Synthesis, spectroscopic characterization, and structural studies of new Cu(I) and Cu(II) complexes containing organophosphorus ligands, and crystal structures of (Ph$_3$P)$_2$Cu[S$_2$PMe$_2$], (Ph$_3$P)$_2$Cu[(OPPh$_2$)$_2$N], Cu[(OPPh$_2$)$_2$N]$_2$, and Cu[(OPPh$_2$)(SPPh$_2$)N]$_2$

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Abstract: The Cu(I) complexes, (Ph$_3$P)$_2$CuL (L = [S$_2$PMe$_2$]$^-$, [OSPR$_2$]$^-$ (R = Me, Ph), [(XPR$_2$)(YPR$'_2$)N]$^-$ (X, Y, R, R$'$ = O, O, Ph, Ph; O, S, Ph, Ph; O, S, OEt, Ph; S, S, Me, Me)) and Cu(II) complexes, CuL$_2$ (L = [(XPR$_2$)(YPR$'_2$)N]$^-$ (X, Y, R, R$'$ = O, O, Ph, Ph; O, S, Ph, Ph)), have been prepared. The Cu(I) derivatives were characterized by multinuclear NMR spectroscopy and in two cases by X-ray crystallography. (Ph$_3$P)$_2$Cu[S$_2$PMe$_2$] (**1**) crystallizes in the orthorhombic space group $P2_12_12_1$ (No. 19) with cell parameters a = 9.782(2), b = 17.808(4), c = 20.216(4) Å, V = 3521(6) Å^3 and Z = 4, and (Ph$_3$P)$_2$Cu[(OPPh$_2$)$_2$N] (**4**) in the triclinic space group $P\bar{1}$ (No. 2) with cell parameters a = 9.8079(2), b = 12.9141(3), c = 22.5666(5) Å, α = 75.714(2), β = 79.465(2), γ = 68.2770(8)°, V = 2559.9(1) Å^3 and Z = 2. In both cases the phosphorus ligands are bidentate, thus resulting in monomeric molecules that contain tetrahedral CuP$_2$S$_2$ and CuP$_2$O$_2$ cores. The molecular structures of two of the Cu(II) derivatives were also determined. Cu[(OPPh$_2$)$_2$N]$_2$ (**8**) and Cu[(OPPh$_2$)(SPPh$_2$)N]$_2$ (**9**) crystallize in the triclinic space group $P\bar{1}$ (No. 2) with cell parameters a = 8.887(2), b = 10.739(2), c = 12.477(3) Å, α = 77.61(3), β = 76.15(5), γ = 79.46(3)°, V = 1118.3(4) Å^3 and Z = 1 for **8**, and a = 9.626(2), b = 14.151(3), c = 24.752(5) Å, α = 88.23(3), β = 79.93(3), γ = 89.77(3)°, V = 3181(1) Å^3 and Z = 3 for **9**. The molecule of Cu[(OPPh$_2$)$_2$N]$_2$ (**8**) has a planar CuO$_4$ core, while in Cu[(OPPh$_2$)(SPPh$_2$)N]$_2$ (**9**) both planar and tetrahedral copper cores are observed in a ratio of 1:2.

Key words: structure, copper, thiophosphinates, oxo- and thio-imidodiphosphinates.

Résumé : On a préparé les complexes suivants du Cu(I), (Ph$_3$P)$_2$CuL (L = [S$_2$PMe$_2$]$^-$, [OSPR$_2$]$^-$ (R = Me, Ph), [(XPR$_2$)(YPR$'_2$)N]$^-$ (X, Y, R, R$'$ = O, O, Ph, Ph; O, S, Ph, Ph; O, S, OEt, Ph; S, S, Me, Me)) et du Cu(II), CuL$_2$ (L = [(XPR$_2$)(YPR$'_2$)N]$^-$ (X, Y, R, R$'$ = O, O, Ph, Ph; O, S, Ph, Ph)). On a caractérisé les dérivés du Cu(I) par spectroscopie RMN multinucléaire et, dans deux cas, par diffraction des rayons X. Les cristaux de (Ph$_3$P)$_2$Cu[S$_2$PMe$_2$] (**1**) sont orthorhombiques, groupe d'espace $P2_12_12_1$ (No. 19) avec a = 9,782(2), b = 17,808(4) et c = 20,216(4) Å, V = 3521(6) Å^3 et Z = 4; ceux du (Ph$_3$P)$_3$Cu[OPPh$_2$)$_2$N] (**4**) sont tricliniques, groupe d'espace $P\bar{1}$ (No. 2) avec a = 9,08079(2), b = 12,9141(3) et c = 22,5666(5) Å, α = 75,714(2), β = 79,465(2) et γ = 68,2770(8)°, V = 2559,9(1) Å^3 et Z = 2. Dans les deux cas, les ligands phosphorés sont bidentates ce qui conduit à des molécules monomères qui comportent des unités centrales CP$_2$S$_2$ et CP$_2$O$_2$ tétraédriques. On a aussi déterminé les structures moléculaires de deux des dérivés du Cu(II). Les cristaux de Cu[(OPPh$_2$)$_2$N]$_2$ (**8**) et de Cu[(OPPh$_2$)(SPPh$_2$)N]$_2$ (**9**) sont tous les deux tricliniques, groupe d'espace $P\bar{1}$ (No. 2) avec a = 8,887(2), b = 10,739(3) et c = 12,477(3) Å, α = 77,61(3), β = 76,15(5) et γ = 79,46(3)°, V = 1118,3(1) Å^3 et Z = 1, pour le composé **8**, et avec a = 9,626(2), b = 14,151(3) et c = 24,752(5) Å, α = 88,23(3), β = 79,93(3) et γ = 89,77(3)°, V = 3181(1) Å^3 et Z = 3, pour le composé **9**. La molécule de Cu[(OPPh$_2$)$_2$N]$_2$ (**8**) comporte une unité centrale de CuO$_4$ qui est plane alors que dans la molécule de Cu[(OPPh$_2$)(SPPh$_2$)N]$_2$ (**9**), on observe la

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Dedicated to Professor Brian James on the occasion of his 65th birthday.

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présence d'unités de cuivre planes et tétraédriques dans un rapport de 1:2.

Mots clés : structure, cuivre, thiophosphinates, oxo- et thio-imidodiphosphinates.

