From bis(imidazole-2-thion-4-yl)phosphane to a flexible P-bridged bis(NHC) ligand and its silver complex
Table of content:

From bis(imidazole-2-thion-4-yl)phosphane to a flexible P-bridged bis(NHC) ligand and its silver complex

Paresh Kumar Majhi, Gregor Schnakenburg and Rainer Streubel
From bis(imidazole-2-thion-4-yl)phosphane to a flexible P-bridged bis(NHC) ligand and its silver complex

Paresh Kumar Majhi,* Gregor Schnakenburg† and Rainer Streubel*‡

Synthesis of the first P(V)-bridged bis(NHC) ligand 7 was achieved via deprotonation of P(V)-functionalized bis(imidazolium) salt 6, which was obtained via oxidative desulfurization of bis(imidazole-2-thion-4-yl)phosphane 2. Bis(imidazolium) salt 6 was also employed to synthesize the corresponding silver complex 8. All new products were firmly established by spectroscopic and spectrometric methods as well as elemental analysis and, in addition, X-ray crystal structure analysis in case of 3.

Introduction

The chemistry of imidazole-2-thiones I (Fig. 1) has been known for more than 100 years. This class of heterocycles have received a considerable amount of attention in the chemical as well as pharmaceutical industries, e.g. as precursors to unusual thion-ylides, tricoordinate sulfuranes, desulfurizing agents for a thirane, in catalyzing cross-linking of polymers, halogen free ionic liquids and as drugs in the field of medicinal chemistry. The N-heterocyclic carbenes (NHCs) II (Fig. 1) derived from imidazole-2-thiones I has witnessed rapid growth in the last two decades in coordination and organometallic chemistry, in catalysis and in medicinal or polymer chemistry. The introduction of an additional donor atom(s) into an imidazol-2-yldene has been the subject of increased attention and functional groups such as amino, alkoxy, and phosphanyl groups have been introduced at the N-centers. Of particular importance are the phosphanyl functionalized imidazol-2-yldene of types III as Nolan et al. demonstrated a successful application of an N-phosphinoethyl-functionalized NHC ligand in a Heck reaction. Since then the field has begun to emerge more rapidly and the structural modification has been done at both nitrogen as well as phosphorus centers leading to rather flexible, often hemilabile metallacycles. Most of the N-phosphanyl substituted imidazol-2-yldenes described in the literature are often designed to preferentially bind one metal center in a chelating fashion. However, the design of non-chelating phosphanyl substituted imidazol-2-yldenes of types IV was first reported by Gates and coworkers by introducing a phosphanyl group at the backbone C\(^4\) position using the reaction of a sterically demanding NHC and a phosphahalkene.

Alternative synthetic strategies were also employed by different research groups to achieve backbone phosphorylated imidazol-2-yldenes as they are very promising candidates to synthesize homo- and heterobimetallic complexes and, hence, for a new catalyst design. On the other hand, the design of poly-NHC ligands with different topologies has increased the architectural diversity and coordination modes in organometallic chemistry. Among them one important class are bis-NHCs of type V (Fig. 1) having an additional donor such as N in the linker scaffold that might be varied and open to the inclusion of atoms such as O, S and P atoms. The trischelating coordination mode of such ligands V has furnished pioneer and tripodal bis-NHC complexes that have attracted great attention and because of their structural flexibility, very often bis-NHCs are known to coordinate one metal center in a chelating mode to form stable metal NHC complexes.

However, the design of non-chelating bis-NHCs is also of great interest in the development of electronic and polymeric materials. Bieławski and co-workers have reported the first bis(carbene) of type VI with facially opposed imidazol-2-yldenes annulated to a common arene core. Meanwhile a series of similar ditopic NHCs (type VI) with different types of linkers have been reported in which the coordination to the same metal is avoided by the linearly opposed disposition of the two carbenes due to rigid backbone. The concept of Janus bis(carbene) ligands were also exploited in the synthesis of new homobimetallic complexes. Hahn et al. have successfully used such ditopic bis-NHCs as building blocks for metallo-supramolecular architectures, e.g. forming multidentate molecular squares and rectangles. From above perspectives, it is particularly enticing to synthesize compounds of type VII (Fig. 1) having a flexible P(III) or P(V) group at the backbone of two NHCs, thus being able to investigate their coordination properties and subsequent applications as novel ligands.

