Diphenyl(1-pyridyl)phosphine Sulfide as a Ligand in Mono- and Binuclear Coinage Metal Complexes

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Ambidentate Ligand

Diphenyl(1-pyridyl)phosphine sulfide, Ph_2pyPS, **1**, gives a 1:1 complex (**2**) with AuCl upon treatment with $(C_4H_8S)AuCl$. According to an X-ray diffraction analysis, this compound is isomorphous with the Ph_3PS complex. $[Ph_3PAu]BF_4$ and **1** give the cationic complex $[Ph_3PAuSPpyPh_2]BF_4$ (**3**) . With two equivalents of the same reagent the binuclear complex **4** is generated, in which the metal atoms are S- and N-bonded. The reaction of 2 equivalents of **1** with $[(tetrahydrothiophene)_2Au]ClO_4$ affords the 2:1 complex **5** with the gold atom exclusively S-bonded. The analogous reaction with $AgBF_4$ gives the 2:1 complex **6**, the structure of which has also been determined by X-ray diffraction. The silver atom is engaged in coordinative bonding with both sulfur and both nitrogen atoms in a quasi-tetrahedral environment. Addition of $AgClO_4$ to compound **5,** and of $[(MeCN)_4Cu]BF_4$ to **6**, gives mixed-metal complexes (**7, 8**) with head-to-head structures, the silver atoms being exclusively S-bonded.

Introduction

Sulfide and thiolate anions can serve as clustering centers for gold(I) cations. The sulfur atoms may accommodate up to four gold atoms to form aggregates with short intermetallic contacts which contribute to the overall stability [1]. The sulfur atoms of phosphine sulfides R_3PS can be expected to have similar acceptor qualities for gold atoms, but the first systematic studies in this area have been carried out only very recently [2].

Any auxiliary donor group in the organic substituents R of the phosphine sulfides should be helpful for the build-up of polynuclear complexes, and therefore a study of complexes with 1-pyridylphosphine sulfides as ligands for the coinage metals was initiated. Diphenyl(1-pyridyl)-phosphine sulfide $Ph_2(1\text{-}C_5H_4N)PS$ was chosen as the model ligand substrate because of its clear and simple substitution pattern.

Results and Discussion

Diphenyl(1-pyridyl)phosphine sulfide ($SPPh_2py$) **1** reacts with an equimolecular amount of chloro(tetrahydrothiophene)gold(I) with displacement of the weakly coordinated thioether ligand to give the neutral complex $[AuCl(SPPh_2py)]$ (**2**) which contains ligand **1** coordinated to the metal centre via the sulfur atom (Scheme 1). The product has been identified by microanalysis, mass spectrometry and NMR spectroscopy (see Experimental), and its solid state structure has been established by a single crystal X-ray diffraction study.

The crystals are monoclinic, space group $P2_1/n$, with Z = 4 formula units in the unit cell. The lattice contains monomeric molecules with the expected linear coordination at the gold atom (Fig. 1). The molecule has no crystallographically imposed symmetry. The structure is isomorphous with that of the triphenylphosphine sulfide complex of AuCl [3, 4] with virtually identical geometrical parameters (Fig. 3). It therefore appears that the pyridine function plays no role in determining the molecular and crystal structure. The pyridine ring is found to simply replace one of the phenyl rings in $Ph_3PSAuCl$ without any major changes in the crystallographic dimensions.

