partial structure expansion gave postions for the *N*-MeIm ligands. Subsequent least-squares refinement (SHELXS-76)[39,40] and difference Fourier syntheses revealed positions for the disordered sulfur atoms. Hydrogen atoms were included as fixed contributors in idealized positions. In the final cycle of least squares, anisotropic thermal coefficients were refined for non-hydrogen atoms and a common isotropic thermal parameter was varied for hydrogen atoms. Owing to the high correlation coefficients (see supplementary material), the S1-S2 and S7-S8 bond lengths were constrained to a free variable (±0.005 Å) preceding each refinement cycle. Successful convergence was indicated by the maximum shift/error (0.07) for the final cycle. The highest peaks in the final difference Fourier map were in the vicinity of the disordered atom S7 (and consequently S2). A final analysis of variance between observed and calculated structure factors showed no apparent systematic errors with respect to Miller index, sin θ, or amplitude.

Refinement of an ordered model in the acentric space group converged with non-positive-definite thermal coefficients, unreasonable bond length ranges (Ni-N, 2.01-2.25 Å, and S-S, 1.87-2.34 Å), distorted imidazole ring geometries, greater residual electron density, and higher agreement factors. Refinement with no constraints in the centric space group converged with nonsensical thermal coefficients for S7. A subsequent Fourier synthesis located maximum residual electron density in the vicinity of atom S7 (and S2). Attempts to refine a more complex model with additional disorder for site S7 were not successful.

Details on the data collection are presented in Table V while atomic coordinates and thermal parameters are listed in Tables VI and VII.

Acknowledgment. This research was supported by the National Science Foundation through Grant DMR-89-20538. We thank Gregory S. Girolami and Shifang Luo for helpful discussions.

Supplementary Material Available: Plots of magnetism data, an ORTEP diagram of the disordered S_8^{2-} anion, and tables of thermal parameters, bond distances and angles, and hydrogen atom positions (8 pages); a structure factor table (11 pages). Ordering information is given on any current masthead page.

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(39) The function minimized was $\Sigma w([F_o] - [F_c])^2$.

(40) Atomic scattering factors were taken from: *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Contribution from the Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742-2021, Department of Chemistry, University of Delaware, Newark, Delaware 19716, Department of Chemistry, City of London Polytechnic, London EC3N 2EY, U.K., and U.S. Naval Research Laboratory, Code 6030, Washington, D.C. 20375

Polydentate Ligands Containing Phosphorus. 13. Synthesis and Molecular Structure of (Tri-*n*-butylphosphine)[tris(diphenylthiophosphinoyl)methanido]silver(I), $(n\text{-}Bu)_3PAg\{[(S)PPh_2]_3C\}$[1]

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The synthesis, NMR spectra, and molecular structure are described for (tri-*n*-butylphosphine)[tris(diphenylthiophosphinoyl)-methanido]silver(I). The compound crystallizes in monoclinic space group $P2_1/c$, with a = 18.192 (3) Å, b = 12.986 (2) Å, c = 21.194 (5) Å, β = 109.42 (1)°, and Z = 4. The molecule possesses pseudotetrahedral geometry about silver with the anionic ligand bonded via the three sulfur atoms in a tripodal, tridentate fashion with an average Ag-S bond length of 2.63 Å. The Ag-P (tri-*n*-butylphosphine) bond length is 2.402 (3) Å. The ^{31}P NMR spectrum at ambient temperature indicates $^1J(^{107}Ag-^{31}P)$ and $^1J(^{109}Ag-^{31}P)$ of 488.3 and 564.0 Hz, respectively, as well as $^3J(^{31}P-^{31}P)$ of 7.3 Hz.