Herein, the oxidation and subsequent oxidative desulfurization of bis(imidazole-2-thion-4-yl)phosphane is presented. Furthermore, the first synthesis of a flexible P(V)-bridged bis(imidazol-2-yldene) ligand as well as a preliminary study on the coordination behavior towards Ag(OTf)\(_2\)PPh\(_3\) will be reported.
Results and discussion

Recently, synthesis of bis(imidazole-2-thion-4-yl)phosphane 2 was reported (Scheme 1),\textsuperscript{40,41} thus demonstrating that the steric demand of the \textit{tert}-butyl group is sufficient to selectively direct lithiation to the C\textsubscript{4} position and, hence, to obtain 2 selectively and in high yields.

Scheme 1. Synthesis of bis(imidazole-2-thion-4-yl)phosphane 2.

To study the reactivity of 2, various oxidation reactions were first performed (Scheme 2). The reactions of 2 with the H\textsubscript{2}O\textsubscript{2}-urea adduct, elemental sulfur and selenium were quantitative according to \textsuperscript{31}P NMR spectroscopy. The phosphane oxide 3 was crystallized from toluene and obtained as white solid whereas phosphane sulfide 4 and selenide derivatives 5 were precipitated from the reaction mixture and obtained in pure form as white solids. The analytical data of the phosphane oxide, sulfide and selenide derivatives 3-5 are given in the experimental section and \textsuperscript{31}P NMR and selected \textsuperscript{13}C{\textsuperscript{1}H} NMR spectroscopic data of 3-5 are given in Table 1. As very often observed for P(V) derivatives, the \textsuperscript{31}P NMR signal of 3-5 was shifted downfield compared to phosphane 2 (δ = -54.7 ppm), whereby the largest shift was observed for the phosphane sulfide 4.

Scheme 2. Various oxidation reactions of phosphane derivative 2.

As can be seen from the Table 1, P(V) derivatives 3-5 show a significantly larger \textsuperscript{1}J\textsubscript{P,C} coupling constant compared to P(III) derivative 2 (\textsuperscript{1}J\textsubscript{P,C} = 4.8 Hz, C\textsuperscript{4}); similar tendencies were observed earlier in the series of imidazole-2-thione phosphane chalcogenides.\textsuperscript{42,43} The \textsuperscript{1}H and \textsuperscript{13}C{\textsuperscript{1}H} NMR spectra of phosphane chalcogenides 3-5 in CDCl\textsubscript{3}, exhibited a single set of signals for the groups of the imidazole-2-thione unit, indicative of a symmetric structure in solution and a free rotation around the P-C\textsubscript{4} bonds.
Table 1: \(^{31}\)P and selected \(^{1}H\) NMR spectroscopic data of 3-5 in ppm.

<table>
<thead>
<tr>
<th></th>
<th>(\delta^{31}P)</th>
<th>(\delta) of imidazole carbon ring nuclei</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>2.5 (ttt, (J_{PH} = 12.9) Hz, (J_{PH} = 3.5) Hz)</td>
<td>119.2 (d, (J_{PC} = 138.4) Hz, C(<em>1)), 124.7 (d, (J</em>{PC} = 20.9) Hz, C(<em>2)), 166.9 (d, (J</em>{PC} = 5.6) Hz, C=S)</td>
</tr>
<tr>
<td>4</td>
<td>10.4 (ttt, (J_{PH} = 14.8) Hz, (J_{PH} = 3.8) Hz)</td>
<td>118.3 (d, (J_{PC} = 117.3) Hz, C(<em>1)), 124.2 (d, (J</em>{PC} = 19.7) Hz, C(<em>2)), 167.0 (d, (J</em>{PC} = 5.0) Hz, C=S)</td>
</tr>
<tr>
<td>5</td>
<td>-5.6 (ttt, (J_{PH} = 766.2) Hz, (J_{PH} = 15.4) Hz, (J_{PH} = 3.5) Hz)</td>
<td>116.1 (d, (J_{PC} = 107.5) Hz, C(<em>1)), 124.5 (d, (J</em>{PC} = 19.1) Hz, C(<em>2)), 167.2 (d, (J</em>{PC} = 4.9) Hz, C=S)</td>
</tr>
</tbody>
</table>

