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Synthesis and Structural Characterization of Neutral Silver(I) Complexes with Arenephosphinothiols. Crystal Structures of [Ag_4{2-(Ph_2P)-6-(Me_3Si)C_6H_6S}$_4$] and [Ag_4{2-(Ph_2PO)-6-(Me_3Si)C_6H_3S}$_4$]

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Silver complexes of the anionic forms of 2-(diphenylphosphino)benzenethiol [2-(Ph_2P)C_6H_4SH] (**1**), 2-(diphenylphosphino)-6-(trimethylsilyl)benzenethiol [2-(Ph_2P)-6-(Me_3Si)C_6H_3SH] (**2**), and 2-(diphenylphosphinyl)-6-(trimethylsilyl)benzenethiol [2-(Ph_2PO)-6-(Me_3Si)C_6H_3SH] (**3**) have been prepared by an electrochemical procedure and characterized by spectroscopic (IR, ^1H, ^{13}C, and ^{31}P NMR) methods, and ligand **3** and [Ag_4{2-(Ph_2P)-6-(Me_3Si)C_6H_3S}$_4$] (**5**) and [Ag_4{2-(Ph_2PO)-6-(Me_3Si)C_6H_3S}$_4$] (**6**) complexes were characterized by X-ray crystallographic techniques. Crystal data for **3**: $C_{21}H_{23}OPSSi$, monoclinic, $P2(1)/n$, $a = 11.3730(4)$ Å, $b = 11.1562(4)$ Å, $c = 17.1153(6)$ Å, $\beta = 103.961(1)°$, $V = 2107.4(1)$ Å^3, $Z = 4$, 2730 reflections with $I_o > 2\sigma(I_o)$, $R = 0.0621$. Crystal data for **5**: $C_{84}H_{88}Ag_4P_4S_4Si_4$, tetragonal, $P4(2)2(1)2$, $a = 18.8454(7)$ Å, $b = 18.8454(7)$ Å, $c = 24.596(2)$ Å, $V = 8735.1(7)$ Å^3, $Z = 4$, 4676 reflections with $I_o > 2\sigma(I_o)$, $R = 0.0286$. Crystal data for **6**: $C_{90}H_{97}Ag_4N_3O_4P_4S_4Si_4$, trigonal, $P1$, $a = 13.4567(1)$ Å, $b = 14.4148(2)$ Å, $c = 14.8080(2)$ Å, $\alpha = 99.130(1)°$, $\beta = 98.815(1)°$, $g = 114.211(1)°$, $V = 2509.38(5)$ Å^3, $Z = 1$, 6345 reflections with $I_o > 2\sigma(I_o)$, $R = 0.0505$. The [Ag_4{2-(Ph_2P)-6-(Me_3Si)C_6H_3S}$_4$] (**5**) compound is tetranuclear with an array of four silver atoms bridged by four sulfur atoms. Each silver atom has a distorted trigonal [AgS_2P] environment with each ligand acting as P,S bidentate S-bridging ligand. The [Ag_4(2-(Ph_2PO)-6-(Me_3Si)C_6H_3S}$_4$] (**6**) complex is also tetranuclear, but in this case two of the silver atoms are [AgO_2S_2] tetracoordinated and the other two Ag atoms are [AgS_2] two coordinated.

Introduction

It is well-known that metal thiolate complexes adopt geometries of variable nuclearities and great structural complexity. These features are the result of the tendency of thiolate ligands to bridge metal centers to yield oligomeric or polymeric species.[1−3] These aggregation phenomena may be limited by a number of expedients. (a) Steric constraints may be introduced by appropriate ligand design, for example, using bulky groups close to the sulfur atom that might modify the degree of aggregation as a result of steric hindrance. Thus, for example, the crystal structure of [$M(SPh)_2$] (M = Zn or Cd),[4] with SPh^- ligands, which may be regarded as prototypes for sterically less hindered ligands, are polynuclear. However, the presence of a methyl group in the ortho position on the phenyl ring gives a heptanuclear cadmium complex,[5] and the presence of three bulkier *tert*-butyl groups in the ring allows the formation of binuclear compounds [$M(SC_6H_2tBu_3$-2,4,6$)_2]_2$ (M = Zn[6] or Cd[7]). A similar situation is found in the silver chemistry. In the case of a relatively unencumbered ligand such as $(Me_3Si)CH_2S^-$, the compound is polymeric, while with the more hindered ligand $(Me_3Si)_2CHS^-$, the compound is octanuclear, and the bulkier ligands $(Me_3Si)_3CS$ and $(Me_2PhSi)_2CS^-$ allow the formation of tetra- and trinuclear complexes, respectively.[8] (b) Auxiliary or coligands may be introduced to block some of the coordination sites around the metal. An example is the monomeric complex [$Zn(SC_6H_2tBu_3$-2,4,6$)_2(NC_5H_3$-2,6-$Me_2)$].[9] (c) Other

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strategies include the incorporation of additional donor atoms in chelating thiolate ligands and (d) the simultaneous exploitation of two or more of these conditions. Thus, the presence of additional donor atoms, such as the N atom in pyridine-2-thione (Hpyt) and pyrimidine-2-thione (Hpymt) and also the introduction of bulky substituents in the ligand modify the nuclearity of the complexes; thus, the cadmium complex with pyridine-2-thione, $[Cd(pyt)_2]$,[10] is polymeric, while the greater steric constraints introduced by the methyl groups of 4,6-dimethypyrimidine-2-thione prevents polymerization and $[Cd(dmpymt)_2]$[11] is hexanuclear. When a more voluminous substituent such as the trimethylsilyl group is introduced, the cadmium complex with 3-(trimethylsilyl)pyridine-2-thione is dinuclear.[12] On the other hand, the presence of coligands, such as 2,2′-bipyridine, 1,10-phenanthroline, bis(diphenylphosphino)methane, or 1,2-bis(diphenylphosphine)ethane), might modify such aggregation processes producing mono- or binuclear thiolate complexes.[13]

As a part of our continuing interest in the chemistry of sterically hindered thiolates,[14] and as a consequence of the paucity of known structures of neutral homoleptic species of the type $[Ag(SR)]_n$,[8,15] we report in this paper the electrochemical synthesis and characterization of a series of complexes of silver(**I**) with 2-(diphenylphosphino)benzenethiol [2-$(Ph_2P)C_6H_4$-SH], 2-(diphenylphosphino)-6-(trimethylsilyl)benzenethiol [2-(Ph_2P)-6-$(Me_3Si)C_6H_3SH$] and 2-(diphenylphosphine oxide)-6-(trimethylsilyl)benzenethiol [2-(Ph_2PO)-6-$(Me_3Si)C_6H_3SH$] ligands which have, in addition to the thiolate sulfur atom, other donor atoms such as phosphorus or oxygen in the same ligand. In addition, some of these ligands also possess a bulky trimethylsilyl group close to the sulfur atom which might modify the degree of aggregation of the thiolate complexes.