Introduction

Tris(diphenylthiophosphinoyl)methanide, $\{[Ph_2P(S)]_3C\}^-$ (**1**), is the prototype of a recently discovered series of uninegative ligands[1a,3-6] that are related to **1** via replacement of the phenyl groups by other organic groups such as methyl[5,7-9] or replacement of one or more sulfur atoms by other chalcogens such as oxygen or selenium.[1a,6,10] These ligands can bond in a tridentate manner as has been shown in the case of a mercury(II) complex, $\{[Ph_2P(S)][Me_2P(S)]_2C\}HgCl$,[5,7] of the tetramethyl analogue of **1** or in a bidentate mode as in a platinum(II) complex, $Et_3PPtCl\{[(S)PPh_2]_3C\}$,[11] of **1** and in scandium, yttrium, and lutetium complexes, $M\{[(O)PPh_2]_3C\}_3$,[12] of the trioxide analogue of **1**.

This paper describes a convenient general method for the synthesis of complexes of this type of ligand as exemplified by the first silver complex, $(n\text{-}Bu)_3PAg\{[(S)PPh_2]_3C\}$ (**2**),[1b,c] containing the trisulfide ligand **1**. Also reported are the molecular structure and multinuclear NMR data for **2**. This is the first crystal structure reported in which **1** behaves as a tripodal ligand.

Experimental Section

$[(n\text{-}Bu)_4N]\{[Ph_2P(S)]_3C\}$ was prepared as described earlier.[4,6] $(n\text{-}Bu)_3P$ was obtained from Strem Chemicals, Inc., and distilled before use. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN.

Synthesis of $(n\text{-}Bu)_3PAg\{[(S)PPh_2]_3C\}$ (2). To a mixture of 0.90 g (1.0 mmol) of $[(n\text{-}Bu)_4N]\{[Ph_2P(S)]_3C\}$ and 0.20 g (1.0 mmol) of (n-

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(1) (a) Part 12: Grim, S. O.; Sangokoya, S. A.; deLaubenfels, E.; Colquhoun, I. J.; McFarlane, W. *Phosphorus Sulfur* **1988**, *38*, 79. (b) First reported at the International Conference on Phosphorus Chemistry, Nice, France, Sept 1983. (c) Grim, S. O. *Phosphorus Sulfur* **1983**, *18*, 283.

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Table I. Crystallographic Data for $(n\text{-Bu})_3\text{PAg}\{[(\text{S})\text{PPh}_2]_3\text{C}\}$ (**2**)

formula	$C_{49}H_{57}AgP_4S_3$	fw	973.93
space group	$P2_1/c$	temp, K	173 ± 2
a, Å	18.192 (3)[a]	μ(Mo Kα)	7.1
b, Å	12.986 (2)	λ, Å	0.71073
c, Å	21.194 (5)	D(calc), g cm^{-3}	1.37
β, deg	109.42 (1)	$R(F)$, %	7.22
V, Å^3	4722 (1)	$R(wF)$, %	8.51
Z	4		

[a] Unit cell parameters obtained from the least-squares best fit of the angular settings of 15 reflections (22° < 2θ < 30°).

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (Å^2 $\times$ 10^3) for **2**[a]