When a freshly prepared solution of $[AuPPh_3][BF_4]$ is treated with ligand **1** in a 1:1 molar ratio, the cationic mononuclear complex $[Au(PPh_3)(SPPh_2py)][BF_4]$ (**3**) is obtained as a

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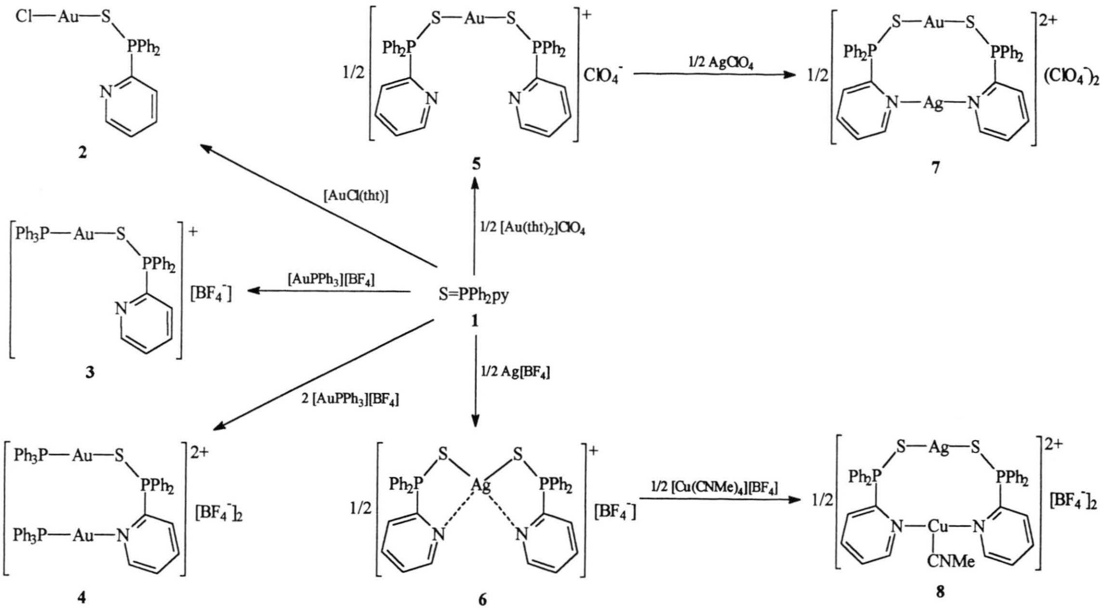

Scheme 1

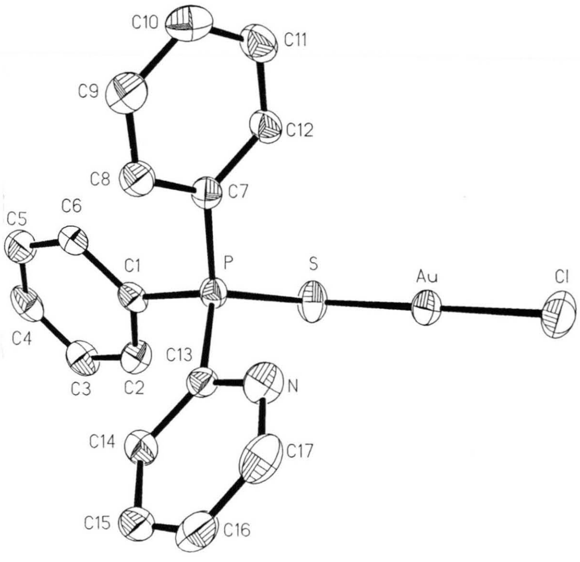

Fig. 1. Molecular structure of compound **2** in the crystal with atomic numbering. (ORTEP, 50% probability ellipsoids; H atoms omitted for clarity; Selected bond lengths [Å] and angles [°]: Au-S 2.263(2), Au-Cl 2.267(2), S-P 2.017(2); S-Au-Cl 174.49(5), P-S-Au 105.85(7).

colorless solid, which also features S-coordination of the phosphine sulfide. Its $^{31}P\{^1H\}$ NMR spectrum shows two signals at δ = 44.4 and 37.1 ppm, corresponding to the phosphorus atoms of ligand **1** and triphenylphosphine, respectively.

