

Novel Types of Tetra-, Hexa-, Octa-, and Dodecanuclear Silver Clusters Containing (2,7-Di-*tert*-butylfluoren-9-ylidene)methanedithiolate[†]José Vicente,[‡] Pablo González-Herrero,^{*,‡} Yolanda García-Sánchez,[‡] and Peter G. Jones[§]

Grupo de Química Organometálica, Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, Apdo. 4021, 30071 Murcia, Spain, and Institut für Anorganische and Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany

Received October 24, 2008

The reaction of AgClO₄ with piperidinium 2,7-di-*tert*-butyl-9H-fluorene-9-carbodithioate (pipH)[S₂C(*t*-Bu-Hfy)] (**1**) (*t*-Bu-Hfy = 2,7-di-*tert*-butylfluoren-9-yl) afforded [Ag_n{S₂C(*t*-Bu-Hfy)}_n] (**2**), which reacted with phosphines to give [Ag{S₂C(*t*-Bu-Hfy)}L₂] [L = PPh₃ (**3a**); L₂ = bis(diphenylphosphino)ethane (dppe, **3b**), 1,1'-bis(diphenylphosphino)ferrocene (dppf, **3c**). By reacting complex **2** with AgClO₄ and piperidine in a 1:1:1 molar ratio, the dodecanuclear cluster [Ag₁₂{S₂C(= *t*-Bu-fy)}₆] (**4**) (*t*-Bu-fy = 2,7-di-*tert*-butylfluoren-9-ylidene) was obtained. Compound **4** can also be directly prepared from the reaction of **1** with AgClO₄ and piperidine in a 1:2:1 molar ratio. The reactions of **1** with AgClO₄, phosphines, and piperidine afforded the compounds [Ag₆{S₂C(= *t*-Bu-fy)}₃L₃] [1:2:2:1 molar ratio; L = PPh₃ (**5a**), P(*p*-To)₃ (**5b**)], [Ag₄{S₂C(= *t*-Bu-fy)}₂(dppf)₂] (**6**) (1:2:1:1 molar ratio), [Ag_n{S₂C(= *t*-Bu-fy)}_{n/2}{P(*i*-Pr)₃}_n] (**7**) (1:2:2:1 molar ratio), or [Ag₈{S₂C(= *t*-Bu-fy)}₄{P(*i*-Pr)₃}₄] (**8**) (1:2:1:1 molar ratio). Complexes **5a, b, 6, 7**, and **8** can be also obtained by reacting **4** with the corresponding phosphine in the appropriate molar ratio. The crystal structures of **4, 5b**, and **8** have been determined by X-ray diffraction studies. The nuclearity of complex **6** was established from its ³¹P{¹H} NMR data, which reveal a very fast dynamic process leading to an average coupling of each of the P atoms of the dppf ligands with four Ag atoms.

Introduction

Silver complexes and clusters with thiolato ligands have been the subject of considerable interest because of their extraordinary structural diversity.^{1,2} The study of their structures, bonding modes, and spectroscopic features has proved to be relevant to the structural elucidation of the metal-binding sites of metallothioneins.³ In recent years, their importance has become apparent for a number of applications in the area of advanced materials, including the synthesis of monolayer-protected clusters⁴ and the thermolytic preparation of nanostructured materials.⁵

1,1-Ethylenedithiolates (XYC=CS₂²⁻) and related dithio ligands have received attention because of their ability to form high-nuclearity clusters,^{6,7} heteronuclear complexes,⁸

and coordination polymers.⁹ Our research group has been involved in the synthesis of polynuclear complexes with this type of ligand, including heterometallic derivatives.^{10,11} However, the previously reported silver complexes with 1,1-

* To whom correspondence should be addressed. E-mail: pgh@um.es.
[†] (Fluoren-9-ylidene)methanedithiolato Complexes, part 6. For previous parts, see refs 11, 18–21.

[‡] Universidad de Murcia.

[§] Technische Universität Braunschweig.

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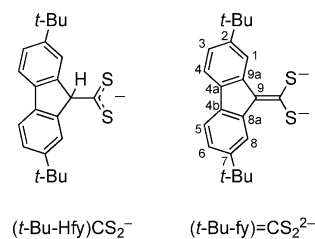
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ethylenedithiolates are very scarce and have been described only with the ligands $(\text{NC})_2\text{C}=\text{CS}_2^{2-}$ (*i*-mnt) and $\{(\text{EtO})_2\text{P}(\text{O})\}(\text{NC})\text{C}=\text{CS}_2^{2-}$ (cpdt). Most of them are anionic clusters, namely, $[\text{Ag}_8(\text{i-mnt})_6]^{4-}$,¹² $[\text{Ag}_6(\text{i-mnt})_6]^{6-}$,¹³ $[\text{Ag}_4(\text{i-mnt})_4]^{4-}$, $[\text{Ag}_8(\text{i-mnt})_6(\text{PPh}_3)_4]^{4-}$, and $[\text{Ag}_6(\text{i-mnt})_6(\text{PPh}_3)_6]^{3-}$.^{7,14} The only neutral complexes are the tetranuclear clusters $[\text{Ag}_4(\text{i-mnt})_2(\text{dppm})_4]^{15}$ and $[\text{Ag}_4(\text{cpdt})_2(\text{dppm})_4]^{16}$ and the coordination polymer $[\text{Ag}_4(\text{i-mnt})_2(\text{HPyS})_4]_n$ (HPyS = pyridine-2-thione).¹⁷ The cationic derivative $[\text{Ag}_5(\text{cpdt})_2(\text{dppm})_4](\text{PF}_6)$ has also been reported.¹⁶

We have recently undertaken the study of the reactivity and photophysical properties of transition metal complexes with (fluoren-9-ylidene)methanedithiolate and several disubstituted derivatives.^{11,18–21} The di-*tert*-butyl-substituted homologue $[(t\text{-Bu-fy})=\text{CS}_2^{2-}$, Chart 1] is particularly suitable for the synthesis of metal complexes, because it normally gives more stable and soluble species. In general, the ligands of this kind show remarkable differences from the previously used 1,1-ethylenedithiolates; these are largely attributable to the absence of strongly electron-withdrawing substituents and affect the photophysical properties and redox behavior of their metal complexes. Thus, the strongly electron-donating

Chart 1



character of these ligands is responsible for the facile oxidation of certain Au(I) and Pt(II) complexes under atmospheric conditions and the unusually low energies of their charge-transfer absorptions and emissions.^{18,20} We have also reported the aerial oxidation of Cu(I) and Cu(II) to Cu(III) complexes with $(t\text{-Bu-fy})=\text{CS}_2^{2-}$ ¹⁹ and the formation of dinuclear derivatives with the condensed dithiolato ligands $\text{S}[(t\text{-Bu-fy})=\text{CS}]_2^{2-}$ and $\text{S}[(t\text{-Bu-fy})=\text{CS}]_3^{2-}$.^{19,21}

In view of the atypical characteristics of the (fluoren-9-ylidene)methanedithiolato ligands, we thought it of interest to carry out an exploration of the chemistry of silver complexes with $(t\text{-Bu-fy})=\text{CS}_2^{2-}$. Here, we present a series of neutral Ag(I) complexes with this ligand and also with its protonated precursor, $(t\text{-Bu-Hfy})\text{CS}_2^-$ (Chart 1). The new dithiolato complexes represent unprecedented types of silver thiolate clusters.

Experimental Section

General Considerations, Materials, and Instrumentation. All preparations were carried out at room temperature under an atmosphere of nitrogen using Schlenk techniques, except in the cases indicated. Synthesis-grade solvents were obtained from commercial sources. Piperidinium 2,7-di-*tert*-butyl-9*H*-fluorene-9-carbodithioate (**1**) was prepared as previously described.²² All other reagents were obtained from commercial sources and used without further purification. NMR spectra were recorded on Bruker Avance 200, 300, or 400 spectrometers, usually at 298 K, unless otherwise indicated. Chemical shifts are referred to internal TMS (¹H and ¹³C{¹H}) or external 85% H₃PO₄ (³¹P{¹H}). The assignments of the ¹H and ¹³C{¹H} NMR spectra were made with the help of HMBC and HSQC experiments. Chart 1 shows the atom numbering of the dithiolato ligand. NMR simulations were carried out with the program gNMR 5.0. Melting points were determined on a Reichert apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba 1106 microanalyzer. Infrared spectra were recorded in the range 4000–200 cm⁻¹ on a Perkin-Elmer Spectrum 100 spectrophotometer using KBr pellets. Electronic absorption spectra were recorded on a Unicam UV500 spectrophotometer.