atom	x	y	z	U[b]
Ag	2477 (1)	728 (1)	1758 (1)	49 (1)
S(1)	1811 (1)	883 (2)	2688 (1)	32 (1)
S(2)	3847 (1)	48 (2)	2439 (1)	32 (1)
S(3)	1784 (1)	−1002 (2)	1175 (1)	34 (1)
P(1)	1827 (1)	−605 (2)	2916 (1)	21 (1)
P(2)	3521 (1)	−855 (2)	3063 (1)	21 (1)
P(3)	2287 (1)	−1924 (2)	1950 (1)	22 (1)
P(4)	2207 (2)	2144 (2)	986 (1)	45 (1)
C(1)	2562 (4)	−1350 (5)	2750 (4)	17 (3)
C(2)	2608 (7)	2068 (9)	302 (6)	67 (6)
C(3)	2496 (10)	977 (12)	−16 (9)	115 (9)
C(4)	2860 (12)	594 (16)	−307 (17)	261 (23)
C(5)	2774 (9)	−452 (11)	−586 (10)	126 (10)
C(6)	2528 (9)	3444 (8)	1301 (6)	93 (7)
C(7)	2586 (9)	3703 (10)	1971 (8)	94 (8)
C(8)	3262 (10)	3390 (10)	2529 (7)	103 (8)
C(9)	3425 (15)	3693 (12)	3162 (8)	203 (15)
C(10)	1188 (7)	2287 (10)	540 (7)	72 (6)
C(11)	712 (9)	2502 (21)	956 (9)	201 (15)
C(12)	−147 (8)	2495 (16)	647 (8)	137 (10)
C(13)	−499 (10)	1402 (12)	634 (8)	134 (9)
C(21)	613 (3)	−2030 (4)	2759 (2)	33 (3)
C(22)	−126	−2437	2434	42 (4)
C(23)	−610	−1985	1845	48 (4)
C(24)	−354	−1126	1581	48 (4)
C(25)	385	−719	1907	36 (3)
C(26)	869	−1171	2496	26 (3)
C(31)	2186 (3)	−1660 (4)	4144 (3)	33 (3)
C(32)	2202	−1764	4804	43 (4)
C(33)	1946	−958	5114	50 (4)
C(34)	1674	−49	4764	58 (5)
C(35)	1657	54	4104	44 (4)
C(36)	1913	−751	3794	25 (3)
C(41)	3859 (4)	−652 (3)	4463 (3)	34 (3)
C(42)	4030	−85	5054	44 (4)
C(43)	4032	989	5033	48 (4)
C(44)	3863	1495	4420	43 (4)
C(45)	3692	928	3829	33 (3)
C(46)	3690	−145	3851	25 (3)
C(51)	3993 (3)	−2768 (4)	3660 (3)	35 (3)
C(52)	4489	−3617	3845	43 (4)
C(53)	5169	−3653	3679	48 (4)
C(54)	5355	−2840	3329	45 (4)
C(55)	4860	−1991	3145	35 (3)
C(56)	4179	−1955	3310	28 (3)
C(61)	1812 (3)	−3645 (4)	2512 (2)	31 (3)
C(62)	1342	−4498	2502	44 (4)
C(63)	716	−4727	1927	55 (5)
C(64)	560	−4103	1361	54 (4)
C(65)	1030	−3250	1371	40 (4)
C(66)	1656	−3021	1946	29 (3)
C(71)	3414 (3)	−3487 (4)	2084 (3)	31 (3)
C(72)	4060	−3920	1968	38 (3)
C(73)	4420	−3398	1574	47 (4)
C(74)	4135	−2444	1297	45 (4)
C(75)	3489	−2012	1413	31 (3)
C(76)	3129	−2534	1807	25 (3)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Bond Lengths (Å) in **2**[a]

Ag–S(1)	2.639 (3)	P(3)–C(66)	1.828 (6)
Ag–S(2)	2.585 (2)	P(3)–C(76)	1.836 (6)
Ag–S(3)	2.670 (2)	P(4)–C(2)	1.828 (15)
Ag–P(4)	2.402 (3)	P(4)–C(6)	1.838 (11)
S(1)–P(1)	1.990 (3)	P(4)–C(10)	1.788 (12)
S(2)–P(2)	1.999 (3)	C(2)–C(3)	1.554 (20)
S(3)–P(3)	1.991 (3)	C(3)–C(4)	1.156 (37)
P(1)–C(1)	1.779 (8)	C(4)–C(5)	1.468 (27)
P(1)–C(26)	1.827 (5)	C(6)–C(7)	1.426 (22)
P(1)–C(36)	1.822 (6)	C(7)–C(8)	1.452 (19)
P(2)–C(1)	1.767 (7)	C(8)–C(9)	1.333 (23)
P(2)–C(46)	1.840 (6)	C(10)–C(11)	1.452 (26)
P(2)–C(56)	1.824 (5)	C(11)–C(12)	1.480 (20)
P(3)–C(1)	1.764 (8)	C(12)–C(13)	1.554 (25)

[a] Estimated standard deviations in the least significant digits are given in parentheses.

