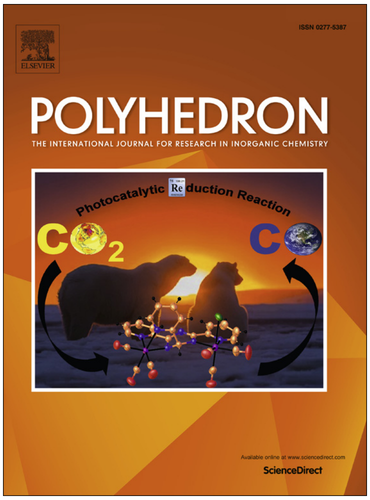

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Structural studies on tribenzylphosphane sulfide complexes of copper(I) and silver(I)

Eric W, Ainscough,* Andrew M. Brodie,* Graham H. Freeman, Paul G. Plieger

Chemistry - Institute of Fundamental Sciences, Massey University, Private Bag 11 222, Palmerston North, New Zealand 4442

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* Corresponding authors. Tel.: +64-6-3569099; fax: +64-6-3505682.
E-mail addresses: e.ainscough@massey.ac.nz (E.W. Ainscough), a.brodie@massey.ac.nz (A.M. Brodie).

ABSTRACT

Tribenzylphosphane sulfide ($SPBn_3$) reacts with $[Cu(CH_3CN)_4]PF_6$ in a 2:1 ratio to give $[Cu(CH_3CN)(SPBn_3)_2]PF_6$ whereas with $[Ag(CH_3CN)_4]PF_6$ in the same ratio it forms $[Ag_2(SPBn_3)_3](PF_6)_2$. The crystal structure of the Cu(I) complex shows it to contain discrete 3-coordinate $[Cu(CH_3CN)(SPBn_3)_2]^+$ cations and $[PF_6]^-$ anions with the Cu atom lying in the plane formed by the two coordinated sulfur atoms and the nitrogen from the coordinated acetonitrile molecule. The Ag complex is a dinuclear species with the one silver atom being 3-coordinate and the other 4-coordinate. Each of the $SPBn_3$ molecules forms a Ag-C η^1-bond with one of the aromatic rings thus blocking the coordination of further $SPBn_3$ ligands. The two Ag centres are linked by a bridging sulfur and a weaker interaction with carbon from the aromatic ring of the same tribenzylphosphane sulfide.

Keywords: Tribenzylphosphane sulfide; Copper(I); Silver(I); Ag(I)-C bond; X-ray crystallography

1. Introduction

The parent molecule to tribenzylphosphane sulfide $(C_6H_5CH_2)_3PS$ ($SPBn_3$) is the bulky tribenzylphosphane (PBn_3) which forms two coordinate complexes of the type $[Cu(PBn_3)_2]X$ (X = $CuCl_2$, $CuBr_2$, PF_6) [1] and $[Ag(PBn_3)_2]PF_6$ and $[Ag(PBn_3)_2]BF_4$ [2] where the driving force for the formation of the linear cations was attributed to interligand ‘embraces’ which prevent secondary coordination of the counter ion to the metals. Here the phenyl groups of PBn_3 swing back over the Ag or Cu in the $[M(PBn_3)_2]^+$ cations to generate a six-fold phenyl embrace. Silver also forms the cluster $[Ag_{13}I_{13}(PBn_3)_6]$, the non-stoichiometric compounds $Ag_{\sim 11.5}Br_{\sim 11.5}(PBn_3)_{16}\cdot\sim 5.5H_2O$ and

$[Ag(PBn_3)_2]_8[AgCl_3]Cl_6$ $6H_2O$. The strength of the driving force of the six-fold phenyl embrace, even in complex clusters, is seen in the latter two non-stoichiometric compounds which also contain discrete $[Ag(PBn_3)_2]^+$ cations with linear P-Ag-P coordination [2]. With this unusual display of behaviour with PBn_3 as a ligand we were interested to observe whether any of these features extended to the chemistry of $SPBn_3$ or if new ones appeared.