Experimental Section

Silver (Ega Chemie) was used as plates (ca. 2 × 2 cm). All other reagents, including acetonitrile, thiophenol, TMEDA (tetramethylethylenediamine), *n*-butyllithium, chlorodiphenylphosphine, and diphenylphosphinic chloride were commercial products (Aldrich) and were used as supplied.

Microanalysis were performed using a Carlo-Erba EA microanalyzer. IR spectra were recorded as KBr disks with a Bruker IF5 66v spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Brucker WN 300 MHz instrument using $CDCl_3$ as solvent; chemical shifts were determined against TMS as internal standard. ^{31}P NMR was recorded on a Brucker AC 500 spectrometer using 85% H_3PO_4 as internal standard. FAB data were recorded on a KRATOS MS 50TC mass spectrometer connected to a DS90 data system, using 3-nitrobenzyl alcohol (3-NOBA) as a matrix material.

Preparation of the Ligands. All manipulations were carried out under argon, using high vacuum and conventional Schlenk techniques. Solvents used to isolate the products were distilled over appropriate drying agents and degassed and saturated with argon by passing argon through them during 1 h. The reactants and products were kept away from light by covering the flasks with aluminum foil to suppress photoinitiated decomposition.

Synthesis of 2-(Diphenylphosphino)benzenethiol (1). The white crystalline solid was prepared from thiophenol (7 g, 63.5 mmol), with TMEDA (22 mL, 142.0 mmol), *n*-butyllithium (2.5 M in hexane, 57 mL, 142.0 mmol), and diphenylphosphine chloride (10 g, 45.5 mmol) equivalent to 5 g (71%) of thiophenol by the procedure of Block et al.[16] The crude product was evaporated to dryness and extracted with diethyl ether. The ether layer was washed with water to remove the acid produced and dried ($MgSO_4$), and the solvents were removed in vacuo to yield 8.7 g (65%, 29.6 mmol) of crude product. The crude product was purified by dissolution in diethyl ether, adding activated charcoal, concentrating in vacuo, and adding hexane to help precipitate the phosphinethiol.

Recrystallization was also accomplished from ether/hexane solution. An analytically pure sample was obtained by chromatographing the crude product with a Chromatotron (4 mm silica plates, hexane/CH_2Cl_2). The isolated phosphinethiol was a colorless solid, mp 98−99 °C. Anal. Calcd for $C_{18}H_{15}PS$: C, 73.34; H, 5.20; S, 10.88. Found: C, 73.45; H, 5.14; S, 10.67. ^1H NMR ($CDCl_3$): δ 7.5−6.7 (m, 14H, phenyl), 4.1 (d, J ($^{31}P-^{1}H$) = 2.2 Hz), 1H, SH). ^{13}C NMR ($CDCl_3$): δ 137.7 (d, ^2J ($^{31}P-^{13}C$) = 30.3 Hz, (C1)), 135.8 (d, ^1J ($^{31}P-^{13}C$) = 7.9 Hz, (C2)), 130.4 (d, ^2J ($^{31}P-^{13}C$) = 3.1 Hz, (C3)), 125.9 (C4), 129.2 (C5), 134.0 (C6), 135.3 (d, ^1J ($^{31}P-^{13}C$) = 9 Hz, (C7)), 133.7 (d, ^2J ($^{31}P-^{13}C$) = 2.8 Hz, (C8)), 128.6 (d, ^3J ($^{31}P-^{13}C$) = 7 Hz, (C9)), 129.0 (C10). ^{31}P NMR ($CDCl_3$): δ −14.51 (relative to external 85% H_3PO_4).

Synthesis of 2-(Diphenylphosphino)-6-(trimethylsilyl)benzenethiol (2). The white solid was prepared from 2-(trimethylsilyl)benzenethiol (9.82 g, 0.054 mol) obtained by the method of Martin and Figuly,[17] with TMEDA (6.5 g, 0.054 mol), *n*-butyllithium (44 mL, 2.5 M hexane solution, 0.11 mol), and diphenylphosphine chloride (9.67 g, 0.044 mol) following the procedure of Block.[17] The reaction product was quenched with concentrated HCl at 0 °C. The mixture was concentrated in vacuo and dissolved in degassed diethyl ether. Residual acid in the organic layer was removed with degassed water. The solution was dried ($MgSO_4$) and concentrated in vacuo to give 15 g of crude product (93%, 0.041 mol). Yield after recrystallization from hexane/CH_2Cl_2 solution was 67% (10.86 g, 0.03 mol). Analytically pure sample was obtained by chromatography on a Chromatotron (hexane/CH_2Cl_2); mp 102−103 °C. Anal. Calcd for $C_{21}H_{23}PSSi$: C, 68.82; H, 6.33; S, 8.74. Found: C, 69.00; H, 6.43; S, 8.67. ^1H NMR ($CDCl_3$): δ 7.6−6.7 (m, 13H, phenyl), 4.6 (d, 1H, ^4J ($^{31}P-^{1}H$) = 11.24 Hz, SH), 0.38 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 143.7 (d, J ($^{31}P-^{13}C$) = 29.9 Hz, (C)), 141.4 (C), 137.2 (d, J ($^{31}P-^{13}C$) = 6.2 Hz, (C)), 135.8 (C), 135.6 (CH), 134.7 (CH), 134.0 (d, J ($3^{31}P-^{13}C$) = 19.2 Hz, (CH)), 128.8 (d, J ($^{31}P-^{13}C$) = 26.5 Hz, (CH)), 128.7 (C), 125.5 (CH), 0.10 ($Si(CH_3)_3$). ^{31}P NMR ($CDCl_3$): δ −15.02 (relative to external 85% H_3PO_4).

