 394.35, crystal dimensions 0.16 x 0.06 x 0.04 mm^3, triclinic, space group P -1 Z = 1, a = 9.9952(5) Å, b = 13.8074(4) Å, c = 14.1857(6) Å, α = 107.357(2)°, β = 104.864(2)°, γ = 94.068(2)°, V = 1782.84(13) Å^3, d = 1.555 mg m^{-3}, μ = 2.427 mm^{-1}, T = 123(2) K, 2θmax = 54°, no. of unique data 7728, R_{int} = 0.0607, R1 (for I > 2σ(I)) = 0.0571, wR2 (for all data) = 0.0658, goodness of fit 0.921, ΔF(max/min) = 0.511/-0.718 e Å^{-3}.

Crystal data for 6. $C_{16}H_{15}NOPS$, HO_4S M = 397.39, crystal dimensions 0.4 × 0.14 × 0.12 mm^3, orthorhombic, space group Pbca Z = 1, a = 8.3334(7)Å, b = 13.5214(10) Å, c = 30.503(3) Å, α = β = γ = 90°, V = 3437.0(5) Å^3, d = 1.536g cm^{-3}, μ = 0.431mm^{-1}, T = 123.15K, 2θmax = 55.998°, Interdependent reflections 4119 [R_{int} = 0.0354, R_{sigma} = 0.0355], R1 (for I > 2σ(I)) = 0.0425, wR2 (for all data) = 0.1047, goodness of fit 1.054, ΔF(max/min) = 0.46/-0.33e Å^{-3}.

Conclusions

We have presented a facile protocol that enables backbone functionalization of thiazol-2-thiones which is lithiation, followed by phosphanylation to afford the first example of aP(III) substituted thiazol-2-thione (**2**). Oxidation reactions of **2** to yield the corresponding P-O, P-S and P-Se P(V) derivatives **3-5** proceeded in a clean fashion. The first P(V) substituted thiazolium salt **6** was obtained via oxidative desulfurization of **2** (or **3**). As demonstrated for **6**, the first P(V) substituted NHC-metal complex **7** was synthesized, using a deprotonation and complexation protocol.

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Synthesis and reactions of *C*-phosphanylated thiazol-2-thiones

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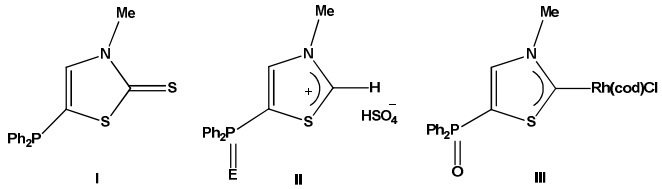
Facile regioselective synthesis of the P(III) substituted thiazole-2-thione **I** is presented. Oxidation reactions of **I** resulted in P(V) chalcogenide thiazole-2-thiones (E = O, S, Se). Oxidative desulfurization of thiazole-2-thione **I** (E = O) using hydrogenperoxide led to the first *C*-phosphanoyl substituted thiazolium salt **II**. Deprotonation of **II** and in *situ* reaction with cyclooctadiene rhodium(I) chloride dimer yielded thiazole-2-ylidene rhodium(I) complex **III**.



I II III