Tris(phenylthiomethyl)phosphane Sulfide and Selenide, $(PhSCH_2)_3PX$ ($X = S, Se$), as Ambidentate Ligand Systems in Copper(I) Complexes

Stefan Fuchs, Klaus Angermaier, Andreas Bauer, and Hubert Schmidbaur*

Anorganisch-chemisches Institut der Technischen Universität München,
Lichtenbergstraße 4, D-85747 Garching, Germany

Received August 2, 1996

Keywords: Sulfides / Selenides / Copper complexes / Ambidentate ligands

Triphenylphosphite has been converted into tris(phenylthiomethyl)phosphane (**1**) by reaction with $LiCH_2SPh$/DABCO, and subsequently into the corresponding sulfide (**2**) and selenide (**3**) by treatment with elemental sulfur or selenium, respectively. Ligands **2** and **3** react with copper(I) halides CuX ($X = Cl, Br, I$) in polar organic solvents to give either 1:1 ($X = Cl$: **4**, **7**, $X = Br$: **5**, **8**) or 1:2 complexes ($X = Br$: **9**, $X = I$: **6**, **10**). The crystal structures of five of these complexes have been determined by single crystal X-ray diffraction studies. All compounds of the type $[(PhSCH_2)_3P{=}S/Se]CuX$ ($X = Cl, Br$) form centrosymmetrical dinuclear complexes featuring a four-membered ring core $Cu_2[S/Se]_2$ fused to two five-membered rings Cu[S/Se]PCS through common *trans* edges. Only one of the three phenyl-thiomethyl functions is involved in coordination to a metal center. The compound $[(PhSCH_2)_3P{=}S](CuI)_2$ (**6**) is associated into a centrosymmetrical tetranuclear complex containing two four-membered rings (ICu_2S) bridged via iodine atoms in 1,3-*cis* positions. The ligand is found to employ two of its $PhSCH_2$ functions for metal coordination, giving rise to two five-membered rings fused to the four-membered rings via neighbouring edges. In all cases, therefore, the P=S/Se functions of the ligands are the preferred donor sites, which are used for the building of bridgehead structural units of polynuclear complexes.

Introduction

Thioethers (RSR′) are important ligands for the coinage metals. Their coordination chemistry is particularly relevant for the role of copper in biological systems[1], but also for the stabilization of copper-containing aqueous solutions employed in electrochemical processes[2] and for the production of copper sulfide based pigments, colloids and nano-particles[3]. Except for the biological aspects, the role of thioethers is similar in the solution chemistry of silver and gold[4]. The soft donor character of the sulfur ligands is an excellent match for the coinage metals in their low positive oxidation states, and the donor properties are even more pronounced in chelating polythioethers[5].

Phosphane sulfides R_3PS (and selenides) are also excellent soft donors, but their affinity for low-valent coinage metals has been probed much less, and the knowledge of the structural chemistry of their complexes is only limited[6]. This is surprising considering the importance of thiophosphanes and thiophosph(on/in)ates in agricultural chemistry and the exposure of these chemicals to metal ions in many environmental compartments[7]. There are also quite diverse selenium sources in the environment, which allow rapid further transformation of S/Se compounds.

Molecules offering a combination of thioether *and* phosphane sulfide/selenide functions are only scarcely represented in the literature[8], and their role as ligands for coinage metals has not been investigated. A study was therefore initiated in this laboratory that should provide basic information on the special features of this new type of ligands. Tris(phenylthiomethyl)phosphane sulfide/selenides $(PhSCH_2)_3P{=}X$ ($X = S, Se$) were chosen as the ligand prototypes, and copper(I) salts CuX as the substrates for coordination.

Results

Ligand Synthesis

Tris(phenylthiomethyl)phosphane, **1**, is prepared from triphenylphosphite and three equivalents of the DABCO complex of phenylthiomethyllithium in a tetrahydrofuran/hexane solvent mixture first at ambient and finally at reflux temperature. An aqueous workup of the reaction mixture gives good yields of a crude liquid product (71%), which is readily identified by its analytical and spectroscopic data (Experimental). Treatment of compound **1** with elemental sulfur or selenium in chloroform and precipitation of the products with pentane affords the corresponding sulfide (**2**) and selenide (**3**), respectively, in high yields as colourless, crystalline derivatives [94% yield, m.p. 100 °C (**2**), 90% yield, m.p. 107 °C (**3**)].

$$\begin{array}{lcccll}
P(OPh)_3 & + & 3\ LiCH_2SPh & \rightarrow & 3\ Li(OPh) + (PhSCH_2)_3P & \mathbf{1} \\
\mathbf{1} & + & S & \rightarrow & (PhSCH_2)_3P{=}S & \mathbf{2} \\
\mathbf{1} & + & Se & \rightarrow & (PhSCH_2)_3P{=}Se & \mathbf{3}
\end{array}$$

Solutions of the three ligands in chloroform show the expected $^{31}P\{^1H\}$-NMR singlet signals with chemical shifts $\delta(P)$ and coupling constants $^2J(^{31}P\text{-}^1H)$ following the oxidation of the phosphorus atoms on going from **1** to **2**/**3**. The $J(^{31}P\text{-}^{77}Se)$ coupling constant in compound **3** (744 Hz) is an important reference value for the changes observed upon complexation (below).