Bu)$_3$P in 40 mL of CHCl$_3$ was added 0.17 g (1.0 mmol) of solid AgNO$_3$. The mixture was stirred under N$_2$ for about 3 h, during which time a colorless solution was formed. Ethanol (50 mL) was added to the solution followed by concentration by rotary evaporation. The white precipitate which formed was recrystallized from CH$_2$Cl$_2$/EtOH (1:1) to give a 58% yield of **2**, mp 210 °C dec. Anal. Calcd for $C_{49}H_{57}AgP_4S_3$: C, 60.43; H, 5.90; P, 12.72. Found: C, 60.53; H, 6.13; P, 12.60.

NMR spectra were recorded on a Bruker WP 200 Fourier transform spectrometer operating at 81.0 MHz for ^{31}P and 50.3 MHz for ^{13}C. Triple-resonance experiments, ^{31}P{^{1}H,^{107}Ag}, were performed with a JEOL FX60 Fourier transform spectrometer with an additional coil wound within the probe, and rf power at the ^{107}Ag resonant frequency was provided by a GenRad Model 1061 frequency synthesizer via a tuned amplifier and matching network. Typically, the available $\gamma B_2/2\pi$ was 200 Hz, thus permitting an initial search for a resonant frequency to be undertaken in steps of 300 Hz. ^{31}P chemical shifts are referenced to external 85% H$_3$PO$_4$ and are reported as positive to the high-frequency (deshielded) side of the reference. ^{13}C chemical shifts are referenced to internal CDCl$_3$.

X-ray Structural Determination. A colorless crystal of **2** obtained by recrystallization from CH$_2$Cl$_2$/Et$_2$O was sealed in a glass capillary tube. Preliminary photographic characterization revealed $2/m$ Laue symmetry; systematic absences in the diffraction data uniquely determined the space group to be $P2_1/c$. No correction for absorption was required.

The structure was solved by heavy-atom methods and completed by a series of difference Fourier syntheses. The butyl groups showed expected high thermal activity and may be present in several similar but unresolvable configurations. Two of the butyl group distances, C(3)–C(4) and C(8)–C(9), are unreasonably short, 1.16 (2) and 1.33 (2) Å, respectively, an artifact of unresolved disorder. All non-hydrogen atoms were refined (blocked-cascade) with anisotropic thermal parameters, and all hydrogen atoms were incorporated as idealized, isotropic contributions. The phenyl rings were treated as rigid hexagons (d_{CC} = 1.395 Å).

Computer programs and sources of scattering factors are contained in the SHELXTL (5.1) program library (G. Sheldrick, Nicolet XRD, Madison, WI). Crystallographic data are given in Table I. Table II contains the atomic coordinates, and Tables III and IV contain selected bond distances and angles, respectively.

Results

The silver complex, $(n\text{-Bu}_3\text{P})\text{Ag}\{[(\text{S})\text{PPh}_2]_3\text{C}\}$ (**2**), has been prepared in 58% yield by the methasis of $[n\text{-Bu}_4]\{[\text{Ph}_2\text{P}(\text{S})]_3\text{C}\}$ and AgNO$_3$ in the presence of n-Bu$_3$P, all in equimolar amounts in chloroform solution. It is a colorless, air-stable, high-melting (210 °C dec) crystalline solid. The molecular structure of **2** has been determined by X-ray crystallography. The structure is shown in Figure 1, with a stereoview given in Figure 2. The phosphorus-31 NMR spectrum at room temperature reveals one-bond coupling of the tributylphosphine phosphorus with ^{107}Ag and ^{109}Ag of 488.3 and 564.0 Hz, respectively, and also three-bond ^{31}P–^{31}P coupling of 7.3 Hz. The spectrum is reproduced in the supplementary material.

