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Inorganica Chimica Acta

Triarylphosphanes with 2-(Et₂NCH₂)C₆H₄ groups. Copper(I) complexes and oxidation derivatives of type EP(C₆H₄CH₂NEt₂-2)_nPh_{3-n} (E = S, Se; n = 1,2).

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Abstract

The triarylphosphanes $P(C_6H_4CH_2NEt_2-2)_nPh_{3-n}$ [n = 1 (1), 2 (2)] were obtained by reacting Ph₂PCl or PhPCl₂ with [2-(Et₂NCH₂)C₆H₄]Li in a 1:1 and a 1:2 molar ratio, respectively. Further oxidation with elemental sulfur or elemental selenium powder resulted in the triorganophosphane chalcogenides $EP(C_6H_4CH_2NEt_2-2)_nPh_{3-n}$ [E = S, n = 1 (3), 2 (5); E = Se; n = 1 (4), 2 (6)]. The copper(I) complexes [CuCl{P(C₆H₄CH₂NEt₂-2)_nPh_{3-n}}] [n = 1 (7), 2 (8)] were prepared by the reactions between the triarylphosphanes 1 and 2 with CuCl in a 1:1 molar ratio. The new species were investigated in solution by NMR spectroscopy. The single crystal X-ray diffraction studies revealed a monomeric structure for the triorganophosphane sulphides 3 and 5, while the copper(I) complexes 7 and 8 form dimers by bridging chlorine atoms. In both copper complexes the phosphane ligands behave as *C*,*N* chelating moieties. For compound 8 the two C₆H₄CH₂NEt₂-2 groups are equivalent in solution, while in solid state only for one of them the N→Cu intramolecular interaction was observed.

Key words: P/N triarylphosphanes; triarylphosphane chalcogenides; copper(I) complexes; solution behaviour; solid state structure;

1. Introduction

Heteropolydentate ligands bearing both phosphorus and nitrogen as donor atoms, so named P/N ligands, are still of high interest, due to their coordination ability towards different transition metals and the potential of the resulted metal complexes in catalysis [1-3]. The combination of the π -acceptor character of phosphorus and the σ -donation ability of nitrogen results in the stabilization of the metal center in a low oxidation state and also in an increased availability for oxidative addition reactions [4]. Different organic groups, *i.e.* amino, imino, pyridine, etc., were used in order to allow a fine tuning of the electronic properties of various P/N ligands, thus allowing to design appropriate compounds for specific catalytic processes [5,6]. Triorganophosphanes bearing aryl groups with pendant arms with nitrogen donor atoms, *i.e.* 2-(Me₂NCR¹R²)C₆H₄ (R¹ = H, R² = H, Me) [7], [2-(Me₂NCR¹R²)]₂C₆H₃ (R¹ = R² = H) [8], were described and used as ligands for different transition metals. In such metal complexes, besides the stabilization effect of the P \rightarrow M interaction, the presence of nitrogen in one or more pendant arms attached to the organic groups in the R₃P ligand usually results in additional N \rightarrow M intramolecular coordination.

Copper compounds stabilized by triarylphosphanes proved to be promising candidates as active species in catalysis, *i.e.* in hydroboration [9], hydrogenation [10], carbene insertion into the N–H bond [11], etc., and, based on their photoluminescent properties, in the design of different types of sensors [12,13].

In copper complexes with the PN₃ ligand P(C₆H₄CH₂NMe₂-2)₃ the phosphane was observed to act as a chelating either *P*,*N*- [14,15] or *P*,*N*,*N*- [16,17] moiety in the mononuclear species [CuX{P(C₆H₄CH₂NMe₂-2)₃] (X = Cl, I). The third pendant arm was involved in coordination to the metal as a chelating moiety in the ionic [{2-(Me₂NCH₂)C₆H₄}PCu]⁺ ClO₄⁻ [16] or the dinuclear [CuX{P(C₆H₄CH₂NMe₂-2)₃]₂ (X = Cl, Br) [15,18], while in other species it remained dangling [17]. We have previously reported some copper(I) compounds of type [CuX{P(C₆H₄CH₂NMe₂-2)_nPh_{3-n}}] (n = 0 - 2; X = Cl, I) and we observed a chelating *P*,*N*- behaviour in the mononuclear [CuCl{PPh₂(C₆H₄CH₂NMe₂-2)] and the dinuclear [CuI{P(C₆H₄CH₂NMe₂-2)Ph₂]₂. For the compound [CuCl{P(C₆H₄CH₂NMe₂-2)₂Ph}] were found two independent molecules in the asymmetric unit, with a different coordination behaviour of the triarylphosphane in each of them, *e.g.* in one of them both nitrogen atoms are intramolecularly interacting with copper, while in the other molecule one nitrogen is interacting with copper and the other with phosphorus [19].

As a continuation of our interest in triarylphosphanes with organic groups bearing pendant arms, we extended our studies upon the triarylphosphanes $P(C_6H_4CH_2NEt_2-2)_nPh_{3-n}$ (n = 1, 2) and we report here their synthesis and structural characterization, as well as the Cu(I) complexes of type $[CuCl{P(C_6H_4CH_2NEt_2-2)_nPh_{3-n}}]$. In addition, the oxidation products $E=P(C_6H_4CH_2NEt_2-2)_nPh_{3-n}$ (E = S, Se) are also discussed.

2. Experimental

2.1. General methods

The intermediates $2-(Et_2NCH_2)C_6H_4Br$ and $[2-(Et_2NCH_2)C_6H_4]Li$ were prepared according to literature procedures [20] and the starting materials, *i.e.* ⁿBuLi, HNEt₂, 2bromobenzyl bromide, PhPCl₂, Ph₂PCl, elemental S and Se powders and CuCl were purchased from Sigma Aldrich and used without further purification. All manipulations involving air sensitive compounds were carried out under argon, by using Schlenk techniques. Solvents were dried and distilled prior to use.