The ^1H and $^{13}C\{^1H\}$-NMR data indicate a symmetrical structure with three equivalent thioether groups at the central P and P=S/Se units. The ligands **1**−**3** can therefore be expected to be tripodal donors through their thioether functions, complemented by donor properties at the P, P=S and P=Se centers, but with a different orientation in space. These additional donor capabilities can make one or more of the thioether functions redundant, if the acceptor properties of the metal component favour bonding to the sulfide/selenide end. In this case the ambidentate ligands may thus act simultaneously through different functionalities.

The Phosphine Sulfide/Selenide Compounds (2, 3) as Ligands in Copper(I) Halide Complexes

Anhydrous copper(I) chloride dissolves in a solution of an equimolar quantity of the ligand **2** in chloroform/acetonitrile. Cooling of the resulting solution gave single crystals, which could be shown to be the 1:1 complex (**4**) by their analytical data. The crystals tend to disintegrate rapidly at ambient temperature and pressure owing to their high contents of crystal chloroform (below), but the solvent-free powder obtained after prolonged exposure of the samples to high vacuum is a colourless, air-stable material (m.p. 119°C, with decomposition).

The 1:1 complex of copper(I) bromide (**5**) is obtained in a similar manner as light pale-green, solvent-free single crystals (m.p. 115°C), albeit in low yield owing to unfavourable solubility characteristics.

By contrast, analogous reactions of ligand **2** and CuI with the same stoichiometry (1:1) gave the 1:2 complex (**6**, single crystals) even in experiments where a deficit of CuI was present.

$$(PhSCH_2)_3P{=}S \; + \; CuX \rightarrow [(PhSCH_2)_3P{=}S]CuX \quad \mathbf{4}\text{: } X{=}Cl$$
$$\mathbf{5}\text{: } X{=}Br$$
$$\mathbf{2} \; + \; 2\,CuI \rightarrow [(PhSCH_2)_3P{=}S](CuI)_2 \quad \mathbf{6}$$

The results with the selenide ligand (**3**) show a similar trend: The CuCl complex (**7**, m.p. 122°C, as a powder) has the 1:1 stoichiometry, and its single crystals contain chloroform solvent, but less than the crystals of the sulfide analogue (**4**). With CuBr, both the 1:1 complex with crystal chloroform (**8**, single crystals) and the 1:2 complex (**9**, as a powder, m.p. 165°C) are obtained. Finally, CuI affords only the 1:2 complex (**10**, as a powder, m.p. 192°C with decomposition). No single crystals could be obtained of any CuI complex of the selenide ligand **3**.

$$(PhSCH_2)_3P{=}Se + \; CuX \rightarrow [(PhSCH_2)_3P{=}Se]CuX \quad \mathbf{7}\text{: } X{=}Cl$$
$$\mathbf{8}\text{: } X{=}Br$$
$$\mathbf{3} \; + 2\,CuX \rightarrow [(PhSCH_2)_3P{=}Se](CuX)_2 \quad \mathbf{9}\text{: } X{=}Br$$
$$\mathbf{10}\text{: } X{=}I$$

The CuCl/CuBr complexes of the sulfide ligand **2** are soluble in chloroform, while the CuI complex is soluble only in dimethylsulfoxide. With the selenide ligand **3**, only the powder samples of the CuCl complex are soluble in $CHCl_3$, however the crystals of the CuCl and CuBr complexes and the powder samples of the CuI complex again dissolve only in Me_2SO.

Solubilities are generally low, and concentrations are sufficiently high for NMR studies only at or above room temperature. Under these conditions the ligands show retention of their virtual threefold symmetry in solution. Since the solid state structures require nonequivalent thioether groups (below), this result indicates rapid site exchange of the metal atoms at the donor functions in solution. For the selenide complexes **7**−**10**, the J(P, Se) coupling constants are reduced significantly as compared with the value for the free ligand, suggesting that the selenium atoms are directly involved in the complexation.

In the FAB mass spectra of the complexes the cations $[LCu]^+$ are the predominating parent species (L = **2**, **3**), formed in the loss of a halide anion from the monomer.

Crystal and Molecular Structures of the Complexes

The crystal structures of the four 1:1 complexes **4**, **5** and **7**, **8**, and of the 1:2 complex **6** have been determined by single crystal X-ray diffraction studies. Crystal and structure solution and refinement data are summarized in Tables 1 and 2, the molecular structures are shown in Figures 1−5, and selected details about bond lengths and angles are given in the captions to these Figures.

It is immediately obvious from these presentations that all 1:1 complexes (Figures 1−4) are present as centrosymmetrical dimers $[LCuX]_2$ based on the same structural principle, with only minor differences in the ligand conformations. They contain a core structure composed of two CuX units bridged by the (P=S/Se) sulfur or selenium atoms. Only one of the three thioether groups of each ligand is engaged in coordination to the copper atoms, whereas the other two are dangling freely in different conformations. A four-membered ring $Cu_2(S/Se)_2$ with the halogens in *trans* positions is thus fused to two five-membered rings CuS_2CP through common CuS edges. The copper atoms are tetrahedrally tetracoordinated, but with short transannular Cu···Cu contacts. The phosphorus atoms are also tetracoordinated, while the (P=X) bridgehead sulfur/selenium atoms have steeply pyramidal threefold coordination.