Lewis basicity data is not available for $SPBn_3$ but proton affinity measurements[3] show that triphenylphosphane is more basic than triphenylphosphane sulfide ($SPPh_3$). Also it was found that by measuring the decrease in the I-C stretching frequency of the linear triatomic molecule ICN as it forms iodine-bonded complexes with phosphine chalcogenides, the soft Lewis base $SPPh_3$ is more basic than triphenylphosphane oxide[4]. Using the same scale, the basicity of $SPPh_3$ is not as high as trimethylphosphane sulfide ($SPMe_3$) (as expected) which is more basic than trimethylphosphane oxide. From these data it is reasonable to extrapolate that $SPBn_3$ would be less basic than $SPMe_3$ but more basic than $SPPh_3$ [4].

Previously it has been shown that $SPMe_3$ forms the complex $[Cu(SPMe_3)_3]ClO_4$ which has a trigonal-planar arrangement of sulfur atoms around the copper atom [5], and the trinuclear complex $[CuCl(SPMe_3)]_3$ where three-coordination of the copper is achieved by sulfur atoms bridging, the copper and sulfur atoms forming a six-membered ring and chlorine atoms occupying the third coordination position on the copper atoms [6]. Other compounds with the same stoichiometry $[CuX(SPMe_3)]_n$ ($X = Br^-$, I^-, $[SCN]^-$) are known and for $X = Br^-$ or I^- the structures are not trinuclear [7, 8]. With $SPPh_3$ the 1:1 compounds $CuX(SPPh_3)$ ($X = Cl^-$, Br^-) are known [9] as well as the 1:2 complex

$[Cu(dmp)(SPPh_3)_2]ClO_4$ (dmp = 2,9-dimethyl-1,10-phenanthroline) [10] where the copper has a pseudo-tetrahedral structure. Interplanar interactions between the phenyl groups on the sulfide ligand and the phenanthroline exist, but are quite less than those reported for the Cu(I) triphenylphosphane analog. The complex displays emission from a single metal-centered charge-transfer state at 77 K which was in contrast to the triphenylphosphane complex which exhibited dual luminescence from a charge-transfer and a intraligand state at 77 K [10].

Triphenylphosphane sulfide reacts with silver trifluoroacetate in a 4:6 ratio to give the complex ($[CF_3C(O)OAg]_6(SPPh_3)_4$) which contains a 24 membered $(AgOCO)_6$ ring built from TPPS as a template molecule, where each sulfur atom caps a triangle of silver atoms providing each silver atom with two Ag-S contacts in addition to its two Ag-O contacts. The μ^3- coordination of the sulfide was unique. The six silver atoms are connected via argentophilic bonding to give a 6-membered metallacycle in a twisted boat conformation that experiences, as shown by NMR studies, great fluxionality in solution suggesting that TPPS can undergo facile intra or intermolecular ‘ring hopping’ to other silver triangles [11].

2. Experimental

2.1. Materials and instrumentation

Analytical grade solvents were used without further purification with all reactions being carried out under nitrogen. [Cu(MeCN)$_4$]PF$_6$ and [Ag(MeCN)$_4$]PF$_6$ were made according to a literature method [12]. Microanalyses were performed by the Campbell Microanalytical Laboratory, University of Otago. IR data were run as KBr discs on a Perkin-Elmer FT-IR Paragon 1000 spectrometer and ^{31}P NMR spectra recorded at 400 MHz with a Bruker Advance 400 spectrometer. ^{31}P NMR spectra were recorded in CD$_2$Cl$_2$ solution at room temperature and chemical shifts were referenced to a 85% H$_3$PO$_4$ standard. Mass spectra were obtained using a Varian VG70-250S double-focusing magnetic sector spectrometer by the method of liquid secondary ion mass spectroscopy (LSIMS) using *m*-nitrobenzyl alcohol as the matrix. Peaks quoted are for the most abundant isotopomer; percentages are relative intensities.