In complex **3** there is still a nitrogen function available, which can be used for further coordination of metal atoms. Such a dinuclear complex is obtained, when ligand **1** is treated with $[AuPPh_3][BF_4]$ in a 1:2 molar ratio. The room temperature $^{31}P\{^1H\}$ NMR spectrum of the product in $CDCl_3$ features three broad signals, which are split into two doublets and a singlet as the temperature is lowered to -60°C. This result is in accordance with the formation of a complex $[(Ph_3PAu)SPPh_2\{2\text{-}C_5H_4N(AuPPh_3)\}][BF_4]_2$ (**4**), with S,N-coordination of ligand **1**. A sulfonium salt structure with the gold atoms solely S-coordinated can thus be ruled out. The stoichiometry of the complex is corroborated by elemental analysis data, which differ clearly from those found for the 1:1 product **3** (see Experimental).

Treatment of $[Au(tht)_2]ClO_4$ (tht = tetrahydrothiophene) with two equivalents of ligand **1** gives the 1:2 complex **5**, and the related silver derivative $[Ag(SPPh_2py)_2][BF_4]$ (**6**) can also be prepared by reacting $Ag[BF_4]$ with ligand **1** in the same molar ratio (Scheme 1). The spectroscopic data are indicative of the coordination of the ligands through their sulfur atoms in the gold complex **5**, but there

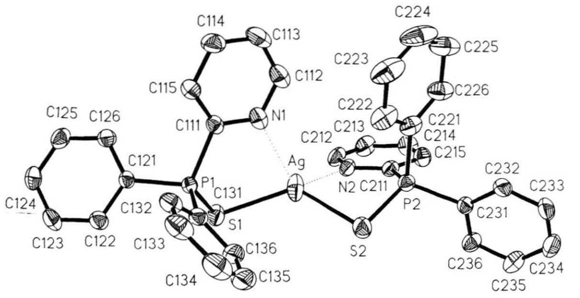

Fig. 2. Molecular structure of compound **6** in the crystal with atomic numbering. (ORTEP, 50% probability ellipsoids; H atoms omitted for clarity; only one of the two enantiomers is shown.) Selected bond lengths [Å] and angles [°]: Ag-S1 2.472(1), Ag-S2 2.545(1), Ag-N1 2.482(3), Ag-N2 2.341(3), P1-S1 1.974(1), P2-S2 1.967(1); S1-Ag-S2 127.35(3), N1-Ag-N2 113.2(1), P1-S1-Ag 95.23(4), P2-S2-Ag 91.72(4).

is no direct evidence for this in the silver species **6**, because in its $^{31}P\{^1H\}$ NMR spectrum no Ag-P coupling is observed. Therefore a single crystal X-ray structure analysis of **6** has been carried out. Crystals of **6** are triclinic, space group $P\bar{1}$, with Z = 2 formula units in the unit cell. The lattice is built of independent BF_4 anions and mononuclear cations. These cations have no crystallographically imposed symmetry. Two enantiomeric chiral cations are related by a crystallographic center of inversion. In the cation the silver atom is coordinated to the ligands mainly through the sulfur centers, but the cation also features weak Ag–N interactions, which lead to a distortion of the linear environment of the silver atom (Fig. 2).

The axis S1-Ag-S2 is strongly bent [127.35(3)°], and together with an angle N1-Ag-N2 = 113.2(1)° the coordination geometry at the metal atom is close to tetrahedral. The silver atom thus is a spiro center of two five-membered rings. The two Ag-S bond lengths are almost equal [2.472(1) and 2.545(1) Å], more so than the two Ag-N distances [2.341(3) and 2.482(3) Å]. Owing to the integration into five-membered rings, the P-S-Ag angles are compressed to 95.23(4)° at S1 and even 91.72(4)° at S2. In the open chain complex **2** this angle Au-S-P is 105.85(7)°.