Specific details are as follows: Complex **4** crystallizes with three mole-equivalents of crystal chloroform in the triclinic cell (space group $P\bar{1}$, $Z = 2$ formula units). This chloroform is lost rapidly at ambient temperature leading to a decay of the lattice. Crystals of the complexes **7** and **8** are isomorphous and contain one mole-equivalent of crystal chloroform in the triclinic cells (space group $P\bar{1}$, $Z = 2$ formula units). Cell dimensions of both compounds (at 205 K) are very similar. Compound **5** crystallizes monoclinically without any chloroform (space group $P2_1/n$, $Z = 4$ formula units).

The 1:2 complex **6** forms centrosymmetrical tetrameric units composed of two dimers linked by iodine bridges out of 1,3-*cis* positions (Figure 5). In each of the dimers the ligand **2** is bridging the two copper atoms through its (P=S) sulfur atom (S4), and two of its three thioether functions (S2, S3) are engaged in metal coordination. Iodine bridging (I2) of the two copper atoms leads to four-membered rings

Table 1. Crystal data, data collection and structure refinement for compounds **4**, **5** and **6**

	4	**5**	**6**
Crystal data			
Empirical formula	$C_{24}H_{24}Cl_{10}CuPS_4$	$C_{21}H_{21}BrCuPS_4$	$C_{21}H_{21}Cu_2I_2PS_4$
M_r	889.68	576.04	813.47
Crystal System	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$ [No. 2]	$P2_1/n$ [No. 14]	$P2_1/n$ [No. 14]
Cryst. Dim. [mm]	0.30, 0.35, 0.45	0.13, 0.25, 0.50	0.30, 0.40, 0.45
a [Å]	10.650(1)	12.585(2)	12.264(2)
b [Å]	11.492(1)	8.487(1)	13.192(2)
c [Å]	15.969(2)	22.272(4)	16.783(3)
α [°]	106.80(1)	90	90
β [°]	103.12(1)	104.59(1)	108.85(1)
γ [°]	93.53(1)	90	90
V [Å^3]	1805.2(3)	2302.1(6)	2569.2(8)
ρ_{calc} [gcm^{-3}]	1.637	1.662	2.103
Z	2	4	4
F(000) [e]	892	1160	1560
μ (Mo K_α) [cm^{-1}]	16.4	31.2	44.5
Data collection			
Diffractometer	Enraf Nonius CAD4		
Radiation	Mo K_α, 0.71069 Å, graphite monochromator		
T (°C)	-62	-62	-62
Scan mode	2ω/θ	ω	ω
hkl range	+13/±14/±19	-16,+15/+10/+27	+15/-16/±21
Measured refl.	7074	5448	6072
Unique refl.	7074	4975	5332
Used refl.	7061	4924	4883 [$F_o \geq 4\sigma(F_o)$]
Absorption correction	no	empirical	empirical
T_{min}/T_{max}	-/-	0.7016/1.0000	0.8001/0.9995
Refinement			
Refined parameters	361	253	271
H atoms [found/calcd.]	0/24	0/21	0/21
R[a]/R1[b]	-/0.0514	-/0.0413	0.0261/-
R_w[a]/wR2[b]	-/0.1474	-/0.1054	0.0290/-
Weighting par.[a,b]	0.0704/4.4176[b]	0.0195/3.8316[b]	Unit weights[a]
ρ_{fin}(max/min) [eÅ^{-3}]	1.30/-0.97	0.42/-0.49	0.63/-1.13

[a] $R = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$. – $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w F_o^2]^{1/2}$. – $w = 1/\sigma^2(F_o)$. – [b] $R1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$. – $wR2 = [\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$. – $w = 1/2\sigma^2(F_o^2) + (ap)^2 + bp, p = (F_o^2 + 2F_c^2)/3$.

Table 2. Crystal data, data collection and structure refinement for compounds **7** and **8**

	7	**8**
Crystal data		
Empirical formula	$C_{22}H_{22}Cl_4CuPS_3Se$	$C_{22}H_{22}BrCl_3CuPS_3Se$
M_r	697.85	742.31
Crystal System	triclinic	triclinic
Space group	$P\bar{1}$ [No. 2]	$P\bar{1}$ [No. 2]
Cryst. Dim. [mm]	0.25, 0.35, 0.50	0.24, 0.50, 0.50
a [Å]	10.246(1)	12.262(2)
b [Å]	10.356(1)	10.394(2)
c [Å]	13.373(2)	13.496(3)
α [°]	103.06(1)	103.29(2)
β [°]	102.25(1)	102.34(2)
γ [°]	92.20(1)	92.31(2)
V [Å^3]	1345.4(3)	1362.6(5)
ρ_{calc} [gcm^{-3}]	1.737	1.809
Z	2	2
F(000) [e]	696	732
μ (Mo K_α) [cm^{-1}]	28.9	42.0
Data collection		
Diffractometer	Enraf Nonius CAD4	
Radiation	Mo K_α, 0.71069 Å, graphite monochromator	
T (°C)	-68	-68
Scan mode	ω/θ	ω
hkl range	-13,+12/-13,+12/+16	+12/±12/±16
Measured refl.	5424	5056
Unique refl.	5417	5049
Used refl.	5408	5047
Absorption correction	empirical	empirical
T_{min}/T_{max}	0.7570/0.9997	0.4588/0.9992
Refinement		
Refined parameters	290	290
H atoms [found/calcd.]	0/22	0/22
R[a]/R1[b]	-/0.0318	-/0.0355
R_w[a]/wR2[b]	-/0.0793	-/0.0900
Weighting par.	0.0432/1.0156[b]	0.0576/0.9851[b]
ρ_{fin}(max/min) [eÅ^{-3}]	0.97/-0.83	1.23/-0.73