Synthesis of 2-(Diphenylphosphinyl)-6-(trimethylsilyl)benzenethiol (3). The white solid was prepared from 2-(trimethylsilyl)benzenethiol (7.23 g, 0.04 mol), with TMEDA (4.62 g, 0.04 mol), *n*-butyllithium (34 mL, 2.5 M hexane solution, 0.085 mol), and diphenylphosphinic chloride (4.54 g, 0.02 mol) following the same method as in the synthesis of **2**. The reaction mixture was quenched with concentrated HCl at 0 °C, and the solvent was evaporated. The residue was extracted into diethyl ether, and excess acid was removed with water. The organic layer was dried ($MgSO_4$), and solvents were removed in vacuo. The residue was washed with ether/hexane 1:9, and the white crystalline product dried in vacuo. An analytically pure sample

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was obtained after chromatografing the crude product using degassed hexane/CH_2Cl_2 mixtures. Crystals suitable for X-ray difffraction were isolated by crystallizing the eluted solution. Yield 4.5 g (59%, 0.012 mol), mp 194−195 °C. Anal. Calcd for $C_{21}H_{23}OPSSi$: C, 65.94; H, 6.06; S, 8.38. Found: C, 69.00; H, 6.43; S, 8.35. ^1H NMR ($CDCl_3$): δ 7.8−6.8 (m, 13H, phenyl), 7.08 (s, 1H, SH), 0.21 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 146.4 (d, J ($^{31}P-^{13}C$) = 7.1 Hz, (CS)), 142.4 (d, J ($^{31}P-^{13}C$) = 5.9 Hz, (CSi)), 138.3 (d, J ($^{31}P-^{13}C$) = 1.9 Hz, (CH)), 135.1 (d, J ($^{31}P-^{13}C$) = 14.5 Hz, (CH)), 132.1 (d, J ($^{31}P-^{13}C$) = 2.0 Hz, (CH)), 132.1 (d, J ($^{31}P-^{13}C$) = 8.3 Hz, (CH)), 131.7 (d, J ($^{31}P-$13C) = 106.0 Hz, (CP)), 128.6 (d, J ($^{31}P-^{13}C$) = 104.8 Hz, (CP)), 128.5 (d, J ($^{31}P-^{13}C$) = 12.0 Hz, (CH)), 123.5 (d, J ($^{31}P-^{13}C$) = 12.0 Hz, (CH)), −0.11 ($Si(CH_3)_3$). ^{31}P NMR ($CDCl_3$): δ 34.1 (relative to external 85% H_3PO_4).

Electrochemical Synthesis of the Complexes. The electrochemical method used in the synthesis of the metal complexes is similar to that described by Tuck.[18] An acetonitrile (50 mL) solution of the corresponding thiolato ligand and a small amount of tetramethylammonium perchlorate (ca. 10 mg) as the supporting electrolyte was electrolyzed using a silver sacrificial anode and a platinum cathode. In all cases, hydrogen evolved at the cathode. These cells can be summarized as: $Pt_{(-)}/CH_3CN + RP\text{-}SH/M_{(+)}$.

Preparation of [Ag{2-(Ph_2P)C_6H_4S}] (4). Electrolysis of an acetonitrile solution (50 mL) containing 2-(diphenylphosphino)benzenethiol (**1**) (0.220 g, 0.75 mmol) at 12 V and 20 mA for 1 h dissolved 85 mg of metal (E_f = 1.05 mol F^{-1}). As the reaction proceeded, a solid was formed immediately at the anode, and hydrogen evolved at the cathode. At the end of the experiment the solid obtained was filtered, washed with cool acetonitrile and ether, and dried under vacuum, 0.26 g (85%). This solid was identified as [Ag{2-(Ph_2P)C_6H_4S}] (**4**). Anal. Calcd for $C_{18}H_{14}AgPS$: C, 53.88; H, 3.32; S, 7.98. Found: C, 53.31; H, 3.49; S, 7.54. IR (KBr, cm^{-1}): 1570 (m), 1437 (s), 1417 (m), 1249 (m), 1095 (s), 1037 (m), 997 (w), 744 (s), 729 (w), 694 (s), 506 (m). ^1H NMR ($CDCl_3$): δ 7.8−6.0 (m, 14H). ^{31}P NMR ($CDCl_3$): δ 32.42 (s).

Preparation of [Ag_4{2-(Ph_2P)-6-(Me_3Si)C_6H_3S}$_4$] (5). Electrochemical oxidation of a silver anode in a solution of 2-(diphenylphosphino)-6-(trimethylsilyl)benzenethiol (**2**) (0.273 g, 0.75 mmol) in acetonitrile (50 mL) at 18 V and 10 mA for 2 h caused 82 mg of Ag to dissolve (E_f = 1.02 mol F^{-1}). During the electrolysis, hydrogen was evolved at the cathode, and after 1 h, white needles appeared on the electrodes and at the bottom of the vessel. The solid was filtered, washed with acetonitrile and ether, and dried under vacuum, 0.31 g (88%). This compound was identified as [Ag{2-(Ph_2P)-6-(Me_3Si)C_6H_3S}] (**5**). Anal. Calcd for $C_{21}H_{22}AgPSSi$: C, 53.29; H, 4.86; S, 6.77. Found: C, 53.11; H, 4.89; S, 6.45. IR (KBr, cm^{-1}): 1552 (m), 1479 (m), 1435 (m), 1349 (s), 1241 (m), 1095 (s), 998 (w), 852 (s), 837 (s), 743 (s), 720 (w), 693 (m), 501 (m). ^1H NMR ($CDCl_3$): δ 7.8−6.3 (m, 22H), 0.46 (s, 9H). ^{31}P NMR ($CDCl_3$): δ 34.11. Recrystallization by diffusion of MeOH into a solution of the compound in $CHCl_3$ produces crystals of [Ag{2-(Ph_2P)-6-(Me_3Si)C_6H_3S}] (**5**) suitable for X-ray studies.