Discussion

The isolation of the anion **1** as an air-stable salt[4,13] with lithium or an onium cation, such as tetra-n-butylammonium, allows easy access to coordination compounds of metal salts via simple metathesis. It is important that an onium salt of **1** rather than the

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Table IV. Bond Angles (deg) in **2**[a]

S(1)–Ag–S(2)	101.9 (1)	C(2)–P(4)–C(6)	100.1 (7)
S(1)–Ag–S(3)	98.4 (1)	Ag–P(4)–C(10)	112.4 (5)
S(2)–Ag–S(3)	101.0 (1)	C(2)–P(4)–C(10)	101.7 (6)
S(1)–Ag–P(4)	114.1 (1)	C(6)–P(4)–C(10)	104.2 (6)
S(2)–Ag–P(4)	125.6 (1)	P(1)–C(1)–P(2)	116.1 (4)
S(3)–Ag–P(4)	111.8 (1)	P(1)–C(1)–P(3)	115.4 (4)
Ag–S(1)–P(1)	97.7 (1)	P(2)–C(1)–P(3)	116.4 (5)
Ag–S(2)–P(2)	97.3 (1)	P(4)–C(2)–C(3)	111.3 (11)
Ag–S(3)–P(3)	96.2 (1)	C(2)–C(3)–C(4)	127.4 (18)
S(1)–P(1)–C(1)	115.6 (3)	C(3)–C(4)–C(5)	127.5 (23)
S(1)–P(1)–C(26)	109.7 (2)	P(4)–C(6)–C(7)	119.2 (10)
C(1)–P(1)–C(26)	110.0 (3)	C(6)–C(7)–C(8)	120.5 (15)
S(1)–P(1)–C(36)	109.8 (2)	C(7)–C(8)–C(9)	125.6 (17)
C(1)–P(1)–C(36)	109.3 (3)	P(4)–C(10)–C(11)	114.9 (10)
C(26)–P(1)–C(36)	101.5 (3)	C(10)–C(11)–C(12)	119.0 (15)
S(2)–P(2)–C(1)	115.9 (3)	C(11)–C(12)–C(13)	112.4 (17)
S(2)–P(2)–C(46)	107.9 (2)	P(1)–C(26)–C(21)	121.2 (2)
C(1)–P(2)–C(46)	111.7 (4)	P(1)–C(26)–C(25)	118.8 (2)
S(2)–P(2)–C(56)	109.8 (2)	P(1)–C(36)–C(31)	121.7 (2)
C(1)–P(2)–C(56)	107.1 (3)	P(1)–C(36)–C(35)	118.2 (2)
C(46)–P(2)–C(56)	103.7 (2)	P(2)–C(46)–C(41)	121.7 (1)
S(3)–P(3)–C(1)	116.3 (3)	P(2)–C(46)–C(45)	118.2 (1)
S(3)–P(3)–C(66)	110.5 (2)	P(2)–C(56)–C(51)	119.6 (2)
C(1)–P(3)–C(66)	108.1 (3)	P(2)–C(56)–C(55)	120.4 (2)
S(3)–P(3)–C(76)	107.6 (2)	P(3)–C(66)–C(61)	120.1 (2)
C(1)–P(3)–C(76)	110.7 (3)	P(3)–C(66)–C(65)	119.9 (2)
C(66)–P(3)–C(76)	102.7 (3)	P(3)–C(76)–C(71)	121.8 (2)
Ag–P(4)–C(2)	116.9 (4)	P(3)–C(76)–C(75)	118.2 (2)
Ag–P(4)–C(6)	119.2 (4)		

[a] Estimated standard deviations in the least significant digits are given in parentheses.