X-ray single-crystal structure analysis was performed for compound 3; suitable crystals were obtained from a saturated methylene chloride solution (-20°C). Compound 3 crystallizes in a monoclinic lattice with space group \(P\ 2_1/c\). The structure and numbering scheme for 3 is shown in Fig. 2. The selected bond parameters are given in the figure caption. For crystallographic data see Table S1 (ESI†). The bond lengths and angles in 3 are in the common range for P(V) substituted imidazole-2-thione derivatives reported earlier \(^{42,43}\) and, hence, will not be discussed here.

As the attempt to synthesize \(P\)-functional bis(imidazol-2-ylidene) by the reductive desulfurization \(^{1}\) of 2 with four equivalents of potassium metal in THF did not afford the desired product, \(^{40}\) another synthetic methodology to access the \(P\)-functional bis(imidazol-2-ylidene) was needed. As oxidative desulfurization of imidazole-2-thiones to get imidazolium salts using hydrogen peroxide is established, \(^{24,2}\) 2 was reacted with 10 equivalents of \(H_2O_2\) in methanolic solution to get the corresponding bis(imidazolium hydrogensulfate) salt \(^{31}\) which was then reacted \(in\ situ\) with \(BaCl_2\cdot2H_2O\) to give the bis-(imidazolium) chloride 6 (Scheme 3). The oxidation of a P(III) to a P(V) center was reflected by the downfield shift of the \(^{31}\)P resonances to \(\delta = 7.4\) (precursor 2 at \(\delta = -54.7\)).

![Molecular structure of compound 3.](image)

**Scheme 3. Oxidative desulfurization of phosphine derivative 2.**

In the \(^{31}\)P \(^{1}H\) NMR spectrum, product 6 appears more downfield at \(\delta = 7.4\) compared to the \(P\)-oxide derivative 3 (\(\delta = 2.5\)). Formation of the bis(imidazolium) derivative 6 was garnered from the \(^1\)H NMR spectra by the appearance of the signal at \(\delta = 9.30\) assigned to the C\(^2\)-proton. Further confirmation came through the \(^{13}\)C \(^{1}H\) NMR spectra showing the C\(^2\)-carbon resonance at \(\delta = 141.5\) having a \(J_{PC}\) value of 5.8 Hz, while the (typical) thione C\(^2\)-carbon resonance at \(\delta = 167.4\) had disappeared. \(^{40}\) Like in 3-5, the \(^1\)H and \(^{13}\)C \(^{1}H\) NMR spectra of compound 6 in D\(_2\)O showed a single set of signals for the various groups for the imidazole-2-thione units. The formation of 6 was independently confirmed by positive and negative ESI mass spectrometry showing m/z 435.1 \([C_{24}H_{24}[CNI]OP]^+\). The presence of the chloride anion was also confirmed by ESI negative mass spectrometry after the addition of a neutral adduct \((C_6H_{11})\_2O_6; m.w. = 1152.9\) to the sample; the m/z value of the chloride adduct ion is given in the experimental section.

The bis(imidazolium salt) 6 was then deprotonated using two equivalents of potassium hexamethyldisilazide (KHMDMS) (-78 °C) to afford the new bis(imidazol-2-ylidene)phosphane oxide 7 (Scheme 4). After removal of potassium chloride via filter cannulation, followed by drying \(in\ vacuo\), a yellow solid was obtained which was spectroscopically characterized. The resonance of the phosphane oxide 7 in the \(^{31}\)P \(^{1}H\) NMR spectrum is slightly highfield shifted to \(\delta = 0.4\) with respect to the imidazolium precursor 6 (\(\delta = 7.4\)). Further constitutional proof for the formation of 7 was obtained from the \(^1\)H NMR spectrum by the disappearance of the C\(^1\)-proton signal and the appearance of a downfield signal (\(\delta = 220.0; J_{PC} = 2.2\) Hz) in the \(^{13}\)C \(^{1}H\) NMR spectrum. Furthermore, the formation of 7 was supported by ESI-mass spectrometry (pos. mode: m/z 435 for \(C_{24}H_{24}[CNI]OP\)).