Preparation of [Ag_4{2-(Ph_2PO)-6-(Me_3Si)C_6H_3S}$_4$] (6). A solution of acetonitrile (50 mL) containing 2-(diphenylphosphinyl)-6-(trimethylsilyl)benzenethiol (**3**) (0.214 g, 0.56 mmol) was electrolyzed at 11 V and 10 mA during 1.5 h, and 61 mg of silver metal was dissolved from the anode (E_f = 1.00 mol F^{-1}). The white microcrystalline precipitate formed was filtered, and crystals suitable for X-ray diffraction studies were isolated from the filtrate, left to concentrate by evaporation at room temperature, and identified as [Ag_4{2-(Ph_2PO)-6-(Me_3Si)C_6H_3S}$_4$]0.3CH_3CN (**6**), 0.225 g (88%). Anal. Calcd for $C_{90}H_{97}Ag_4N_3O_4P_4S_4Si_4$: C, 52.05; H, 4.72; N, 2.02; S, 6.16. Found: C, 51.45; H, 4.58; N, 1.98; S, 6.50. IR (KBr, cm^{-1}): 1555 (m), 1483 (m), 1436 (m), 1352 (s), 1243 (s), 1172 (s), 1116 (m), 1040 (m), 998 (w), 851 (s), 748 (s), 727 (w), 694 (s), 625 (m), 556 (s). ^1H NMR ($CDCl_3$): δ 7.8−6.7 (m, 22H), 0.5 (s, 9H). ^{31}P NMR ($CDCl_3$): δ 35.12.

X-ray Crystallography of 3, 5, and 6. Crystals of **3**, **5**, and **6** were mounted on a glass fiber, and data were recorded on a CAD4 diffractometer with graphite monochromated Mo−Kα radiation at room temperature. The *hkl* range was $-9 < h < 15$, $-14 < k < 14$, $-22 < l < 21$ for **3**, $-16 < h < 25$, $-23 < k < 25$, $-32 < l < 32$ for **5**, and $-17 < h < 11$, $-18 < k < 19$, $-14 < l < 19$ for **6**. 7954 reflections were collected for **3** in the range $\theta = 1.95-22.49°$, 31422 reflections for **5** in the range $\theta = 1.36-21.00°$, and 10321 in the range $\theta = 1.44-22.50°$ for (**6**).

Structure Solution and Refinement. For these compounds, full matrix least-squares calculations were carried out on F^2. Refinements were carried out using 2730 reflections for **3**, 4676 reflections for **5**, and 6345 reflections for **6** with $F > 2.0\sigma(F_o)$. For compound **3** the final cycle of full-matrix least-squares based on 226 variable parameters converged to $R = \sum(|F_o| - |F_c|)/(F_o) = 0.0621$ and $Rw = [(\sum w(|F_o| - |F_c|)^2]^{1/2} = 0.1366$. The maximum and minimum peaks on the final difference Fourier map were 0.263 and −0.221 e$Å^{-3}$. For compound **5** the final cycle of full-matrix least-squares based on 379 variable parameters converged to $R = \sum(|F_o| - |F_c|)/(F_o) = 0.0286$ and $Rw = [(\sum w(|F_o| - |F_c|)^2]^{1/2} = 0.0530$. The maximum and minimum peaks on the final difference Fourier map were 0.199 and −0.170 e$Å^{-3}$. For compound **6** the final cycle of full-matrix least-squares based on 505 parameters converged to $R = \sum(|F_o| - |F_c|)/(F_o) = 0.0505$ and $Rw = [(\sum w(|F_o| - |F_c|)^2]^{1/2} = 0.1337$. The maximum and minimum peaks on the final difference Fourier map were 1.034 and −0.395 e$Å^{-3}$. Atomic scattering factors were taken from International Tables for X-ray Crystallography.[19] Crystallographic data and final *R* indices for all three compounds are given in Table 1. Significant bond distances and angles for **3**, **5**, and **6** are given in Tables 2, 3, and 4, respectively. Complete crystallographic details are given in the Supporting Information. ORTEP diagrams of the molecules are shown in Figures 1, 2, and 4.

Results and Discussion

The synthesis of homoleptic silver(I) phosphino- and phosphinylthiolate complexes [Ag(RP−S)] can be readily accomplished in good yield by the electrochemical method described, a methodology similar to previous work on related systems.[20−23]

The electrochemical efficiency, defined as moles of metal dissolved per Faraday of charge, was found to have an average value of 1.0 ± 0.05 mol F^{-1}. These results, together with the evolution of hydrogen at the cathode, are compatible with the occurrence of the following electrode reactions

$$\text{cathode: } RP{-}SH + e^- \rightarrow 1/2H_2 + RP{-}S^-$$

$$\text{anode: } RP{-}S^- + Ag \rightarrow [Ag(RP{-}S)] + e^-$$

where RP−SH stands for the neutral ligand.

[Ag{2-(Ph_2P)C_6H_4S}] (**4**) was obtained as a white insoluble solid which precipitated after several minutes of electrolysis. The IR spectrum of the complex shows that the free ligand band ν(S−H) at 2400−2500 cm^{-1} is absent, indicating that deprotonation of this group occurred and that it is coordinated as an anionic ligand. Moreover, the spectrum also shows bands at 1600−1580 cm^{-1} assigned to ν(C═C) of the aromatic ring and at 1000 cm^{-1} and 720−730 cm^{-1} attributed to ν(P−C) and ν(C−S), respectively. The room temperature ^1H NMR spectrum shows signals in the range 7.8−6.0 ppm due to the phenyl protons and also the disappearance of the signal attributable to

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Table 1. Crystal Data and Structure Refinement for **3**, **5**, and **6**