X-Ray Structure Determinations. Crystals of **4**, **5b**, and **8** suitable for X-ray diffraction studies were obtained from C₆H₆/hexane (**4**) or CH₂Cl₂/MeCN (**5b**, **8**). Numerical details are presented in Table 1. The data for **4** were collected on an Oxford Diffraction Nova O diffractometer using mirror-focused Cu K α radiation in the ω -scan mode. The data for **5b** and **8** were collected on an Oxford Diffraction Xcalibur S diffractometer using monochromated Mo K α radiation in the ω -scan mode. The structures were solved by direct methods and refined anisotropically on F^2

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Table 1. Crystallographic Data for **4**·C₆H₁₄·4C₆H₆, **5b**·CH₂Cl₂·3MeCN, and **8**·CH₂Cl₂·3MeCN

	4 ·C ₆ H ₁₄ ·4C ₆ H ₆	5b ·CH ₂ Cl ₂ ·3MeCN	8 ·CH ₂ Cl ₂ ·3MeCN
formula	C ₁₆₂ H ₁₈₂ Ag ₁₂ S ₁₂	C ₁₇₈ H ₁₈₈ Ag ₆ Cl ₂ N ₃ P ₅ S ₆	C ₁₃₁ H ₁₉₁ Ag ₈ Cl ₂ N ₃ P ₄ S ₈
fw	3808.24	3434.82	3122.09
<i>T</i> (K)	103(2)	100(2)	100(2) K
λ (Å)	1.54184	0.71073	0.71073
cryst syst	monoclinic	triclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	14.5153(3)	16.5832(5)	26.7245(5)
<i>b</i> (Å)	31.7686(6)	17.4121(5)	20.9427(5)
<i>c</i> (Å)	34.3104(6)	32.9195(10)	25.0333(6)
α (deg)	90	75.352(3)	90
β (deg)	90.769(3)	75.838(3)	93.527(3)
γ (deg)	90	63.234(3)	90
<i>V</i> (Å ³)	15820.2(5)	8116.5(4)	13984.2(5)
<i>Z</i>	4	2	4
ρ_{calcd} (Mg m ⁻³)	1.599	1.414	1.483
μ (mm ⁻¹)	13.469	0.937	1.345
<i>R</i> 1 ^a	0.0594	0.0543	0.0270
w <i>R</i> 2 ^b	0.1765	0.1282	0.0628

^a $R1 = \sum |F_o| - |F_c| / \sum |F_o|$ for reflections with $I > 2\sigma(I)$. ^b $wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and *a* and *b* are constants set by the program.

using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen).²³ Restraints to local aromatic ring symmetry or light-atom displacement factor components were applied in some cases. Special features of refinement are as follows: The structure of **4** contains four benzene molecules and one hexane, as well as at least one solvent site that could not be identified. Much of the solvent does not refine well. Furthermore, some *t*-Bu groups are poorly resolved. In view of these problems, C atoms were refined isotropically. For compound **5b**, extensive regions of residual electron density presumably correspond to solvent molecules but could not be refined satisfactorily. Accordingly, the program SQUEEZE (A. L. Spek, University of Utrecht, Netherlands) was used to remove mathematically the effects of the solvent. For calculations of formula mass and so forth, an idealized solvent content of one CH₂Cl₂ and three MeCN molecules was assumed. *t*-Bu hydrogens were assigned assuming ideally staggered methyl groups. *p*-Tolyl methyl groups were modeled using idealized geometry but may suffer from rotational disorder. For compound **8**, residual electron density was tentatively identified as one MeCN site and one superimposed site with CH₂Cl₂ and MeCN. However, this model could not be refined adequately. The program SQUEEZE was therefore used to cancel the effect of the solvent. For the calculation of mass-dependent parameters, an idealized composition of one CH₂Cl₂ and three MeCN molecules was assumed. The *t*-Bu group at C15 is disordered.

[Ag_n{S₂C(*t*-Bu-Hfy)}_n] (**2**). To a solution of piperidinium 2,7-di-*tert*-butyl-9*H*-fluorene-9-carbodithioate (**1**) (583 mg, 1.22 mmol) in acetone (15 mL) was added AgClO₄ (246 mg, 1.19 mmol). An orange precipitate immediately formed, which was filtered off, recrystallized from CH₂Cl₂/MeOH, and vacuum-dried to give **2** as a red solid. Yield: 508 mg, 93%. Anal. calcd for C₂₂H₂₅AgS₂: C, 57.26; H, 5.46; S, 13.90. Found: C, 56.94; H, 5.56; S, 13.79. Mp: 198 °C (dec). IR (KBr, cm⁻¹): ν (CS₂), 1020. ¹H NMR (400.9 MHz, CDCl₃): δ 7.38 (d, ³*J*_{HH} = 8.0 Hz, 2 H each, H4, H5), 7.22 (s, 2 H, H1, H8), 7.17 (d, ³*J*_{HH} = 8.0 Hz, 2 H, H3, H6), 5.64 (s, 1 H, H9), 1.02 (s, 18 H, *t*-Bu). ¹³C{¹H} NMR (100.8 MHz, CDCl₃): δ 151.1 (C2, C7), 146.2 (C8a, C9a), 138.7 (C4a, C4b), 125.8 (C3, C6), 121.7 (C1, C8), 119.6 (C4, C5), 72.2 (C9), 35.5 (CMe₃), 32.2 (CMe₃).

[Ag{S₂C(*t*-Bu-Hfy)}(PPh₃)₂] (**3a**). To a solution of PPh₃ (118 mg, 0.45 mmol) in CH₂Cl₂ (15 mL) was added complex **2** (96 mg,

0.21 mmol), and the resulting orange solution was stirred for 30 min. The solvent was removed under a vacuum, and the residue was treated with hexane (20 mL) to give a pale brown precipitate, which was filtered off, washed with hexane (2 × 2 mL), and vacuum-dried to give **3a**. Yield: 171 mg, 84%. Anal. calcd for C₅₈H₅₅AgP₂S₂: C, 70.65; H, 5.59; S, 6.49. Found: C, 70.38; H, 5.62; S, 6.50. Mp: 134 °C. IR (KBr, cm⁻¹): ν (CS₂), 1012. ¹H NMR (400.9 MHz, CDCl₃): δ 7.85 (s, 2 H, H1, H8), 7.62 (d, ³*J*_{HH} = 8.0 Hz, 2 H, H4, H5), 7.37 (dd, ³*J*_{HH} = 8.0 Hz, ⁴*J*_{HH} = 1.6 Hz, 2 H, H3, H6), 7.33–7.29 (m, 18 H, *o*-H + *p*-H, Ph), 7.19–7.16 (m, 12 H, *m*-H, PPh₃), 5.66 (s, 1 H, H9), 1.25 (s, 18 H, *t*-Bu). ¹³C{¹H} NMR (50.1 MHz, CDCl₃): δ 259.6 (CS₂), 149.4 (C2, C7), 146.1 (C8a, C9a), 138.3 (C4a, C4b), 133.8 (d, ¹*J*_{C-P} = 27.0 Hz, *i*-C, Ph), 133.3 (*o*-C, Ph), 129.7 (*p*-C, Ph), 128.6 (d, ³*J*_{CP} = 14.7 Hz, *m*-C, Ph), 124.3 (C3, C6), 122.7 (C1, C8), 118.7 (C4, C5), 72.6 (C9), 34.9 (CMe₃), 31.6 (CMe₃). ³¹P{¹H} NMR (162.3 MHz, CDCl₃, 223 K): δ 6.96 (2 d, ¹*J*_{P-107Ag} = 355 Hz, ¹*J*_{P-109Ag} = 407 Hz).

