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SYNTHESIS AND MULTINUCLEAR NMR STUDIES ON COPPER AND SILVER COMPLEXES OF MULTIDENTATE PHOSPHINE AND MIXED PHOSPHA/THIA LIGANDS. SINGLE CRYSTAL STRUCTURE OF $[Cu(P_2S_2)]PF_6$ ($P_2S_2 = Ph_2PCH_2CH_2SCH_2CH_2SCH_2CH_2PPh_2$)

CHRISTOPHER L. DOEL, ALEXANDER M. GIBSON and
GILLIAN REID*

Department of Chemistry, University of Southampton, Highfield,
Southampton SO17 1BJ, U.K.

and

CHRISTOPHER S. FRAMPTON

Roche Products Ltd, Welwyn Garden City, Herts AL7 3AY, U.K.

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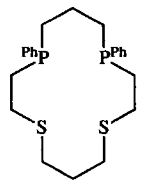
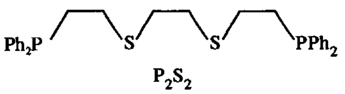
Abstract—Reaction of $[Cu(MeCN)_4]PF_6$ or $AgBF_4$ with 1 molar equiv. of L (L = tetraphos-1, P_2S_2) in degassed acetone followed by addition of diethyl ether yielded the complexes of stoichiometry $[M(L)]^+X^-$, M = Cu, $X^- = PF_6^-$; M = Ag, $X^- = BF_4^-$, in high yield. ^1H, ^{31}P and ^{109}Ag NMR spectroscopic data consistent with this formulation are presented. The complex $Cu(L)PF_6$ contains discrete $[Cu(P_2S_2)]^+$ cations and PF_6^- anions. The Cu^I ion is tetra-ligated to the P_2S_2 ligand via both the P- and S-donor atoms, Cu—S = 2.385(2), 2.367(2), Cu—P = 2.233(2), 2.242(2) Å. The geometry at Cu^I is a severely distorted and flattened tetrahedron, with the angles at Cu^I involved in the five-membered chelate rings showing only small deviations from 90°, while the unrestricted P(1)—Cu—P(2) angle is much more open at 134.88(6)°. The complexes $[Cu(L')_2]PF_6$ ($L' = PhHPCH_2CH_2PHPh$ or $PhHPCH_2CH_2CH_2PHPh$) were obtained by reaction of $[Cu(MeCN)_4]PF_6$ with 2 molar equiv. of the appropriate disecondary phosphine in degassed CH_2Cl_2. Variable-temperature ^{31}P and ^{63}Cu NMR spectroscopic studies confirmed the 1:2 Cu:L′ stoichiometry and indicated an approximately tetrahedral arrangement of the four P donors around the Cu^I ion in each case.

The coordination chemistry of phosphine ligands has been studied intensively in recent years, and these have been shown to be extremely good ligands for transition metal ions, being both better σ-donor and π-acceptor ligands than, for example, thioethers.[1] We have been studying the synthesis and coordination chemistry of macrocyclic ligands incorporating phosphine donor atoms. As part of this work we have recently prepared and structurally characterized the mixed phospha–thia macrocyclic cations $[Pt(Ph_2[14]aneP_2S_2)]^{2+}$ and *trans*-



$Ph_2[14]aneP_2S_2$



P_2S_2

tetraphos-1

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*Author to whom correspondence should be addressed.

$[RhCl_2(Ph_2[14]aneP_2S_2)]^+$ ($Ph_2[14]aneP_2S_2$ = 1,5-diphenyl-1,5-diphospha-8,12-dithiacyclotetradecane).[2] As a parallel to this work we are also investigating the related open-chain ligands tetraphos-1 and P_2S_2 in an attempt to establish the differences in their metal ion chemistry. A feature common to the acyclic ligands is the presence of terminal phosphine functions. We wondered whether the presence of the better σ-donor ligands at the termini would tend to discourage "unzipping" of the ligand and hence demetallation of these complexes. We now wish to report the high yield syntheses and properties of complexes of Cu^I and Ag^I with these acyclic phosphine and phospha–thia ligands. The single-crystal structure of $[Cu(P_2S_2)]PF_6$ is also reported.

The disecondary phosphine complexes $[Cu(L')_2]PF_6$ (L' = $PhHPCH_2CH_2PHPh$ or $PhHPCH_2CH_2CH_2PHPh$) have also been prepared and characterized by multinuclear (^1H, ^{31}P and ^{63}Cu) NMR studies. Most of the homoleptic Cu^I and Ag^I phosphine complexes reported to date incorporate mono- or bidentate tertiary phosphine ligands.[3–6] Several thioether macrocyclic complexes of Cu^I and Ag^I are also known.[7] A few other examples of primary and secondary phosphine complexes of Cu^I and Ag^I are also known.[3,8]