**Scheme 4. Synthesis of bis(imidazol-2-ylidene)phosphane 7.**

In stark contrast to monotopic NHCs, less attention has been directed towards the development of discrete multitopic carbenes that are designed to bind multiple metal centers. \(^{44}\) To start the exploration of the coordination chemistry of P-bridged bis(NHCs) a preliminary study was carried out. Therefore, the bis(imidazolium) salt 6 was mixed with KO\(_2\)Bu (2 eq.) and Ag(OtF)\(_2\) (2 eq.) in THF and heated at 60 °C, which afforded the desired bis(NHC) silver complex 8d (Scheme 5). After removal of potassium chloride via filter cannulation, followed by drying the residue \(in\ vacuo\), 8 was obtained as white solid.
Complex 8 was fully characterized by multinuclear NMR spectroscopy [\(^{1}\text{H}, \ ^{13}\text{C}\{\ ^{1}\text{H}\}, \ ^{31}\text{P}\{\ ^{1}\text{H}\}]$. The \(^{31}\text{P}\{\ ^{1}\text{H}\}$ NMR spectrum of 8 showed two signals at $\delta = 8.5$ and $\delta = 29.5$. The former resonance at $\delta = 8.5$, assigned to the PhP(O) group, did not change much compared to the starting material 6 ($\delta = 7.4$), whereas a significant downfield shift was observed for the latter resonance, which was assigned to PhP(O) group. Further confirmation for 8 came from the \(^{13}\text{C}\{\ ^{1}\text{H}\}$ NMR spectrum as the $C^2$ resonance of the imidazolium salt ($\delta = 141.5$) had disappeared and, instead, a new signal at $\delta = 178.2$ having a $J_{P,H}$ value of 3.6 Hz had appeared, being assigned to the $C^2$ carbon. This chemical shift is in the typical range for NHC silver(I) complexes, reported earlier.\(^{44}\) The coordination of the bis(NHC) ligand to the silver ion was also confirmed by ESI mass spectrometry showing the following $m/z$ values: 774.9 [(PPh$_3$)$_2$AgCl]$^+$, 633.0 [(PPh$_3$)$_2$Ag]$^+$, 507.1 [(PPh$_3$)Ag(C$_6$H$_5$N$_2$)]$^+$, 383.1 [Ag(C$_6$H$_5$N$_2$)$_2$]$^+$. It should be noted that a similar ditopic bis(NHC) silver complex based on benzimidazol-2-ylidene has been reported by Bielawski and co-workers.\(^{36(a)}\)

**Conclusions**

The phosphorus-centered oxidation of bis(imidazole-2-thion-4-yl)phosphine 2 with various chalcogens afforded the corresponding P(V)-E products 3-5 (E = O, S, Se) selectively. Oxidative desulfurization of phosphane 2 with hydrogen peroxide furnished the P(V)-bridged bis(imidazolium) salt 6, which could be used to gain access to the first example of a flexible P(V)-bridged bis(NHC) (7) via depotonation. The coordination ability of 7 was demonstrated via the synthesis of the dinuclear silver(I) complex 8 using in situ prepared 7. Current studies are aiming at the use of such bis(NHC)s as building blocks for metalo-supramolecular architectures or coordination polymers.