[Ag{S₂C(*t*-Bu-Hfy)}(dppe)] (**3b**). This pale orange compound was prepared as described for **3a**, from **2** (63 mg, 0.14 mmol) and dppe (61 mg, 0.15 mmol). Yield: 100 mg, 86%. Anal. calcd for C₄₈H₄₉AgP₂S₂: C, 67.05; H, 5.74; S, 7.46. Found: C, 67.04; H, 5.88; S, 7.05. Mp: 181 °C (dec). IR (KBr, cm⁻¹): ν (CS₂), 1011. ¹H NMR (400.9 MHz, CDCl₃): δ 7.93 (s, 2 H, H1, H8), 7.66 (d, ³*J*_{HH} = 8.0 Hz, 2 H, H4, H5), 7.41–7.39 (m, 10 H, H3, H6 + Ph), 7.30–7.26 (m, 4 H, Ph), 7.17–7.14 (m, 8 H, Ph), 5.71 (s, 1 H, H9), 2.36 (s, 4 H, CH₂), 1.25 (s, 18 H, *t*-Bu). ¹³C{¹H} NMR (100.8 MHz, CDCl₃): δ 149.5 (C2, C7), 146.1 (C8a, C9a), 138.4 (C4a, C4b), 133.1 (*i*-C, Ph), 132.7 (*o*-C, Ph), 130.0 (*p*-C, Ph), 128.8 (*m*-C, Ph), 124.3 (C3, C6), 122.7 (C1, C8), 118.8 (C4, C5), 72.7 (C9), 34.9 (CMe₃), 31.6 (CMe₃), 24.8 (CH₂) (CS₂ not observed). ³¹P{¹H} NMR (162.3 MHz, CDCl₃, 223 K): δ 3.16 (2 d, ¹*J*_{P-107Ag} = 351 Hz, ¹*J*_{P-109Ag} = 405 Hz).

[Ag{S₂C(*t*-Bu-Hfy)}(dppf)] (**3c**). This orange compound was obtained as a monohydrate following the procedure described for **3a**, from **2** (126 mg, 0.27 mmol) and dppf (163 mg, 0.29 mmol). Yield: 235 mg, 85%. Anal. calcd for C₄₈H₅₅AgOP₂S₂: C, 65.06; H, 5.36; S, 6.20. Found: C, 65.13; H, 5.29; S, 6.12. Mp: 156 °C (dec). IR (KBr, cm⁻¹): ν (CS₂), 1011. ¹H NMR (400.9 MHz, CDCl₃): δ 7.93 (br, 2 H, H1, H8), 7.63 (d, ³*J*_{HH} = 8.0 Hz, 2 H, H4, H5), 7.54–7.50 (m, 10 H, Ph), 7.37 (dd, ³*J*_{HH} = 8.0 Hz, ⁴*J*_{H-H} = 1.5 Hz, 2 H, H3, H6), 7.34–7.23 (m, 10 H, Ph), 5.72 (s, 1 H, H9), 4.27 (t, ³*J*_{H-H} = 1.7 Hz, 4 H, H2, H5, Cp), 4.11 (br, 4 H, H3, H4, Cp), 1.21 (s, 18 H, *t*-Bu). ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ

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259.5 (CS₂), 149.4 (C2, C7), 146.1 (C8a, C9a), 138.3 (C4a, C4b), 134.5 (vt, *N* = 24.2 Hz, *i*-C, Ph), 133.9 (vt, *N* = 19.1 Hz, *o*-C, Ph), 129.7 (*p*-C, Ph), 128.4 (vt, *N* = 9.5 Hz, *m*-C, Ph), 124.2 (C3, C6), 122.5 (C1, C8), 118.6 (C4, C5), 74.0 (vt, *N* = 28.1 Hz, C2, C5, Cp), 72.7 (br, C9), 71.8 (br, C3, C4, Cp), 34.8 (CMe₃), 31.5 (CMe₃) (C1 of Cp not observed). ³¹P{¹H} NMR (162.3 MHz, CDCl₃, 223 K): δ -5.9 (2 d, ¹J_{P-107Ag} = 338 Hz, ¹J_{P-109Ag} = 389 Hz).

[Ag₁₂{S₂C=(*t*-Bu-fy)}₆] (4). **Method A.** To a solution of **1** (203 mg, 0.42 mmol) and AgClO₄ (170 mg, 0.82 mmol) in THF (15 mL) was added piperidine (44 μL, 0.44 mmol), and the resulting orange solution was stirred for 48 h. The solvent was removed under a vacuum, and the residue was treated with MeOH (30 mL), whereupon a brown precipitate formed, which was filtered off and recrystallized from CHCl₃/pentane to give **4** as a yellowish orange solid. Yield: 130 mg, 56%.

Method B. To a solution of complex **2** (202 mg, 0.44 mmol) and AgClO₄ (90 mg, 0.44 mmol) in THF (15 mL) was added piperidine (44 μL, 0.44 mmol), and the resulting orange solution was stirred for 6 h. The solvent was removed under a vacuum, and the residue was treated with MeOH (30 mL), whereupon an orange precipitate formed, which was filtered off and recrystallized from CHCl₃/pentane to give **4**. Yield: 85 mg, 35%.

Method C. A suspension of complex **5a** (431 mg, 0.197 mmol) in distilled THF (30 mL) was stirred for 48 h under atmospheric conditions. An orange solution was obtained. The solvent was removed under a vacuum, and the residue was treated with MeOH (30 mL), whereupon an orange precipitate formed, which was filtered off, washed with MeOH (2 mL), and vacuum-dried to give **4**. Yield: 186 mg, 83%. Anal. calcd for C₁₃₂H₁₄₄Ag₁₂S₁₂: C, 46.50; H, 4.26; S, 11.28. Found: C, 46.65; H, 4.13; S, 10.63. Mp: 192 °C (dec). IR (KBr, cm⁻¹): ν(C=CS₂), 1503, 1473. ¹H NMR (400.9 MHz, CDCl₃): δ 9.11, 9.02, 9.01 (all d, ⁴J_{HH} = 1.5 Hz, 2 H each, H1, H8), 7.57–7.52 (m, 6 H, H4, H5), 7.32, 7.29, 7.21 (all dd, ⁴J_{HH} = 1.5 Hz, ³J_{HH} = 8.0 Hz, 2 H each, H3, H6), 1.32, 1.26, 1.04 (all s, 18 H each, *t*-Bu). ¹³C{¹H} NMR (100.8 MHz, CDCl₃): δ 149.8, 149.5, 149.4 (C2, C7), 144.2 (br, CS₂), 139.5, 139.4, 138.9 (C8a, C9a), 137.7, 137.6, 137.4 (C4a, C4b), 135.2, 134.9 (C9), 125.6, (C3, C6), 125.1, 125.0, 124.9, 124.7 (C1, C8, C3, C6), 118.3, 118.1, 118.0 (C4, C5), 35.1, 35.0 (CMe₃), 32.0, 31.8, 31.7 (CMe₃).

[Ag₆{S₂C=(*t*-Bu-fy)}₂{PPh₃}]₅ (**5a**). To a solution of dithioate **1** (154 mg, 0.32 mmol) in MeCN (15 mL) were added AgClO₄ (131 mg, 0.63 mmol), PPh₃ (175 mg, 0.67 mmol), and piperidine (32 μL, 0.32 mmol), and the mixture was stirred for 0.5 h. A bright yellow precipitate gradually formed, which was filtered off, washed with MeCN (3 × 3 mL), and vacuum-dried to give **5a**. Yield: 286 mg, 83%. Anal. calcd for C₁₅₆H₁₄₇Ag₆P₅S₆: C, 62.12; H, 4.91; S, 6.38. Found: C, 61.87; H, 5.07; S, 5.71. Mp: 139 °C (dec). IR (KBr, cm⁻¹): ν(C=CS₂), 1489. ¹H NMR (400.9 MHz, CDCl₃): δ 9.28 (d, ⁴J_{HH} = 1.5 Hz, 6 H, H1, H8), 7.59 (d, ⁴J_{HH} = 7.9 Hz, 6 H, H4, H5), 7.24–7.18 (m, 36 H, H3, H6 + *m*-H, Ph), 7.12 (m, 30 H, *o*-H, Ph), 6.95 (m, 15 H, *p*-H, Ph), 1.24 (s, 54 H, *t*-Bu). ¹³C{¹H} NMR (75.5 MHz, CDCl₃): δ 148.2 (C2, C7), 140.5 (C8a, C9a), 136.3 (C4a, C4b), 133.5 (d, ³J_{CP} = 17.2 Hz, *o*-C, Ph), 133.2 (C9), 131.7 (d, ¹J_{CP} = 53.4 Hz, *i*-C, Ph), 129.3 (*p*-C, Ph), 128.5 (d, ⁴J_{CP} = 8.5 Hz, *m*-C, Ph), 124.7 (C1, C8), 122.2 (C3, C6), 117.1 (C4, C5), 34.9 (CMe₃), 31.8 (CMe₃) (CS₂ not observed). ³¹P{¹H} NMR (81.0 MHz, CDCl₃): δ 4.9 (br).