[a] $R = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$. – $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w F_o^2]^{1/2}$. – $w = 1/\sigma^2(F_o)$. – [b] $R1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$. – $wR2 = [\Sigma w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$. – $w = 1/2\sigma^2(F_o^2) + (ap)^2 + bp, p = (F_o^2 + 2F_c^2)/3$.

Cu_2SI, and these rings are connected via the remaining iodine atoms (I1). The copper atoms are again tetrahedrally tetracoordinated with short transannular Cu···Cu contacts. It appears very likely that the selenium analogues (**9**, **10**) have similar structures, but no single crystals could be obtained for further investigation.

Conclusions

The present studies have shown that the new thioether/phosphane sulfide/selenide mixed functional ligands of the type $(PhSCH_2)_3P{=}S/Se$ (**2**, **3**) can form dinuclear 1:1 (**4**, **5**, **7**, **8**) and tetranuclear 1:2 complexes (**6**, **9**, **10**) with copper(I) halides. In these coordination compounds the phosphane sulfide/selenide groups are the preferred donor sites which become bridgehead atoms between neighbouring metal centers. Coordination to the halide anions is retained throughout, and the thioether functions are only partially employed for dative bonding to the extent that they can finally secure tetrahedral tetracoordination of the metal atoms. In all structures the copper atoms are components of four-membered rings with transannular metal-metal contacts, which very surprisingly are much shorter for the selenium compounds (ca. 2.76 Å) as compared to the analogous sulfur compounds (ca. 2.82 Å). All compounds are diamagnetic, as judged from NMR studies, and strongly Vis-luminescent upon UV irradiation. They are stable in air and soluble in polar solvents. In solution rapid donor site exchanges occur leading to an equilibration of all thioether functions on the NMR time scale.

This work was supported by *Deutsche Forschungsgemeinschaft* and by *Fonds der Chemischen Industrie*. The authors are indebted to Mr. *J. Riede* for establishing the X-ray data sets.

Experimental Section

General: All experiments were routinely carried out in an atmosphere of dry nitrogen. Solvents were dried and saturated with nitrogen; glassware was oven-dried and filled with nitrogen. Standard analytical and spectroscopic equipment was used throughout. Starting materials were commercially available or prepared and purified following published procedures.

Figure 1. Molecular structure of the complex $[(PhSCH_2)_3P{=}S]CuCl(CHCl_3)_3$, **4**$(CHCl_3)_3$, with atomic numbering; the solvent molecules are not shown; hydrogen atoms are omitted (ORTEP, 50% probability ellipsoids; the complex is aggregated to give dimers with a crystallographic center of inversion); selected bond lengths [Å] and angles [°]: Cu–Cl 2.259(1), Cu–S1 2.317(1), Cu–S2 2.485(1), Cu–S2' 2.379(1), Cu–Cu' 2.822(1), P–S2 1.990(1); Cl–Cu–S1 126.53(5), Cl–Cu–S2' 117.80(5), S1–Cu–S2' 101.86(4), Cl–Cu–S2 103.35(5), S1–Cu–S2 95.09(4), S2–Cu–S2' 109.10(4), P–S2–Cu 99.68(5), P–S2–Cu' 101.08(5), Cu–S2–Cu' 70.90(4)

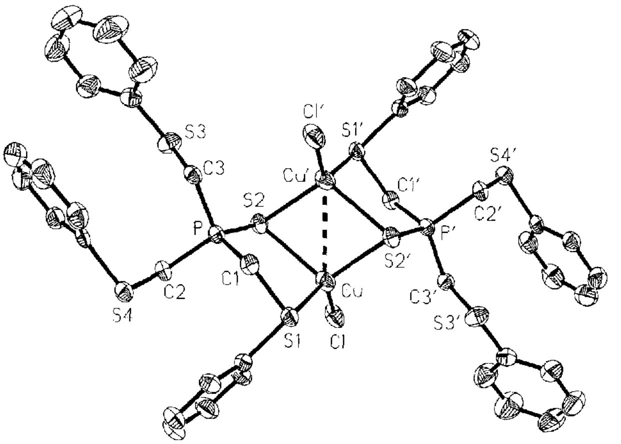
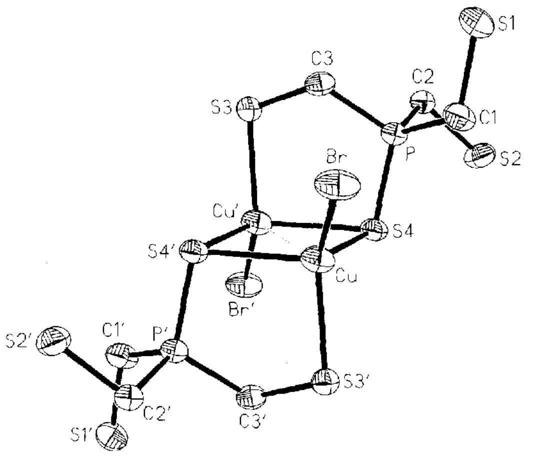