RESULTS AND DISCUSSION

Tetradentate ligand complexes

Reaction of $[Cu(MeCN)_4]PF_6$ or $AgBF_4$ with 2 molar equiv. of L (L = tetraphos-1 or P_2S_2) in degassed $MeCN/CH_2Cl_2$ followed by precipitation with Et_2O gave good yields of complexes of stoichiometry $[Cu(L)]PF_6$ or $[Ag(L)]BF_4$ as white solids. FAB-mass spectrometry shows a molecular ion peak with the correct isotropic distribution in each case corresponding to $[M(L)]^+$ (calc. for $[^{63}Cu(P_2S_2)]^+$ m/z 581, found m/z 581; calc. for $[^{109}Ag(P_2S_2)]^+$ m/z 627, found m/z 627; calc. for $[^{63}Cu(tetraphos\text{-}1)]^+$ m/z 733, found m/z 733; calc. for $[^{109}Ag(tetraphos\text{-}1)]^+$ m/z 780, found m/z 779). These data, together with IR and ^1H NMR spectroscopic data and microanalyses, confirm the above 1 : 1 formulations.

^{31}P NMR spectra (145.8 MHz, $CDCl_3$, 300 K) were recorded for all four complexes. $[Cu(P_2S_2)]PF_6$ shows a singlet at $\delta + 1.0$ due to the coordinated P donors of the P_2S_2 ligand, and a septet at δ −146.3 from the non-coordinating PF_6^- anions. These signals integrate as 2 : 1, consistent with a mononuclear Cu^I cation coordinated to a single P_2S_2 ligand. The resonance for the coordinated P_2S_2 ligand is shifted downfield by approximately 17 ppm relative to free P_2S_2 ($\delta^{31}P$ −16.3), and is broadened due to the interaction of the ^{31}P nuclear spin with the ^{63}Cu and ^{65}Cu nuclei, both of which are quadrupolar ($I = 3/2$). A more complicated ^{31}P NMR spectrum is seen for $[Cu(tetraphos\text{-}1)]PF_6$, with a broad multiplet in the range δ +17.7–5.8 arising from coordinated tetraphos-1 and a septet at δ −145.9 (PF_6^-). The complexity of the ligand resonances probably arises from the presence of two P environments and the possibility of different diastereoisomers for tetraphos-1 (DL and *meso*) due to the chirality of the internal P-donors, and the interaction of these ^{31}P nuclei with the ^{63}Cu and ^{65}Cu quadrupolar nuclei. However, the substantial downfield shift relative to free tetraphos-1 and the 4 : 1 ratio for the ligand : PF_6^- resonances are consistent with the mononuclear complex $[Cu(tetraphos\text{-}1)]PF_6$.

The ^{31}P NMR spectrum of $[Ag(P_2S_2)]BF_4$ shows two overlapping doublets indicative of the two equivalent ligand phosphines coupling to the two $I = 1/2$ silver nuclei, ^{107}Ag (51%) and ^{109}Ag (49%), $J(^{107}AgP)$ = 445 Hz, $J(^{109}AgP)$ = 510 Hz. The ratio of the coupling constants for ^{107}Ag—P : ^{109}Ag—P of 0.87 is in agreement with that expected based on the respective nuclear magnetic moments of the two isotopes. The magnitudes of the Ag—P coupling constants in $[Ag(P_2S_2)]^+$ are approximately twice those for $[Ag(dppe)_2]^+$, which involves a P_4 donor set, $J(^{107}AgP)$ = 231, $J(^{109}AgP)$ = 266 Hz.[6] A similar decrease in the Ag—P coupling constants with increasing number of coordinated phosphines has been observed by ^{31}P CP-MAS NMR spectroscopy for the series $[Ag(PPh_3)_nNO_3]$, n = 1–4. Thus, for $[Ag(PPh_3)_4]NO_3$(P_4 donor set) J(AgP) = 109 Hz; $[Ag(PPh_3)_3NO_3]$ (P_3O donor set) J(AgP) = 310 Hz; $[Ag(PPh_3)_2NO_3]$ (P_2O_2 donor set) J(AgP) = 470 Hz.[9] Thus, the coupling constants for $[Ag(P_2S_2)]^+$ are also consistent with two phosphines bound to Ag^I. The ^{109}Ag NMR spectrum of $[Ag(P_2S_2)]BF_4$ (16.75 MHz, $CH_2Cl_2/CDCl_3$) recorded at 220 K (Fig. 1) is consistent with this showing a triplet at $\delta + 1117$ [$^1J(^{109}AgP)$ = 510 Hz] arising from the Ag^I centre ligated to two phosphine functions. No ^{109}Ag NMR resonances were observed for this complex at 300 K, suggesting that the thioether donor atoms may be exchanging on the NMR time-scale at this temperature.

As for $[Cu(tetraphos\text{-}1)]PF_6$, the presence of different P environments and diastereoisomers in $[Ag(tetraphos\text{-}1)]BF_4$ leads to greater complexity in the ^{31}P NMR spectrum, which shows a multiplet in the range δ +3.5 to +0.5. As a result the Ag—P coupling constants could not be assigned.