[Traduit par la Rédaction]

Introduction

Relatively few copper complexes containing both neutral donors and *O*,*O′*-diorganodithiophosphato ligands have been structurally characterized (1, 2). For Cu(I) derivatives, the presence of the P-neutral ligand affords tetrahedral mononuclear $(Ph_3P)_2Cu[S_2P(OR)_2]$ (R = Et (**3**), $(OR)_2$ = $(OCH_2)_2CMe_2$ (**4**)) or dinuclear $[(Ph_3P)Cu\{S_2P(OEt)_2\}]_2$ (**5**) complexes. Polynuclear phosphine adducts of Cu(I) thiolates have also been reported (6, 7). Recent studies on neutral Cu(I) thiocarboxylates with triphenylphosphine demonstrate that complexes of different stoichiometry and structure can be obtained with small changes in the thio ligand. Thus, for example, using 1:1:1 stoichiometric ratios of CuCl:Na[S(O)CR]:PPh_3, the thioacetate anion gave the tetramer $[Cu\{S(O)CMe\}(PPh_3)]_4$, while for R = Ph a 4:4:3 complex $[Cu_4\{S(O)CPh\}_4(PPh_3)_3]$ was isolated. Attempts to prepare a 4:4:3 derivative for R = Me failed; only the tetrameric complex being isolated. Thioacetate and thiobenzoate ligands both gave products of 1:1:2 stoichiometry, but for R = Me the complex was a dimer $[Cu\{S(O)CMe\}(PPh_3)_2]_2$, whereas for R = Ph it was a monomer (8). In the absence of a neutral ligand, a polynuclear Cu(I) cluster complex, $[Cu\{S_2P(O\text{-}i\text{-}Pr)_2\}]_4$, has been isolated (9). On the other hand, the use of $[(XPR_2)_2N]^-$ (X = S, Se) ligands, which are characterized by flexible XPNPX skeletons and a larger X⋯X bite, resulted in the displacement of a coordinated triphenylphosphine, leading to trigonal, mononuclear Cu(I) complexes, $(Ph_3P)Cu[(XPR_2)_2N]$ (R = Ph, X = S (10), Se (11)). Reaction of Cu(II) salts with dithio ligands of the type $(SPR_2)(SPR'_2)NH$ resulted in polynuclear Cu(I) complexes such as trinuclear $[Cu\{(XPR_2)(YPR'_2)N\}]_3$ (R, R′ = *i*-Pr, *i*-Pr; *i*-Pr, Ph; *i*-Pr, OPh; OEt, OPh (12)) or tetranuclear $[Cu^I_4\{(SPPh_2)_2N\}_3][Cu^ICl_2]$ (R, R′ = Ph, Ph (13, 14)). By contrast, with *O*,*S*- and *O*,*O*-phosphorus ligands of the type $[OSPR_2]^-$ and $[(OPR_2)(YPR'_2)N]^-$, no Cu(I) complexes have been reported to date, and only one Cu(II) complex $Cu[\{OP(OPh)_2\}_2N]_2$ (15) has been reported. Therefore, we decided to examine the differences that result in copper complexes using related ligands when the organic groups and (or) the chalcogens attached to the phosphorus atoms are changed.

We report on the synthesis and spectroscopic characterization of new $(Ph_3P)_2CuL$ and CuL_2 complexes of anionic phosphorus ligands, as well as the crystal and molecular structures of two Cu(I) derivatives, $(Ph_3P)_2Cu[S_2PMe_2]$ and $(Ph_3P)_2Cu[(OPPh_2)_2N]$, along with two Cu(II) derivatives, $Cu[(OPPh_2)_2N]_2$ and $Cu[(OPPh_2)(SPPh_2)N]_2$.

Experimental

Materials

Starting materials were prepared according to published methods: $NaS_2PMe_2\cdot 2H_2O$ (16), $NaOSPMe_2\cdot 1.5H_2O$ (17), NH_4OSPPh_2 (18, 19), $Na[(OPPh_2)_2N]$ (20), $K[(OPPh_2)(SPPh_2)N]$ (21), $K[\{OP(OEt)_2\}(SPPh_2)N]$ (22), and $K[(SPMe_2)_2N]$ (23). All solvents were dried and distilled prior to use.

Physical measurements

The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian Gemini 300S instrument operating at 299.5, 75.4, and 121.4 MHz, respectively, using solutions in dried $CDCl_3$. The ^1H and ^{13}C and ^{31}P chemical shifts are reported in ppm relative to TMS and external H_3PO_4 85%, respectively. Electron spin resonance (ESR) measurements were performed at room temperature on a Radiopan SE/X-2543 9GHz ESR spectrometer, using a 100 kHz field modulation.

Preparation of $(Ph_3P)_2CuL$ compounds (1–7)

Typically, stoichiometric amounts of $(PPh_3)_2CuNO_3$ (0.54 g, 0.83 mmol) and $NaS_2PMe_2\cdot 2H_2O$ (0.15 g, 0.81 mmol) were placed in a round-bottom flask and solvent (CH_2Cl_2, ca. 20 mL) was added. The reaction mixture was stirred for 2 h at room temperature, followed by filtration to remove $NaNO_3$. Concentration under vacuum gave $(Ph_3P)_2Cu[S_2PMe_2]$ (**1**), as a colorless solid. Recrystallization from a CH_2Cl_2–*n*-hexane mixture gave crystals suitable for X-ray diffraction studies, yield 70% (0.35 g), mp 185–187°C. ^1H NMR δ: 1.77 (d, $^2J_{P,H}$ = 12.8 Hz, 6H, P-CH_3), 7.24 (t, $^3J_{H,H}$ = 7.2 Hz, 12H, $P(C_6H_5)_3$-*meta*), 7.34 (t, $^3J_{H,H}$ = 7.1 Hz, 6H, $P(C_6H_5)_3$-*para*), 7.45 (dd, $^3J_{H,H}$ = 8.5, $^3J_{P,H}$ = 9.2 Hz, 12H, $P(C_6H_5)_3$-*ortho*). ^{13}C NMR δ: 31.84 (d, $^1J_{P,C}$ = 48.2 Hz, P-CH_3), 128.40 (d, $^2J_{P,C}$ = 8.7 Hz, $P(C_6H_5)_3$-*ortho*), 129.44 ($P(C_6H_5)_3$-*para*), 134.11 (d, $^3J_{P,C}$ = 14.6 Hz $P(C_6H_5)_3$-*meta*). ^{31}P NMR δ: –4.1 (2P, PPh_3), 60.7 (1P, PMe_2).

In the same fashion the following compounds were prepared:

$(Ph_3P)_2Cu[OSPMe_2]$ (**2**)*:* from $(PPh_3)_2CuNO_3$ (0.46 g, 0.70 mmol) and $NaOSPMe_2\cdot 1.5H_2O$ (0.11 g, 0.69 mmol) Recrystallization gave colorless crystals, yield 88% (0.44 g), mp 143–145°C. ^1H NMR δ: 1.54 (d, $^2J_{P,H}$ = 12.7 Hz, 6H, P-CH_3); 7.32 (m, 30H, $P(C_6H_5)_3$). ^{31}P NMR δ: –2.7 (2P, PPh_3), 64.1 (1P, PMe_2).