Multinuclear (¹H, ¹³C, ³¹P and ⁷⁷Se) NMR spectra were recorded at room temperature in CDCl₃ on a BRUKER DRX 400 instrument, operating at 400.13, 100.61, 161.92 and 76.28 MHz, respectively. The chemical shifts (δ) are reported in ppm relative to TMS (¹H and ¹³C), H₃PO₄ 85% (³¹P) and Me₂Se (⁷⁷Se). The ¹H and ¹³C chemical shifts were assigned based on 2D NMR experiments using standard BRUKER XWIN-NMR pulse sequencies. The NMR spectra were processed using the MestReC and MestReNova software [21]. The mass spectra were measured on a LTQ-OrbitrapXL mass spectrometer equipped with a standard ESI/APCI source.

2.2. Syntheses

Synthesis of P(C₆H₄CH₂NEt₂-2)Ph₂ (1)

PPh₂Cl (3.5 mL, $\rho = 1.2$ g/mL, 19.0 mmol) in THF (5 mL) was added dropwise to a solution of [2-(Et₂NCH₂)C₆H₄]Li (3.21 g; 19.0 mmol) in THF (25 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 2 h, then it was allowed to reach the room temperature and the solvent was removed under vacuum. The remaining oily product was extracted in hexane. The solid residue was filtered off and from the clear solution the solvent was removed under vacuum to give the title compound as a yellowish oil. Yield: 4.7 g (71%). ¹H NMR (CDCl₃): 0.89 (t, 6H,

CH₂-CH₃, ${}^{3}J_{HH}$ 7.16 Hz), 2.47 (q, 4H, CH₂-CH₃, ${}^{3}J_{HH}$ 7.11 Hz), 3.82 (s, br., 2H, CH₂N), 6.92 (dd, 1H, H₆, ${}^{3}J_{HH}$ 4.42, ${}^{3}J_{PH}$ 7.51 Hz), 7.16 (t, 1H, H₅, ${}^{3}J_{HH}$ 7.61 Hz), 7.27-7.42 (m, 10H, P-C₆H₅ortho+meta+para, + 1H H₄), 7.62 (m, 1H, H₃). ${}^{13}C$ NMR (CDCl₃): 11.53 (s, CH₂-CH₃), 46.42 (s, CH₂-CH₃), 57.11 (d, CH₂N, ${}^{3}J_{PC}$ 19.8 Hz), 127.36 (s, C₅), 128.95 (d, C₆H₅-meta, ${}^{3}J_{PC}$ 8.2 Hz), 128,92 (d, C₆H₅-para, ${}^{4}J_{PC}$ 2.54 Hz), 129.08 (s, C₄), 129.73 (d, C₃, ${}^{3}J_{PC}$ 5.83 Hz), 134.33 (d, C₆H₅-ortho, ${}^{2}J_{PC}$ 19.8 Hz), 134.49 (br, C₆), 137.02 (d, C₁, ${}^{1}J_{PC}$ 14.4 Hz), 138.67 (d, C₂, ${}^{2}J_{PC}$ 11.2 Hz), 146.04 (d, C₆H₅-ipso, ${}^{1}J_{PC}$ 22.9 Hz). ${}^{31}P$ NMR (CDCl₃): -16.03 (s).

P(**C**₆**H**₄**CH**₂**NEt**₂-**2**)₂**Ph** (**2**) was prepared similarly, from PPhCl₂ (2 mL, $\rho = 1.32$ g/mL, 14.7 mmol) and [2-(Et₂NCH₂)C₆H₄]Li (4.97 g, 29.4 mmol), as a yellowish oil. Yield: 4.8 g (76%). ¹H NMR (CDCl₃): 0.85 (t, 12H, CH₂-CH₃, ³J_{HH} 7.16 Hz), 2.42 (q, 8H, CH₂-CH₃, ³J_{HH} 7.12 Hz), 3.71 (ABX spin system with δ_A 3.69 and δ_B 3.72, 4H, CH₂N, ²J_{HH} 14.15, ⁴J_{PH} 3.11 Hz), 6.78 (ddd, 2H, H₆ ³J_{HH} 6.53, ⁴J_{HH} 1.12, ³J_{PH} 4.3 Hz), 7.09 (t, 2H, H₅, ³J_{HH} 7.4 Hz), 7.19-7.21 (m, 2H, H₅), 7.27-7.31 (m, 5H C₆H₅-*ortho*+*meta*+*para* + 2H H₄), 7.59 (dd, 2H, C₆H₅-*ortho*, ³J_{HH} 6.86, ⁴J_{HH} 4.09 Hz). ¹³C NMR (CDCl₃): 11.41 (s, CH₂-CH₃), 46.38 (s, CH₂-CH₃), 56.00 (d, ³J_{PC} 21.4 Hz), 126.68 (s, C₅), 128.36 (d, C₆H₅-*meta*, ³J_{PC} 17.4 Hz), 128.26 (d, C₆H₅-*para*, ⁴J_{PC} 6.1 Hz), 128.76 (d, C₃, ³J_{HH} 5.34 Hz), 133.65 (s, C₄), 134.98 (d, C₆H₅-*ortho*, ²J_{PC} 20.5 Hz), 136.21 (d, C₁, ¹J_{PC} 13.9 Hz), 137.58 (d, C₂, ²J_{PC} 9.2 Hz), 144.71 (d, C₆H₅-*ipso*, ¹J_{PC} 24.9 Hz). ³¹P NMR (CDCl₃): -25.9 s.