2.2. Syntheses

2.2.1. SPBn$_3$

To a solution of 1.5 g (4.93 mmol) of tribenzylphosphane (PBn$_3$) in 30 mL of toluene was added 0.17 g (5.3 mmol) of sulfur washed in with a further 10 mL of toluene. The reaction mixture was refluxed, under dinitrogen, for 2 h then cooled on ice. The resulting white powder was filtered, washed with cold toluene and then hexane to give 1.3 g of the crude product in 78 % yield. Recrystallization from hot toluene gave fluffy white crystals, mp. 278-279^{o} C (lit. 274^{o} C [13], 282-283.3^{o} C [14]). *Anal.* Calc. for C$_{21}$H$_{21}$PS: C, 74.97; H, 6.29. Found : C. 75.24; H, 6.53 %.

2.2.2. [Cu(CH_3CN)($SPBn_3$)$_2$]PF_6

[Cu(MeCN)$_4$]PF_6 (0.200 g, 0.536 mmol) was dissolved in 20 mL of 2:1 CH_2Cl_2/methanol and a further 30 mL of CH_2Cl_2 was added. Solid $SPBn_3$ (0.361 g, 1.073 mmol) was added and the reaction mixture refluxed for 10 min then cooled and filtered. The filtrate was reduced in volume and the resulting white precipitate was filtered and air-dried to give a white crystalline product. Yield 0.41 g (83 % yield). Crystals suitable for X-ray analysis were grown by slow evaporation of the filtrate. The compound has a tendency to lose the occluded solvent molecules. mp. 211- 213 ^oC. *Anal.* Calc. for $C_{44}H_{45}CuF_6NP_3S_2 \cdot 0.5CH_2Cl_2$: C, 55.39; H, 4.81; N, 1.45%. Found: C, 55.51; H, 4.84; N, 1.48%.

2.2.3. [Ag_2($SPBn_3$)$_3$](PF_6)$_2$

[Ag(MeCN)$_4$]PF_6 (0.124 g, 0.297 mmol) was dissolved in 20 mL of 2:1 CH_2Cl_2 /methanol and a further 30 mL of CH_2Cl_2 was added. Solid $SPBn_3$ (0.200 g, 0.595 mmol) was added and the reaction mixture refluxed for 10 min. Hexane was added until the solution became slightly cloudy and the flask was placed in a refrigerator to cool for 30 min. The resulting precipitate was filtered and air-dried to give 0.146 g (65 % yield) of crude product. Diffusion of diethyl ether vapor into a concentrated acetonitrile solution of the crude product afforded white needles suitable for X-ray analysis. mp. 194-198 ^oC. *Anal.* Calc. for $C_{63}H_{63}Ag_2F_{12}P_5S_3$: C, 49.95; H, 4.19%. Found: C, 49.99; H, 4.08%.

2.3. X-ray Crystallography

X-ray data were collected on a Siemens SMART diffractometer using graphitemonochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å). The data were corrected for Lorentz and polarization effects and semiempirical absorption corrections (SADABS) were applied. The structures were solved by direct methods and refined against F^2 using all data by full matrix least-squares techniques (SHELXTL) [15]. In the refinement of the structures all non-hydrogen atoms were made anisotropic. Hydrogen atoms were inserted at calculated positions with isotropic thermal parameters at 1.2 times the equivalent isotropic displacement parameters of the atoms to which they are attached. Disordered solvent regions in $[Cu(CH_3CN)(SPBn_3)_2]PF_6$ were treated in the manner described by van der Sluis and Spek [16], as 109 e^- per cell, approximating $0.7(CH_2Cl_2)$ (= 116 e^-) per formula unit. The carbon aton (C3A) on the methyl group on the bound acetonitrile molecule was postionally disordered over two sites in the ratio of 0.71:0.29.

Crystal data for $[Cu(CH_3CN)(SPBn_3)_2]PF_6$ $C_{44}H_{45}CuF_6NP_3S_2$, $M_r = 922.38$, colourless prism, 0.40 x 0.20 x 0.18 mm, monoclinic, $P2_1/n$, $a = 14.687(2)$, $b = 18.931(3)$, $c = 17.290(3)$ Å, $\beta = 102.653(1)°$, $U = 4690.7(13)$ Å^3, $Z = 4$, $\mu = 0.711$ mm^{-1}, $F(000) = 1904$, $T = 203(2)$ K. A total of 21526 reflections were collected in the range $4.64° < 2\theta < 50.69°$. The 8350 independent reflections [$R(\mathrm{int}) = 0.051$] were used after absorption correction ($T_{\min} = 0.558$, $T_{\max} = 1.000$). Refinement of 526 parameters converged to $R_1 = 0.0566$ [for 8350 reflections having $I > 2\sigma(I)$], $wR_2 = 0.1451$ and goodness-of-fit of 0.935 (for all 21526 F^2 data). Peak/hole 0.83/-0.41 e Å^{-3}.