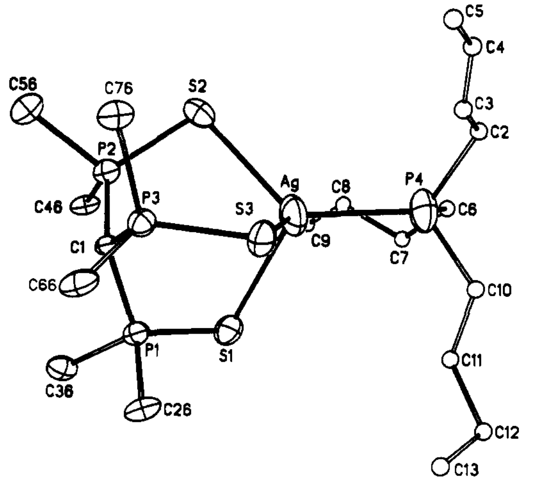

Figure 1. Molecular structure and labeling scheme for $(n\text{-Bu})_3$PAg{[(S)PPh$_2$]$_3$C}. Phenyl rings are depicted as the ipso carbon atoms only for clarity. Thermal ellipsoid probability is 50%.

lithium salt be used in the specific case of silver(I) because the lithium salt causes partial reduction to metallic silver. The lithium salt has been used successfully for the metathetical syntheses of other complexes of **1**.[5]

The molecular structure determination shows that silver has pseudotetrahedral geometry with coordination to phosphorus of the neutral tributylphosphine ligand and to the three sulfurs of **1**, which behaves as an anionic tripod. The cage of six-membered chelate rings is rather flat at the tricoordinated bridgehead carbon (mean ∠PCP = 116.0 (6)°) but less so at the silver bridgehead (mean ∠SAgS = 100.4 (15)°). The angles subtended at sulfur within the cage are small (mean ∠PSAg = 97.1 (6)°) compared to the angles at sulfur in the monodentate phosphine sulfide copper(I) complex [Me$_3$PS)$_3$Cu]ClO$_4$,[14] whose ∠PSCu's range from 104.3 (3) to 110.3 (3)°. The structural parameters in $(n\text{-Bu})_3$PAg{[(S)PPh$_2$]$_3$C} are quite similar to those in the analogous mercury cage complex {[Ph$_2$P(S)][Me$_2$P(S)]$_2$C}HgCl,[5] in which the mean PCP and PSHg angles are 116.4 (7) and 96.2 (11)°, respectively. In the silver complex, the mean P–C and P–S bond lengths are 1.770 (10) and 1.993 (5) Å, respectively, compared to 1.753 (8) and 2.019 (3) Å (for the Ph$_2$P–S group), respectively, for the same bonds in the mercury complex.

Table V. Structural and NMR Parameters for [Ph$_2$P(S)]$_3$CH and Derivatives

parameter[a]	[Ph$_2$P(S)]$_3$CH (**3**)[b]	anion **1**[c]	Ag complex **2**
mean d(P–S), Å	1.944	1.980	1.992
mean d(P–C), Å	1.883	1.759	1.776
mean ∠PCP, deg	115.3	119.9	115.5
mean ∠CPS, deg	112.5	117.5	116.6
^2J(P–P)[d]	<2	24.5	12.8
^1J(P–C)	22.3	75.7	50.7
δ(P)	46.9	44.0	42.7
$\delta(C_{\text{methine}})$	52.1	33.1	32.9
$\delta(C_{\text{ipso}})$	130.5	138.3	134.7
$\delta(C_{\text{ortho}})$	133.2	134.2	134.0
$\delta(C_{\text{meta}})$	129.2	125.8	126.6
$\delta(C_{\text{para}})$	130.7	128.4	129.8
$^1J(P{-}C_{\text{ipso}})$	84.2	86.7	89
$^3J(P{-}C_{\text{ipso}})$	1.5	2.8	
$^2J(P{-}C_{\text{ortho}})$	10.7	10.4	9.8
$^3J(P{-}C_{\text{meta}})$	13.2	12.2	12.2
$^4J(P{-}C_{\text{para}})$	2.9	<2	<2

[a] δ in ppm and J in Hz. [b] Reference 29. [c] Reference 13. [d] Calculated from the ^{13}C resonance of the phenyl ipso carbon, which is the A part of an AXX'$_2$ spin system.