Compounds **5** and **6** were used as precursors for the synthesis of mixed metal (Ag/Au: **6**, Ag/Cu: **7**) complexes. Treatment of the gold complex **5** with $AgClO_4$ in acetone leads to the colourless crystalline product $[AgAu(\mu\text{-}SPPh_2py)_2](ClO_4)_2$ (**7**), which is assumed to have a non-centrosymmetrical "head-to-head" structure in solution ($CDCl_3$), as suggested by its $^{31}P\{^1H\}$ NMR spectrum (see Experimental), with the gold atom coordinated only to the S-donor sites and the silver atoms exclusively engaged in bonding with the N-donor ends.

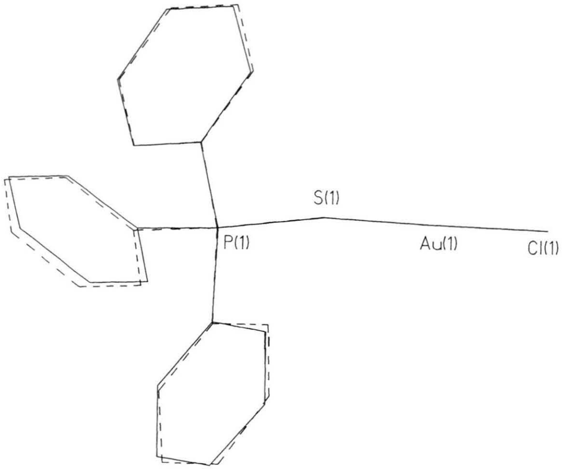

Fig. 3. Superposition of the molecules of compound **2** (dotted lines) and of (triphenylphosphine)sulfide-gold(I)chloride [3], showing the virtually identical geometric parameters of both complexes.

Similarly, complex **6** reacts with equimolecular amounts of $[Cu(MeCN)_4][BF_4]$ in dichloromethane to give the product $[AgCu(\mu\text{-}SPPh_2py)_2(MeCN)][BF_4]_2$ (**8**) as an air-sensitive yellow solid. In this case all analytical and spectroscopic data are also consistent with a "head-to-head" structure, with the silver atom bonded to the sulfur atoms and the copper atom coordinated to both nitrogen atoms. One molecule of acetonitrile appears to be strongly coordinated in the product, most likely as an additional ligand for the copper atom.

Experimental

General: All experiments were carried out at room temperature without special precautions against moisture, except for the mixed metal complex **8**. Silver complexes must be protected against daylight. Warning: Perchlorate salts may be explosive. $[AuPPh_3][BF_4]$ was prepared in situ by the reaction of $AgBF_4$ with $AuClPPh_3$ in THF. Diphenyl(1-pyridyl)phosphine sulfide was obtained by reacting commercially available diphenyl(1-pyridyl)phosphine with elemental sulfur. [AuCl(tht)], $[Au(tht)_2]ClO_4$[5] and $[Cu(CNMe)_4]BF_4$[6] were pre-

Table I. Crystal data, data collection, and structure refinement for compounds **2** and **6**.

	2	**6**
Crystal data		
Formula	$C_{17}H_{14}AuClNPS$	$C_{34}H_{28}AgBF_4N_2P_2S_2$
M_r	527.74	785.32
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$ [No. 14]	$P\bar{1}$ [No. 2]
a (Å)	12.075(1)	10.536(1)
b (Å)	9.285(1)	12.460(1)
c (Å)	14.764(1)	13.806(2)
α (°)	90	78.05(1)
β (°)	96.48(1)	68.32(1)
γ (°)	90	81.33(1)
V (Å^3)	1645.0(2)	1642.3(3)
ρ_{calc} (gcm^{-3})	2.131	1.588
Z	4	2
F(000) (e)	1000	792
μ (Mo K$_a$) (cm^{-1})	93.23	8.90
Data collection		
Diffractometer	Enraf Nonius CAD4	Enraf Nonius CAD4
Radiation	Mo K$_\alpha$, 0.71073 Å	Mo K$_\alpha$, 0.71073 Å
T (°C)	-68	-74
Scan mode	ω	ω
hkl Range	-15→+15, 0→+11, 0→+18	-13→+13, 0→+15, -16→+17
$\sin(\theta/\lambda)_{\max}$ (Å^{-1})	0.64	0.64
Measured refl.	3306	6784
Unique refl.	3306	6778
Observed refl.	3306	6758
Absorption correction	Ψ-scans	none
$T_{\min}/T_{\max}$	0.265/0.999	- / -
Refinement		
Refined parameters	199	461
H atoms (found/calcd.)	0/14	0/28
$R1$[a]	0.0307	0.0434
$wR2$[b]	0.0853	0.1139
(shift/error)$_{\max}$	<0.001	<0.001
ρ_{fin}(max/min) (eÅ^{-3})	+1.593/-2.021	+3.210/-1.326