**Experimental section**

**General considerations:**

The sulfurization, selenization, the synthesis of the imidazol-2-ylidine and its silver complex was performed under an argon atmosphere, using common Schlenk techniques and dry solvents. Tetrahydrofuran, toluene, diethyl ether, n-pentane were dried over sodium wire/benzophenone and further purified by subsequent distillation. Complex [Ag(OTf)PPh$_3$] was prepared following the literature protocol.\(^{45}\) All other chemicals and solvents were used as purchased. 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 NMR spectra were referenced to the residual proton resonances and the $^{13}$C NMR signals of the deuterated solvents and $^{31}$P to 85% H$_3$PO$_4$ 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 FT-IR spectrometer with an attenuated total reflection (ATR) attachment. The UV/Vis spectra were recorded in solution on a Shimadzu UV-1950 PC spectrometer. The X-ray analyses were performed on a Bruker X8-KappaAPEX TT type diffractometer at 100(2) K. The structures was solved by direct methods refined by full-matrix least-squares technique in anisotropic approximation for non-hydrogen atoms using SHELEX97 and SHELXL97\(^{46}\) 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-1013837 (3), which can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

**Synthesis of bis(1-tert-butyl-3-methyl-imidazole-2-thion-4-yl)phenylphosphane oxide (3)**

To 3.81 g (8.53 mmol) of the phosphane derivative 2, dissolved in 40 mL of chloroform, 0.80 g (8.53 mmol) of the hydrogen peroxide-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. The reaction mixture was then filtered through a funnel equipped with filter paper to remove the urea, the filtrate was concentrated to dryness in vacuo ($\times 10^{1}$ mbar). The crude product was purified via crystallization from hot toluene and the obtained crystalline material was washed with n-pentane ($\times 20$ mL) and dried in vacuo ($\times 10^{2}$ mbar).

**Synthesis of phosphane sulfide 4 and phosphane selenide 5**

To a solution of phosphane derivative 2 (0.89 mmol each) in 10 mL of toluene, 0.028 g (0.89 mmol) of elemental sulfur or 0.070 g (0.89 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 crystals. The obtained crystals were...
washed with *n*-pentane (2 × 4 mL) and dried in vacuo (8×10⁻³ mbar).

**Bis(1-tert-butyl-3-methyl-imidazol-2-thione-4-yi)-phenylphosphane sulfide (4)**

Yield: 0.39 g (0.81 mmol, 91%), white solid, m.p. > 230 °C. **¹H NMR (300.1 MHz, CDCl₃, 25 °C): δ = 1.71 (s, 18H, Bu-CH₃), 3.60 (s, 6H, N₂CH₃), 3.65 (d, 1J_P,H = 3.8 Hz, 2H, C₃H₂), 7.52–7.81 (m, 5H, 5CH₃, 2Ph).** **¹³C [¹H] NMR (75.5 MHz, CDCl₃, 25 °C): δ = 27.8 (s, Bu-CH₃), 43.1 (s, N₂-CH₃), 60.4 (s, Bu-C), 118.3 (d, 1J_P,C = 117.3 Hz, C₃), 124.2 (d, 1J_P,C = 19.7 Hz, C₂), 128.2 (d, 1J_P,C = 97.5 Hz, iso-P,C₅₇), 129.3 (d, 1J_P,C = 13.9 Hz, C₃), 131.8 (d, 1J_P,C = 12.5 Hz, C₃), 133.3 (d, 1J_P,C = 3.1 Hz, C₂), 167.0 (d, 1J_P,C = 5.0 Hz, C, 3Ph).** IR (ATR, ν [cm⁻¹]): ν = 3053 (w), 2978 (w), 2935 (w), 1583 (w), 1545 (vs), 1437 (s), 1280 (vs), 1130 (s), 1096 (s), 823 (s), 756 (s), 740 (s), 716 (vs), 680 (s), UV/Vis (CHCl₃): λmax [nm] (abs.): 287 (1.501), 230 (0.829). MS (EI, 70 eV): m/z (%) 478 (76) [M⁺], 446 (10) [M-Se⁺], 421 (12) [M-Se₂⁺], 366 (100) [M-Se₃⁺], 332 (24) [M-Se₄⁺], 239 (32) [C₁₂H₁₉₅N₆P⁺], 57 (20) [C₆H₆⁺]. HR-MS: found: 478.1447, calc: 478.1448. EA: calc for C₂₃H₂₁N₆P₂S: C 55.20, H 6.53, N 11.70, S 20.10 found: C 54.42, H 6.36, N 11.34, S 19.35.