These ^{31}P NMR spectroscopic data indicate that the four complexes studied in this work probably

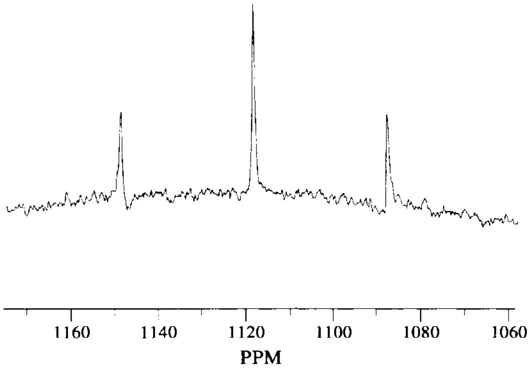

Fig. 1. ^{109}Ag NMR spectrum of $[Ag(P_2S_2)]BF_4$ (16.75 MHz, $CH_2Cl_2/CDCl_3$, 220 K).

exist as mononuclear complexes in solution,[*] and the observation of coupling between the Ag and P nuclei suggest that they are not exchanging on the NMR time-scale, and cooling to 220 K does not alter the ^{31}P NMR spectra significantly, although the absence of a resonance in the ^{109}Ag NMR spectrum of $[Ag(P_2S_2)]BF_4$ at 300 K suggests that the thioether donors may be exchanging at this temperature. This behaviour contrasts with that of several copper and silver complexes incorporating mono- and bidentate phosphines, which often exchange P-donors at room temperature and can form polynuclear complexes with bridging diphosphines.[5]

In order to establish the geometry of the complex cation formed between Cu^{I} and P_2S_2, and to confirm the 1 : 1 Cu : P_2S_2 ratio, a single-crystal X-ray study was undertaken. Small, colourless prismatic crystals of $[Cu(P_2S_2)]PF_6$ suitable for single-crystal X-ray analysis were obtained by layering a solution of the complex in CH_2Cl_2 with hexane at -15°C. The structure determination shows (Fig. 2) the Cu^{I} ion tetra-ligated to the P_2S_2 ligand, giving discrete $[Cu(P_2S_2)]^+$ cations and PF_6^- anions, Cu—P(1) = 2.233(2), Cu—P(2) = 2.242(2), Cu—S(1) = 2.385(2) and Cu—S(2) = 2.367(2) Å. The angles around the central Cu atom deviate markedly from the 109° expected for a regular tetrahedral environment. In particular, those involving five-membered chelate rings are close to 90°, reflecting the small bite size of the PCH_2CH_2S and SCH_2CH_2S linkages, while those that have no such restriction are much more open, e.g. P(1)—Cu—P(2) = 134.88(6)°. The result of this is that the stereochemistry at Cu^{I} is a flattened and severely distorted tetrahedron. The Cu—S and Cu—P distances in $[Cu(P_2S_2)]^+$ are similar to those observed for other Cu^{I} thioether and Cu^{I} phosphine complexes.[3,4,7]

These results confirm that the tetradentate ligands tetraphos-1 and P_2S_2 can readily form stable 1 : 1 complexes with Cu^{I} and Ag^{I} ions.

Disecondary phosphine complexes

The complexes $[Cu(L')_2]PF_6$ (L′ = $PhHPCH_2CH_2PHPh$ or $PhHPCH_2CH_2CH_2PHPh$) are obtained by reaction of $[Cu(MeCN)_4]PF_6$ with 2 molar equiv. of L′ in degassed CH_2Cl_2. These complexes have been identified by IR spectroscopy (ν_{P-H} = 2331 and 2328 cm^{-1}, respectively), FAB-mass spectrometry, which shows molecular ion peaks inconsistent with $[^{63}Cu(L')_2]^+$ (m/z = 555 and 583, respectively) and $[^{63}Cu(L')]^+$ (m/z = 309 and 323, respectively), ^{1}H NMR spectroscopy ($^{1}J_{PH}$ *ca* 320 Hz for both complexes) and microanalytical data. Variable-temperature ^{31}P (145.8 MHz, $CDCl_3$) and ^{63}Cu[†] (95.5 MHz, $CDCl_3$) NMR spectra were recorded for both complexes over the temperature range 210–325 K. At temperatures greater than 325 K the NMR samples decomposed. In addition to a sharp septet at δ -146.2 (PF_6^- anion), the $^{31}P\{^{1}H\}$ NMR spectra show a broad resonance at $\delta = -32.2$ and -45.0 for L′ = $PhHPCH_2CH_2PHPh$ and $PhHPCH_2CH_2CH_2PHPh$, respectively (Fig. 3). These ligand P : PF_6^- signals integrate as 4 : 1. Coupling to $^{63/65}$Cu is not resolved within the temperature range studied, although the resonances do sharpen a little upon cooling. These signals broaden further in the ^{1}H-coupled ^{31}P NMR spectrum, indicating retention of the P-bound protons upon coordination of the disecondary phosphines to Cu^{I}. The ^{63}Cu NMR spectra show broad resonances at $\delta +180$ and $+297$ for L′ = $PhHPCH_2CH_2PHPh$ and $PhHPCH_2CH_2CH_2PHPh$, respectively (Fig. 4). These shifts are to the high frequency end of the range usually observed for Cu^{I} phosphine complexes, and are comparable with the shifts observed for $[Cu(PMe_2Ph)_4]^+$ and $[Cu(PPhH_2)_4]^+$ ($\delta +265$ and $+250$, respectively).[3] The high quadrupole moment of the ^{63}Cu nucleus (-0.211×10^{-28} m^2) usually means that resonances are only observed where the symmetry at Cu^{I} is close to tetrahedral. Hence these data support assignment of an approximately tetrahedral stereochemistry for the $[Cu(L')_2]^+$ cations. As in the ^{31}P NMR spectrum, the coupling of the

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[*] *Note added in proof*: Wild and co-workers[16] have recently reported the single-crystal X-ray structure of the helical, binuclear species $[Ag_2(\text{tetraphos-1})_2](BF_4)_2$ prepared using optically pure (S, S)-(+)-tetraphos-1.