Crystal data for $[Ag_2(SPBn_3)_3](PF_6)_2$ $C_{63}H_{63}Ag_2F_{12}P_5S_3$, $M_r = 1514.90$, colourless block, 0.65 x 0.30 x 0.18 mm, triclinic, $P\bar{1}$, $a = 11.3370(1)$, $b = 13.5875(2)$, $c = 21.3610(3)$ Å, α

= 75.0200(9), β = 87.5080(10), γ = 83.0180(10)°,U = 3154.85(7) Å^3, Z = 2, μ = 0.922 mm^{-1}, F(000) = 1532, T =203 (2) K. A total of 29491 reflections were collected in the range 3.20° < 2θ < 55.2°. The 13595 independent reflections [R(int) = 0.019] were used after absorption correction (T_{min} = 0.774, T_{max} = 0.935). Refinement of 766 parameters converged to R_1 = 0.0339 [for 13595 reflections having $I > 2\sigma(I)$], wR_2 = 0.0823 and goodness-of-fit of 1.03 (for all 13595 F^2 data). Peak/hole 0.56/-0.91 e Å^{-3}.

3. Results and Discussion

3.1. Syntheses and characterization

Reaction of $SPBn_3$ with $[Cu(MeCN)_4]PF_6$ afforded the 1:2 complex, $[Cu(CH_3CN)(SPBn_3)_2]PF_6$, whereas its reaction with $[Ag(MeCN)_4]PF_6$ gave a 2:3, compound, *viz.* $[Ag_2(SPBn_3)_3](PF_6)_2$, regardless of the ratio of ligand to metal used. In the infrared spectra both complexes showed the expected downward shift of the ν(P=S) stretching frequency in the free ligand from 577 cm^{-1} to 558 cm^{-1} consistent with sulfur coordination [17]. For $[Cu(CH_3CN)(SPBn_3)_2]PF_6$, the positive ion liquid secondary ionization mass spectrum showed the most intense peak at *m/z* 399 (100%) assignable to $[Cu(SPBn_3)]^+$ with weaker peaks at *m/z* 735 (64%) and 217 (22%) due to the $[Cu(SPBn_3)_2]^+$ and ($[Cu(SPBn)]^+$ ions. Similarly $[Ag_2(SPBn_3)_3](PF_6)_2$ exhibits peaks at *m/z* 781 (83%), 445 (100%) and 261 (20%) assignable to the $[Ag(SPBn_3)_2]^+$, $[Ag(SPBn_3)]^+$ and $[Ag(SPBn)]^+$ respectively indicating dissociation of the solid state dimer in the gas phase. Similarly, apart from the expected $[PF_6]^-$ septet at 145 ppm, solution ^{31}P NMR spectra (in CD_2Cl_2) exhibit a sharp resonance at 54 ppm for both complexes (cf 45 ppm for the uncomplexed ligand [18]) indicating that the solid state structure is maintained in solution.