	3	**5**	**6**
empirical formula	$C_{21}H_{23}POSSi_4$	$C_{84}H_{88}Ag_4P_4S_4Si_4$	$C_{90}H_{97}Ag_4N_3O_4P_4S_4Si_4$
formula weight	382.51	1893.50	2080.67
crystal size (mm)	0.40 × 0.40 × 0.40	0.10 × 0.10 × 0.10	0.10 × 0.10 × 0.10
temperature (K)	298(2)	298(2)	298(2)
wavelength (Å)	0.71073	0.71073	0.71073
crystal system	monoclinic	tetragonal	triclinic
space group	*P*2(1)/*n*	*P*4(2)2(1)2	*P*1
unit cell dimensions			
a, Å	11.3730(4)	18.8454(7)	13.4567(1)
b, Å	11.1562(4)	18.8454(7)	14.4148(2)
c, Å	17.1153(6)	24.596(2)	14.8080(2)
α, deg			99.130(1)
β, deg	103.961(1)		98.815(1)
γ, deg			114.211(1)
volume, $Å^3$	2107.4(1)	8735.1(7)	2509.38(5)
Z	4	4	1
density (calcd), mg/m^3	1.206	1.440	1.377
absorption coefficient, cm^{-1}	2.92	11.48	10.10
final *R* indices [$I > 2\sigma(I)$]			
*R*1	0.0621	0.0286	0.0505
*wR*2	0.1366	0.0530	0.1337
$R1 = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	$wR2 = \{\Sigma[w(F_o^2 - F_c^2)]/\Sigma[w(F_o^2)^2]\}^{1/2}$		

SH which in the free ligand appears at 4.1 ppm. On the other hand, the ^{31}P NMR spectrum shows a signal at 32.42 ppm, which has shifted downfield from its position in the free ligand spectrum, −14.51 ppm. This fact is taken as proof of coordination of the phosphorus atom. In the FAB mass spectrum of **4**, the largest *m*/*z* peak, 910, corresponds to $[Ag_3\{2\text{-}(Ph_2P)C_6H_4S\}_2]^+$. The spectrum also shows the peaks associated with $[Ag_2\{2\text{-}(Ph_2P)C_6H_4S\}]^+$ and $[2\text{-}(Ph_2P)C_6H_4S]^+$ at *m*/*z* 509 and *m*/*z* 294, respectively. The peak clusters have the appropriate isotope distribution. Elemental analysis is consistent with this formulation, but the structure is not apparent from spectroscopy data. Attempts to obtain crystals suitable for X-ray studies were unsuccessful. Most likely, the compound is polymeric or as least tetrameric with a structure similar to that found for **5** and **6** (vide infra).

Compounds **5** and **6** are obtained by oxidation of a silver anode as white crystalline solids formed slowly at the bottom of the cell as the reactions proceeded. The presence of trimethylsilyl groups on the ligands increases their solubility in the reaction medium. The IR spectra of these complexes are similar to that of **4** with the addition of a strong band at 850 cm^{-1} characteristic of the rocking mode of the $SiMe_3$ group and a band in **6** at 1172 cm^{-1} assignable to ν(P−O). The ^1H NMR spectra show signals of the aromatic protons and also a signal ca. 0.4 ppm assignable to the trimethylsilyl group. The ^{31}P NMR spectra show only signals at 34.1 and 35.1 ppm for **5** and **6**, respectively. FAB mass spectra of these complexes show the molecular peaks for $[Ag_3(RP{-}S)_2]^+$ at *m*/*z* 1052, 1086, $[Ag_2(RP{-}S)]^+$ at *m*/*z* 589, 598, and $[Ag(RP{-}S)]^+$ at *m*/*z* 473 and 498, respectively, for both compounds.

Description of the Structures. The structure of the ligand $2\text{-}(Ph_2PO)6\text{-}(Me_3Si)C_6H_3SH$ (**3**) is illustrated in Figure 1, and the relevant metrical parameters are summarized in Table 2.

The bond angles and lengths (Table 2) in the rings are essentially identical to those found in other (phenyl)P═O and are unremarkable. The geometry around the central P atom is slightly distorted tetrahedral, being bound to one oxygen atom and one carbon atom of each one of the three phenyl rings. The O−P−C angles, 110.1(2)−113.1(1)°, are slightly greater that the corresponding C−P−C angles, 106.4(2)-107.7(2)°, but they are in the range found in similar ligands, 111.6−114.5° for O−P−C and 103.4−108.8° for C−P−C angles.[24] The P−O distance, 1.493(3) Å, is similar to those found in other $O{=}PR_3$ ligands,[24,25] 1.475−1.498 Å, and they are in agreement the value proposed for a P═O bond.[26] The C−P distances, 1.813(4)−1.829(4) Å, are also comparable with the above ligands (1.780−

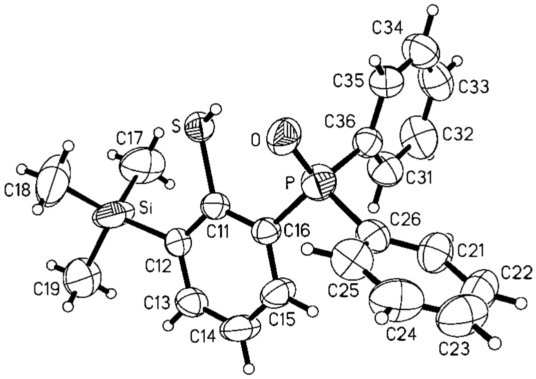

Figure 1. Molecular structure of $[2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3SH]$ (**3**).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **3**

S−C(11)	1.784(4)	P−O	1.493(3)
P−C(36)	1.813(4)	P−C(26)	1.821(4)
P−C(16)	1.829(4)	Si−C(18)	1.874(6)
Si−C(17)	1.880(6)	Si−C(19)	1.883(5)
Si−C(12)	1.913(4)		
O−P−C(36)	112.6(2)	O−P−C(26)	110.1(2)
C(36)−P−C(26)	106.7(2)	O−P−C(16)	113.1(2)
C(36)−P−C(16)	106.4(2)	C(26)−P−C(16)	107.7(2)
C(18)−Si−C(17)	112.9(3)	C(18)−Si−C(19)	108.2(3)
C(17)−Si−C(19)	108.4(3)	C(18)−Si−C(12)	110.7(2)
C(17)−Si−C(12)	108.9(2)	C(19)−Si−C(12)	107.6(2)