$(Ph_3P)_2Cu[OSPPh_2]$ (**3**)*:* from $(PPh_3)_2CuNO_3$ (0.47 g, 0.72 mmol) and NH_4OSPPh_2 (0.18 g, 0.71 mmol). Recrystallization gave colorless crystals, yield 98% (0.49 g), mp 148–151°C. ^1H NMR δ: 7.22 (m, 36H, $P(C_6H_5)_3$, P-C_6H_5-*meta* + *para*), 7.75 (dd, $^3J_{H,H}$ = 6.9, $^3J_{P,H}$ = 12.6 Hz, 4H, P-C_6H_5-*ortho*). ^{13}C NMR δ: 127.60 (d, $^3J_{P,C}$ = 12.8 Hz, P-C_6H_5-meta), 128.45 (d, $^2J_{P,C}$ = 8.5 Hz, $P(C_6H_5)_3$-*ortho*), 129.60 ($P(C_6H_5)_3$-*para*, P-C_6H_5-*para*), 130.80 (d, $^2J_{P,C}$ = 9.9 Hz, P-C_6H_5-*ortho*), 134.00 (d, $^3J_{P,C}$ = 13.8 Hz, $P(C_6H_5)_3$-*meta*). ^{31}P NMR δ: –3.8 (2P, PPh_3), 55.3 (1P, PPh_2).

$(Ph_3P)_2Cu[(OPPh_2)_2N]$ (**4**)*:* from $(PPh_3)_2CuNO_3$ (0.38 g, 0.58 mmol) and $Na[(OPPh_2)_2N]$ (0.26 g, 0.59 mmol). Recrystallization gave colorless crystals, yield 84% (0.42 g), mp 168–170°C. ^1H NMR δ: 7.15 (m, 42H,

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$P(C_6\mathit{H}_5)_3$, $P\text{-}C_6\mathit{H}_5$-meta + *para*), 7.68 (dd, $^3J_{H,H}$ = 7.4, $^3J_{P,H}$ = 11.1 Hz, 8H, $P\text{-}C_6\mathit{H}_5$-*ortho*). ^{13}C NMR δ: 127.43 (d, $^3J_{P,C}$ = 12.8 Hz, $P\text{-}\mathit{C}_6H_5$-meta), 128.17 ($P(\mathit{C}_6H_5)_3$-*ortho*), 129.10 ($P(\mathit{C}_6H_5)_3$-*para*), 129.28 ($P\text{-}\mathit{C}_6H_5$-*para*), 131.36 (d, $^2J_{P,C}$ = 9.2 Hz, $P\text{-}\mathit{C}_6H_5$-*ortho*), 134.13 (d, $^3J_{P,C}$ = 7.8 Hz, $P(\mathit{C}_6H_5)_3$-meta). ^{31}P NMR δ: –6.5 (2P, $\mathit{P}Ph_3$), 18.9 (2P, $\mathit{P}Ph_2$).

*$(Ph_3P)_2Cu[(OPPh_2)(SPPh_2)N]$ (**5**):* from $(PPh_3)_2CuNO_3$ (0.34 g, 0.52 mmol) and $K[(OPPh_2)(SPPh_2)N]$ (0.24 g, 0.50 mmol). Recrystallization gave colorless crystals, yield 94% (0.47 g), mp 170°C. ^{1}H NMR δ: 7.22 (m, 42H, $P(C_6\mathit{H}_5)_3$, $P\text{-}C_6\mathit{H}_5$-*meta + para*), 7.59 (ddd, $^3J_{H,H}$ = 7.0, $^4J_{H,H}$ = 1.1, $^3J_{P,H}$ = 12.1 Hz, 4H, $P(O)\text{-}C_6\mathit{H}_5$-*ortho*), 7.85 (ddd, $^3J_{H,H}$ = 7.5, $^4J_{H,H}$ = 1.4, $^3J_{P,H}$ = 13.5 Hz, 4H, $P(S)\text{-}C_6\mathit{H}_5$-*ortho*). ^{13}C NMR δ: 127.46 (d, $^3J_{P,C}$ = 11.4 Hz, $P\text{-}\mathit{C}_6H_5$-*meta*), 127.61 (d, $^3J_{P,C}$ = 10.9 Hz, $P\text{-}\mathit{C}_6H_5$-*meta*), 128.21 (d, $^2J_{P,C}$ = 8.0 Hz, $P(\mathit{C}_6H_5)_3$-*ortho*), 129.04 ($P(\mathit{C}_6H_5)_3$-*para*), 129.43 ($P\text{-}\mathit{C}_6H_5$-*para*), 129.54 ($P\text{-}\mathit{C}_6H_5$-*para*), 130.93 (d, $^2J_{P,C}$ = 10.3 Hz, $P(O)\text{-}\mathit{C}_6H_5$-*ortho*), 131.26 (d, $^2J_{P,C}$ = 9.1 Hz, $P(S)\text{-}\mathit{C}_6H_5$-*ortho*), 134.12 (d, $^3J_{P,C}$ = 15.2 Hz, $P(\mathit{C}_6H_5)_3$-*meta*). ^{31}P NMR δ: –5.7 (2P, $\mathit{P}Ph_3$), 18.1 (1P, $\mathit{P}(O)Ph_2$), 30.0 (1P, $\mathit{P}(S)Ph_2$).

*$(Ph_3P)_2Cu\text{-}[\{OP(OEt)_2\}(SPPh_2)N]$ (**6**):* from $(PPh_3)_2CuNO_3$ (0.46 g, 0.71 mmol) and $K[\{OP(OEt)_2\}(SPPh_2)N]$ (0.29 g, 0.71 mmol). Recrystallization gave colorless crystals, yield 92% (0.46 g), mp 160°C. ^{1}H NMR δ: 1.01 (t, $^3J_{H,H}$ = 6.9 Hz, 6H, $P\text{-}O\text{-}CH_2C\mathit{H}_3$), 3.67 (dq, $^3J_{H,H}$ = 6.9, $^3J_{P,H}$ = 7.1 Hz, 4H, $P\text{-}O\text{-}C\mathit{H}_2CH_3$), 7.24 (m, 36H, $P(C_6\mathit{H}_5)_3$, $P\text{-}C_6\mathit{H}_5$-*meta + para*), 7.90 (dd, $^3J_{H,H}$ = 7.4, $^3J_{P,H}$ = 13.4 Hz, 4H, $P\text{-}C_6\mathit{H}_5$-*ortho*). ^{31}P NMR δ: –5.2 (2P, $\mathit{P}Ph_3$), 4.4 (1P, $\mathit{P}(OEt)_2$), 34.2 (1P, $\mathit{P}Ph_2$).

*$(Ph_3P)_2Cu[(SPMe_2)_2N]$ (**7**):* from $(PPh_3)_2CuNO_3$ (0.41 g, 0.63 mmol) and $K[(SPMe_2)_2N]$ (0.15 g, 0.62 mmol). Recrystallization gave colorless crystals, yield 80% (0.40 g), mp 149–152°C. ^{1}H NMR δ: 1.81 (d, $^2J_{P,H}$ = 12.0 Hz, 12H, $P\text{-}C\mathit{H}_3$), 7.35 (m, 30H, $P(C_6\mathit{H}_5)_3$). ^{31}P NMR δ: –2.9 (2P, $\mathit{P}Ph_3$), 40.0 (2P, $\mathit{P}Me_2$).