[†] ^{63}Cu, I = 3/2, 69% abundant, D_c = 345.

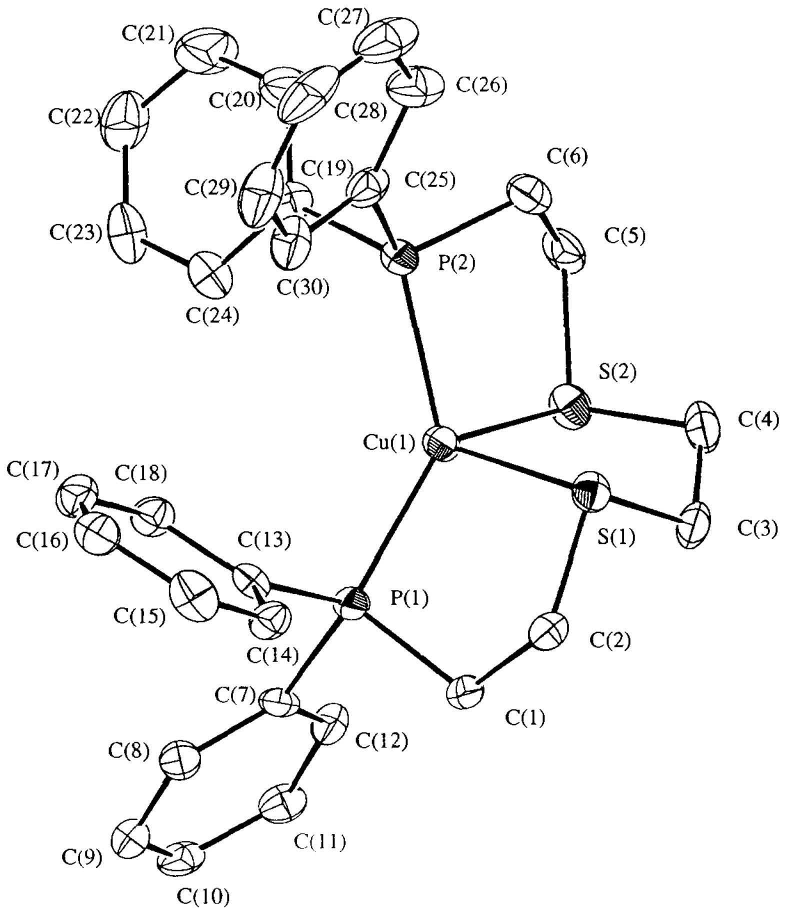

Fig. 2. View of the structure of $[Cu(P_2S_2)]^+$ with numbering scheme adopted.

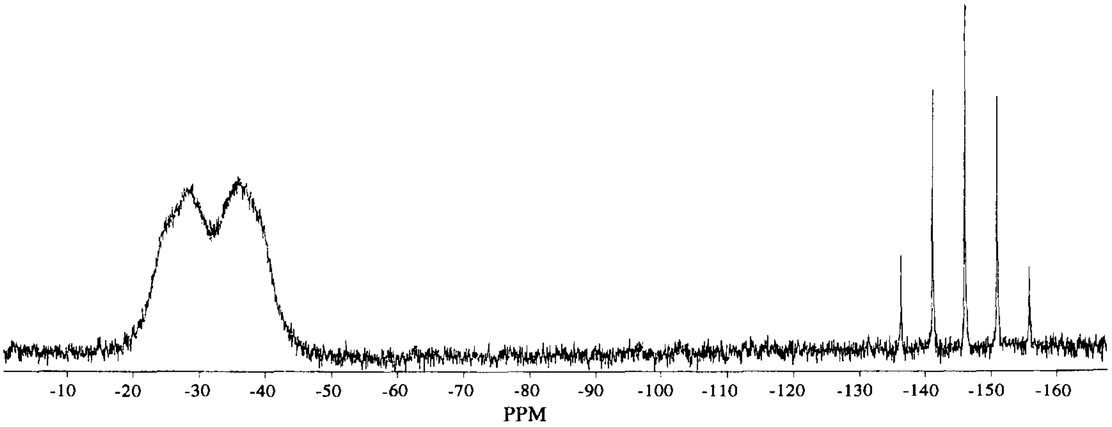

Fig. 3. $^{31}P\{^1H\}$ NMR spectrum of $[Cu(PhHPCH_2CH_2PHPh)_2]PF_6$ (145.8 MHz, $CDCl_3$, 300 K).