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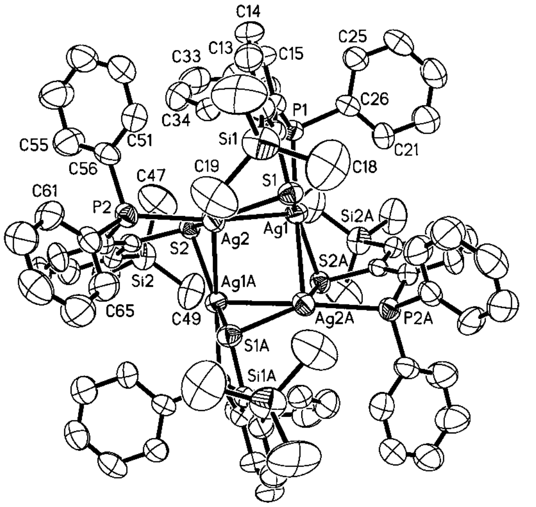

Figure 2. An ORTEP view of the structure of [Ag_4{2-(Ph_2P)-6-(Me_3Si)C_6H_3S}$_4$] (**5**).

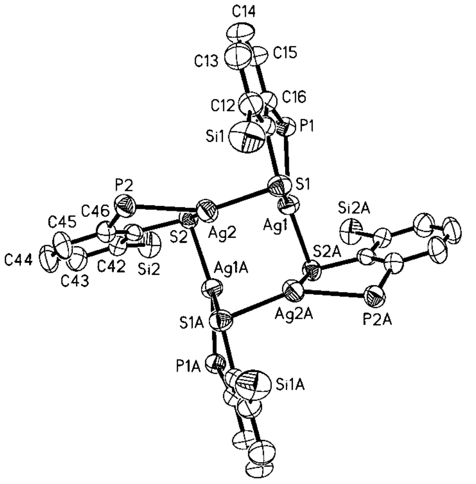

Figure 3. Perspective view of the coordination spheres of the metals in [Ag_4{2-(Ph_2P)-6-(Me_3Si)C_6H_3S}$_4$] (**5**).

Table 3. Selected Lengths (Å) and Angles (deg) for **5**

Ag(1)−P(1)	2.4282(14)	Ag(1)−S(2)[a]	2.4481(14)
Ag(1)−S(1)	2.6289(14)	Ag(1)−Ag(2)	2.9356(6)
Ag(1)−Ag(2)[a]	2.9694(6)	Ag(2)−P(2)	2.426(2)
Ag(2)−S(1)	2.448(2)	Ag(2)−S(2)	2.6435(14)
P(1)−C(26)	1.822(3)	P(1)−C(36)	1.808(3)
P(2)−C(46)	1.815(3)	P(1)−C(16)	1.840(3)
P(2)−C(56)	1.821(3)	P(2)−C(66)	1.813(3)
S(2)−C(41)	1.781(3)	S(1)−C(11)	1.786(3)
P(1)−Ag(1)−S(2)[a]	145.23(5)	P(1)−Ag(1)−S(1)	82.52(5)
S(2)[a]−Ag(1)−S(1)	128.94(4)	P(2)−Ag(2)−S(2)	79.90(5)
P(2)−Ag(2)−S(1)	145.19(5)		
S(1)−Ag(2)−S(2)	128.57(5)		

[a] Symmetry transformations used to generate equivalent atoms: *y*, *x*, −*z* + 2.

1.833 Å).[24,25] The S−C(11) distance, 1.784(4) Å, is within the accepted range for S−C single bonds.[26]

The molecular structure of [Ag_4{2-(Ph_2P)-6-(Me_3Si)C_6H_3S}$_4$] (**5**) is shown in Figure 2, together with the atomic numbering scheme adopted. For the sake of clarity, a view of the coordination sphere of the metals has been represented in Figure 3. Selected bond distances and angles are listed in Table 3. The structure contains discrete molecules having a crystallographically imposed symmetry with four molecules in the unit cell.

The structure consists of a tetranuclear array of silver atoms, consisting of a highly distorted tetrahedron of four silver atoms bridged by the sulfur atoms of four thiolate anions. The distances between silver atoms are in the range 2.93 to 3.52 Å, showing that no significant silver−silver interactions exist in the compound. Each silver atom is coordinated to one phosphorus atom and the bridging sulfur atom of two thiolate ligands. Therefore, each ligand acts as a η^2(P-μ^2-S) six-electron donor ligand. Each silver atom is in a distorted trigonal-planar environment [$AgPS_2$], with a deviation of the Ag atom from the best least squares donor atom plane of 0.327 (2) Å for Ag(2) and 0.237 (2) Å for Ag(1). The bond angles between silver and the atoms of the chelate rings are significantly smaller than the idealized limit of 120°, (82.52(5)°, and 79.90(5)°), whereas the angles involving donor atoms of different ligands have values larger than 120°, 145.23(5)−145.19(5) for PAgS and 128.94(4)−128.57(5)° for SAgS. These large deviations from the theoretical values give rise to a highly distorted three-coordinate geometry. The Ag(1)−S(2) and Ag(2)−S(1′) distances, 3.293(5) and 3.337(6) Å, are considerably longer that the other Ag−S distances observed in this complex and even greater than the sum of the van der Waals radii of the silver and sulfur atoms,[27] indicating that the S(2) and S(1′) are not coordinated to the Ag(1) and Ag(2) sites, respectively.

The silver atoms are linked through asymmetric sulfur bridges, as the Ag−S distances are significantly different. Thus, the Ag−S bond distances are of two types: the shorter bonds have values of 2.448(2) and 2.4481(14) Å, and the longer have distances of 2.6289(14) and 2.6435(14) Å. The latter distances correspond to the Ag−S bonds of the chelate rings. The shorter set of bond lengths is close to those found in other silver(I) complexes with heterocyclic thiones involving sulfur atom bridges and a trigonal environment around silver atoms.[28] However, the longer Ag−S bond lengths of **5** are greater that those found in the above-cited tricoordinated silver(I) compounds. The steric strain in the five-member chelate rings and the small "bite" of the ligand appear to be primarily responsible for the lengthening of the metal−sulfur bonds. The Ag−P bond distances, 2.4282(14) and 2.426(2) Å, are similar to those found in other three-coordinated silver(I) complexes, 2.390−2.524 Å.[29]

Each of the phenyl rings is planar, but the sulfur and phosphorus atoms lie out of the plane of the phenyl ring to which they are bound (by 0.0216 and 0.0407 Å for P(1) and S(1), respectively, and 0.0844 and 0.2130 Å for S(2) and P(2), respectively).The interplanar angle between the phenyl ring of ligands that are bonded to adjacent silver have values of ca. 84°.