Preparation of $Cu[(OPPh_2)_2N]_2$ (8)

Stoichiometric amounts of $CuCl_2\cdot 2H_2O$ (0.095 g, 0.56 mmol) and $K[(OPPh_2)_2N]$ (0.51 g, 1.12 mmol) were placed in a round-bottom flask and solvent (MeOH, ca. 20 mL) was added. The reaction mixture was stirred for 12 h at room temperature and the solvent was removed to dryness under vacuum. The blue-greenish residual solid was extracted twice with CH_2Cl_2 (ca. 20 mL) to remove KCl and unreacted starting materials. Concentration of the blue solution under vacuum then gave $Cu[(OPPh_2)_2N]_2$ (**8**) as a blue solid. Recrystallization from a CH_2Cl_2–*n*-hexane mixture gave crystals suitable for X-ray diffraction studies, yield 72% (0.36 g), mp 273 to 274°C. ESR (X band): $g_\perp$ = 2.017 ± 0.004, $g_\parallel$ = 2.086 ± 0.004, A = 140 ± 10 Gs, B = 30 ± 10 Gs.

Preparation of $Cu[(OPPh_2)(SPPh_2)N]_2$ (9)

Stoichiometric amounts of $CuCl_2\cdot 2H_2O$ (0.092 g, 0.54 mmol) and $K[(OPPh_2)(SPPh_2)N]$ (0.5 g, 1.06 mmol) were placed in a round-bottom flask and CH_2Cl_2 (20 mL) was added. The reaction mixture, which immediately turned brown, was stirred for 6 h at room temperature before KCl was filtered off to leave a brown solution. Concentration under vacuum gave $Cu[(OPPh_2)(SPPh_2)N]_2$ (**9**) as a dark brown solid. Recrystallization from a CH_2Cl_2–*n*-hexane mixture gave crystals suitable for X-ray diffraction studies, yield 66% (0.33 g), mp 90–91°C. ^{31}P NMR δ: 21.5 (1P), 23.5 (1P, $\mathit{P}(O)Ph_2$, $\mathit{P}(S)Ph_2$).

X-ray crystallographic analysis

Colourless, block crystals of $(Ph_3P)_2Cu[S_2PMe_2]$ (**1**) and $(Ph_3P)_2Cu[(OPPh_2)_2N]$ (**4**), a blue block crystal of $Cu[(OPPh_2)_2N]_2$ (**8**), and a dark brown block crystal of $Cu[(OPPh_2)(SPPh_2)N]_2$ (**9**) were mounted on glass fibres. Data for **1**, **4**, and **8** were collected on an Enraf Nonius KappaCCD area detector (ϕ scans and ω scans to fill Ewald sphere) at the University of Southampton EPSRC National Crystallography Service. For **9**, data collection and processing was carried out by G. Yapp, then at the University of Windsor, using a Siemens SMART/CCD system. Cell refinement (24) gave cell constants corresponding to orthorhombic (for **1**) and triclinic (for **4**, **8**, and **9**) cells whose dimensions are given in Table 1, along with other experimental parameters. An absorption correction was applied (25), which resulted in transmission factors ranging from 0.870 to 0.825 for **1**, 0.943 to 0.842 for **4**, 0.937 to 0.773 for **8**, and 0.927 to 0.861 for **9**.

The structures were solved by direct methods (26). All of the nonhydrogen atoms were treated anisotropically. Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. The data for **1** and **4** were of much better quality than that for **8**, and the positions of the higher residual peaks in the latter made no chemical sense. The final cycle of full-matrix least-squares refinement (27) was based on 8027 (**1**), 10601 (**4**), 3925 (**8**), and 9164 (**9**) observed reflections (4949 (**1**), 6343 (**4**), 3289 (**8**), and 7548 (**9**) for $F^2 > 4\sigma(F^2)$) and 399 (**1**), 613 (**4**), 269 (**8**), and 799 (**9**) variable parameters and converged (largest parameter shift was 0.001 times its esd). The absolute configuration parameter for **1** was –0.017(12). Selected distances and bond angles are given in Tables 2–5 and the molecules are displayed in the ORTEP diagrams in Figs. 1–4.[2]

Results and discussion

The preparation of the Cu(I) complexes ($(Ph_3P)_2CuL$) is achieved by the reaction of stoichiometric amounts of

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[2] Supplementary material including the final atomic coordinates and equivalent isotropic thermal parameters for the nonhydrogen atoms, anisotropic thermal parameters for the nonhydrogen atoms, final fractional coordinates and thermal parameters for hydrogen atoms, and all bond distances and angles, have been deposited and may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council of Canada, Ottawa, ON, Canada, K1A 0S2 (http://www.nrc.ca/cisti/irm/unpub_e.shtml). Tables of atomic coordinates for the structures reported in this paper have also been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (fax: 44-1223-336033 or e-mail:deposit@ccdc.cam.ac.uk). Structure factor amplitudes are no longer being deposited and may be obtained directly from the author.

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Table 1. Crystal data and structure refinement for $(Ph_3P)_2Cu(S_2PMe_2)$ (**1**), $(Ph_3P)_2Cu[(OPPh_2)_2N]$ (**4**), $Cu[(OPPh_2)_2N]_2$ (**8**), and $Cu[(OPPh_2)(SPPh_2)N]_2$ (**9**).