[Ag₆{S₂C=(*t*-Bu-fy)}₃{P(*p*-To)}₃}]₅ (**5b**). This bright yellow compound was prepared as described for **5a**, from **1** (221 mg, 0.46 mmol), AgClO₄ (192 mg, 0.92 mmol), P(*p*-To)₃ (290 mg, 0.95 mmol), and piperidine (50 μL, 0.51 mmol). Yield: 454 mg, 91%. Anal. calcd for C₁₇₁H₁₇₇Ag₆P₅S₆: C, 63.65; H, 5.53; S, 5.96. Found:

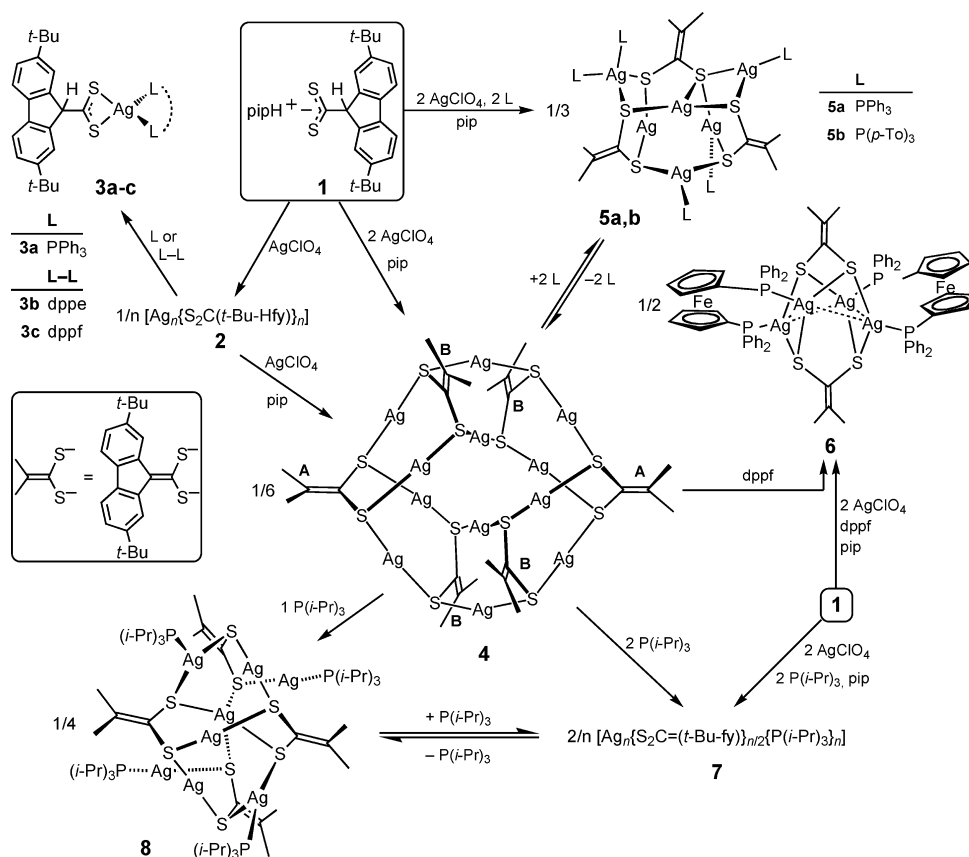
C, 63.37; H, 5.83; S, 5.78. Mp: 158 °C (dec). IR (KBr, cm⁻¹): ν(C=CS₂), 1496. ¹H NMR (400.9 MHz, CDCl₃): δ 9.31 (d, ⁴J_{HH} = 1.6 Hz, 6 H, H1, H8), 7.59 (d, ³J_{HH} = 8.0 Hz, 6 H, H4, H5), 7.19 (dd, ⁴J_{HH} = 1.6 Hz, ³J_{HH} = 8.0 Hz, 6 H, H3, H6), 7.02 (m, 30 H, To), 6.60 (br, 30 H, To), 2.10 (s, 45 H, Me, To), 1.18 (s, 54 H, *t*-Bu). ¹³C{¹H} NMR (100.8 MHz, CDCl₃): δ 151.9 (br, CS₂), 148.2 (C2, C7), 140.9 (C8a, C9a), 139.1 (*p*-C, To), 136.2 (C4a, C4b), 133.5 (d, ²J_{CP} = 17 Hz, *o*-C, To), 132.1 (C9), 130.1 (br, *i*-C, To), 129.2 (d, ³J_{CP} = 9 Hz, *m*-C, To), 124.8 (C1, C8), 121.8 (C3, C6), 116.9 (C4, C5), 34.9 (CMe₃), 31.8 (CMe₃), 21.3 (Me, To). ³¹P{¹H} NMR (162.3 MHz, CDCl₃): δ 3.5 (br).

[Ag₄{S₂C=(*t*-Bu-fy)}₂(dppf)₂] (**6**). **Method A.** A solid mixture of **1** (104 mg, 0.22 mmol), AgClO₄ (85 mg, 0.41 mmol), and dppf (124 mg, 0.22 mmol) was suspended in MeCN (15 mL). Piperidine (24 μL, 0.24 mmol) was then added, and the mixture was stirred for 30 min. A yellow solid gradually precipitated, which was filtered off, washed with MeCN (2 × 3 mL), and vacuum-dried. Yield: 221 mg, 96%.

Method B. To a solution of compound **4** (104 mg, 0.06 mmol) in CH₂Cl₂ (10 mL) was added dppf (116 mg, 0.21 mmol), and the mixture was stirred for 35 min. A small amount of a yellow solid gradually precipitated. The solvent was partially evaporated under a vacuum (5 mL), and Et₂O was added to complete the precipitation. The solid was then filtered off and vacuum-dried to give **6**. Yield: 164 mg, 80%. Anal. calcd for C₁₁₂H₁₀₄Ag₄Fe₂P₄S₄: C, 59.91; H, 4.67; S, 5.71. Found: C, 59.98; H, 4.70; S, 5.82. Mp: 179 °C (dec). IR (KBr, cm⁻¹): ν(C=CS₂), 1484. ¹H NMR (400.9 MHz, CDCl₃): δ 9.55 (d, ⁴J_{HH} = 1.5 Hz, 4 H, H1, H8), 7.62 (d, ³J_{HH} = 7.9 Hz, 4 H, H4, H5), 7.48–7.43 (m, 16 H, *o*-H, Ph), 7.19–7.13 (m, 12 H, H3, H6 + *p*-H, Ph), 6.95 (t, ²J_{HH} = 7.2 Hz, 16 H, *m*-H, Ph), 4.83 (br, 8 H, Cp), 3.79 (s, 8 H, Cp), 1.13 (s, 36 H, *t*-Bu). ¹³C{¹H} NMR (100.8 MHz, CDCl₃): δ 152.3 (CS₂), 147.8 (C2, C7), 141.1 (C8a, C9a), 135.2 (C4a, C4b), 133.8 (*i*-C, Ph), 133.4 (m, *o*-C, Ph), 133.0 (C9), 129.7 (*p*-C, Ph), 128.4 (m, *m*-C, Ph), 123.9 (C1, C8), 121.0 (C3, C6), 117.3 (C4, C5), 75.8 (d, ²J_{CP} = 14.6 Hz, C1, Cp), 74.1 (d, ³J_{CP} = 36.2 Hz, C2, C5, Cp), 72.5 (m, C3, C4, Cp), 34.9 (CMe₃), 31.9 (CMe₃). ³¹P{¹H} NMR (162.3 MHz, CDCl₃): δ -0.53 (quint m, ¹J_{P-107Ag} = 457 Hz, ¹J_{P-109Ag} = 524 Hz, calculated constants, see text).