Figure 2. Molecular structure of the complex $[(PhSCH_2)_3P{=}S]CuBr$, **5**, with atomic numbering; the crystals contain no solvent molecules (ORTEP, 50% probability ellipsoids; the dimers have a crystallographic center of inversion; phenyl groups and hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: Cu–Br 2.374(1), Cu–S4 2.377(1), Cu–S4' 3.438(1), Cu-S3' 2.328(1), Cu–Cu' 2.817(1), P–S4 1.986(1); Br–Cu–S4 118.60(3), Br–Cu–S4' 103.87(3), Br–Cu–S3' 127.11(3), S4–Cu–S3' 99.14(4), S4–Cu–S4' 108.41(3), S3'–Cu–S4' 96.84(4), P–S4–Cu 101.63(5), P–S4–Cu' 99.17(5), Cu–S4–Cu' 71.59(3)



Tris(phenylthiomethyl)phosphane (**1**): Triphenylphosphite (20.9 ml, 80 mmol) is dissolved in tetrahydrofuran (50 ml), cooled to 0°C, and treated with a solution of phenylthiomethyllithium[9] (DABCO-complex, 240 mmol) in hexane with stirring. The solution turns brown. Stirring is continued for 2 h at 20°C and for 4 h at reflux temperature. For workup, two 100 ml portions of 2.5 M aqueous ammonium chloride solution are added. The organic phase is removed and dried with magnesium sulfate before the solvent is removed in a vacuum to leave the product as a brown oil (22.6 g, 71% yield). Attempted distillation results is extensive decomposition. – ^{1}H NMR ($CDCl_3$): δ = 3.28 [d, J(P,H) = 5.4 Hz, 2H, CH_2]; 7.15–7.45 (m, 5H, Ph). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 28.4 [d, J(P,C) = 26.4 Hz, CH_2]; 126.3, 128.9, 129.6 (s, for *ortho-*, *para-*, and *meta*-CH), 136.3 [d, J(P,C) = 3.9 Hz, *ipso*-C]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −27.0 (s). – MS (EI): m/z = 400 [M^+], 291 [M^+ – SPh]. – $C_{21}H_{21}PS_3$ (400.55): calcd. C 62.97, H 5.28, P 7.73, S 24.01; found C 62.65, H 5.38, P 7.91, S 22.85.

Figure 3. Molecular structure of the complex $[(PhSCH_2)_3P{=}Se]CuCl(CHCl_3)$, **7**$(CHCl_3)$, with atomic numbering; two monomers are aggregated to give a centrosymmetrical dimer; the chloroform molecules are not shown; phenyl groups and hydrogen atoms are omitted for clarity (ORTEP, 50% probability ellipsoids); selected bond lengths [Å] and angles [°]: Cu–Cl 2.266(1), Cu–Se 2.608(1), Cu–Se' 2.492(1), Cu–S3 2.316(1), Cu–Cu' 2.773(1), P–Se 2.136(1); Cl–Cu–Se 102.91(4), Cl–Cu–Se' 116.50(4), Cl–Cu–S3 126.94(4), Se–Cu–Se' 114.17(2), S3–Cu–Se 95.23(4), S3–Cu–Se' 99.61(4), P–Se–Cu 96.12(4), P–Se–Cu' 97.63(4), Cu–Se–Cu' 65.83(2)

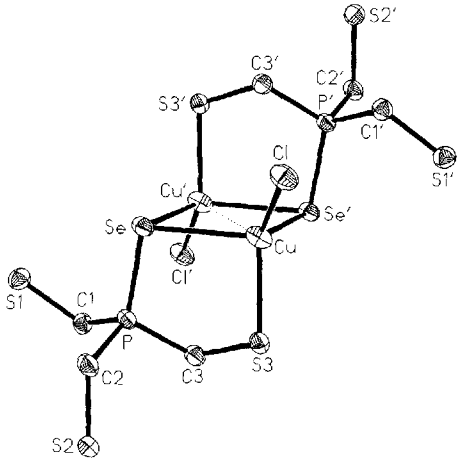
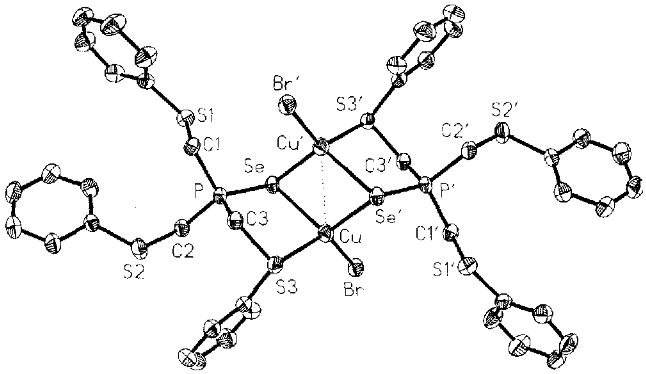
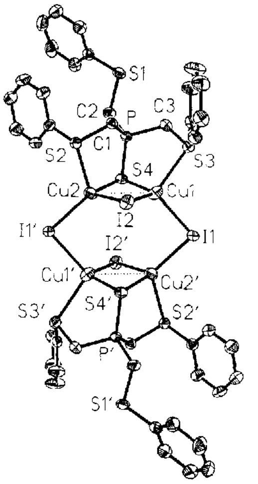