	1	**4**	**8**	**9**
Empirical formula	$C_{38}H_{36}P_3S_2Cu$	$C_{60}H_{50}NO_2P_4Cu$	$C_{48}H_{40}N_2O_4P_4Cu$	$C_{48}H_{40}N_2O_2P_4S_2Cu$
FW	713.24	1004.43	896.24	928.36
T (°C)	298(2)	298(2)	298(2)	298(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic	Triclinic	Triclinic
Space group	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	9.782(2)	9.8079(2)	8.887(2)	9.626(2)
b (Å)	17.808(4)	12.9141(3)	10.739(2)	14.151(3)
c (Å)	20.216(4)	22.5666(5)	12.477(3)	24.752(5)
α (°)		75.714(2)	77.61(3)	88.23(3)
β (°)		79.465(2)	76.15(3)	79.93(3)
γ (°)		68.2770(8)	79.46(3)	89.77(3)
Volume (Å^{-3})	3521.6(1)	2559.9(1)	1118.3(4)	3318(1)
Z	4	2	1	3
$\rho_{calcd.}$ (g cm^{-3})	1.345	1.303	1.331	1.394
μ (mm^{-1})	0.901	0.596	0.677	0.774
$F(000)$	1480	1044	463	1437
Crystal size (mm)	0.25 × 0.15 × 0.10	0.30 × 0.15 × 0.10	0.10 × 0.10 × 0.10	0.20 × 0.10 × 0.10
θ range for data collection (°)	3.05–27.89	3.00–27.47	3.21–25.03	1.64–23.24
Limiting indices	$-9 \le h \le 12$, $-18 \le k \le 23$, $-25 \le l \le 25$	$-12 \le h \le 12$, $-16 \le k \le 16$, $-22 \le l \le 28$	$-10 \le h \le 10$, $-12 \le k \le 12$, $-14 \le l \le 14$	$-10 \le h \le 10$, $-15 \le k \le 15$, $0 \le l \le 27$
Reflections collected	21154	16010	9925	9164
Independent reflections	8028 (R_{int} = 0.0623)	10601 (R_{int} = 0.0422)	3925 (R_{int} = 0.0428)	9164 (R_{int} = 0.0496)
Max. and min. transmissions	0.870 and 0.825	0.943 and 0.842	0.937 and 0.773	0.9266 and 0.8605
Refinement method	Full-matrix least-squares on F^2			
Data/restraints/ parameters	8027/0/399	10601/0/613	3925/0/269	9164/0/799
GoF on F^2	0.971	1.003	1.062	1.060
Final R indices [$F^2 > 4\sigma(F^2)$]	R_1 = 0.0455, wR_2 = 0.0788	R_1 = 0.0499, wR_2 = 0.0967	R_1 = 0.0702, wR_2 = 0.2010	R_1 = 0.0423, wR_2 = 0.1129
R indices (all data)	R_1 = 0.1059, wR_2 = 0.0937	R_1 = 0.1048, wR_2 = 0.1134	R_1 = 0.0806, wR_2 = 0.2129	R_1 = 0.0538, wR_2 = 0.1193
Largest diff. peak and hole (e Å^3)	0.220 and –0.279	0.412 and –0.419	2.305 and –0.477	0.708 and –0.312

Table 2. Selected bond lengths (Å) and angles (°) for $(PPh_3)_2CuS_2PMe_2$ (**1**).

Bond lengths (Å)			
Cu(1)—P(1)	2.2718(10)	Cu(1)—P(2)	2.2796(10)
Cu(1)—S(1)	2.4343(12)	Cu(1)—S(2)	2.4797(12)
S(1)—P(3)	1.997(2)	S(2)—P(3)	2.000(2)
Bond angles (°)			
P(1)-Cu(1)-P(2)	117.09(4)	P(1)-Cu(1)-S(1)	117.60(4)
P(2)-Cu(1)-S(1)	107.08(4)	P(1)-Cu(1)-S(2)	114.20(4)
P(2)-Cu(1)-S(2)	111.43(4)	S(1)-Cu(1)-S(2)	85.07(4)
P(3)-S(1)-Cu(1)	80.75(5)	P(3)-S(2)-Cu(1)	79.56(5)
C(1)-P(1)-Cu(1)	113.83(11)	C(19)-P(2)-Cu(1)	117.34(13)
C(7)-P(1)-Cu(1)	112.16(11)	C(25)-P(2)-Cu(1)	113.45(11)
C(13)-P(1)-Cu(1)	119.02(13)	C(31)-P(2)-C(19)	103.1(2)
S(1)-P(3)-S(2)	112.47(7)	C(37)-P(3)-C(38)	103.7(3)

Table 3. Selected bond lengths (Å) and angles (°) for $(Ph_3P)_2Cu[(OPPh_2)_2N]$ (**4**) and $Cu[(OPPh_2)_2N]_2$ (**8**).

4		**8**	
Bond lengths (Å)			
Cu(1)—O(1)	2.122(2)	Cu(1)—O(1)	1.917(3)
Cu(1)—O(2)	2.165(2)	Cu(1)—O(2)	1.918(3)
Cu(1)—P(1)	2.2554(7)	P(1)—O(1)	1.515(3)
Cu(1)—P(2)	2.2449(7)	P(2)—O(2)	1.508(3)
P(3)—O(1)	1.505(2)	P(1)—N(1)	1.579(3)
P(4)—O(2)	1.503(2)	P(2)—N(1)	1.575(4)
P(3)—N(1)	1.586(2)		
P(4)—N(1)	1.586(2)		
Bond angles (°)			
O(1)-Cu(1)-P(1)	103.55(5)	O(1)-Cu(1)-O(2)	94.67(13)
O(1)-Cu(1)-P(2)	109.51(5)	O(1)-Cu(1)-O(1)′	180.0
O(2)-Cu(1)-P(1)	106.91(5)	O(2)-Cu(1)-O(1)′	85.33(13)
O(2)-Cu(1)-P(2)	107.50(5)	P(1)-O(1)-Cu(1)	131.60(17)
P(1)-Cu(1)-P(2)	126.10(3)	O(1)-P(1)-N(1)	117.35(18)
O(1)-Cu(1)-O(2)	100.32(7)	P(1)-N(1)-P(2)	125.6(2)
P(3)-O(1)-Cu(1)	119.13(11)	O(2)-P(2)-N(1)	117.09(19)
O(1)-P(3)-N(1)	118.43(11)	P(2)-O(2)-Cu(1)	132.6(2)
P(3)-N(1)-P(4)	129.5(2)		
O(2)-P(4)-N(1)	118.56(12)		
P(4)-O(2)-Cu(1)	119.14(10)		

Note: Symmetry equivalent position (–*x* + 2, –*y* + 1, –*z* + 2) given by a prime.

$(Ph_3P)_2CuNO_3$ with the ammonium or alkali salt of the appropriate organophosphorus acid in CH_2Cl_2 as solvent, in accord with rxn. [1]

$$[1] \qquad (Ph_3P)_2CuNO_3 + ML \rightarrow (Ph_3P)_2CuL + MNO_3$$

where L = (S_2PMe_2) (**1**), $(OSPR_2)$ (R = Me (**2**), Ph (**3**)), $[(XPR_2)(YPR'_2)N]$ (X, Y, R, R′ = O, O, Ph, Ph (**4**), O, S, Ph, Ph (**5**), O, S, OEt, Ph (**6**), S, S, Me, Me (**7**)).

All of the compounds are isolated in good yields as crystalline colorless solids and X-ray quality crystals are obtained for **1** and **4**. In previous reports, the use of $[(XPR_2)_2N]^-$ (X = S, Se) ligands was found to result in displacement of a coordinated triphenylphosphine and isolation of trigonal $(Ph_3P)Cu[(XPR_2)_2N]$ (R = Ph, X = S (10), Se (11)). By contrast, for all reactions (eq. [1]) investigated in this work, the isolated products are found to preserve two neutral phosphine ligands coordinated to the metal atom, even though similar reaction conditions were used. This suggests that changes in the organic groups and (or) chalcogens on phosphorus can influence the stoichiometry of the isolated Cu(I) adducts.