[Ag_{*n*}{S₂C=(*t*-Bu-fy)}_{*n*/2}{P(*i*-Pr)}_{*n*}] (**7**). To a solution of **1** (102 mg, 0.21 mmol) in MeCN (15 mL) were added AgClO₄ (83 mg, 0.40 mmol), P(*i*-Pr)₃ (82 μL, 0.43 mmol), and piperidine (22 μL, 0.22 mmol), and the mixture was stirred for 1 h. A yellow solid gradually precipitated, which was filtered off, washed with MeCN (2 mL), and vacuum-dried to give **7**. Yield: 124 mg, 69%. Anal. calcd for C₄₀H₆₆Ag₂P₂S₂: C, 54.06; H, 7.49; S, 7.22. Found: C, 53.82; H, 7.69; S, 7.16. Mp: 152 °C (dec). IR (KBr, cm⁻¹): ν(C=CS₂), 1482. ¹H NMR (300.1 MHz, CDCl₃): δ 9.51 (br, 4 H, H1, H8), 7.60 (d, ³J_{HH} = 8.0 Hz, 4 H, H4, H5), 7.19 (dd, ⁴J_{HH} = 1.5 Hz, ³J_{HH} = 8.0 Hz, 4 H, H3, H6), 1.94 (m, 12 H, CHMe₂), 1.37 (s, 36 H, *t*-Bu), 1.09 (dd, ³J_{HH} = 7.0 Hz, ³J_{HP} = 14.4 Hz, 72 H, CHMe₂). ¹³C{¹H} NMR (50.1 MHz, CDCl₃): δ 147.4 (C2, C7), 141.3 (C8a, C9a), 134.8 (C4a, C4b), 131.8 (C9), 124.5 (C1, C8), 120.2 (C3, C6), 116.7 (C4, C5), 35.0 (CMe₃), 32.0 (CMe₃), 22.6 (d, ¹J_{CP} = 8.7 Hz, CHMe₂), 20.5 (d, ²J_{CP} = 5.8 Hz, CHMe₂) (CS₂ not observed). ³¹P{¹H} NMR (162.3 MHz, CDCl₃, 213 K): δ 39.8 (2 d, ¹J_{P-107Ag} = 460 Hz, ¹J_{P-109Ag} = 530 Hz).

[Ag₈{S₂C=(*t*-Bu-fy)}₄{P(*i*-Pr)}₃}]₄ (**8**). To a solution of AgClO₄ (205 mg, 0.99 mmol) and **1** (234 mg, 0.49 mmol) in THF (10 mL) were added piperidine (49 μL, 0.49 mmol) and P(*i*-Pr)₃ (107 μL, 0.49 mmol). The resulting yellowish orange solution was stirred for 15 min and concentrated under reduced pressure (4 mL). The addition of MeCN (20 mL) led to the precipitation of a yellow

Scheme 1^a

^a To = tolyl; pip = piperidine; dppe = 1,2-bis(diphenylphosphino)ethane; dppf = 1,1'-bis(diphenylphosphino)ferrocene.

solid, which was filtered off, recrystallized from $CH_2Cl_2/MeCN$, and vacuum-dried to give **8**. Yield: 300 mg, 84%. Anal. calcd for $C_{124}H_{180}Ag_8P_4S_8$: C, 51.11; H, 6.23; S, 8.80. Found: C, 51.03; H, 6.26; S, 8.71. Mp: 168 °C (dec). IR (KBr, cm^{-1}): $\nu(C=CS_2)$, 1496, 1464. 1H NMR (400.9 MHz, CD_2Cl_2 , 203 K): δ 9.22 (s, 4 H, H1, H8), 9.06, 8.63 (both s, 2 H each, H1, H8), 7.63, 7.59, 7.45, 7.39 (all d, $^3J_{HH} = 8.0$ Hz, 2 H each, H4, H5), 7.22, 7.16, 7.12, 6.94 (all d, $^3J_{HH} = 8.0$ Hz, 2 H each, H3, H6), 1.87, 1.63 (both br m, 6 H each, $CHMe_2$), 1.28, 1.26, 1.24 (all s, 18 H each, *t*-Bu), 1.03–0.98 (br m, 18 H, $CHMe_2$), 0.84–0.64 (br m, 54 H, $CHMe_2$), 0.51 (s, 18 H, *t*-Bu). $^{31}P\{^1H\}$ NMR (162.3 MHz, $CDCl_3$, 203 K): δ 48.6 (2 d, $^1J_{P-^{107}Ag} = 521$ Hz, $^1J_{P-^{109}Ag} = 594$ Hz), 45.2 (2 d, $^1J_{P-^{107}Ag} = 477$ Hz, $^1J_{P-^{109}Ag} = 549$ Hz). Data for isomer **8*** (see the NMR section) is as follows. 1H NMR (400.9 MHz, CD_2Cl_2 , 203 K): δ 9.17 (d, $^4J_{HH} = 1.4$ Hz, 2 H, H1, H8), 7.58 (d, $^3J_{HH} = 8.0$ Hz, 2 H, H4, H5), 7.26 (dd, $^4J_{HH} = 1.4$ Hz, $^3J_{HH} = 8.0$ Hz, 2 H, H3, H6), 1.55 (br m, 3 H, $CHMe_2$), 1.30 (s, 18 H, *t*-Bu) ($CHMe_2$ signals overlapped by those from **8**). $^{31}P\{^1H\}$ NMR (162.3 MHz, $CDCl_3$, 203 K): δ 50.8 (2 d, $^1J_{P-^{107}Ag} = 543$ Hz, $^1J_{P-^{109}Ag} = 626$ Hz).

Results and Discussion

Synthesis of Silver(I) Complexes with the $(t-Bu-Hfy)CS_2^-$ Ligand. The synthesis of Ag(I) complexes with $(t-Bu-Hfy)CS_2^-$ (Chart 1) was undertaken in order to explore their suitability as precursors for the preparation of complexes with the dithiolato ligand $(t-Bu-fy)=CS_2^{2-}$. As we have shown in our previous reports, metal complexes with the (fluorene-9-ylidene)methanedithiolato ligand and its 2,7-disubstituted derivatives can be obtained by reacting appropriate metal

precursors with the corresponding piperidinium 9*H*-fluorene-9-carbodithioate in the presence of a base. In some cases, dithioato complexes were obtained when the reactions were carried out in the absence of a base.^{18,19}

By reacting dithioato **1** with $AgClO_4$ in a 1:1 molar ratio in acetone, the red complex $[Ag_n\{S_2C(t-Bu-Hfy)\}_n]$ (**2**) precipitated in almost quantitative yield (Scheme 1). The reactions of this compound with PPh_3 , 1,2-bis(diphenylphosphino)ethane (dppe), or 1,1'-bis(diphenylphosphino)ferrocene (dppf) in the appropriate molar ratios allowed the preparation of the tetracoordinated complexes $[Ag\{S_2C(t-Bu-Hfy)\}L_2]$ [$L = PPh_3$ (**3a**); $L_2 = dppe$ (**3b**), dppf (**3c**)]. Although it proved impossible to grow crystals of complexes **2** and **3a–c**, their elemental analyses are consistent with a 1:1 dithioato/silver ratio.

Synthesis of Silver(I) Complexes with the $(t-Bu-fy)=CS_2^{2-}$ Ligand. The attempts to obtain anionic complexes with the dithiolato ligand $(t-Bu-fy)=CS_2^{2-}$ through the deprotonation of the dithioato complexes **2** or **3a–c** with piperidine or $(Pr_4N)OH$ led in all cases to complicated mixtures. However, the deprotonation of the dithioato ligand in **2** with piperidine was successful in the presence of an additional equivalent of $AgClO_4$, leading to the formation of a neutral complex, which, according to its elemental analysis, has a 2:1 silver to dithiolate ratio. An X-ray diffraction study revealed that the product of this reaction is the dodecanuclear cluster $[Ag_{12}\{S_2C(t-Bu-fy)\}_6]$ (**4**; Scheme 1). This compound can

also be directly obtained from the reaction of dithioate **1** with AgClO_4 and piperidine in a 1:2:1 molar ratio in THF.

We then attempted the direct synthesis of neutral $\text{Ag}(\text{I})$ complexes with $(t\text{-Bu-fy})=\text{CS}_2^{2-}$ and phosphine ligands by reacting dithioate **1** with AgClO_4 , phosphines, and piperidine in a molar ratio of 1:2:2:1 in MeCN. These reactions afforded neutral clusters of various nuclearities, depending on the nature of the phosphine. When PPh_3 or $\text{P}(p\text{-To})_3$ (To = tolyl) was employed, the hexanuclear clusters $[\text{Ag}_6\{\text{S}_2\text{C}=(t\text{-Bu-fy})\}_3\text{L}_5]$, where L = PPh_3 (**5a**) or $\text{P}(p\text{-To})_3$ (**5b**), were isolated in high yields as bright yellow precipitates. The elemental analyses of **5a** and **5b** are consistent with a 6:3:5 silver/dithiolate/phosphine ratio, which was confirmed for **5b** by means of an X-ray single-crystal structure analysis (see below). Complexes **5a** and **5b** are only moderately stable in solution, and they slowly lose phosphine. When the complexes are stirred in distilled THF for 48 h, the dodecanuclear cluster **4** eventually forms. The formation of **4** from **5a,b** requires the presence of atmospheric oxygen and also requires that the solvent be free of peroxide inhibitors, which suggests that the oxidation of the dissociated phosphine is crucial for the transformation to occur. This process is reversible, and the reaction of **4** with PPh_3 or PTO_3 in a 1:12 molar ratio gave complex **5a** or **5b**, respectively.