Figure 4. Molecular structure of the complex $[(PhSCH_2)_3P{=}Se]CuBr(CHCl_3)$, **8**$(CHCl_3)$, with atomic numbering; the crystals are isomorphous to those of complex **7** (ORTEP, 50% probability ellipsoids; the dimer has a crystallographic center of inversion); hydrogen atoms are omitted; selected bond lengths [Å] and angles [°]: Cu–Br 2.404(1), Cu–Se 2.604(1), Cu–Se' 2.493(1), Cu–S3 2.324(1), Cu–Cu' 2.746(1), P–Se 2.144(1); Br–Cu–Se 102.66(3), Br–Cu–Se' 116.05(3), Br–Cu–S3 125.56(3), Se–Cu–Se' 114.85(2), Se–Cu–S3 95.70(3), Se'–Cu–S3 100.81(3), P–Se–Cu 95.98(3), P–Se–Cu' 99.11(3), Cu–Se–Cu' 65.15(2)



Tris(phenylthiomethyl)phosphane Sulfide (**2**): A solution of compound **1** (17.90 g, 45 mmol) in chloroform (50 ml) is allowed to react with elemental sulfur (1.44 g, 45 mmol) for 2 h. The product

Figure 5. Molecular structure of the complex $[(PhSCH_2)_3P{=}S](CuI)_2$, **6**, with atomic numbering; two dinuclear units are associated to give a centrosymmetrical tetranuclear aggregate (ORTEP, 50% probability ellipsoids); hydrogen atoms are omitted; selected bond lengths [Å] and angles [°]: Cu1–I1 2.579(1), Cu1–I2 2.598(1), Cu2–I2 2.648(1), Cu2–I1′ 2.527(1), Cu1–S4 2.385(1), Cu2–S4 2.423(1), Cu1–S3 2.488(1), Cu2–S2 2.374(1), Cu1–Cu2 2.830(1), P–S4 1.984(1); Cu1–I2–Cu2 65.3(1), Cu1–I1–Cu2′ 93.8(1), Cu1–S4–Cu2 72.1(1), Cu1–S4–P 91.8(1), Cu2–S4–P 97.8(1), I1–Cu1–I2 113.5(1), I1′–Cu2–I2 120.3(1), I1–Cu1–S4 115.9(1) I1′–Cu2–S4 113.8(1)



is precipitated by careful addition of pentane (20 ml), collected by filtration, washed with small amounts of pentane, and dried in a vacuum (18.3 g, 94% yield; white powder, m.p. 100 °C, soluble in di- and trichloromethane and other polar, non-protic solvents). – ^1H NMR ($CDCl_3$): δ = 3.51 [d, *J*(P,H) = 7.9 Hz, 2H, CH_2]; 7.21–7.37 (m, 5H, Ph). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 33.8 [d, *J*(P,C) = 48.5 Hz, CH_2]; 127.4, 129.2, 130.3 (s, *ortho*-, *para*-, and *meta*-CH), 134.6 [d, *J*(P,C) = 4.4 Hz, *ipso*-CH]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 49.7 (s). – MS (EI): *m*/*z* = 432 [M^+], 323 [M^+ – SPh]. – $C_{21}H_{21}PS_4$ (432.61): calcd. C 58.30, H 4.89, P 7.16, S 29.64; found C 56.63, H 4.57, P 7.10, S 29.94.

Tris(phenylthiomethyl)phosphane Selenide (**3**): The procedure is the same as described for **2**, using 15.00 g of compound **1** (37.4 mmol) and 3.00 g of grey selenium (37.4 mmol); yield 16.4 g, 90%, colourless powder, m.p. 107 °C, soluble in polar, non-protic organic solvents. – ^1H NMR ($CDCl_3$): δ = 3.62 [d, *J*(P,H) = 7.8 Hz, 2H, CH_2]; 7.17–7.39 (m, 5H, Ph). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 33.5 [d, *J*(P,C) = 40.2 Hz, CH_2]; 127.5, 129.3, 130.4 (s, *ortho*-, *para*-, and *meta*-CH), 134.4 [d, *J*(P,C) = 5.0 Hz, *ipso*-CH]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 36.7 [s/d, *J*(P,Se) = 744 Hz]. – MS (EI): *m*/*z* = 480 [M^+], 400 [M^+ – Se], 371 [M^+ – SPh]. – $C_{21}H_{21}PS_3Se$ (479.51): calcd. C 52.60, H 4.41, P 6.46, S 20.06, Se 16.47; found C 52.99, H 4.44, P 6.44, S 20.20, Se 15.70.