[a] $R = \sum(|F_o|-|F_c|)/\sum|F_o|$; [b] $wR2 = \{[\sum w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; a = 0.0560 (**2**), 0.0567 (**6**); b = 5.84 (**2**), 3.32 (**6**).

pared by following the literature procedures. MS: Varian MAT 311A spectrometer; NMR: JEOL GX 400 spectrometer, $CDCl_3$ or CD_2Cl_2 (**8**) as solvents with TMS as internal standard for ^{1}H and aqueous H_3PO_4 (85%) as external standard for $^{31}P\{^1H\}$.

[AuCl(SPPh$_2$py)] (**2**): To a solution of ligand **1** (0.4 mmol, 0.118 g) in dichloromethane was added [AuCl(tht)] (0.4 mmol, 0.128 g) and the solution was stirred for 30 min. The solution was then concentrated in a vacuum and diethylether (15 ml) was added to precipitate complex **2** as a white solid, yield 0.190 g (90%). - ^{1}H NMR: δ = 7.51-8.01 (m, Ph, 10H + py, 2H), 8.63 (m, py, 1H), 8.78 (m, py, 1H). - $^{31}P\{^1H\}$ NMR: δ = 36.6 (s). - MS (FAB): m/z (%) = 527.1 (1.41) [M]$^+$; 492.1 (10.86) [M-Cl]$^+$. -

$C_{17}H_{14}AuClNPS$ (527.76)
Calcd C 38.69 H 2.67 N 2.65 S 6.07%,
Found C 38.60 H 2.68 N 2.57 S 5.90%.

[(Ph$_3$PAu)SPPh$_2$py][BF$_4$] (**3**): To a freshly prepared solution of (triphenylphosphine)gold(I) tetrafluoroborate (0.2 mmol, 0.109 g) in THF was added ligand **1** (0.2 mmol, 0.059 g). After 1 h of stirring the solution was concentrated in a vacuum. Addition of 15 ml of diethylether led to the precipitation of **3** as a white solid, yield 0.110 g (66%). - ^{1}H NMR: δ = 7.36-7.77 (m, Ph, 25H + py, 2H),

8.01 (m, py, 1H), 8.19 (m, py, 1H). - $^{31}P\{^{1}H\}$ NMR: δ = 44.4 (broad, $SPPh_2py$, 1P), 37.1 (broad, PPh_3, 1P). - MS (FAB): m/z (%) = 754.3 (100) $[M\text{-}BF_4]^+$; 492.1 (3.45) $[M\text{-}BF_4\text{-}PPh_3]^+$; 459.2 (43.16) $[M\text{-}BF_4\text{-}SPPh_2py]^+$.

$C_{35}H_{29}AuBF_4NP_2S$ (841.40)
Calcd C 49.96 H 3.47 N 1.67 S 3.81%,
Found C 49.66 H 3.33 N 1.42 S 4.39%.