The reaction of **1** with AgClO_4 , dppf, and piperidine in a 1:2:1:1 molar ratio in MeCN afforded the tetranuclear derivative $[\text{Ag}_4\{\text{S}_2\text{C}=(t\text{-Bu-fy})\}_2(\text{dppf})_2]$ (**6**) as a yellow precipitate. Alternatively, compound **6** can be obtained by reacting cluster **4** with dppf in a 1:6 molar ratio in CH_2Cl_2 . In contrast to **5a** and **5b**, complex **6** exhibits a remarkable stability in solution, even under atmospheric conditions. Its nuclearity was established from the $^{31}\text{P}\{\text{H}\}$ NMR data (see the NMR section).

By reacting **1** with AgClO_4 , $\text{P}(i\text{-Pr})_3$, and piperidine in a 1:2:2:1 molar ratio in MeCN, a compound with the stoichiometry $[\text{Ag}_n\{\text{S}_2\text{C}=(t\text{-Bu-fy})\}_{n/2}\{\text{P}(i\text{-Pr})_3\}_n]$ (**7**) was obtained as a yellow precipitate. Complex **7** can also be prepared from the reaction of **4** with $\text{P}(i\text{-Pr})_3$ in a 1:12 molar ratio. The nuclearity of **7** could not be unequivocally established (see the NMR section). Complex **7** is moderately labile in solution, and it slowly decomposes, giving a complicated mixture. One of the decomposition products is the octanuclear cluster $[\text{Ag}_8\{\text{S}_2\text{C}=(t\text{-Bu-fy})\}_4\{\text{P}(i\text{-Pr})_3\}_4]$ (**8**), which results from the loss of $n/2$ equiv of $\text{P}(i\text{-Pr})_3$ from **7**. Compound **8** crystallized in an attempt to obtain crystals of **7** from $\text{CH}_2\text{Cl}_2/\text{MeCN}$ and was structurally characterized by means of an X-ray diffraction study; it can be independently obtained in high yield by reacting a solution of **4** in THF with $\text{P}(i\text{-Pr})_3$ in a 1:6 molar ratio.

Crystal Structures. The crystal structure of the dodecanuclear cluster **4** is shown in Figure 1; it displays no imposed crystallographic symmetry. Selected bond distances and angles are listed in Table 2. Each of the six dithiolates acts as a bridging ligand toward four Ag atoms. All 12 metal centers are in approximately linear coordination environments, with S–Ag–S angles in the range 154.68–176.84°; the most appreciable deviations from linearity are observed for the Ag(11) and Ag(8) atoms [S(6)–Ag(8)–S(1),

161.00(7)°; S(4)–Ag(11)–S(12), 154.68(8)°]. The Ag–S distances lie in the range 2.373–2.428 Å and are normal for dicoordinated silver thiolato complexes.^{1,24} The molecule can be viewed as two interlocked Ag_6S_6 macrocycles, held together by the C atoms of the CS_2 moieties. If we consider linear S–Ag–S segments, the shape of each of the macrocycles resembles the twist-boat conformation of cyclohexane (Figure 2). The cluster has approximate D_2 symmetry, with one pseudo-2-fold axis passing through the Ag(11), Ag(1), Ag(2), and Ag(8) atoms; a second axis through the C(104) and C(134) atoms; and a third axis through the midpoint of the Ag(1)–Ag(2) segment. The shape of the Ag_{12} core is rather flat, with eight of the Ag atoms [Ag(1), Ag(2), and Ag(7–12)] being almost coplanar (mean deviation from plane: 0.068 Å), while the other four make up a slightly twisted rectangle (main deviation from plane: 0.267 Å), perpendicular to the Ag_8 mean plane (Figure 3). There are 21 $\text{Ag}\cdots\text{Ag}$ metallophilic contacts in the range 2.875–3.367 Å, which, in view of the low coordination number of the Ag atoms, must play a crucial role in the stabilization of the cluster. Notably, the innermost metal centers, Ag(1) and Ag(2), establish a total of eight contacts with neighboring Ag atoms, while the rest of metals are involved in one to four $\text{Ag}\cdots\text{Ag}$ contacts.

The crystal structure of **5b**, which has no imposed symmetry (Figure 4, Table 3), reveals that three of the Ag atoms [Ag(2), Ag(3), Ag(4)] have trigonal AgS_2P coordination, while the others are in trigonal AgS_3 [Ag(1)], linear AgS_2 [Ag(5)], or tetrahedral AgS_2P_2 [Ag(6)] environments. Five of the S atoms are doubly bridging, while S(2) is triply bridging. The Ag–S bond distances range from 2.382 to 2.798 Å, the shortest corresponding to the linearly coordinated Ag(5) atom. The Ag_6S_6 core as depicted in Figure 4 has very approximate mirror symmetry, although the distance Ag(1)–S(1) is too long (4.228 Å). There are six short $\text{Ag}\cdots\text{Ag}$ metallophilic contacts in the range 2.886–3.143 Å. As far as we are aware, the arrangement of the silver atoms has no precedent in other silver thiolato complexes. The complex $[\text{Ag}_6(\text{SC}_6\text{H}_4\text{Cl-}p)_6(\text{PPh}_3)_5]$ has the same Ag/S/P ratio, but the Ag_6S_6 core has a very different structure, with one doubly bridging and five triply bridging S atoms.²⁵

The molecular structure of compound **8**, which displays crystallographic 2-fold symmetry [the axis passes through Ag(1) and Ag(2)], is represented in Figures 5 and 6. Selected bond distances and angles are listed in Table 4. As observed for **4**, all of the dithiolates act as quadruply bridging ligands. The Ag(1) atom is in a distorted tetrahedral AgS_4 environ-

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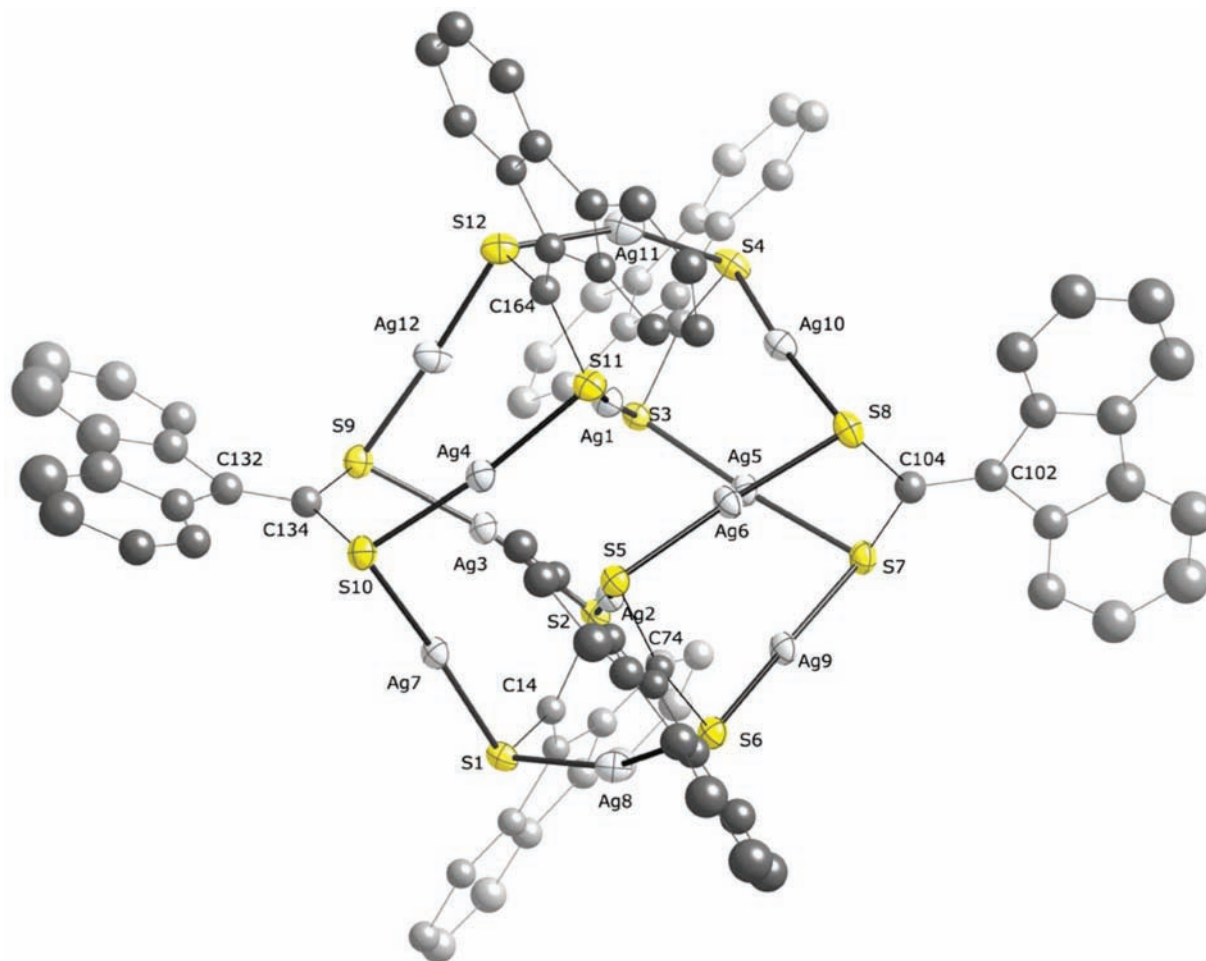


Figure 1. Thermal ellipsoid representation (30% probability; isotropic light atoms as spheres) of the structure of complex **4**. H atoms and *t*-Bu groups have been omitted for clarity.