*Complex [(**2**)CuCl]₂* (**4**): Copper(I) chloride (70 mg, 0.71 mmol) is dissolved in acetonitrile (25 ml) and treated with a solution of compound **1** (305 mg, 0.70 mmol) in chloroform (25 ml) at 20 °C for 12 h. The solvent is removed in a vacuum to leave a colourless powder (135 mg, 36% yield, m.p. 119 °C with decomposition, soluble in chloroform and other polar non-protic solvents). Reducing the volume of the reaction mixture to only one half in a vacuum and initiation of crystallization by cooling the solution to –30 °C gives a small amount of colourless crystals containing three mole-equivalents of chloroform. These crystals disintegrate rapidly in air with loss of solvent. – ^1H NMR ($CDCl_3$): δ = 3.63 [d, *J*(P,H) = 6.7 Hz, 2H, CH_2]; 7.20–7.43 (m, 5H, Ph). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 32.5 [d, *J*(P,C) = 47.8 Hz, CH_2]; 126.6, 128.9, 129.1 (s, *ortho*-, *para*-, and *meta*-CH), 135.0 [d, *J*(P,C) = 5.5 Hz, *ipso*-CH]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 59.5 (s). *Note:* The same order of notation and assignment of NMR data applies for the spectra of all other complexes (below). MS (FAB): *m*/*z* = 495 [M^+ – Cl]. – $C_{21}H_{21}PS_4CuCl$ (531.62): calcd. C 47.44, H 3.98, Cu 11.9, Cl 6.70; found C 47.40, H 4.01, Cu 11.8, Cl 6.80.

*Complex [(**2**)CuBr]₂* (**5**): The procedure is the same as for complex **4**, with CuBr (150 mg, 1.05 mmol) and ligand **2** (450 mg, 1.05 mmol); yield 115 mg (19%) of crystallized, solvent-free material, m.p. 115 °C; soluble in chloroform and other polar, non-protic solvents). – ^1H NMR ($CDCl_3$): δ = 3.63 (7.9); 7.25–7.44. – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 33.0 (45.9); 127.8, 129.3, 130.7, 133.8 (3.7). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 70.9. MS (FAB): *m*/*z* = 495 [M^+ – Br]. – $C_{21}H_{21}PS_4CuBr$ (576.04): calcd. C 43.79, H 3.67, P 5.38, S 22.26, Cu 11.03, Br 13.87; found C 42.63, H 3.51, P 5.01, S 23.68, Cu 10.7, Br 13.48.

*Complex [(**2**)(CuI)₂]₄* (**6**), was prepared as described for **4** from CuI (130 mg, 0.69 mmol) and ligand **2** (300 mg, 0.69 mmol); yield 76 mg, 27%, of crystallized, solvent-free material, m.p. 147 °C with decomposition; soluble only in dimethylsulfoxide with slow decomposition. – ^1H NMR ([D_6]DMSO): δ = 3.80 (6.8); 7.25–7.49. – $^{13}C\{^1H\}$ NMR ([D_6]DMSO): δ = 32.6 (46.0); 127.2, 129.1, 129.4; 133.5 (4.0). – $^{31}P\{^1H\}$ NMR ([D_6]DMSO): 58.8. – $C_{21}H_{21}PS_4Cu_2I_2$ (813.51): calcd. C 31.01, H 2.60, P, 3.81, S 15.76, Cu 15.62, I 31.20; found C 31.17, H 2.85, P 3.62, S 15.91, Cu 15.3, I 30.82.

*Complex [(**3**)CuCl]₂* (**7**): As described for complex **4**, from CuCl (160 mg, 1.6 mmol) and ligand **3** (770 mg, 1.6 mmol); yield 435 mg, 47%; colourless, air-stable powder, m.p. 122 °C with decomposition, soluble in chloroform; single crystals contain one mole-equivalent of $CHCl_3$. – ^1H NMR ($CDCl_3$): 3.80 (7.0); 7.25–7.48. – $^{13}C\{^1H\}$ NMR ($CDCl_3$): 32.2 (37.5); 127.9, 129.3, 130.9; 133.3 (3.3). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): 43.6 (668). – MS (FAB): *m*/*z* = 543 [M^+ – Cl]. – $C_{21}H_{21}PS_3SeCuCl$ (578.51): calcd. C 43.60, H 3.66, P 5.35, S 16.63, Se 13.65, Cu 11.0, Cl 6.1; found C 43.55, H 3.60, P 5.41, S 17.9, Se 13.4, Cu 10.6, Cl 5.93.