^{63}Cu nuclei to the four-coordinated P-donors is not resolved in the ^{63}Cu NMR spectra within the temperature range studied. The ^{63}Cu spectra were observed between 325 and 240 K; below this the Cu signals broaden and disappear. The sensitivity of ^{63}Cu NMR spectroscopy to geometric distortions is exemplified by the fact that we were unable to observe a signal for either $[Cu(P_2S_2)]^+$ or $[Cu(tetraphos\text{-}1)]^+$ by ^{63}Cu NMR spectroscopy over the temperature range 220–300 K.

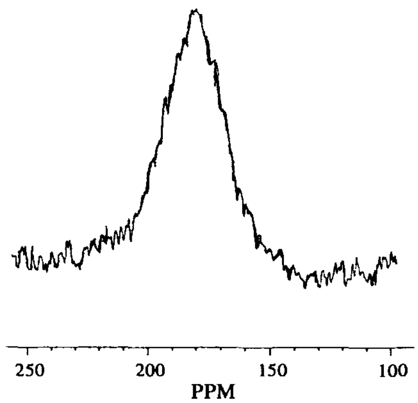

Fig. 4. ^{63}Cu NMR spectrum of [Cu(PhHPCH$_2$CH$_2$PHPh)$_2$]PF$_6$ (95.5 MHz, CDCl$_3$, 300 K).

EXPERIMENTAL

IR spectra were measured as KBr or CsI discs or as Nujol mulls using a Perkin–Elmer 983 spectrometer over the range 200–4000 cm^{-1}. Mass spectra were obtained by electron impact or fast-atom bombardment (FAB) using 3-NOBA (3-nitrobenzyl alcohol) as matrix on a VG Analytical 70-250-SE Normal Geometry Double Focusing Mass Spectrometer. ^{1}H NMR spectra were recorded using a Bruker AM300 spectrometer operating at 300 MHz. ^{31}P, ^{63}Cu and ^{109}Ag NMR spectra were recorded in 10 mm NMR tubes containing 10–15% deuterated solvent using a Bruker AM360 spectrometer operating at 145.8, 95.5 and 16.75 MHz, respectively, and are referenced to 85% H$_3$PO$_4$ (^{31}P $\delta = 0$), [Cu(MeCN)$_4$]BF$_4$ in MeCN solution (^{63}Cu $\delta = 0$) and 9.1 mol dm^{-3} Ag$^+$ in water (^{109}Ag $\delta = -47$).[10] TEMPO (2,2,6,6-tetramethyl-l-piperidenyloxy, free radical) was also added to the NMR sample as a relaxation agent prior to recording ^{109}Ag NMR spectra. Microanalyses were obtained from the Imperial College microanalytical laboratory. Tetraphos-1 was purchased from Strem, PhHPCH$_2$CH$_2$PHPh and PhHPCH$_2$CH$_2$CH$_2$PHPh[11] were prepared by the literature methods and P$_2$S$_2$[12] by a slight modification of a literature method.

Synthesis of [Cu(P$_2$S$_2$)][PF$_6$]

To a degassed solution of P$_2$S$_2$ (50 mg, 0.096 mmol) in CH$_2$Cl$_2$ (10 cm^3) was added a degassed solution of [Cu(MeCN)$_4$][PF$_6$][13] (35.7 mg, 0.096 mmol) in MeCN (10 cm^3). The resulting mixture was stirred for 1 h under dinitrogen. The solvent was removed *in vacuo* to leave a white solid. Recrystallization from a minimum amount of CH$_2$Cl$_2$ and Et$_2$O afforded a white precipitate (yield: 37 mg, 52%). Found: C, 44.8; H, 4.2. Calc. for [C$_{30}$H$_{32}$CuP$_2$S$_2$]PF$_6$·CH$_2$Cl$_2$: C, 45.7; H, 4.0%; FAB-mass spectrum (3-NOBA matrix): found $m/z = 581$; calc. for [^{63}Cu(P$_2$S$_2$)]$^+$ $m/z = 581$. ^{31}P NMR spectrum (145.8 MHz, CH$_2$Cl$_2$/CDCl$_3$, 300 K): δ 1.0 (*s*, 2P, P$_2$S$_2$), -146.3 (*septet*, 1P,PF$_6^-$). ^{1}H NMR spectrum (300 MHz, CDCl$_3$, 300 K): δ 7.65–7.35 (*m*, phenyl, 10H), 3.12–2.53 (*m*, CH$_2$, 6H). IR spectrum (KBr disc): 2923m, 1481w, 1433m, 1259w, 1101m, 838vs, 743m, 694m, 558s, 519w, 483w cm^{-1}.

Single-crystal structure determination on [Cu(P$_2$S$_2$)]PF$_6$

Colourless prismatic crystals of the complex were obtained by layering a solution of the complex in CH$_2$Cl$_2$ with hexane at -15°C. The selected crystal ($0.20 \times 0.10 \times 0.20$ mm) was coated in silicone oil and mounted on a glass fibre.