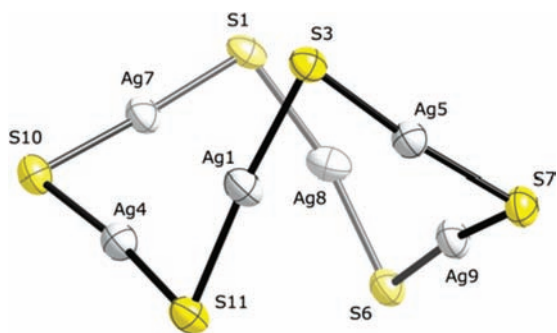


Figure 2. Perspective view of one of the Ag_6S_6 macrocycles in the structure of **4** (thermal ellipsoids with 50% probability).

ment, with S–Ag–S angles in the range $90.07\text{--}141.10^\circ$. The Ag(2), Ag(4), and Ag(5) atoms are in approximately linear environments, the first two with AgS_2 coordination and the third with AgSP coordination. The Ag(3) atom is in a distorted trigonal AgS_2P coordination. The Ag–S bond distances lie in the range $2.381\text{--}2.688\text{ \AA}$, the shortest being associated with the linearly coordinated Ag(2), Ag(4), and Ag(5) atoms. The molecule displays a total of 11 $\text{Ag}\cdots\text{Ag}$ short contacts in the range $2.835\text{--}3.258\text{ \AA}$.

NMR Spectra, Solution Structure, and Dynamic Behavior. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of complexes **2** and **3a–c** show one set of signals for the protons and

carbon atoms of the dithioato ligand slightly modified with respect to those of the free dithioate **1**,²² with the H9 resonance in the range of $5.64\text{--}5.78\text{ ppm}$ and the CS₂ resonance around 259 ppm. The NMR data of **2** suggest a highly symmetrical, oligomeric structure for this complex. The polymeric $[\text{Ag}_n(\text{S}_2\text{C-}o\text{-To})_n]$ ²⁶ is comprised of repeating tetranuclear subunits (Chart 2, *a*), and some pyridine adducts of Ag(I) dithiobenzoates, such as $[\text{Ag}_4(\text{S}_2\text{CMes})_4(\text{py})_3]$ and $[\text{Ag}_4(\text{S}_2\text{C-}o\text{-To})_4(\text{py})_4]$ ²⁷ (Mes = mesityl; To = tolyl; *b* and *c*, respectively), as well as the related $[\text{Ag}_4\{\text{S}_2\text{CC}(\text{PPh}_3)_2\}_4]^{4+}$ (*d*),²⁸ are tetranuclear species. The ^1H NMR data of complexes **3a–c** are compatible with mononuclear structures with tetrahedral coordination around silver. Their $^{31}\text{P}\{^1\text{H}\}$ NMR spectra display the resonance arising from the phosphines as somewhat broad singlets at room temperature, which is attributable to phosphine dissociation and exchange processes in solution.²⁹ For this reason, we measured the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra at low temperatures,

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Table 2. Selected Bond Distances (Å) and Angles (deg) for **4**

Ag(1)–S(3)	2.4185(19)	Ag(6)–S(8)	2.382(2)
Ag(1)–S(11)	2.428(2)	Ag(6)–S(5)	2.4156(19)
Ag(1)–Ag(11)	2.9338(10)	Ag(6)–Ag(9)	2.9098(8)
Ag(1)–Ag(12)	3.0113(10)	Ag(7)–S(10)	2.373(2)
Ag(1)–Ag(5)	3.0303(8)	Ag(7)–S(1)	2.375(2)
Ag(1)–Ag(10)	3.0494(9)	Ag(8)–S(6)	2.394(2)
Ag(1)–Ag(4)	3.1071(8)	Ag(8)–S(1)	2.396(2)
Ag(1)–Ag(3)	3.2660(8)	Ag(9)–S(6)	2.409(2)
Ag(1)–Ag(2)	3.2999(8)	Ag(9)–S(7)	2.410(2)
Ag(1)–Ag(6)	3.3669(9)	Ag(10)–S(4)	2.380(2)
Ag(2)–S(2)	2.4077(18)	Ag(10)–S(8)	2.388(2)
Ag(2)–S(5)	2.4099(18)	Ag(10)–Ag(11)	3.2871(10)
Ag(2)–Ag(8)	2.8747(8)	Ag(11)–S(4)	2.419(2)
Ag(2)–Ag(6)	3.0144(8)	Ag(11)–S(12)	2.427(2)
Ag(2)–Ag(3)	3.0318(8)	Ag(12)–S(9)	2.403(2)
Ag(2)–Ag(9)	3.0404(8)	Ag(12)–S(12)	2.405(2)
Ag(2)–Ag(7)	3.0649(8)	S(1)–C(14)	1.788(8)
Ag(2)–Ag(4)	3.2912(8)	S(2)–C(14)	1.785(8)
Ag(2)–Ag(5)	3.3658(8)	S(3)–C(44)	1.784(8)
Ag(3)–S(9)	2.387(2)	S(4)–C(44)	1.776(8)
Ag(3)–S(2)	2.4165(19)	S(5)–C(74)	1.771(7)
Ag(3)–Ag(7)	2.8865(8)	S(6)–C(74)	1.783(7)
Ag(3)–Ag(12)	3.2800(9)	S(7)–C(104)	1.793(8)
Ag(4)–S(10)	2.389(2)	S(8)–C(104)	1.785(8)
Ag(4)–S(11)	2.410(2)	S(9)–C(134)	1.792(8)
Ag(4)–Ag(12)	2.8991(9)	S(10)–C(134)	1.776(8)
Ag(5)–S(7)	2.405(2)	S(11)–C(164)	1.777(8)
Ag(5)–S(3)	2.427(2)	S(12)–C(164)	1.784(8)
Ag(5)–Ag(10)	2.8984(8)		
S(3)–Ag(1)–S(11)	175.12(8)	C(74)–S(5)–Ag(2)	106.6(2)
S(2)–Ag(2)–S(5)	176.08(7)	C(74)–S(5)–Ag(6)	103.9(3)
S(9)–Ag(3)–S(2)	168.69(7)	Ag(2)–S(5)–Ag(6)	77.32(6)
S(10)–Ag(4)–S(11)	172.32(7)	C(74)–S(6)–Ag(8)	103.2(3)
S(7)–Ag(5)–S(3)	172.74(7)	C(74)–S(6)–Ag(9)	106.9(3)
S(8)–Ag(6)–S(5)	170.78(7)	Ag(8)–S(6)–Ag(9)	92.47(7)
S(10)–Ag(7)–S(1)	176.82(7)	C(104)–S(7)–Ag(5)	105.1(3)
S(6)–Ag(8)–S(1)	161.00(7)	C(104)–S(7)–Ag(9)	108.8(3)
S(6)–Ag(9)–S(7)	173.04(7)	Ag(5)–S(7)–Ag(9)	91.91(7)
S(4)–Ag(10)–S(8)	170.40(8)	C(104)–S(8)–Ag(6)	108.2(3)
S(4)–Ag(11)–S(12)	154.68(8)	C(104)–S(8)–Ag(10)	101.3(3)
S(9)–Ag(12)–S(12)	176.75(8)	Ag(6)–S(8)–Ag(10)	90.58(8)
C(14)–S(1)–Ag(7)	106.1(2)	C(134)–S(9)–Ag(3)	110.2(3)
C(14)–S(1)–Ag(8)	99.7(3)	C(134)–S(9)–Ag(12)	99.6(3)
Ag(7)–S(1)–Ag(8)	96.03(7)	Ag(3)–S(9)–Ag(12)	86.43(7)
C(14)–S(2)–Ag(2)	105.7(2)	C(134)–S(10)–Ag(7)	105.7(3)
C(14)–S(2)–Ag(3)	103.9(3)	C(134)–S(10)–Ag(4)	106.1(3)
Ag(2)–S(2)–Ag(3)	77.87(5)	Ag(7)–S(10)–Ag(4)	91.08(7)
C(44)–S(3)–Ag(1)	104.7(2)	C(164)–S(11)–Ag(4)	105.6(3)
C(44)–S(3)–Ag(5)	104.9(3)	C(164)–S(11)–Ag(1)	103.3(3)
Ag(1)–S(3)–Ag(5)	77.41(6)	Ag(4)–S(11)–Ag(1)	79.91(6)
C(44)–S(4)–Ag(10)	111.2(3)	C(164)–S(12)–Ag(12)	106.7(3)
C(44)–S(4)–Ag(11)	101.9(3)	C(164)–S(12)–Ag(11)	96.1(3)
Ag(10)–S(4)–Ag(11)	86.47(7)	Ag(12)–S(12)–Ag(11)	106.28(8)