The molecular structure of [Ag_4{2-(Ph_2PO)-6-(Me_3Si)-C_6H_3S}$_4$] (**6**) is shown in Figure 4, together with the atomic numbering scheme adopted. For clarity, a view of the coordination sphere of the metals has been represented in Figure 5. Selected bond distances and angles are listed in Table 4. The structure contains discrete molecules having crystallographically imposed symmetry with one molecule of complex and three acetonitrile molecules in the unit cell.

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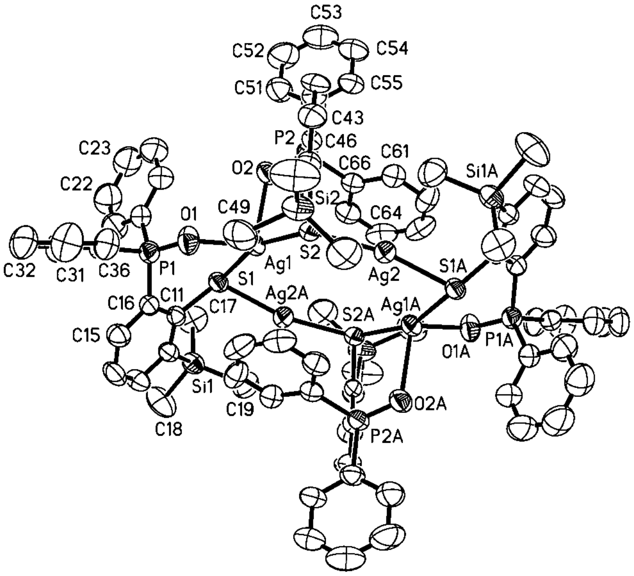

Figure 4. An ORTEP view of the structure of [$Ag_4\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_4$] (**6**).

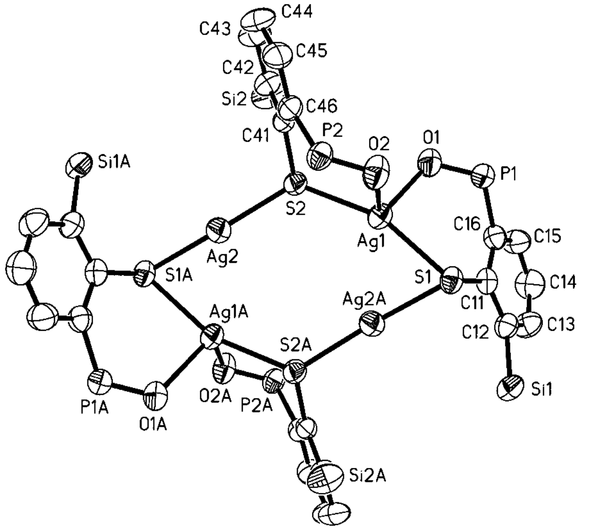

Figure 5. Perspective view of the coordination spheres of the metals in [$Ag_4\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_4$] (**6**).

Table 4. Selected Lengths (Å) and Angles (deg) for **6**

Ag(1)−O(1)	2.388(5)	Ag(1)−S(2)	2.462(2)
Ag(1)−O(2)	2.489(5)	Ag(1)−S(l)	2.507(2)
Ag(1)−Ag(2)[a]	2.8546(7)	Ag(2)−S(2)	2.392(2)
Ag(2)−S(1)[a]	2.417(2)	P(1)−O(1)	1.490(5)
P(2)−O(2)	1.483(5)		
O(1)−Ag(1)−S(2)	99.92(12)	O(1)−Ag(1)−O(2)	106.3(2)
S(2)−Ag(1)−O(2)	89.86(11)	O(1)−Ag(1)−S(1)	92.27(12)
S(2)−Ag(I)−S(1)	158.47(6)	O(2)−Ag(1)−S(1)	103.75(12)
S(2)−Ag(2)−S(1)[a]	160.27(6)		

[a] Symmetry transformations used to generate equivalent atoms: $-x + 1, -y + 2, -z + 1$.

The structure of **6** also consists of a tetranuclear array of silver atoms, but in contrast to **5** the structure of **6** can be best described as being based on a distorted parallelogram of four silver atoms, symmetrically disposed around the inversion center, and held together by four ligands. The silver atoms are bridged by the sulfur atoms of four thiolate anions. Two of the sulfur atoms are above the plane formed by the four silver atoms (+ 0.5144 Å) and the other two below it (−0.3052 Å). The four sulfur atoms are coplanar, and the dihedral angle formed by the sulfur plane and the silver plane is 167.46(3)°. The silver−silver distances [2.8546(7) and 2.8560(8) Å] shorter than in **5** and even slightly shorter than the distance in metallic silver (2.88 Å),[30] suggest no significant silver−silver interaction. Moreover, in contrast to **5**, where all silver atoms are three-coordinate in a trigonal disposition around the metal, the four silver atoms in compound **6** can be divided into two different pairs according to their coordination environment. One pair containing Ag(1) and Ag(1′) atoms possesses a very distorted [AgO_2S_2] tetrahedral coordination. The other group containing Ag(2) and Ag(2′) shows a [AgS_2] digonal coordination. Thus, the Ag(1) and Ag(1′) atoms are four coordinated by the oxygen and the sulfur atoms from two η^2(O-μ^2-S) bridging bidentate thiolate ligands acting as five-electron donors. The tetrahedral geometry around these silver atoms is highly distorted, with bond angles in the range 158.47(6)−89.86(11)°, which are significantly different from the value of 109° for regular tetrahedral geometry. The other two silver atoms are coordinated by two sulfur atoms, each one from a bridging bidentate thiolate ligand, resulting in a digonal environment with an S(2)−Ag(2)−S(1′) angle of 160.27(6)°.