Comparisons of NMR and structural data are given in Table V for the neutral parent [Ph$_2$P(S)]$_3$CH (**3**), the uncomplexed anion **1**, and the silver cage complex **2**. Upon anion formation, the central C–P bonds shorten and the PCP angles increase. Both of these changes are due to the change of hybridization, i.e. an increase in s character, of the central carbon from that of four-coordination in **3** to three-coordination in **1**. Mesomeric stabilization in **1** contributes to making the P–C bond order in **1** greater than unity. At the same time, ^1J(P–C) and ^2J(P–P) both increase from **3** to **1** (anion formation), as expected from the greater s character of the C hybrids. Upon complex formation by the anion (**1** to **2**), the central carbon is no longer planar and the PCP angles decrease to an average of 116°. However, since the carbon is only three-coordinate, some mesomeric character remains. As a consequence, the P–C bond lengths in complex **2** increase slightly from the anion **1** values and ^1J(P–C) and ^2J(P–P) are intermediate between those in **3** and **1**. The mean P–S bond length increases from **3** to the anion **1**, as would be expected from a decrease of the contribution of the P═S canonical form and an increase of the P$^+$—S$^-$ canonical form in going from the neutral **3** to the anion **1**. A slight further lengthening is observed upon coordination of the anion (**1** to **2**), as is expected when phosphine chalcogenides undergo complexation.

The phosphorus-31 NMR spectrum (24.2 MHz) in conjunction with ^{31}P{^{107}Ag,^{1}H} triple-resonance experiments confirms that this structure (Figure 1) is essentially maintained in solution and shows that even at room temperature exchange of the ligands is slow on an NMR time scale. The resonance due to $(n\text{-Bu})_3$P (δ −4.8 ppm) is a pair of doublets owing to splitting by ^{107}Ag [$I = {}^1/_2$; natural abundance 51.82%; ^1J(Ag–P) = 488.3 Hz] and ^{109}Ag [$I = {}^1/_2$; natural abundance 48.18%; ^1J(Ag–P) = 564.0 Hz], and each component is further split into a 1:3:3:1 quartet by coupling to the three equivalent phosphorus nuclei of the tripodal ligand with ^3J(P–P) = 7.3 Hz. The phosphorus nuclei of the tripod resonate at δ 42.7 ppm and show doublet splittings due to ^3J(P–P) of 7.3 Hz and a mean ^2J(^{107,109}Ag–P) of 4.0 Hz. The ^{107}Ag chemical shift is −235 ppm relative to {Ag[(EtO)$_3$P]$_4$}NO$_3$.[15]

In tetrahedral (sp^3) silver complexes ^1J(^{107}Ag–^{31}P) is normally in the range 190–235 Hz for tertiary phosphines[16-22] with

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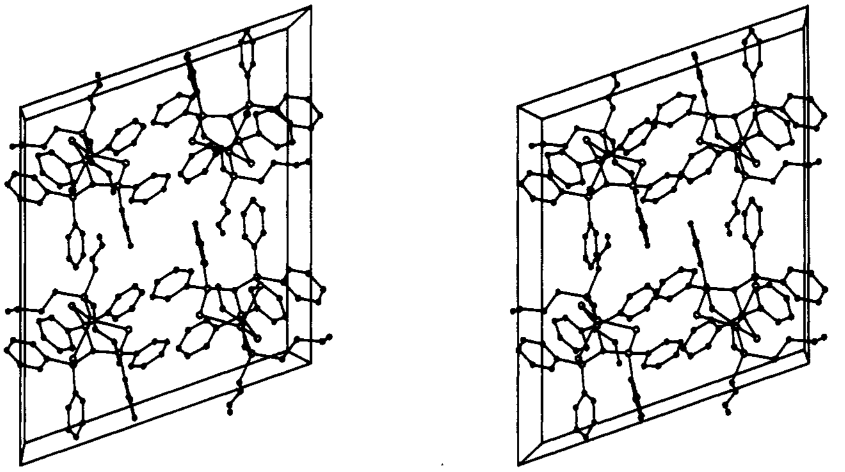