$[(Ph_3PAu)SPPh_2\{2\text{-}C_5H_4N(AuPPh_3)\}][BF_4]_2$ (**4**): To a freshly prepared solution of (triphenylphosphine)-gold(I) tetrafluoroborate (0.3 mmol, 0.164 g) in THF was added ligand **1** (0.15 mmol, 0.044 g). The mixture was stirred for 1 h and the solution was then concentrated in a vacuum. Addition of diethylether leads to the precipitation of complex **4** as a white solid, yield 0.100 g (48%). - ^{1}H NMR: δ = 7.11-7.80 (m, Ph, 40H + py, 2H), 8.01 (m, py, 1H), 8.32 (m, py, 1H). - $^{31}P\{^{1}H\}$ NMR (22°C): δ = 43.6 (broad, $SPPh_2py$, 1P), 36.5 (broad, Ph_3P -Au-S, 1P), 31.5 (broad, Ph_3P -Au-N); -60°C: δ = 44.1 (d, $^{3}J_{PP}$ = 7.6 Hz, $SPPh_2py$, 1P), 36.6 (d, Ph_3P -Au-S, 1P), 32.4 (s, Ph_3P -Au-N). - MS (FD): m/z (%) = 754.0 (100) $[Au(PPh_3)(SPPh_2py)]^+$.

$C_{53}H_{44}Au_2B_2F_8NP_3S$ (1387.47)
Calcd C 45.88 H 3.20 N 1.01 S 2.31%,
Found C 45.62 H 3.27 N 0.87 S 2.22%.

$[Au(SPPh_2py)_2]ClO_4$ (**5**): To a solution of ligand **1** (0.4 mmol, 0.118 g) in dichloromethane (20 ml) was added $[Au(tht)_2]ClO_4$ (0.2 mmol, 0.095 g). After 1 h of stirring at room temperature the solution was concentrated in a vacuum. Addition of diethylether led to the precipitation of **5** as a white solid. Yield 0.135 g (76%). - ^{1}H NMR: δ = 7.27-7.77 (m, Ph, 20H + py, 2 H), 7.91 (m, py, 2H), 8.00 (m, py, 2H), 8.73 (m, py, 2H). - $^{31}P\{^{1}H\}$ NMR: δ = 38.6 (s). - MS (FAB): m/z (%) = 787.2 (100) $[M\text{-}ClO_4]^+$; 492.0 (21.46) $[Au(SPPh_2py)]^+$.

$C_{34}H_{28}AuClN_2O_4P_2S_2$ (887.10)
Calcd C 46.03 H 3.18 N 3.16 S 7.23%,
Found C 45.70 H 3.09 N 3.10 S 7.31%.

$[Ag(SPPh_2py)_2]BF_4$ (**6**): To a solution of silver tetrafluoroborate (0.2 mmol, 0.039 g) in 20 ml of acetone was added ligand **1** (0.4 mmol, 0.118 g), and the solution was stirred for 1 h in the dark. The solution was then concentrated in a vacuum and 15 ml of diethylether was added to precipitate **6** as a white solid, yield 0.108 g (69%). - ^{1}H NMR: δ = 7.41 (m, py, 2H), 7.50 (m, py, 2H), 7.54-7.70 (m, Ph, 20H), 7.80 (m, py, 2H), 7.91 (m, py, 2H). - $^{31}P\{^{1}H\}$ NMR: δ = 47.8 (s).

$C_{34}H_{28}AgBF_4N_2P_2S_2$(785.36)
Calcd C 52.00 H 3.59 N 3.57 S 8.16%,
Found C 51.15 H 3.78 N 3.43 S 8.63%.

$[AgAu(\mu\text{-}SPPh_2py)_2](ClO_4)_2$ (**7**): To an acetone solution (10 ml) of silver perchlorate (0.2 mmol, 0.041 g) was added **5** (0.2 mmol, 0.177 g), and the mixture was stirred at room temperature in the dark for 30 min. The solution was concentrated in a vacuum and 20 ml of diethylether was added to give **7** as a yellow solid, yield 0.160 g (73%). - ^{1}H NMR: δ = 7.60-7.70 (m, Ph, 20H + py, 4 H), 8.01 (m, py, 2H), 8.51 (m, py, 2H). - $^{31}P\{^{1}H\}$ NMR: δ = 45.0 (s). - MS (FAB): m/z (%) = 994.8 (4.75) $[M\text{-}ClO_4]^+$; 786.9 (81.23) $[M\text{-}2ClO_4\text{-}Ag]^+$; 698.8 (100) $[M\text{-}2ClO_4\text{-}Au]^+$.