3.2. Molecular structures

3.2.1. $[Cu(CH_3CN)(SPBn_3)_2]PF_6$

The crystal structure of $[Cu(CH_3CN)(SPBn_3)_2]PF_6$ shows it to contain discrete 3-coordinate $[Cu(CH_3CN)(SPBn_3)_2]^+$ cations and $[PF_6]^-$ anions (Fig. 1 and Table 1). The Cu atom lies in the plane formed by the two coordinated sulfur atoms and the nitrogen from the coordinated acetonitrile molecule. The two Cu-S bond lengths at 2.2825(11) and 2.2453(12) Å are similar to those found in the trigonal-planar trimethylphosphane sulfide complex, $[Cu(SPMe_3)_3]ClO_4$ [2.253(5)-2.264(5) Å][5] and to those in the complex, $[CuCl(SPMe_3)]_3$, where the sulfide is bridging [2.264(1)-2.267(2) Å][7]. Cu(I) coordinated acetonitrile complexes are not uncommon [19] [20] [21]. Not unexpectedly, the Cu-N1A bond distance at 1.975(4) Å is shorter than the range [2.054(3) – 2.097(1) Å] observed for the 4-coordinate copper(I) acetonitrile complexes where triphenylphosphane is the co-ligand *viz.* for the complexes $[Cu(CH_3CN)(PPh_3)_3]X$ ($X = ClO_4$, BF_4, SiF_5 and PF_6) [21]. Possibly due to steric crowding in the $SPBn_3$ case, the Cu1-N1A-C2A angle at 167.2(4)°, is close to the Cu-N-C angles found for the SiF_5^- and PF_6^- complexes [165.8(1) and 166.1(1)°] rather than the essentially linear angles in the ClO_4^- and BF_4^- complexes [178.0(2) and 176.6(3)°].

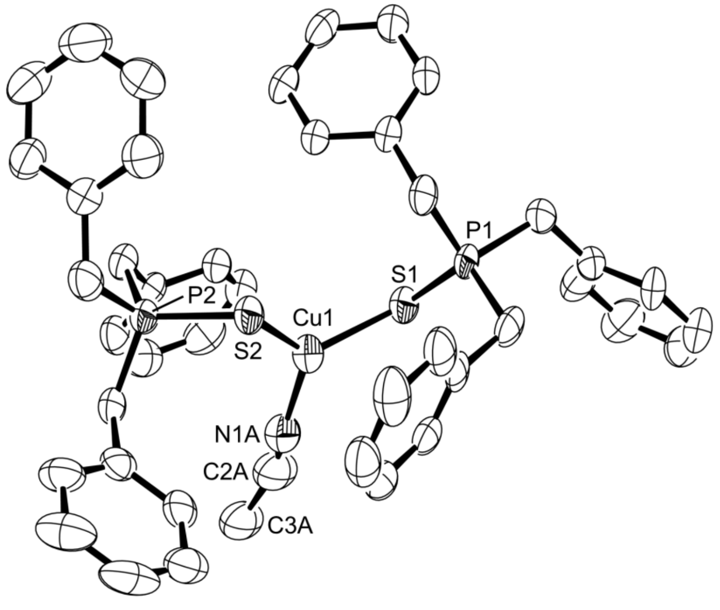

Fig. 1. Solid state structure of [Cu(CH_3CN)($SPBn_3$)$_2$]PF_6. The hydrogen atoms and the PF_6^- anion have been removed for clarity. Ellipsoids are drawn at the 50% probability level.

Table 1

Selected bond lengths (Å) and angles (°) for the complexes.

$[Cu(CH_3CN)(SPBn_3)_2]PF_6$

Atoms	Bond lengths	Atoms	Angles
Cu1 - S1	2.2854(11)	S1- Cu1 - S2	128.05(4)
Cu1 - S2	2.2453(12)	S1 – Cu1 - N1A	104.80(11)
Cu1 - N1A	1.975(4)	S2 – Cu1 - N1A	127.10(11)
S1 - P1	1.9930(14)	Cu1 - S1 - P1	107.56(6)
S2 - P2	2.0008(13)	Cu1 - S2 - P2	104.92(6)
		Cu1 -N1A - C2A	167.2(4)

$[Ag_2(SPBn_3)_3](PF_6)_2$

Atoms	Bond lengths	Atoms	Angles
Ag1 - S1	2.4819(7)	S1 - Ag1 - S3	131.82(2)
Ag1 - S3	2.4834(7)	S1 - Ag1 - C136	101.93(6)
Ag1 - C136	2.633(3)	S3 - Ag1 - C136	125.02(6)
Ag2 - S2	2.4650(7)	S2 - Ag2 - S3	126.34(2)
Ag2 - S3	2.5535(6)	S2 - Ag2 - C236	104.28(6)
Ag2 - C236	2.594(2)	S3 - Ag2 - C236	105.45(6)
Ag2 - C316	2.691 (3)	S2 - Ag2 - C316	117.23 (6)
S1 - P1	1.9887(9)	S3 - Ag2 - C316	87.72 (6)
S2 - P2	1.9951(9)		
S3 - P3	2.0205(8)		