Synthesis of SP(C₆H₄CH₂NEt₂-2)Ph₂ (3)

Elemental sulfur (0.04 g; 1.25 mmol) was added to a solution of $P(C_6H_4CH_2NEt_2-2)Ph_2$ (2) (0.43 g; 1.25 mmol) in anhydrous THF. The reaction mixture was stirred for 48 h, then it was filtered to remove traces of unreacted sulfur. The solvent was removed from the filtrate under vacuum and the obtained solid was washed with n-hexane. The title product was obtained as a pale yellow solid. Yield: 0.34 g (72%). M.p. = 116 °C. Anal. Calc. for C₂₃H₂₆NPS (MW 379.50): C, 72.79; H, 6.91; N, 3.69; S, 8.45 %. Found: C, 72.84; H, 6.98; N, 3.65; S, 8.11%. ¹H NMR (CDCl₃): 0.87 (s, br., 6H, CH₂-CH₃), 2.39 (s, br., 4H, CH₂-CH₃), 3.82 (s, br., 2H, CH₂N), 6.88 (1H, dd, H_6 , ³J_{HH} 7.9, ³J_{PH} 15.1 Hz), 7.13 (t, 1H, H₅, ³J_{HH} 6.9 Hz), 7.40-7.55 (m, 6H C₆H₅*meta+para* + 1H H₄), 7.84 (dd, 4H, C₆H₅-*ortho*, ³J_{HH} 7.2 Hz, ³J_{PH} 13.2 Hz), 8.1 (br., H₃). ¹³C

NMR (CDCl₃): 11.55 (s, v. br., CH₂-CH₃), 46.73 (s, 2H, CH₂-CH₃, 55.42 (s, br., CH₂N), 129.39 (s, br., C₅), 127.43 (d, ${}^{2}J_{PC}$ 12.1 Hz, C₂), 128.60 (d, C₆H₅-*meta*, ${}^{3}J_{PC}$ 12.7 Hz), 129.21 (d, C₆H₅-*ipso*, ${}^{1}J_{PC}$ 80.2 Hz), 129.29 (d, C₁, ${}^{1}J_{PC}$ 48.3 Hz), 130.69 (d, C₃, ${}^{3}J_{PC}$ 11.5 Hz), 131.62 (br., C₆H₅-*para*), 131.95 (d, C₄, ${}^{3}J_{PC}$ 9.1 Hz), 132.28 (d, C₆H₅-*ortho*, ${}^{3}J_{HH}$ 10.9 Hz), 132.55 (d, C₆, ${}^{2}J_{PC}$ 11.3 Hz). ${}^{31}P$ NMR (CDCl₃): 41.45 (s, ${}^{1}J_{PC}$ 80.2 Hz).

Compounds **4** – **6** were prepared similarly:

SeP(C₆H₄CH₂NEt₂-2)Ph₂ (4) from elemental selenium powder (0.29 g; 3.7 mmol) and [2-(Et₂NCH₂)C₆H₄]Ph₂P (1.29 g; 3.7 mmol). Yield: 1.12 g (71%). M.p. = 129 °C. Anal. Calc. for C₂₃H₂₆NPSe (MW 426.39): C, 64.79; H, 6.15; N, 3.28 %. Found: C, 64.82; H, 6.33; N, 3.42 %. ¹H NMR (CDCl₃): 0.89 (s, br., 6H, CH₂-CH₃), 2.47 (s, br., 4H, CH₂-CH₃), 3.87 (s, br., 2H, CH₂N), 6.85 (1H, dd, H_6 , ${}^{3}J_{HH}$ 7.1, ${}^{3}J_{PH}$ 15.3 Hz), 7.13 (t, 1H, H_5 , ${}^{3}J_{HH}$ 7.3 Hz), 7.3 (br., 1H, H₄), 7.38-7.54 (m, 6H C₆H₅-*meta*+*para* + 1H H₄), 7.80 (dd, 4H, C₆H₅-*ortho*, ${}^{3}J_{HH}$ 8.1 Hz, ${}^{3}J_{PH}$ 13.6 Hz), 8.2 (br., H_3). ¹³C NMR (CDCl₃): 11.32 (s, br., CH₂-CH₃), 46.71 (s, 2H, CH₂-CH₃, 55.17 (s, br., CH₂N), 126.57 (d, br., C₅, ${}^{3}J_{PC}$ 8.2 Hz), 127.72 (d, C₂, ${}^{2}J_{PC}$ 12.7 Hz), 128.67 (d, C₆H₅-*meta* ${}^{3}J_{PC}$ 9.6 Hz), 131.77 (d, C₆H₅-*para*, ${}^{4}J_{PC}$ 2.4 Hz), 132.02 (s, br., C₄), 132.45 (d, C₆, ${}^{2}J_{PC}$ 12.2 Hz), 132.85 (d, C₆H₅-*ortho*, ${}^{3}J_{HH}$ 10.5 Hz). ³¹P NMR (CDCl₃): 30.83 (s, ¹J_{PC} 75.8 Hz, ¹J_{PSe} 722.2 Hz). ⁷⁷Se NMR (CDCl₃): -260.1 (d, br., ¹J_{PSE} 728.7 Hz).