Crystal data. C$_{30}$H$_{32}$P$_2$S$_2$Cu$^+$·PF$_6^-$, $M = 727.2$, monoclinic, space group $P2_1/n$, $a = 13.288(2)$, $b = 14.692(2)$, $c = 16.308(3)$ Å, $\beta = 104.68(1)°$, $U = 3079.9(7)$ Å^3 [from 2θ values of 20 reflections measured at $\pm\omega$ ($18.9 \leqslant 2\theta \leqslant 21.1°$, $\lambda = 0.71069$ Å)], $Z = 4$, $D_{\text{calc}} = 1.568$ g cm^{-3}, $T = 123$ K, $\mu = 1.050$ mm^{-1}, $F(000) = 1488$.

Data collection and processing. Rigaku AFC 7R four-circle diffractometer, using graphite-monochromated Mo-K_α X-radiation, $T = 123$ K, ω–2θ scans with ω scan width = $(1.10 + 0.35\tan\theta)°$, 5284 data collected, 5048 unique ($R_{\text{int}} = 0.038$; $2\theta_{\max}$ 48°, $h0- > 15$, $k0- > 16$, $l-18- > 18$), giving 3287 reflections with $F \geqslant 5\sigma(F)$ for use in all calculations. No significant crystal decay or movement was observed. As there were no identifiable faces, the data were corrected for Lorentz and polarization effects and absorption empirically using ψ-scans (max. and min. transmission factors = 0.9995 and 0.9262, respectively).

Structure solution and refinement. The structure was solved by direct methods[14] and developed by using iterative cycles of full-matrix least-squares refinement and difference Fourier syntheses which located all non-H atoms.[15] The [Cu(P$_2$S$_2$)]$^+$ cation was found to be ordered, while the PF$_6^-$ anion was disordered about one plane. Partial F atoms were used for these equatorial F atoms giving two orientations for these atoms in a 45 : 55 ratio, such that the total number of F atoms around the P atom was six. All non-hydrogen atoms except for partially occupied F atoms were refined anisotropically, while hydrogen atoms were included in fixed, calculated positions. The weighting scheme $w^{-1} = \sigma^2(F)$ gave satisfactory agreement analyses. At final convergence R, $R_w = 0.044$, 0.044, respec-

Table 1. Selected bond lengths (Å) and angles for $[Cu(P_2S_2)]^+$

Cu(1)—S(1)	2.385(2)	Cu(1)—S(2)	2.367(2)
Cu(1)—P(1)	2.233(2)	Cu(1)—P(2)	2.242(2)
S(1)—C(2)	1.828(5)	S(1)—C(3)	1.821(5)
S(2)—C(4)	1.830(6)	S(2)—C(5)	1.827(6)
P(1)—C(1)	1.841(5)	P(1)—C(7)	1.828(5)
P(1)—C(13)	1.825(5)	P(2)—C(6)	1.829(6)
P(2)—C(19)	1.828(5)	P(2)—C(25)	1.828(5)
C(1)—C(2)	1.528(7)	C(3)—C(4)	1.526(8)
C(5)—C(6)	1.520(8)		
S(1)—Cu(1)—S(2)	90.21(5)	S(1)—Cu(1)—P(1)	90.85(5)
S(1)—Cu(1)—P(2)	111.87(5)	S(2)—Cu(1)—P(1)	129.22(6)
S(2)—Cu(1)—P(2)	90.61(5)	P(1)—Cu(1)—P(2)	134.88(6)
Cu(1)—S(1)—C(2)	102.1(2)	Cu(1)—S(1)—C(3)	96.6(2)
C(2)—S(1)—C(3)	102.4(2)	Cu(1)—S(2)—C(4)	99.8(2)
Cu(1)—S(2)—C(5)	100.0(2)	C(4)—S(2)—C(5)	100.7(3)
Cu(1)—P(1)—C(1)	102.7(2)	Cu(1)—P(1)—C(7)	129.3(2)
Cu(1)—P(1)—C(13)	110.5(2)	C(1)—P(1)—C(7)	100.2(2)
C(1)—P(1)—C(13)	107.1(2)	C(7)—P(1)—C(13)	104.8(2)
Cu(1)—P(2)—C(6)	100.5(2)	Cu(1)—P(2)—C(19)	118.3(2)
Cu(1)—P(2)—C(25)	122.1(2)	C(6)—P(2)—C(19)	104.2(3)
C(6)—P(2)—C(25)	106.4(3)	C(19)—P(2)—C(25)	103.4(2)
S(1)—C(2)—C(1)	115.1(4)	P(1)—C(1)—C(2)	114.4(4)
S(2)—C(4)—C(3)	111.3(4)	S(1)—C(3)—C(4)	110.3(4)
P(2)—C(6)—C(5)	109.9(4)	S(2)—C(5)—C(6)	115.2(4)

tively, $S = 1.76$ for 378 refined parameters. The final ΔF synthesis showed no peaks above 1.05 or below -0.54 e Å^{-3} and the maximum $\Delta/\sigma = 0.00$. Selected bond lengths, angles and torsion angles are given in Table 1.

Additional deposited material comprises atom coordinates, thermal parameters and observed and calculated structure factors.