The Ag−S bond to the four-coordinated silver atom [Ag(1)−S(2) 2.462(2) and Ag(1)−S(2) 2.507(2) Å] is consistently longer than that to the dicoordinated metal atom [Ag(2)−S(1′) 2.417(2) and Ag(2)−S(2) 2.392(2) Å)]. The larger bond lengths are shorter than the Ag−S distances found in other examples of four-coordinated complexes, 2.721−2.568 Å,[31] but are similar to those found in other silver−sulfur complexes, 2.537−2.464 Å, when the metal is three-coordinated.[28] However, the shorter bond lengths are considerably shorter than those in the above cited complexes but are similar to those found in the dicoordinated complexes, for example, 2.362(8)−2.396(8) Å in [$AgSC(SiMe_3)_3$][4] and 2.387(4)−2.418(4) Å in [$AgSCH(SiMe_3)_2$]$_8$.[8]

The Ag−O bond distances are significantly different, 2.489(2) Å for Ag(1)−O(2) and 2.388(5) Å for Ag(1)−O(1), but fall in the 2.251(7)−2.64(2) Å range found in the other tetracoordinated silver−oxygen compounds.[32]

As in **5**, the phenyl groups of **6** are planar, with the sulfur S(1) and S(2) (0.216, 0.1097 Å) and phosphorus P(1) and P(2) (0.2914, 0.1437 Å) atoms out the plane of the phenyl rings. The solvent acetonitrile molecules do not interact with the silver complex in any significant manner, and there are no noteworthy intermolecular contacts.

The Tetranuclear Core in the Structural Chemistry of Cu(I)- and Ag(I)-Thiolates. The tetranuclear core presents a persistent structural motif in the chemistry of Cu(I) and Ag(I) thiolates. The Cu(I)-thiolates exhibit two families of tetranuclear clusters, the anionic [$Cu_4(SR)_6$]$^{2-}$ cages[33−42] and the neutral [$Cu_4(SR)_4$]. The former are characterized by an octahedral arrangement of the six sulfur donor atoms with the Cu(I) centers occupying half of the triangular faces of the S_6 octahedron in a tetrahedral arrangement. The Cu(I) coordination geometry is distorted trigonal {CuS_3}. The [$Cu_4(SR)_4$] class, in the absence of additional donor groups is restricted to [$Cu_4\{SC_6H_3$-2,6-

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$(SiMe_3)_2\}_4]$[42] and $[Cu_4(SC_6H_2\text{-}{}^iPr_3)_4]$.[43] Both structures are based on a Cu_4S_4 ring with diagonal $\{CuS_2\}$ copper sites. The Cu_4S_4 rings in both instances fold along one S···S axis to produce a butterfly motif. When additional donor groups are present, the core geometry is modified to accommodate the expansion of the Cu(I) coordination sphere. In contrast to the prototypical $[Cu_4(SR)_4]$ structures described above, $[Cu_4\{(2\text{-mercaptoethyl})\text{picolylamine}\}_4]$[44] and $[Cu_4\{SC_6H_4(CH_2NMeCH_2CH_2OMe)\}_4]$[45] exhibit a flattened tetrahedral Cu_4 core with trigonal $\{CuS_2N\}$ coordination at the Cu(I) sites, as a consequence of the constraints imposed by chelate ring formation. The most unusual structure is displayed by $[Cu_4(PPh_3)_4(SPh)_4]$[38] which consists of a central $\{Cu_2S_2\}$ rhomb linked to 2-folded outer quadrilaterals. There are two distinct Cu(I) coordination sites, trigonal $\{CuPS_2\}$ and tetrahedral $\{CuPS_3\}$. The structure of $[Cu_4(PPh_3)_4(SPh)_4]$ demonstrates that the cluster shapes adopted by these thiolates are dictated by an interplay of structure-directing factors including the coordination flexibility of the metal, steric influences, and the presence of additional donor groups.

In contrast to the Cu(I) chemistry, there is a single example of a $[Ag_4(SR)_6]^{2-}$ cluster, $[Ag_4(SCH_2C_6H_4CH_2S)_3]^{2-}$ [46] which exhibits the characteristic Ag_4 tetrahedron within the S_6 octahedron. The organotelluride $[Ag_4(TeC_4H_3S)_6]^{2-}$ [47] is structurally analogous.

The prototypical $[Ag_4(SR)_4]$ structure is provided by $[Ag_4\{SC(SiMe_3)_3\}_4]$[8] which consists of an $\{Ag_4S_4\}$ ring arranged in a shallow crown with a maximum deviation of 0.1 Å from the best least squares plane. The same structure is observed for the selenium analogue $[Ag_4\{SeCCSiMe_3)_3\}_4]$.[48] With less sterically encumbering thiolate ligands, additional aggregation is observed to give higher oligomers in which the tetranuclear unit appears as a structural building block. This is most apparent in the structures of $[Ag_4(SC_6H_4\text{-o-}SiMe_3)_4]_2$[49] and $[Ag_4\{SCH(SiMe_3)_2\}_4]_2$[8] which consist of octanuclear clusters constructed from two fused $\{Ag_4S_4\}$ units. The polymeric $[Ag_4\{SCH_2(SiMe_3)\}_3(OMe)]$[8] is also constructed of fused $\{Ag_4S_4\}$ units.

The compounds of this study represent the first examples of the $[Ag_4(SR)_4]$ family with additional donor groups. The structure of the $\{Ag_4S_4\}$ core of $[Ag_4\{Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S_4]$ is similar to that of the shallow crown of $[Ag_4\{SC(SiMe_3)_3\}_4]$. The Ag−O distances are rather long, and, consequently, the steric influence of the phosphorus bound phenyl groups may be minimized. More significantly, the introduction of the oxo-donor expands the chelate ring {Ag−O−P−C−C−S−} and relieves chelate strain. In contrast, the structure of $[Ag_4\{2\text{-}(Ph_2P)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_4]$ is quite unusual, even for $[M_4(SR)_4]$ cores with additional ligation. While the folding of the structure must reflect some compromise of influences including metal coordination preferences, ligand steric influences, and chelation, the relative weights of such factors in determining geometry remain difficult to assess.

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Supporting Information Available: X-ray crystallographic files for the structure determinations of **3**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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