SP(C₆H₄CH₂NEt₂-2)₂Ph (5) from elemental sulfur (0.10 g; 3.1 mmol) and P(C₆H₄CH₂NEt₂-2)₂Ph (1.35 g; 3.1 mmol). Yield: 1.18 g (82%). M.p. = 102 °C. Anal. Calc. for C₂₈H₃₇N₂PS (MW 464.65): C, 72.38; H, 8.03; N, 6.03; S, 6.90 %. Found: C, 72.41; H, 8.15; N, 6.22; S, 6.74 %. ¹H NMR (CDCl₃): 0.84 (t, 12H, CH₂-CH₃, ³J_{HH} 7.16 Hz), 2.33 (q, 8H, CH₂-CH₃, ³J_{HH} 7.12 Hz), 3.84 (AB spin system with δ_A 3.76 and δ_B 3.93, 4H, CH₂N, ²J_{HH} 15.2 Hz), 7.11 – 7.18 (m, 4H, H₆ + H₅) 7.42 - 7.55 (m, 3H C₆H₅-*meta*+*para* + 2H H₄), 7.74 (dd, 2H, C₆H₅-*ortho*, ³J_{HH} 6.8, ³J_{PH} 12.4 Hz), 8.04 (m, H₃). ¹³C NMR (CDCl₃): 12.07 (s, CH₂-CH₃), 46.7 (s, CH₂-CH₃), 56.27 (s, NCH₂), 125.51 (d, C₅, ³J_{PC} 12.4 Hz), 128.41 (d, C₆H₅-*meta*, ³J_{PC} 12.5 Hz), 129.76 (d, C₃, ³J_{PH} 9.6 Hz), 130.15 (d, C₁, ¹J_{PC} 82.3 Hz), 131.51 (d, C₄, ⁴J_{PC} 2.8 Hz), 131.64 (d, C₆H₅-*para*, ⁴J_{PC} 2.7 Hz),

132.35 (d, C₆, ${}^{2}J_{PC}$ 10.7 Hz), 132.5 (d, C₆H₅-*ipso*, ${}^{1}J_{PC}$ 83.2 Hz), 132.93 (d, C₆H₅-*ortho*, ${}^{2}J_{PC}$ 11.8 Hz), 146.05 (d, C₂, ${}^{2}J_{PC}$ 8.2 Hz). ${}^{31}P$ NMR (CDCl₃): 41.2s, ${}^{1}J_{PC}$ 82.3 Hz.

SeP(C₆H₄CH₂NEt₂-2)₂Ph (6) from elemental selenium (0.10 g, 1.3 mmol) and P(C₆H₄CH₂NEt₂-2)₂Ph (0.56 g; 1.3 mmol). Yield: 0.48 g (73%). M.p. = 121 °C. Anal. Calc. for C₂₈H₃₇N₂PSe (MW 511.54): C, 65.74; H, 7.29; N, 5.48 %; Found: C, 65.77; H, 7.28; N, 5.45 %; ¹H NMR (CDCl₃): 0.84 (t, 12H, CH₂-CH₃, ³J_{HH} 7.5 Hz), 2.32 (q, 8H, CH₂-CH₃, ³J_{HH} 7.5 Hz), 3.80 (AB spin system, δ_A 3.67 and δ_B 3.91, 4H, CH₂N, ¹J_{HH} 16.2 Hz), 7.14 – 7.25 (m, 4H H₆ + H₅), 7.42 - 7.54 (m, 3H C₆H₅-meta+para + 2H H₄), 7.78 (dd, 2H, C₆H₅-ortho, ³J_{HH} 7.5, ³J_{PH} 12.1 Hz), 8.03 (dd., 2H H₃). ¹³C NMR (CDCl₃): 12.13 (s, CH₂-CH₃), 46.86 (s, CH₂-CH₃), 56.50 (d, NCH₂, ²J_{PC} 5.1 Hz), 126.26 (d, C₅, ³J_{PC} 12.3 Hz), 128.52 (d, C₁, ¹J_{PC} 72.3 Hz), 128.57 (d, C₆H₅-meta, ³J_{PC} 13.1 Hz), 129.81 (d, C₃, ³J_{PH} 10.3 Hz), 131.12 (d, C₆H₅-ipso, ¹J_{PC} 74.5 Hz), 131.70 (d, C₄, ⁴J_{PC} 2.6 Hz), 131.84 (d, C₆H₅-para, ⁴J_{PC} 2.7 Hz), 132.69 (d, C₆H₅-ortho, ²J_{PC} 11.3 Hz), 133.67 (d, C₆, ²J_{PC} 10.5 Hz), 146.04 (d, C₂, ²J_{PC} 8.5 Hz). ³¹P NMR (CDCl₃): 26.63 (s, ¹J_{PC} 74.6 Hz, ¹J_{PSe} 710.6 Hz). ⁷⁷Se NMR (CDCl₃): - 191.57 (d, br., ¹J_{PSe} 709.6 Hz).

Synthesis of $[CuCl{P(C_6H_4CH_2NEt_2-2)Ph_2}]$ (7)