$C_{34}H_{28}AgAuCl_2N_2O_8P_2S_2$ (1094.42)
Calcd C 36.31 H 2.58 N 2.57 S 5.86%,
Found C 36.91 H 2.88 N 2.47 S 5.86%.

$[AgCu(\mu\text{-}SPPh_2py)_2(CNMe)][BF_4]_2$ (**8**): To a solution of $[Cu(NCMe)_4]BF_4$ (0.2 mmol, 0.063 g) in dichloromethane (15 ml) was added **6** (0.2 mmol, 0.157 g), and the reaction mixture was stirred in the dark for 1 h under nitrogen. The solution was concentrated in a vacuum and diethylether was added to precipitate complex **8** as a yellow solid, yield 0.141 g (72%). - ^{1}H NMR: δ = 4.05 (s, NCMe, 3H), 7.58-7.78 (m, Ph, 20H + py, 4H), 8.54 (m, py, 2H), 8.10 (m, py, 2H). - $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ = 51.7 (s). - MS (FD): m/z (%) = 849.0 (3.36) $[M\text{-}BF_4\text{-}NCMe]^+$; 740.1 (14.05) $[M\text{-}2BF_4\text{-}Cu]^+$; 699.1 (40.71) $[Ag(SPPh_2py)_2]^+$; 653.1 (100) $[Cu(SPPh_2py)_2]^+$.

$C_{36}H_{31}AgB_2CuF_8N_3P_2S_2$ (976.76)
Calcd C 44.27 H 3.20 N 4.32 S 6.56%,
Found C 44.64 H 3.56 N 4.41 S 5.69%.

Crystal structure determinations: Suitable single crystals of compounds **2** and **6** were sealed into glass capillaries and used for measurement of precise cell constants and intensity data collection. During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed for both compounds. Diffraction intensities were corrected for Lorentz and polarization effects. An absorption correction was applied for compound **2**. The structures were solved by Patterson methods and refined by full matrix least-squares calculations against F^2. The thermal motion of all non-hydrogen atoms was treated anisotropically. The BF_4^- anion of **6** showed disorder and was refined in split positions. All hydrogen atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions ($U_{iso(fix)} = 1.5 \cdot U_{eq}$ of the attached C atom). As mentioned, compound **2** is isomorphous to the triphenyl phosphine analogue[4, 5]. In fact, a superposition of both compounds (Fig. 3) showed no significant differences. Thus, the unambiguous recognition of the nitrogen atom on the basis of conformational changes compared to the nitrogen-free analogue, or by means of the temperature factors C versus N, have failed. Further information on crystal data, data collection, and structure refinement are summarized in Table I. Important interatomic distances and angles are shown in the corresponding figure captions. Anisotropic thermal parameters, tables of interatomic distances and angles, and atomic coordinates have been deposited with the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. The data are available on request on quoting CSD-406397 (**2**) and CSD-406398 (**6**).

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[1] H. Schmidbaur, Chem. Soc. Rev. **24**, 391 (1995).
[2] M. Preisenberger, A. Bauer, H. Schmidbaur, Chem. Ber., in press (and references therein).
[3] P. G. Jones, E. Bembenek, J. Crystallogr. Spectrosc. **22**, 397 (1992).
[4] M. Hussain, E. O. Schlemper, Acta Crystallogr. C **43**, 450 (1987).
[5] R. Usón, A. Laguna, M. Laguna, J. Jiménez, M. P. Gómez, A. Sáinz, P. G. Jones;*J.* Chem. Soc., Dalton Trans. **1990**, 3457.
[6] D. F. Shriver, "Inorganic Syntheses" vol 19, p. 90, Wiley-Interscience, New York (1979).