3.2.2. $[Ag_2(SPBn_3)_3](PF_6)_2$

The silver complex is a dinuclear species with the one silver atom (Ag1) being 3-coordinate and the other (Ag2) 4-coordinate (Fig. 2 and Table 1). An interesting feature of the structure is the way in which each terminal tribenzylphosphane sulfide forms a Ag-C η^1-bond [2.594(2) and 2.633(3) Å] with one of the aromatic ring carbon atoms thus blocking the coordination of further $SPBn_3$ ligands. The two Ag centres are linked by a bridging sulfur (S3) and a weaker η^1-interaction [2.691(3) Å] with carbon (C316) from the aromatic ring of the same tribenzylphosphane. The Ag(1) atom is at the centre of a near 'S_2C' trigonal-planar coordination sphere while the coordination sphere of the Ag(2) is in approximately 'S_2C_2' tetrahedral. There are numerous examples in the literature for Ag-C η^1-interactions with aromatic carbon atoms but few have a sulfur atom as a co-ligand [22-25]. The Ag-C η^1-bond lengths observed for $[Ag_2(SPBn_3)_3](PF_6)_2$ are similar to that observed [2.619(5) Å] in a compound where the ligated sulfur atom is in an aliphatic-S from an S_2O_3 macrocycle [24].

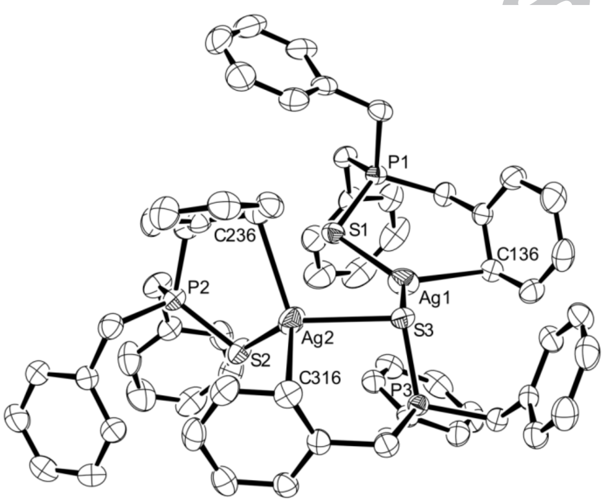

Fig. 2. Solid state structure of $[Ag_2(SPBn_3)_3](PF_6)_2$. The hydrogen atoms and the two PF_6^- anions have been removed for clarity. Ellipsoids are drawn at the 50% probability level.

4. Conclusions

Tribenzylphosphane sulfide reacted with $[Cu(MeCN)_4]PF_6$ to give the 1:2 complex, $[Cu(CH_3CN)(SPBn_3)_2]PF_6$, rather than a complex with three phosphane sulfides coordinated. It appears that the coordination of a third phosphane sulfide is blocked by the bulkiness of the other two. In contrast the reaction of the sulfide with the larger Ag(I) centre afforded a 2:3, compound, *viz.* $[Ag_2(SPBn_3)_3](PF_6)_2$, which contains both 3- and 4-coordinate Ag(I) centres achieved via bridging sulfur atoms and Ag-C η^1-bonds. If it can, silver(I) readily increases its coordination sphere by interacting with other donor groups. For example, with diphenyl(2-pyridyl)phosphane sulfide, $SPPh_2py$, the Ag complex, $[Ag(SPPh_2py)_2]BF_4$, is not 2-coordinated but lies in a quasi-tetrahedral sphere with both S and both N atoms bound [26]. In contrast the parent phosphane, PBn_3, forms two-coordinate complexes of the type $[Cu(PBn_3)_2]PF_6$ and $[Ag(PBn_3)_2]PF_6$ since the ligand can block further coordination by non-covalent interactions between the phenyl groups of the two ligands which sweep back over the metal to an intramolecular form of the sixfold phenyl embrace.