To a solution of P(C₆H₄CH₂NEt₂-2)Ph₂ (0.49 g, 1.4 mmol) in anhydrous chloroform was added CuCl (0.14 g, 1.4 mmol). The reaction mixture was refluxed for 4 h and left under stiring over night. The next day the solvent was removed under reduced pressure. The remaining solid was washed with toluene, and dried under vacuum to give the title compound as a colorless solid. Yield: 0,57 g (91%). M.p. = 152 °C. Anal. Calc. for C₂₃H₂₆ClCuNP (MW 446.43): C, 61.88; H, 5.87; N, 3.14 %; Found: C, 61.63; H, 5.81; N, 3.33 %; ¹H NMR (CDCl₃): 1.17 (t, 6H, CH₂-CH₃, ³J_{HH} 7.5 Hz), 2.75 (d, 2H, CH₂-CH₃, ³J_{HH} 7.5 Hz), 3.56 (s, 2H, CH₂N), 6.89 (t, 1H, H_6 , ³J_{HH} 7.8 Hz), 7.28-7.31 (m, 2H, $H_4 + H_5$), 7.36-7.43 (m, 4H P-C₆H₅-*meta* + 1H H₃), 7.44-7.49 (m, 6H P-C₆H₅-*ortho*+*para*). ¹³C NMR (CDCl₃): 10.91 (s, CH₂-CH₃), 50.09 (s, CH₂-CH₃,), 58.88 (d, CH₂N, ³J_{PH} 5.6 Hz), 128.99(d, C₅, ³J_{PC} 4.9 Hz), 129.26 (d, C₆H₅-*ortho*, ³J_{PC} 10.2 Hz), 130.18 (d, C₆H₅-*ipso*, ¹J_{PC} 35.3 Hz), 130.37 (s, br., C₃), 130.86 (s., br., C₆H₅-*para*), 131.54 (d, C₁, ¹J_{PC} 29.5 Hz), 133.25 (s, br., C₄ + C₆), 134.37 (d, C₆H₅-*meta*, ³J_{PC} 14.6 Hz), 139.91 (d, C₂, ²J_{PC} 16.6 Hz). ³¹P NMR (CDCl₃): -10.93s. ESI+ MS (m/z, %): 410.11 (100) [{CuP(C₆H₄CH₂NEt₂-2)Ph₂⁺].

[CuCl{P(C₆H₄CH₂NEt₂-2)₂Ph}] (8) was prepared silmilarly, from P(C₆H₄CH₂NEt₂-2)₂Ph (0.27 g, 0.62 mmol) and CuCl (0,061 g; 0.62 mmol), as a colorless solid. Yield: 0.27 g (82%). M.p. = 142 °C. Anal. Calc. for C₂₈H₃₇ClCuN₂P (MW 532.59): C, 63.14; H, 7.19; N 5.26 %; Found: C, 63.31; H, 7.11; N, 5.44 %. ¹H NMR (CDCl₃): 0.96 (s, br., 12H, CH₂-CH₃), 2.57 (s, br., 4H, CH₂-CH₃), 3.71 (AB spin system, δ_A 3.67, δ_B 3.74, br., 2H, CH₂N, ¹J_{HH} 11.6 Hz), 6.81 (t, 2H, H₆, ³J_{HH} 7.6 Hz), 7.21 (t, 2H, H₅, ³J_{HH} 7.1 Hz), 7.29-7.57 (m, 5H C₆H₅-ortho+meta+para + 4H, H_{4,3}. ¹³C NMR (CDCl₃): 10.72 (s, CH₂-CH₃), 47.79 (s, CH₂-CH₃), 58.23 (s, br., CH₂N), 128.05 (s, C₅), 129.15 (d, C₆H₅-ortho, ³J_{PC} 11.2 Hz), 130.25 (s, br., C₄), 130.28 (d, C₆H₅-para, ⁴J_{PC} 8.1 Hz), 130.67 (d, C₃, ³J_{PC} 12.1 Hz), 131.61 (d, br., C₄, ⁴J_{PC} 7.5 Hz), 133.17 (s, br., C₆), 134.84 (d, C₆H₅-meta, ²J_{PC} 17.1 Hz), 142.29 (s., br., C₂) ³¹P NMR (CDCl₃): -20.61 (s, br.). ESI+ MS (m/z, %): 531.18 (38) [CuCl{P(C₆H₄CH₂NEt₂-2)₂Ph} + H⁺], 495.20 (100) [Cu{P(C₆H₄CH₂NEt₂-2)₂Ph}⁺].

2.3. Crystal structure determination

For $SP(C_6H_4CH_2NEt_2-2)Ph_2$ (3), $SP(C_6H_4CH_2NEt_2-2)_2Ph$ (5) and the copper(I) complexes $[CuCl{P(C_6H_4CH_2NEt_2-2)Ph_2}]$ (7) and $[CuCl{P(C_6H_4CH_2NEt_2-2)_2Ph}]$ (8) X-ray quality crystals were obtained from chloroform / n-hexane mixtures (1/4, v/v).

Block crystals of **3**, **5**, **7** and **8** were attached with epoxy glue on cryoloops and the data were collected at about 200 K or at room temperature (see Table 1) on an Oxford-Diffraction XCALIBUR E CCD diffractometer (for **3**, **5** and **8**) and a Bruker SMART APEX CCDC diffractometer (for **7**), using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction [22] for **3**, **5** and **8** and SADABS - Bruker/Siemens [23] for **7**. The structures were solved by direct methods using the Olex2 [24] software with the SHELXS structure solution program (for **3**, **5** and **8**) or the SHELXTL Version 6.10 - 2000 (for **7**) and refined by full-matrix least-squares on F² with SHELXL-2016/4 [25]. Atomic displacements for non-hydrogen atoms were refined using an anisotropic model. Hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. The carbon atoms of the ethyl groups in compound **3** (C14, C15, C16 and C17) are disordered over two positions with a contribution of 0.56:0.44 each of them). In compound **8** the carbon atoms of one ethyl group (C25, C26, C27 and C28) are disordered over two positions as well, with a contribution of 0.62:0.38. The

positional parameters of the disordered ethyl fragments in **3** and **8** were refined in combination with PART and SADI restrains using anisotropic/isotropic model for non-H atoms. Table 1 provides a summary of the crystallographic data together with refinement details for compounds **3**, **5**, **7** and **8**. The drawings were created with the Diamond program [26].