Synthesis of $[Ag(P_2S_2)][BF_4]$

Synthesis as for $[Cu(P_2S_2)][PF_6]$ except that the experiment was carried out at 0°C, using P_2S_2 (50 mg, 0.096 mmol) and $AgBF_4$ (19 mg, 0.096 mmol) in degassed CH_2Cl_2 (10 cm^3). Recrystallization afforded a white solid (yield: 53 mg, 77%). Found: C, 48.9; H, 4.3. Calc. for $[C_{30}H_{32}AgP_2S_2]BF_4$: C, 50.5; H, 4.5%. FAB-mass spectrum (3-NOBA matrix): found $m/z = 627$; calc. for $[^{109}Ag(P_2S_2)]^+$ $m/z = 627$. ^{31}P NMR spectrum (145.8 MHz, $CH_2Cl_2/CDCl_3$, 300 K): δ -1.75 [two overlapping doublets, $^1J(^{107}AgP) = 445$ Hz, $^1J(^{109}AgP) = 510$ Hz]. ^{109}Ag NMR spectrum (16.75 MHz, $CH_2Cl_2/CDCl_3$, 220 K): δ $+1117$ [triplet, $^1J(^{109}Ag\text{-}P) = 510$ Hz]. ^1H NMR spectrum (300 MHz, $CDCl_3$, 300 K): δ 7.70–7.35 (*m*, phenyl, 10H), 3.08–2.62 (*m*, CH_2 6H). IR spectrum (KBr disc): 2923m, 1481w, 1432m, 1383w, 1260w, 1083vs, 805w, 744m, 695m, 513w, 478w cm^{-1}.

Synthesis of [Cu(tetraphos-1)]$[PF_6]$

Method as for $[Cu(P_2S_2)][PF_6]$ above except that tetraphos-1 (50 mg, 0.075 mmol) dissolved in degassed CH_2Cl_2 (15 cm^3) was added to a solution of $[Cu(MeCN)_4]PF_6$ (29 mg, 0.075 mmol) in degassed MeCN (15 cm^3). Recrystallization from $CHCl_3/Et_2O$ afforded a white precipitate (yield: 56 mg, 85%). Found: C, 54.1; H, 4.6. Calc. for $[C_{42}H_{42}CuP_4]PF_6 \cdot CH_2Cl_2$: C, 53.5; H, 4.6%. FAB-mass spectrum (3-NOBA matrix): found $m/z = 733$, 656, 547, 520, 443, 411, 385, 248; calc. for $[^{63}Cu(\text{tetraphos-1})]^+$ $m/z = 733$, $[^{63}Cu(Ph_2P(CH_2)_2PPh(CH_2)_2PPh(CH_2)_2PPh)]^+$ $m/z = 656$, $[^{63}Cu(Ph_2P(CH_2)_2PPh(CH_2)_2PPh(CH_2)_2)]^+$ $m/z = 548$, $[^{63}Cu(Ph_2P(CH_2)_2PPh(CH_2)_2PPh)]^+$ $m/z = 520$, $[^{63}Cu(Ph_2P(CH_2)_2PPh(CH_2)_2P)]^+$ $m/z = 443$, $[^{63}Cu(Ph_2P(CH_2)_2PPh(CH_2)_2]^+$ $m/z = 412$, $[^{63}Cu(Ph_2P(CH_2)_2PPh)]^+$ $m/z = 384$, $[^{63}Cu(Ph_2P)]^+$ $m/z = 248$. ^{31}P NMR spectrum (145.8 MHz, $CHCl_3/CDCl_3$, 300 K): δ 17.7–5.8 (*br m*, 4P), -145.9 (*septet*, 1P, PF_6^-). ^1H NMR spectrum (300 MHz, $CDCl_3$, 300 K): δ 7.65–6.85 (*m*, phenyl, 15H), 2.77–1.81 (*m*, CH_2, 6H). IR spectrum (KBr disc): 2923m, 1481w, 1432w, 1100w, 837vs, 741w, 694m, 556m, 519w, 489w cm^{-1}.

Synthesis of [Ag(tetraphos-1)][BF_4]