*Complexes [(**3**)CuBr]₂ (**8**), and [(**3**)(CuBr)₂]₄* (**9**): Prepared as described for complex **5**, from CuBr (400 mg, 2.8 mmol) and ligand **3** (1.34 g, 2.8 mmol). A small number of single crystals of complex **8** containing one mole-equivalent of chloroform, which are unstable at 20 °C, was obtained on cooling the solution to –30 °C. Rapid precipitation by removal of most of the solvent gave the 1:2 complex **9** as a colourless, air-stable powder with the following analytical data. – ^1H NMR ([D_6]DMSO): 3.86 (7.3), 7.26–7.43. – $^{13}C\{^1H\}$ NMR ([D_6]DMSO): 31.5 (38.4); 126.7, 128.6, 129.0, 133.2 (2.0). – $^{31}P\{^1H\}$ NMR ([D_6]DMSO): 45.4 (680). MS (FAB): *m*/*z* = 543 [M^+ – Br]. – $C_{21}H_{21}PS_3SeCu_2Br_2$ (766.41): calcd. C 32.91, H 2.76, P 4.04, S 12.55, Se 10.3, Cu 16.6, Br 20.9; found C 32.60, H 2.88, P 4.0, S 13.39, Se 9.9, Cu 16.7, Br 21.9.

*Complex [(**3**)(CuI)₂]₂* (**10**), was prepared as described for compound **6** from CuI (300 mg, 1.6 mmol) and ligand **3** (770 mg, 1.6 mmol); yield 205 mg, 30%, colourless powder, m.p. 192 °C with decomposition, soluble in dimethylsulfoxide with slow decomposition. – ^1H NMR ([D_6]DMSO): 3.87 (7.7), 7.23–7.46. – $^{13}C\{^1H\}$ NMR ([D_6]DMSO): 30.3 (37.5); 125.5, 127.3, 127.9; 131.7 (3.9). – $^{31}P\{^1H\}$ NMR ([D_6]DMSO): 48.5 (680). – MS (FAB): *m*/*z* = 543 [M^+ – I]. – $C_{21}H_{21}PS_3SeCu_2I_2$ (860.41): calcd. C 29.32, H 2.46, P 3.60, S 11.2, Se 9.2, Cu 14.77, I 29.5; found C 29.42, H 2.44, P 3.55, S 11.30, Se 9.0, Cu 14.2, I 31.9.

Crystal Structure Determination: Suitable single crystals of compounds **4**, **5**, **6**, **7** and **8** were sealed under Argon in glass capillaries and examined with an Enraf Nonius CAD4-diffractometer with Mo-K_α radiation (λ = 0.71069 Å). During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed in any case. Intensity data were corrected for Lorentz polarization and absorption effects (except for **4**). Structures were solved by direct methods[10] and refined by full-matrix least-squares calculations against F^2 (**4**, **5**, **7**, **8**)[11] or F (**6**)[10]. The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms were calculated in idealized positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions ($U_{iso(fix)}$ = 0.08 Å^2 for **5** and **6**), or their isotropic thermal parameters were tied to that of the adjacent carbon atom by a factor of 1.5 (for **4**, **7** and **8**). Further information on crystal data, data collection and structure refinement is summarized in Tables 1 and 2. Important interatomic distances and angles are given in the corresponding figure captions. Further information may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-59413, the names of the authors, and the full journal citation.

[1] [1a] *Biological and Inorganic Copper Chemistry*, (Ed.: K. D. Karlin, J. Zubieta), Adenine, Guilderland, New York, **1986**, Vol. I. – [1b] *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives* (Ed.: K. D. Karlin, J. Zubieta), Adenine, Guilderland, New York, **1983**.

[2] [2a] T. C. Woon, A. W. Addison, S. P. Connors, S. K. Mandal, R. McDonald, L. K. Thompson, *J. Chem. Soc. Dalton Trans.* **1986**, 2381–2386. – [2b] S. Mandal, P. K. Bharadwaj, *Polyhedron* **1992**, *11*, 1037–1042.

[3] J. S. Bradley in *Clusters and Colloids – From Theory to Applications* (Ed.: G. Schmid), VCH, Weinheim, **1994**, chapter 6.

[4] S. G. Murray, F. R. Hartley, *Chem. Rev.* **1981**, 365–414.

[5] [5a] F. Olbrich, H. Maelger, G. Klar, *Transition Met. Chem.* **1992**, *17*, 525–529. – [5b] A. J. Blake, R. O. Gould, G. Reid, M. Schröder, *J. Chem. Soc. Chem. Commun.* **1990**, 974–976. – [5c] H. Maelger, F. Olbrich, J. Kopf, D. Abeln, E. Weiss, *Z. Naturforsch.* **1992**, *47b*, 1276–1280.

[6] T. S. Lobana, *Prog. Inorg. Chem.* **1989**, *37*, 495–588.

[7] S. Franke, S. Hildebrand, J. Schwarzbauer, M. Link, W. Francke, *Fresenius' J. Anal. Chem.* **1995**, *353*, 39–49.

[8] D. J. Pederson, *J. Org. Chem.* **1967**, *32*, 1717–1720.

[9] E. J. Corey, D. Seebach, *J. Org. Chem.* **1966**, *31*, 4097–4098.

[10] Sheldrick, G. M., *SHELXTL-PLUS, Release 4.0 for Siemens R3 Crystallographic Research Systems*, Siemens Analytical X-ray Instruments, Inc., Madison, WI, **1989**.

[11] Sheldrick, G. M., *SHELXL-93*, Göttingen, **1993**.

[96162]