	3	5	7	8
Empirical formula	C ₂₃ H ₂₆ NPS	$C_{28}H_{37}N_2PS$	$C_{46}H_{52}Cl_2Cu_2N_2P_2$	C ₂₈ H ₃₇ ClCuN ₂ P
Formula weight	379.48	464.63	892.81	531.56
Temperature, K	296(4)	200.00(14)	294(2)	199.9(6)
Wavelength, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	P2(1)/c	P2(1)/c	P -1	P2(1)/c
<i>a</i> (Å)	12.907(10)	8.9525(14)	9.5546(18)	13.7305(9)
<i>b</i> (Å)	9.375(4)	22.940(2)	10.1300(19)	15.9477(10)
<i>c</i> (Å)	18.611(11)	12.8369(14)	12.454(2)	12.7585(7)
α (°)	90	90	103.837(4)	90
β (°)	106.88(7)	101.697(12)	97.059(3)	103.251(6)
γ (°)	90	90	110.220(3)	90
Volume, Å ³	2155(2)	2581.6(5)	1070.0(4)	2719.3(3)
Ζ	4	4	1	4
Density (calculated), g/cm ³	1.170	1.195	1.386	1.298
Absorption coefficient, mm ⁻¹	0.231	0.206	1.228	0.979
F(000)	808	1000.0	464	1120.0
Crystal size, mm	0.16 x 0.04 x 0.02	0.20 x 0.15 x 0.03	0.39 x 0.33 x 0.28	0.15 x 0.15 x
				0.04
θ range for data collections (°)	2.40 to 24.71	1.78 to 25.03	1.729 to 24.997	1.52 to 25.03
Reflections collected	6844	12173	10180	10649
Independent reflections	6845	4566	3745	4806
	$[R_{int} = 0.0000]$	$[R_{int} = 0.0630,$	$[R_{int} = 0.0453]$	$[R_{int} = 0.0567]$
Refinement method	Full-matrix least-squares on F ²			
Data / restraints / parameters	6845 / 13 / 231	4566/1/293	3745 / 0 / 246	4806/7/289
Goodness-of-fit on F ²	0.695	1.044	0.967	1.033
Final <i>R</i> indicies [I>2sigma(I)]	R1 = 0.0843,	$R_1 = 0.0813$,	R1 = 0.0397,	$R_1 = 0.0612$,
	wR2 = 0.1695	$wR_2 = 0.1723$	wR2 = 0.0868	$wR_2 = 0.1211$
<i>R</i> indicies (all data)	R1 = 0.2718,	$R_1 = 0.1260,$	R1 = 0.0572,	$R_1 = 0.0950,$
	wR2 = 0.2050	$wR_2 = 0.1975$	wR2 = 0.0925	$wR_2 = 0.1358$
Largest diff. peak and hole, eÅ ⁻³	0.331 and -0.373	0.99 and -0.41	0.349 and -0.288	0.79 and -0.73

Table 1. Crystal data and structure refinement for $SP(C_6H_4CH_2NEt_2-2)Ph_2$ (**3**), $SP(C_6H_4CH_2NEt_2-2)_2Ph$ (**5**), $[CuCl{P(C_6H_4CH_2NEt_2-2)Ph_2}]$ (**7**) and $[CuCl{P(C_6H_4CH_2NEt_2-2)_2Ph}]$ (**8**)

3. Results and discussion

3.1. Synthesis and spectroscopic characterization

The triaryl phosphanes $P(C_6H_4CH_2NEt_2-2)_nPh_{3-n}$ [n = 1 (1), 2 (2)] were prepared by reacting the lithiated derivative [2-(Et_2NCH_2)C_6H_4]Li, previously obtained *in situ* by the ortho lithiation of 2-(Et_2NCH_2)C_6H_4Br, with Ph_2PCl and PhPCl_2, respectively, in the appropriate molar ratio. Further oxidation with elemental sulfur or elemental selenium powder resulted in the triaryl

phosphane chalcogenides $EP(C_6H_4CH_2NEt_2-2)_nPh_{3-n}$ [E = S, n = 1 (3), 2 (5); E = Se; n = 1 (4), 2 (6)]. The reaction of 1 and 2 with CuCl in a 1:1 molar ratio lead to the copper(I) complexes $[CuCl{P(C_6H_4CH_2NEt_2-2)_nPh_{3-n}}]$ [n = 1 (7), 2 (8)]. The described transformations are depicted in Scheme 1.

$$n [2-(Et_2NCH_2)C_6H_4]Li \xrightarrow{PPh_{3-n}Cl_n} P(C_6H_4CH_2NEt_2-2)_nPh_{3-n} n = 1 (1), 2 (2) P(C_6H_4CH_2NEt_2-2)_nPh_{3-n} \xrightarrow{E} E=P(C_6H_4CH_2NEt_2-2)_nPh_{3-n} n = 1; E = S (3), Se (4) n = 2; E = S (5), Se (6) P(C_6H_4CH_2NEt_2-2)_nPh_{3-n} \xrightarrow{CuCl} [CuCl{P(C_6H_4CH_2NEt_2-2)_nPh_{3-n}}] n = 1 (7), 2 (8) Scheme 1$$

The triarylphosphanes 1 and 2 were isolated as yellowish oils, while the other compounds are pale yellow (3 - 6) or colourless (7 and 8) microcrystalline solids. All compounds were characterized in solution by NMR spectroscopy (¹H, ¹³C, ³¹P and ⁷⁷Se where appropriate). The copper(I) complexes were investigated also by mass spectrometry.