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Appendix A. Supplementary material

CCDC 1406094 and 1406095 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or from the CCDC, 12 Union Road, Cambridge, CB21EZ,UK; E-mail: deposit@ccdc.cam.ac.uk.

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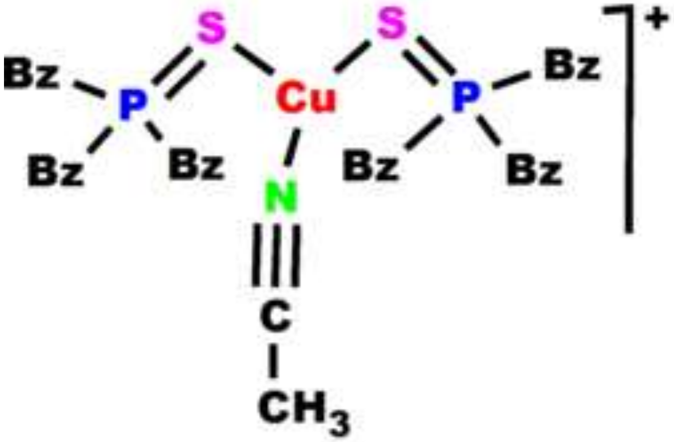
Graphical Abstract

The bulky tertiary phosphane sulfide, $SPBn_3$, reacts with Cu(I) to form 3-coordinate $[Cu(CH_3CN)(SPBn_3)_2]PF_6$ whereas with Ag(I) it forms dinuclear $[Ag_2(SPBn_3)_3](PF_6)_2$ which contains both 3- and 4-coordinated Ag. The Ag atoms are linked by a bridging sulfur and a carbon from the aromatic ring of the same $SPBn_3$.



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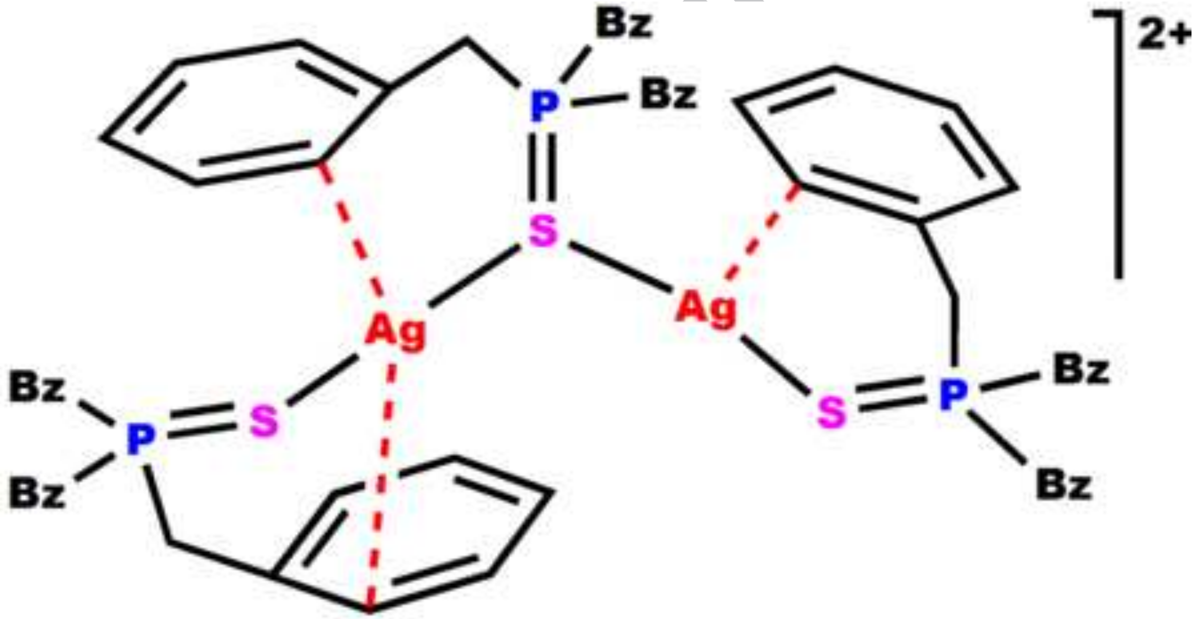

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