Figure 2. Stereo packing diagram for $(n\text{-Bu})_3PAg\{[(S)PPh_2]_3C\}$ as viewed along the *b* axis.

somewhat higher values for phosphites[15,16] and aminophosphines.[21] In the series $(R_3P)_nAgX$, $^1J(^{107}Ag-^{31}P)$ increases with decreasing n; i.e., the lower the coordination number of silver, the greater the s character of the silver hybrid and the larger the coupling constant. In addition, the Ag–P bond length generally decreases with decreasing n, larger s character in the silver hybrid, and less steric hindrance about silver. For example, in the series L_nAgX where n = 1–4 the values of $^1J(^{107}Ag-^{31}P)$ for L = Ph_3P and X = NO_3^- are 780, 470, 310, and 190 Hz, respectively.[23] For L = $(n\text{-Bu})_3P$ and X = BF_4^- the respective values are 759, 470, 304, and 219 Hz.[21] The Ag–P bond lengths in $(Ph_3P)_nAgNO_3$ for n = 1–4 are 2.369, 2.441 (mean), 2.566 (mean), and 2.657 (mean) Å, respectively.[23] $^1J(^{107}Ag-^{31}P)$ for **2** is a very large value (488 Hz) for tetrahedral Ag(I) complexes and actually falls in the range of two-coordinate silver phosphine complexes. Also, the Ag–P bond length of 2.402 (3) Å in **2** is very short compared to those of other tertiary phosphine complexes and is smaller than those normally observed in two-coordinate L_2Ag^+ complexes, for which the range is 2.440–2.519 Å.[17] $[(Me_2N)_3P]_2Ag^+$ has a Ag–P bond length of 2.39 Å. All three Ag–S bonds (range 2.585–2.670 Å) in **2** are significantly longer than the nonbridging Ag–S bonds (range 2.433–2.487 Å)[24-26] observed in tetrahedral thiourea complexes of silver. These observations indicate a very high s character in the silver hybrid orbital bonded to $(n\text{-Bu})_3P$ and correspondingly high p character for the Ag–S bonds.

In comparison with a recently published[27] structure of $[AgCH_2P(S)Ph_2]_2$, a dimer in which each $[CH_2P(S)Ph_2]^-$ ligand bonds to two different Ag atoms via carbon of the CH_2– group and sulfur of the P(S)– group, the mean P–C distance (1.770 Å) and the mean P–S distance (1.993 Å) in **2** are of about the same magnitude as the respective P–C and P–S distances (1.795 and 2.007 Å) in the dimer. However, all three Ag–S bond lengths in **2** are signficantly longer than the Ag–S bond (2.382 Å) in the dimer. This probably arises from both the silver (vide infra) and sulfur hybrid orbitals in **2** containing less s character than in the case of the dimer, in which the coordination about silver is two-coordinate and nearly linear (∠CAgS = 173.7°) although there is also a Ag–Ag interaction at 2.990 Å.

The s character of the silver hybrid to $(n\text{-Bu})_3P$ calculated[27] from the six angles about silver in the crystal structure of **2** is 52%. The mean p character of each of the hybrids to the three sulfurs is 84%. The 52% s character of the silver hybrid to $(n\text{-Bu})_3P$ places this four-coordinate silver complex in the range of two-coordinate silver complexes as far as the properties of the P–Ag bond are concerned and is also in accord with the very large value of $^1J(^{107}Ag-^{31}P)$ as noted above. The large s character may also explain the unusual kinetic stability of the $(n\text{-Bu})_3P$–Ag bond at room temperature. Except for chelating di(tertiary phosphines)[20] and bulky tertiary phosphines,[18] R_3P–Ag complexes normally undergo rapid exchange on an NMR time scale in solution at room temperature.

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Supplementary Material Available: A figure of the ^{31}P NMR spectrum of **2** and tables of crystallographic and refinement parameters, bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates (6 pages); a table of observed and calculated structure factors (58 pages). Ordering information is given on any current masthead page.

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