The ¹H and the ¹³C NMR spectra present the expected resonances for the organic groups attached to phosphorus. For the compounds bearing two 2-(Et₂NCH₂)C₆H₄ groups the NMR spectra suggest their equivalence in solution. The ¹H NMR resonances of the CH₂N(CH₂CH₃)₂ moieties bring no clear evidence for an intramolecular N→P or N→Cu coordination in solution, where such a behaviour is expected. For the triaryl phosphanes **1** and **2** a triplet and a quartet characteristic for the ethyl protons, accompanied by a broad singlet in **1** and an ABX spin system in **2**, characteristic for the C₆H₄CH₂N protons, are present. For the triorganophosphorus chalcogenides **3** and **4** bearing one 2-(Et₂NCH₂)C₆H₄ group, only broad resonances were observed in the aliphatic region, while for compounds **5** and **6**, with two 2-(Et₂NCH₂)C₆H₄ groups, the resonances for the aliphatic protons are well resolved, giving rise to a triplet and a quartet for the ethyl protons and an AB spin system for the diastereotopic C₆H₄CH₂N protons. This behaviour might be consistent with the more crowded environment in case of the species bearing two groups with pendant arms. For the copper(I) complexes the resonances corresponding to the ethyl protons in **7** are resolved in a triplet and a quartet, while those

observed for the complex **8** are broad singlets. In addition, the $C_6H_4CH_2N$ protons appear as a broad singlet in **7** and an AB spin system in **8**.

The ¹³C NMR spectra present the expected number of resonances, in most cases split as doublets due to the coupling with phosphorus.

The ³¹P{H} NMR spectra present in all cases only one singlet resonance, thus being consistent with the presence of only one species in solution. For the selenium containing species, the ³¹P NMR resonance is accompanied by ⁷⁷Se satellites determined by the ³¹P – ⁷⁷Se coupling. For compound **6** the ⁷⁷Se NMR resonance could not be detected, but for compound **4** a doublet was observed at δ -260.1 ppm, with a coupling constant ¹J_{PSe} of 728.7 Hz, almost identical to the value found in the ³¹P NMR spectrum of this compound, respectively ¹J_{PSe} 722.2 Hz.

The ESI+ MS spectra of the copper(I) complexes present the peak characteristic for the ion $[M - Cl]^+$ at m/z 410.11 in 7 and at m/z 495.20 in 8 as base peak. Only in compound 8 was observed a peak at m/z 531.18 with a lower intensity (38 %), corresponding to the pseudo-molecular ion [{P(C₆H₄CH₂NEt₂-2)₂Ph}CuCl + H⁺],

3.2. Single-crystal X-ray diffraction studies

3.2.1. Crystal and molecular structure of $SP(C_6H_4CH_2NEt_2-2)Ph_2$ (3) and $SP(C_6H_4CH_2NEt_2-2)_2Ph$ (5)

The thermal ellipsoids representation for compounds **3** and **5** are depicted in Figures 1 and 2, respectively.



Figure 1. Thermal ellipsoids representation at 30% probability and atom numbering scheme of 3. Only the carbon atoms with a major contribution (56%) are represented in the disordered ethyl groups (C14 – C17). Hydrogen atoms were omitted for clarity.



Figure 2. Thermal ellipsoids representation at 30% probability and atom numbering scheme of 5. Hydrogen atoms were omitted for clarity.

The two compounds have monomeric structures, with a distorted tetrahedral coordination geometry about phosphorus, with bond angles ranging in 3/5 from $103.0(3)^{\circ}/103.45(19)^{\circ}$ (C1–P1–C18) to $114.1(2)^{\circ}/116.60(14)^{\circ}$ (C18–P1–S1). The P=S interatomic distances in both compounds are consistent with a double bond (1.947(3) Å in **3** and 1.9552(16) Å in **5**, *vs*. Ph₂P(=S)–N=P(–SMe)Ph₂: P=S 1.954(1), P–S 2.071(1) Å [27], and of a similar magnitude with the values observed in the related [2-(Me₂NCH₂)C₆H₄]₃P=S or [2-(Me₂NCH₂)C₆H₄]₂PhP=S [28].

3.2.2. Crystal and molecular structure of $[CuCl{P(C_6H_4CH_2NEt_2-2)Ph_2}]$ (7) and $[CuCl{P(C_6H_4CH_2NEt_2-2)Ph_2}]$ (8)

The thermal ellipsoids representation for $[7]_2$ and $[8]_2$ are given in Figures 3 and 4, respectively, while selected interatomic distances and angles are given in Table 2.

The copper(I) complexes 7 and 8 have dimeric structures, with a distorted tetrahedral environment about each copper atom. In both compounds the triorganophosphane ligand behaves as a bidentate chelating P,N moiety towards the metal centre.



Figure 3. Thermal ellipsoids representation at 30% probability and atom numbering scheme of R_{NI}, S_{NI} -[7]₂. Hydrogen atoms were omitted for clarity.



Figure 4. Thermal ellipsoids representation at 30% probability and atom numbering scheme of $R_{NI}, S_{NI'}$ -[**8**]₂. Only the carbon atoms with a major contribution (62%) are represented in the disordered ethyl groups (C25 – C28). Hydrogen atoms were omitted for clarity.