The $(Ph_3P)_2CuL$ derivatives are readily dissolved in chloroform, which is therefore used as the preferred solvent for recording NMR spectra. In all cases, both ^1H and ^{31}P NMR data are consistent with a 2:1 molar ratio between the neutral and anionic ligands. For $(Ph_3P)_2Cu[OSPR_2]$ (R = Me, Ph) derivatives, the magnitude of the ^{31}P chemical shifts is indicative of an *O,S*-bidentate coordination of the monothio ligand moieties δ: R = Me, 64.1 (*P*Me$_2$) (cf. $Me_2P(S)OMe$ 94.3 (28), $Me_2P(O)SMe$ 45.9 (29)), R = Ph 55.3 (*P*Ph$_2$) (cf. $Ph_2P(S)OMe$ 83.5 (29), $Ph_2P(O)SMe$ 42.8 (29)). The ^{31}P chemical shifts assigned for the phosphorus atoms of the anionic ligand in the spectra of the Cu(I) imidodiphosphinato complexes $(Ph_3P)_2Cu[(XPR_2)(YPR'_2)N]$, are also consistent with a chelated ligand. This behavior suggests that tetrahe-

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Table 4. Selected bond lengths (Å) and angles (°) for Cu[(OPPh$_2$)(SPPh$_2$)N]$_2$ (**9**).

9a		**9b**	
Bond lengths (Å)			
Cu(1)—O(1)	1.940(2)	Cu(2)—O(3)	1.940(2)
Cu(1)—O(2)	1.934(2)	Cu(2)—O(3)′	1.940(2)
Cu(1)—S(1)	2.2837(11)	Cu(2)—S(3)	2.3398(13)
Cu(1)—S(2)	2.2931(11)	Cu(2)—S(3)′	2.3398(13)
P(1)—O(1)	1.517(2)	P(5)—O(3)	1.517(3)
P(1)—N(1)	1.590(3)	P(5)—N(3)	1.583(3)
P(2)—N(1)	1.590(3)	P(6)—N(3)	1.595(3)
P(2)—S(1)	2.0311(14)	P(6)—S(3)	2.0216(15)
P(3)—O(2)	1.518(2)		
P(3)—N(2)	1.577(3)		
P(4)—N(2)	1.578(3)		
P(4)—S(2)	2.0344(14)		
Bond angles (°)			
O(1)-Cu(1)-S(1)	100.12(8)	O(3)-Cu(2)-S(3)	97.47(8)
O(1)-Cu(1)-S(2)	149.35(8)	O(3)-Cu(2)-S(3)′	82.53(8)
O(1)-Cu(1)-O(2)	88.91(11)	O(3)-Cu(2)-O(3)′	180
O(2)-Cu(1)-S(1)	140.59(8)	O(3)′-Cu(2)-S(3)	82.53(8)
O(2)-Cu(1)-S(2)	100.74(8)	O(3)′Cu(2)-S(3)′	97.47(8)
S(1)-Cu(1)-S(2)	90.76(5)	S(3)-Cu(2)-S(3)′	180
Cu(1)-O(1)-P(1)	130.10(15)	Cu(2)-O(3)-P(5)	125.37(16)
O(1)-P(1)-N(1)	117.42(15)	O(3)-P(5)-N(3)	117.45(15)
P(1)-N(1)-P(2)	125.53(19)	P(5)-N(3)-P(6)	120.93(19)
S(1)-P(2)-N(1)	117.69(12)	S(3)-P(6)-N(3)	115.43(12)
Cu(1)-S(1)-P(2)	106.06(6)	Cu(2)-S(3)-P(6)	104.19(5)
Cu(1)-O(2)-P(3)	132.82(15)		
O(2)-P(3)-N(2)	116.78(15)		
P(3)-N(2)-P(4)	132.57(19)		
S(2)-P(4)-N(2)	118.91(12)		
Cu(1)-S(2)-P(4)	107.00(5)		

Note: Symmetry equivalent position (*–x*, *–y*, *–z*) given by a prime.

dral structures similar to that established in the solid state for (Ph$_3$P)$_2$Cu[S$_2$PMe$_2$] (**1**) and (Ph$_3$P)$_2$Cu[(OPPh$_2$)$_2$N] (**4**) (see below), are preserved in solution. However, a recent report (8) demonstrates that the nature of the anionic ligand may result in significant structural modifications so that, in the solid state, (Ph$_3$P)$_2$Cu[S(O)CPh] is mononuclear with only a weak intramolecular Cu···O interaction (2.439(2) Å), while [(Ph$_3$P)$_2$Cu(OSCMe)]$_2$ is dinuclear with different coordination modes for the monothiocarboxylato moieties (*S*-bridging and *O*,*S*-bridging).

The Cu(II) complexes, Cu[(OPPh$_2$)(YPPh$_2$)N]$_2$ (Y = O (**8**), S (**9**)), are obtained by reacting stoichiometric amounts of CuCl$_2$·2H$_2$O with the potassium salt of the imidodiphosphinato acid in organic solvent at room temperature, in accord with rxn. [2].

$$[2]\qquad \mathrm{CuCl_2{\cdot}2H_2O + K[(OPPh_2)(YPPh_2)N] \rightarrow Cu[(OPPh_2)(YPPh_2)N]_2 + 2KCl + 2H_2O}$$

Blue crystals of the dioxo derivative **8** are also formed directly in an NMR tube during evaporation in open atmosphere of a CDCl$_3$ solution of (Ph$_3$P)$_2$Cu[(OPPh$_2$)$_2$N] (**4**) (*m*/*z* 896 (molecular ion), and identical spectroscopic properties as a pure sample of the same compound). In the EPR spectrum of **8**, the characteristic hyperfine structure for Cu(II) ions is observed. The hyperfine tensor exhibits axial symmetry with the strongest interaction for the case when the magnetic field is parallel to the deformation axis of the paramagnetic center. For the perpendicular orientation the splitting is too small and the four lines cannot be separated. The analysis of the spectrum was carried out with the axially symmetric spin Hamiltonian, the nuclear quadrupole interaction being neglected. The values of the hyperfine tensor *A* and *B* (parallel and perpendicular components to the tetragonal axis) and of the *g*-factors were calculated. The *g*-factors are consistent with a $|x^2 - y^2 >$ ground state of the paramagnetic ion, while the magnitude of the *A* value suggests a relatively large electronic density at the Cu nucleus.

The brown crystals of the monothio derivative **9** are readily soluble in organic solvents, and the ^{31}P NMR spectrum of its CDCl$_3$ solution exhibited two broad resonance signals. A more detailed examination of its spectroscopic properties, both in solution and the solid state, is being undertaken.

Crystal structure of (Ph$_3$P)$_2$Cu[S$_2$PMe$_2$] (1)

The dithiophosphinato derivative (Ph$_3$P)$_2$Cu[S$_2$PMe$_2$] (**1**), is monomeric. Its molecular structure is displayed as an ORTEP diagram (Fig. 1), and important bond distances and bond angles are given in Table 2. The dithio ligand is essentially isobidentate (Cu(1)—S(1) 2.4343(12), Cu(1)—S(2) 2.4797(12) Å), resulting in approximately tetrahedral

Fig. 1. ORTEP plot of the molecule $(Ph_3P)_2Cu(S_2PMe_2)$ (**1**). The atoms are drawn with 50% probability ellipsoids.