Method as for [Cu(P_2S_2)][PF_6] above using tetraphos-1 (50 mg, 0.075 mmol) dissolved in degassed CH_2Cl_2 (15 cm^3), which was added to $AgBF_4$ (15 mg, 0.075 mmol) in degassed CH_2Cl_2 (10 cm^3). Recrystallization from $CHCl_3$ afforded a white precipitate (yield: 42 mg, 65%). Found: C, 48.0; H, 4.2. Calc. for $[C_{42}H_{42}AgP_4]BF_4\cdot 2CHCl_3$: C, 47.9; H, 4.0%. FAB-mass spectrum (3-NOBA matrix): found $m/z = 779, 701, 594, 565, 457, 429, 353, 321$; calc. for $[^{109}Ag(tetraphos\text{-}1)]^+$ $m/z = 780$, $[^{109}Ag(Ph_2P(CH_2)_2PPh(CH_2)_2PPh(CH_2)_2PPh)]^+$ $m/z = 702$, $[^{109}Ag(Ph_2P(CH_2)_2PPh(CH_2)_2PPh(CH_2)_2)]^+$ $m/z = 594$, $[^{109}Ag(Ph_2P(CH_2)_2PPh(CH_2)_2PPh)]^+$ $m/z = 566$, $[^{109}Ag(Ph_2P(CH_2)_2PPh(CH_2)_2)]^+$ $m/z = 458$, $[^{109}Ag(Ph_2P(CH_2)_2PPh)]^+$ $m/z = 430$, $[^{109}Ag(Ph_2P(CH_2)_2P)]^+$ $m/z = 353$, $[^{109}Ag(Ph_2P(CH_2)_2)]^+$ $m/z = 322$. ^{31}P NMR spectrum (145.8 MHz, $CH_2Cl_2/CDCl_3$, 300 K): δ 3.5–0.5 (*m*, tetraphos-1P, 4P). ^1H NMR spectrum (300 MHz, $CDCl_3$, 300 K): δ 7.55–6.96 (*m*, phenyl, 20H), 2.95–1.65 (*m*, CH_2, 6H). IR spectrum (KBr disc): 3051m, 2923m, 1481w, 1432w, 1383w, 1260w, 1083vs, 743w, 695w, 598w, 515w cm^{-1}.

Synthesis of [Cu($PhHPCH_2CH_2PHPh$)$_2$]PF_6

A degassed solution of $[Cu(MeCN)_4]PF_6$ (76 mg, 0.205 mmol) dissolved in CH_2Cl_2 (10 cm^3) was added to $PhHPCH_2CH_2PHPh$ (0.1 cm^3, 0.41 mmol) in degassed CH_2Cl_2 (15 cm^3). After stirring this solution under dinitrogen for 2 h the solvent was removed *in vacuo* to give an oily white solid. Recrystallization from a minimum volume of CH_2Cl_2 and Et_2O gave the product as a white microcrystalline solid (yield: 65 mg, 70%). Found: C, 48.0; H, 4.6. Calc. for $[C_{28}H_{32}CuP_4]PF_6$: C, 48.0; H, 4.1%. FAB-mass spectrum (3-NOBA matrix): found $m/z = 555$ and 309; calc. for $[^{63}Cu(PhHPCH_2CH_2PHPh)_2]^+$ $m/z = 555$; $[^{63}Cu(PhHPCH_2CH_2PHPh)]^+$ $m/z = 309$. ^1H NMR spectrum (300 MHz, $CDCl_3$, 300 K): δ 7.8–7.2 (*br m*, Ph, 20H), 5.4 (*br m*, P*H*, 4H, $^1J_{PH}$ *ca* 320 Hz), 2.5–1.7 (*br m*, C*H*, 12H). $^{31}P\{^1H\}$ NMR spectrum (145.8 MHz, $CDCl_3$, 300 K): δ -32.2 (*br*, 4P, $W_{1/2}$ *ca* 2670 Hz), -146.2 (*septet*, PF_6^-, 1P). ^{63}Cu NMR spectrum (95.5 MHz, $CDCl_3$, 300 K): δ $+180$ (*br*). IR spectrum (KBr disc): 3050w, 2930w, 2331w, 1586w, 1570m, 1480w, 1435m, 1410w, 1190m, 1095m, 1000w, 837vs, 740m, 695m, 557vs, 521w, 481m, 413w cm^{-1}.

Synthesis of [Cu($PhHPCH_2CH_2CH_2PHPh$)$_2$]PF_6

Method as for $[Cu(PhHPCH_2CH_2PHPh)_2]PF_6$, using $[Cu(MeCN)_4]PF_6$ (71 mg, 0.190 mmol) and $PhHPCH_2CH_2CH_2PHPh$ (0.1 cm^3, 0.38 mmol). The product was isolated as a white solid (yield: 113 mg, 81%). Found: C, 51.1; H, 5.0. Calc. for $[C_{30}H_{36}CuP_4]PF_6$: C, 49.4; H, 4.9%. FAB-mass spectrum (3-NOBA matrix): found $m/z = 583$ and 323; calc. for $[^{63}Cu(PhHPCH_2CH_2CH_2PHPh)_2]^+$ $m/z = 583$; $[^{63}Cu(PhHPCH_2CH_2CH_2PHPh)]^+$ $m/z = 323$. ^1H NMR spectrum (300 MHz, $CDCl_3$, 300 K): δ 7.7–7.1 (*br m*, Ph, 20H), 5.5 (*br m*, P*H*, 4H), 2.9–2.0 (*br m*, C*H*$_2$, 8H). $^{31}P\{^1H\}$ NMR spectrum (145.8 MHz, $CDCl_3$, 300 K): δ -45 (*br*, 4P), -146.4 (*septet*, PF_6^-, 1P). ^{63}Cu NMR spectrum (95.5 MHz, $CDCl_3$, 300 K): δ $+297$ (*br*). IR spectrum (KBr disc): 3080w, 2930w, 2328w, 1480m, 1430m, 1190m, 1115m, 1025w, 838vs, 740m, 695m, 557vs, 484 cm^{-1}.

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