**Bis(1-tert-butyl-3-methyl-imidazol-2-thione-4-yi)-phosphane oxide (7)**

To a solution of 1.73 g (3.87 mmol) of 2 in 30 mL of methanol, 3.85 mL (38.73 mmol) of H₂O₂ (35% in water) was added at 0°C. The reaction mixture was stirred at 0 °C for 30 min, then at r.t. for 10 h. After the reaction was completed (**³¹P NMR control**), 1.90 g (7.74 mmol) of BaCl₂·2H₂O in 10 mL water was added into it and stirred for additional two hours. The reaction mixture was then filtered through a frit equipped with a layer of celite to remove barium sulfate; the filtrate was collected and concentrated in vacuo (8×10⁻³ mbar). The residual syrup-like fluid was crystallized from isopropanol at -20 °C followed by washing with *n*-pentane (2 × 10 mL) and then dried in vacuo.

**Synthesis of bis(1-tert-butyl-3-methyl-imidazol-2-yi)-chloride-4-yi)-phosphane oxide (6)**

In a Schlenk tube, 0.266 g (1.33 mmol) of potassium hexamethyldisilazide and 0.316 g (0.66 mmol) of bis(imidazolium) salt 6 were combined and then dissolved in 10 mL of tetrahydrofuran at -78°C. The reaction mixture was stirred for 12 hours while warming up to ambient temperature. The THF was removed in vacuo (8×10⁻³ mbar), and the residue was dissolved in 20 mL of diethyl ether and the solid potassium chloride was removed via filter cannulation. The solvent was then removed in vacuo.

**Synthesis of bis(1-tert-butyl-3-methyl-imidazol-2-yi)-phosphane sulfide (7)**

In a Schlenk tube, 0.300 g (0.63 mmol) of bisimidazolium salt 6, 0.141 g (1.26 mmol) of potassium tert-butoxide and 0.656 g (1.26 mmol) of AgOTf·PPh₃ were combined and then dissolved in 15 mL of tetrahydrofuran. The reaction mixture was heated at 60 °C for 16 h. The formed potassium chloride was separated via filter cannulation. The clear solution was then concentrated in vacuo (8×10⁻³ mbar) followed by washing with *n*-pentane (2 × 5 mL) and then dried in vacuo.

**Synthesis of bis(NHC-silver) complex 8**

In a Schlenk tube, 0.300 g (0.63 mmol) of bisimidazolium salt 6, 0.141 g (1.26 mmol) of potassium tert-butoxide and 0.656 g (1.26 mmol) of AgOTf·PPh₃ were combined and then dissolved in 15 mL of tetrahydrofuran. The reaction mixture was heated at 60 °C for 16 h. The formed potassium chloride was separated via filter cannulation. The clear solution was then concentrated in vacuo (8×10⁻³ mbar) followed by washing with *n*-pentane (2 × 5 mL) and then dried in vacuo.

**Synthesis of bis(NHC-silver) complex 8**

In a Schlenk tube, 0.300 g (0.63 mmol) of bisimidazolium salt 6, 0.141 g (1.26 mmol) of potassium tert-butoxide and 0.656 g (1.26 mmol) of AgOTf·PPh₃ were combined and then dissolved in 15 mL of tetrahydrofuran. The reaction mixture was heated at 60 °C for 16 h. The formed potassium chloride was separated via filter cannulation. The clear solution was then concentrated in vacuo (8×10⁻³ mbar) followed by washing with *n*-pentane (2 × 5 mL) and then dried in vacuo.
dalton transactions
46. (a) G. M. Sheldrick, SHELXS97 Program for the Solution of Crystal Structure; University of Goettingen, Germany, 1997; (b) G. M. Sheldrick, SHELXL 97 Program for the Refinement of Crystal Structure, University of Goettingen, Germany, 1997.