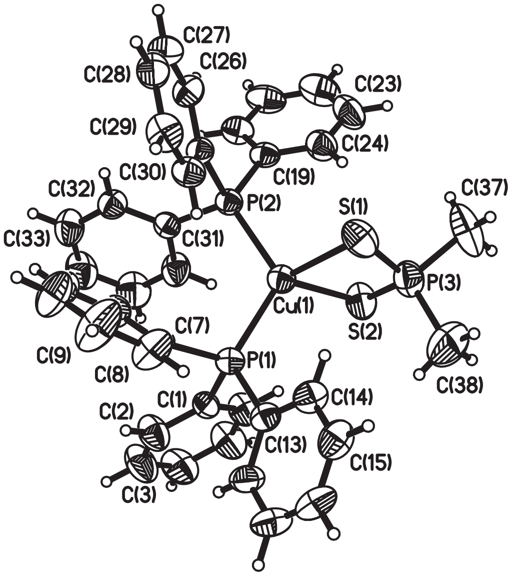
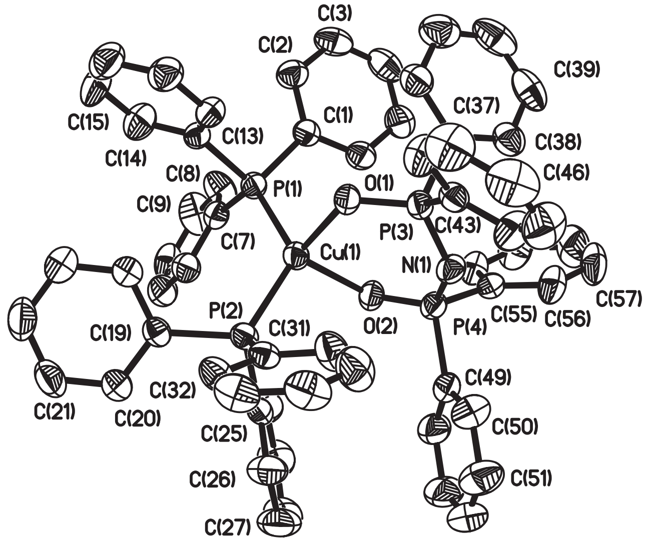


Fig. 2. ORTEP plot of the molecule $(Ph_3P)_2Cu[(OPPh_2)_2N]$ (**4**). The atoms are drawn with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.



CuP_2S_2 coordination (dihedral angle Cu(1)-P(1)-P(2) – Cu(1)-S(1)-S(2) 86.9°). The four-membered CuS_2P chelate ring is nonplanar but folded about the S(1)–S(2) axis (17.3°). The overall molecular structure is very similar to that of the related dithiophosphato derivative, $(Ph_3P)_2Cu[S_2P(OEt)_2]$ (3). The main difference is in the relative magnitudes of the phosphorus sulfur bond lengths (1.997(2), 2.000(2) Å in **1** vs. 1.967(2), 1.973(2) Å), reflecting the nature of the phosphorus ligands, which contain P–C or P–OC bonds.

Crystal structure of $(Ph_3P)_2Cu[(OPPh_2)_2N]$ (4)

The molecular structure of the Cu(I) imidodiphosphinate, $(Ph_3P)_2Cu[(OPPh_2)_2N]$ (**4**), is displayed as an ORTEP diagram (Fig. 2), and important bond distances and bond angles

Fig. 3. ORTEP plot of the molecule $Cu[(OPPh_2)_2N]_2$ (**8**). The atoms are drawn with 50% probability ellipsoids. Carbon atoms of the phenyl rings other than the ipso atoms and hydrogen atoms are omitted for clarity. Copper located at –1 symmetry center.

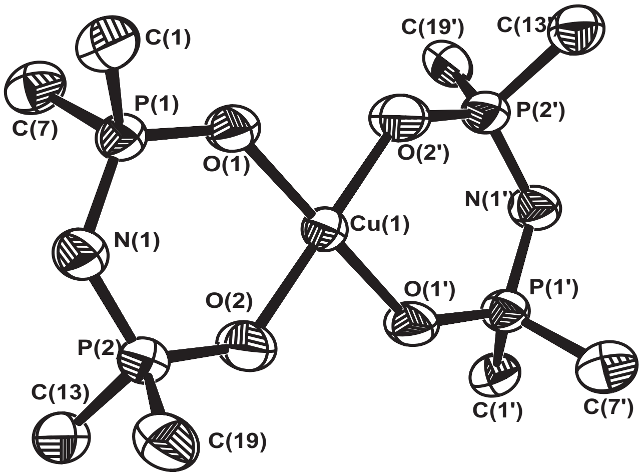
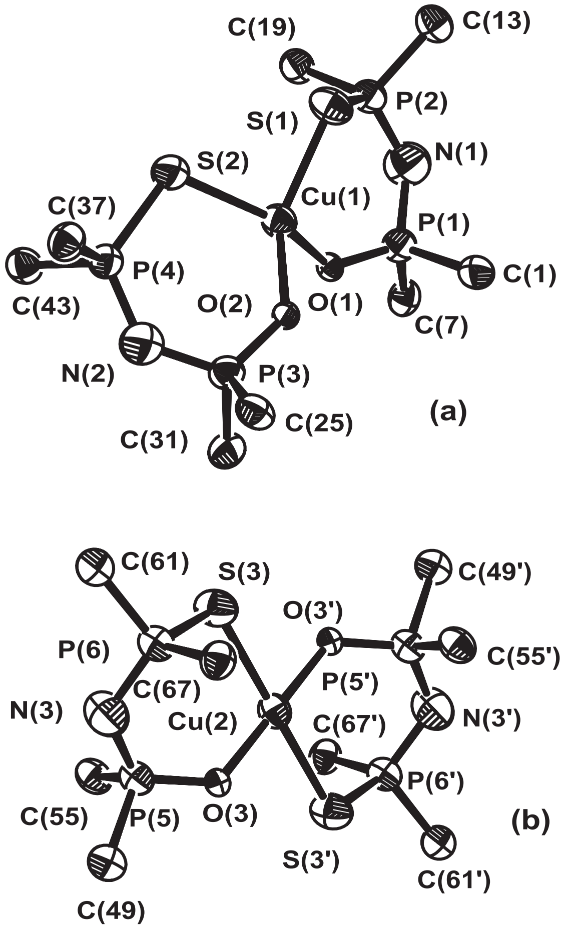


Fig. 4. ORTEP plot of the molecule $Cu[(OPPh_2)(SPPh_2)N]_2$ (**9**) showing the two copper environments: (*a*) tetrahedral, with Cu located at a general position; and (*b*) square planar, with Cu located at –1 symmetry center. The atoms are drawn with 50% probability ellipsoids. Carbon atoms of the phenyl rings other than the ipso atoms and hydrogen atoms are omitted for clarity.