	7	8	
Cu1–P1	2.1870(9)	2.1998(14)	
Cu1–Cl1	2.3773(9)	2.4224(12)	
Cu1…N1	2.193(2)	2.190(4)	
Cu1…Cl1'	2.3593(9)	2.3318(13)	
Cu1'…Cl1	2.3593(9)	2.3317(13)	
P1–Cu1–N1	99.87(7)	100.00(11)	
P1–Cu1–Cl1	117.34(3)	109.53(5)	
N1–Cu1–Cl1	108.67(6)	107.26(10)	
P1–Cu1–Cl1'	124.20(3)	130.41(5)	
N1–Cu1–Cl1'	106.99(7)	108.97(11)	
Cl1–Cu1–Cl1'	99.04(3)	99.30(4)	
Cu1–Cl1–Cu1'	80.96(3)	80.70(4)	

Table 2. Selected interatomic distances (Å) and angles (°) in $[CuCl{P(C_6H_4CH_2NEt_2-2)Ph_2}]$ (7) and $[CuCl{P(C_6H_4CH_2NEt_2-2)Ph_2}]$ (8)

The dimeric association is realized in both compounds by bridging chlorine atoms (Cu1···Cl1' 2.3593(9) Å in 7 and 2.3317(13) Å in 8, vs. Σr_{vdW}(Cu,Cl) 3.20 Å [29,30]). The dimeric structure observed for compound 7 resembles that one previously reported for the copper(I) complexes $[CuX{P(C_6H_4CH_2NMe_2-2)Ph_2}]$ (X = Cl, I) [19]. In compound 8 the two 2-(Et₂NCH₂)C₆H₄ groups attached to phosphorus behave in a different way: one of them is intramolecularly coordinated to copper through a strong N \rightarrow Cu interaction (2.19 Å vs. $\Sigma r_{vdW}(Cu,N)$ 2.94 Å [29,30]), while the other one remains dangling, with the N2/N2' atoms pushed far away from the coordination sphere of phosphorus or copper. This behaviour of the $P(C_6H_4CH_2NEt_2-2)_2Ph$ ligand is different from that one observed in the copper(I) complex $[CuCl{P(C_6H_4CH_2NMe_2-2)_2Ph}]$ where both nitrogen atoms are intramolecularly coordinated, one of them to copper and the other one to phosphorus. Such a behaviour preserve the distorted tetrahedral coordination geometry about phosphorus with bond angles ranging in 7/8 from 102.73(13)° (C7-P1-C18)/101.33(15)° (C7-P1-Cu1)to 118.13(10)°/ 124.10(14)° (C18–P1–Cu1). The N \rightarrow Cu interactions in compounds 7 and 8 are close to the values previously

observed in the copper complexes with the related methyl substituted ligands, $[CuX{P(C_6H_4CH_2NMe_2-2)_2Ph}]$ or $[CuX{P(C_6H_4CH_2NMe_2-2)Ph_2}]$ (X = Cl, I) [19]. The intramolecular N→Cu interaction results in two six membered CuPC₃N rings in each dimer, which are not planar, but folded about the imaginary axes P1…C7 and P1…C7' in 7 and P1…C13 and P1…C13' in 8, respectively, with twisted boat conformations. The intramolecular N→Cu coordination induces planar chirality [31] and the compounds crystallize as mixtures of *R* and *S* isomers which are interconnected in $R_{NI}, S_{NI'}$ and $S_{NI}, R_{NI'}$ dimers in both compounds. Alternatively, by applying the skew line convention [31], the structure of the copper compounds might be discussed in terms of λ and δ isomers. Therefore, compounds 7 and 8 crystalize as a racemate of $\lambda_{Cu1}/\delta_{Cu1'}$ and $\delta_{Cu1}/\lambda_{Cu1'}$ dimers, where δ and λ refer to the chirality of the sixmembered chelate rings associated with copper.

The two dimeric structures are tricyclic systems with planar Cu_2Cl_2 cores and the ligands displayed *trans* each other with respect to the relative positions of the nitrogen and the phosphorus atoms towards the planar Cu_2Cl_2 central unit.

Conclusions

The liquid phosphanes $P(C_6H_4CH_2NEt_2-2)Ph_2$ (1) and $P(C_6H_4CH_2NEt_2-2)_2Ph$ (2) were used in oxidation reactions with elemental chalcogens (sulfur and selenium), as well as in complexation reactions with CuCl. The ¹H NMR spectra of the reported species brought no clear evidences for a *C*,*N* coordination pattern of the 2-Et₂NCH₂C₆H₄ group in solution. For the species bearing two aryl groups 2-Et₂NCH₂C₆H₄, each of them with a pendant arm capable for intramolecular coordination, the ¹H and the ¹³C NMR spectra suggest their equivalence in solution. For the copper complex **8** the solid state structure determined by single crystal X ray diffraction revealed a different behaviour of the two 2-Et₂NCH₂C₆H₄ groups, one of them behaving as a *C*,*N* chelating moiety towards copper, while the pendant arm of the other is pushed far away from the coordination sphere of the metal or the phosphorus atom.

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Supplementary material

CCDC 1557271 for **3**, 1557270 for **5**, 1558371 for **7** and 1558370 for **8** contain the supplementary crystallographic data for this contribution. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data_request/cif</u>

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Graphical abstract

The triarylphosphanes $P(C_6H_4CH_2NEt_2-2)_nPh_{3-n}$ (n = 1, 2) behave as *P,N*-chelating ligands in their copper(I) complexes $[CuCl{P(C_6H_4CH_2NEt_2-2)_nPh_{3-n}}]$. Both copper derivatives have dimeric solid state structures with bridging chlorine atoms. The oxidation with elemental S or Se resulted in the P(V) species $EP(C_6H_4CH_2NEt_2-2)_nPh_{3-n}$ (E = S, Se).

Highlights

- Triorganophosphanes with aryl groups with pendant arms, of type $P(C_6H_4CH_2NEt_2-2)_nPh_{3-n}$ (n = 1, • 2)
- Dimeric copper(I) complexes of type $[CuCl{P(C_6H_4CH_2NEt_2-2)_nPh_{3-n}}]_2$
- *P*,*N*-chelating behaviour towards Cu(I) in both complexes •

- Planar chirality determined by the intramolecular $N \rightarrow Cu$ coordination ٠
- .es Oxidation with S or Se resulted in triarylphosphane chalcogenides •