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are given in Table 3. This mononuclear compound contains a chelating dioxo ligand (Cu(1)—O(1) 2.122(2), Cu(1)—O(2) 2.165(2) Å), and the resulting tetrahedral CuP_2O_2 core is characterized by a dihedral angle Cu(1)-P(1)-P(2) – Cu(1)-O(1)-O(2) 88.1° close to that observed in **1**. The six-membered CuO_2P_2N chelate ring displays a twisted boat conformation being folded about the P(3)–O(2) axis (dihedral angle O(2)-Cu(1)-O(1)-P(3) – O(2)-P(4)-N(1)-P(3) 29.0°). Similar tetrahedral, mononuclear structures have also been reported for related β-diketonato derivatives, such as $(R_3P)_2Cu[(OCCF_3)_2C]$ (R = Ph (30), Cy (31)).

Crystal structure of $Cu[(OPPh_2)_2N]_2$ (8)

The crystal of the Cu(II) complex **8** contains discrete molecules of $Cu[(OPPh_2)_2N]_2$ displayed as an ORTEP diagram in Fig. 3. Both imidodiphosphinato ligands act as chelating units, leading to a distorted square planar CuO_4 core, with *trans*-O-Cu-O angles of 180° and *endocyclic*-O-Cu-O angles (94.67(13)°) larger than *exocyclic* (85.33 (13)°). Not only is the CuO_4 core planar (dihedral angle Cu(1)-O(1)-O(2) – Cu(1)-O(1′)-O(2′) 0°), but the whole spiro-bicyclic system is almost planar (deviations from the CuO_4 plane: P(1) –0.136, P(2) 0.076, N(1) –0.002 Å). The quasi-planarity of the six-membered CuO_2P_2N ring in **8** is in strong contrast to the twisted boat conformation observed in **4**, pointing out the high flexibility of the OPNPO skeleton. The Cu—O bond distances are considerably shorter in **8** (1.917(3), 1.918(3) Å) than in **4** (2.122(2), 2.165(2) Å), while the P—O and P—N distances are similar as are the O-P-N angles. However, the P-N-P and Cu-O-P angles are larger in **8** than in **4** (ca. 4 and 13°, respectively, (Table 3)), which is presumably required to achieve the planarity of the chelate ring. The overall structure is similar to that of the related derivative, $Cu[\{OP(OPh)_2\}_2N]_2$ (15), indicating that at least in this case, replacement of phenoxy by phenyl groups on phosphorus atoms does not result in significant structural changes.

Crystal structure of $Cu[(OPPh_2)(SPPh_2)N]_2$ (9)

The most interesting feature of the solid state structure of the monothio derivative, $Cu[(OPPh2)(SPPh_2)N]_2$ (**9**), is the presence of both tetrahedral (*a*) and square-planar (*b*) copper environments in a 2:1 ratio, as displayed as an ORTEP diagram in Fig. 4. Important bond distances and bond angles are given in Table 4.

The copper atom is in a special position in the square-planar molecule (Fig. 9*b*) to give the *trans*-CuO_2S_2 core (O(3)-Cu(2)-O(3′) and S(3)-Cu(2)-S(3′) of 180°) with the *endocyclic* O(3)-Cu(2)-S(3) angle (97.47(8)°) again larger than the *exocyclic* O(3)-Cu(2)-S(3′) (82.53(8)°). A similar coordination geometry is found in one of the two independent molecules of $Cu[(OCPh)(SCNEt_2)CH]_2$ (32) in which the crystals contain one molecule with a *trans*-arrangement of the square-planar CuO_2S_2 core and a second molecule with a *cis*-arrangement of the chalcogen atoms around the metal center. In contrast to the dioxo derivative **8**, the six-membered $CuOSP_2N$ ring in **9b** exhibits a twisted boat conformation which is folded about the P(6)–O(3) axis (dihedral angle O(3)-Cu(2)-S(3)-P(6) – O(3)-P(5)-N(3)-P(6) 44.3°).

The other molecule (Fig. 9a) exhibits tetrahedral distortion, with a dihedral angle Cu(1)-O(1)-S(1) – Cu(1)-O(2)-S(2) of 46.51°. The two $CuOSP_2N$ rings, which are not related by symmetry, also exhibit distorted boat conformations, but one ring is folded about the P(1)–S(1) axis (dihedral angle S(1)-Cu(1)-O(1)-P(1) – S(1)-P(2)-N(1)-P(1) 145.2°), while the other is folded about the Cu(1)–N(2) axis (dihedral angle Cu(1)-O(2)-P(3)-N(2) – Cu(1)-S(2)-P(4)-N(2) 26.5°). The P-N-P angles within the two chelate rings in **9a** are significantly different (125.53(19) and 132.57(19)°); both being larger than in **9b** (120.93(19)°).

The Cu—O, P—O, P—S, and P—N bond distances in the two independent molecules are similar (Table 4), but the Cu—S bond distances in the square-planar core of **9b** (2.3398(13) Å) are significantly longer than in the tetrahedral core of **9a** (2.2837(11), 2.2931(1) Å) or in the *trans*-$Cu[(OCPh)(SCNEt_2)CH]_2$ complex (*trans*-isomer 2.254(1) Å, *cis*-isomer 2.236(2), 2.244(2) Å).

Concluding comments

Previous reports have indicated that ligands such as $[(XPPh_2)_2N]^-$ (X = S, Se) tend to displace coordinated triphenylphosphine resulting in the isolation of trigonal $(Ph_3P)Cu[(XPR_2)_2N]$ species. By contrast, monomeric, tetrahedral Cu(I) complexes of the type $(Ph_3P)_2CuL$ (L = $[(XPR_2)(YPR'_2)N]^-$ (X, Y, R, R′ = O, O, Ph, Ph; O, S, Ph, Ph; O, S, OEt, Ph, S, S, Me, Me)), $[S_2PMe_2]^-$, $[OSPR_2]^-$ (R = Me, Ph) are formed by treatment of $(Ph_3P)_2CuNO_3$ with salts of the appropriate organophosphorus acid, regardless of the nature of the organophosphorus ligands. The presence of a tetrahedral Cu^IX_4 core is confirmed by the X-ray structures of $(Ph_3P)_2Cu[S_2PMe_2]$ (**1**) and $(Ph_3P)_2Cu[(OPPh_2)_2N]$ (**4**), and NMR studies indicate that the tetrahedral coordination environment at the Cu(I) atom is also preserved in solution.

For related Cu(II) complexes, $Cu[(OPPh_2)_2N]_2$ (**8**) has the expected planar CuO_4 core but, remarkably, the whole spiro-bicyclic system is almost planar. Even more surprising is the existence of copper in both planar and tetrahedral environments in the case of the monothio derivative $Cu[(OPPh_2)(SPPh_2)N]_2$ (**9**), with the planar and tetrahedral molecules being in a ratio of 1:2.

The conformations of the six-membered $CuOXP_2N$ (X = O, S) rings differ considerably in **1**, **4**, and **8**, providing further evidence of the high flexibility of the OPNPX skeleton.

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