which allowed observation of the Ag–P couplings (see the Experimental Section).

The ^1H and ^{13}C NMR data of cluster **4** are in agreement with its solid-state structure. Thus, its D_2 symmetry in solution leads to two types of dithiolato ligands, labeled as A and B in Scheme 1. The two type-A ligands lie along one of the 2-fold axes and thus give rise to one signal for the *t*-Bu groups in the ^1H NMR spectrum, while the four type-B ligands do not contain equivalent atoms and give rise to two different signals for the *t*-Bu groups. The three signals of equal intensity observed for each of the pairs of aromatic protons H1/H8, H3/H6, and H4/H5 (see Chart 1 for the atom numbering) are explained in the same manner. The ^{13}C NMR spectrum of **4** shows the expected two signals for the C9 atoms of the *t*-Bu-fy groups at 135.2 and 134.9 ppm, with relative intensities of approximately 2:1, while the CS_2 carbon

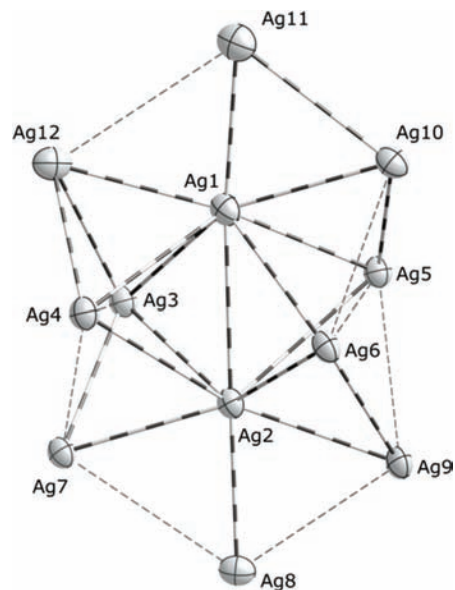


Figure 3. The Ag_{12} cluster in the structure of **4**. The $\text{Ag}\cdots\text{Ag}$ contacts in the range 2.875–3.367 Å are represented as banded cylinders. Longer Ag–Ag distances are represented by dashed lines. Thermal ellipsoids at 50% probability.

atoms give rise to a broad signal centered at 144.2 ppm, probably as a consequence of unresolved Ag–C couplings. The present NMR data indicate that the structure of **4** is essentially nonfluxional in solution.

The room-temperature ^1H NMR spectra of the dithiolato complexes **5a** and **5b** show only one resonance for the *t*-Bu substituents and each of the pairs of aromatic protons H1/H8, H3/H6, and H4/H5 of the fluoren-9-ylidene groups. These data are thus indicative of structures with equivalent and symmetrical dithiolato ligands in solution. However, in view of the crystal structure of **5b**, it is clear that complex dynamic processes take place, which result in the interchange of coordination environments between all of the silver atoms and eventually make the dithiolato ligands equivalent on the NMR time scale. The room-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **5a** and **5b** show a very broad resonance, which is also indicative of exchange processes. Unfortunately, the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **5a,b** could not be measured at low temperatures because of their very low solubilities.

The ^1H NMR data of the dppf complex **6** are also indicative of a structure with symmetrical and equivalent dithiolato ligands. It is therefore striking that its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at room temperature displays the resonance corresponding to the P atoms of the PPh_2 groups as a quintuplet of apparent quintuplets, with almost constant spacings of 122.4 and 8.7 Hz (Figure 7). If the structure of **6** in solution was regular, all of the P atoms would be equivalent, and therefore only one resonance should be observed, which would appear as two doublets because of the coupling with the ^{107}Ag and ^{109}Ag isotopes. The observed multiplicity suggests that **6** undergoes a very fast dynamic process in solution by means of which the P atoms exchange their positions. To confirm this possibility, we measured the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **6** at different temperatures, which show that the quintuplet broadens as the temperature decreases. However, the complex is scarcely soluble below

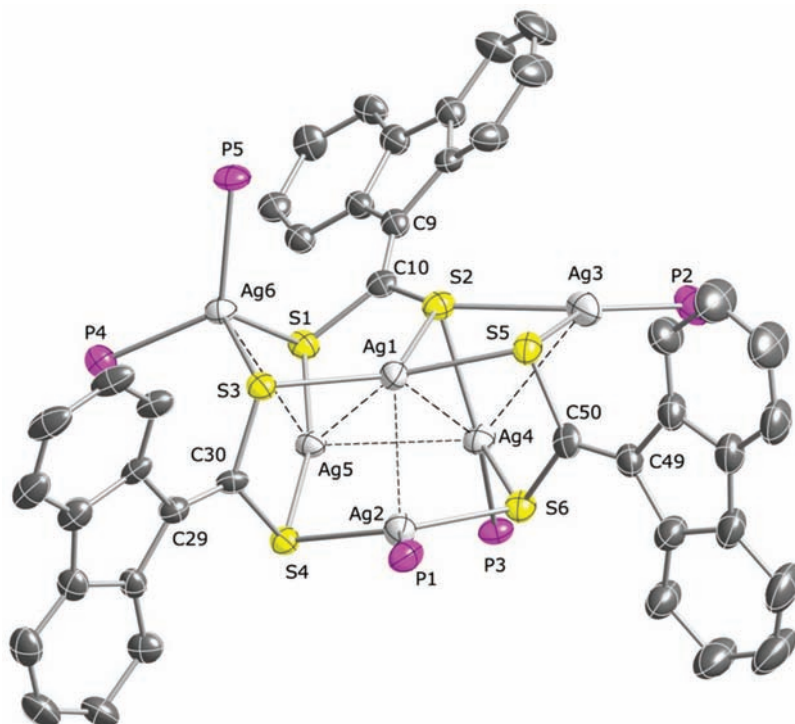


Figure 4. Thermal ellipsoid representation (50% probability) of complex **5b**. H atoms and *t*-Bu and *p*-To groups have been omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **5b**

Ag(1)–S(3)	2.4242(12)	Ag(5)–S(1)	2.3823(13)
Ag(1)–S(5)	2.5066(13)	Ag(5)–S(4)	2.4058(13)
Ag(1)–S(2)	2.6495(13)	Ag(5)–Ag(6)	2.9410(5)
Ag(1)–Ag(2)	2.8857(6)	Ag(6)–P(5)	2.4646(14)
Ag(1)–Ag(5)	2.9790(5)	Ag(6)–P(4)	2.4879(14)
Ag(1)–Ag(4)	3.1429(5)	Ag(6)–S(3)	2.6581(13)
Ag(2)–P(1)	2.4304(15)	Ag(6)–S(1)	2.7975(13)
Ag(2)–S(6)	2.5289(13)	S(1)–C(10)	1.765(5)
Ag(2)–S(4)	2.5690(13)	S(2)–C(10)	1.780(5)
Ag(3)–P(2)	2.3896(15)	S(3)–C(30)	1.768(5)
Ag(3)–S(5)	2.4858(13)	S(4)–C(30)	1.780(5)
Ag(3)–S(2)	2.6709(13)	S(5)–C(50)	1.779(5)
Ag(3)–Ag(4)	3.1359(6)	S(6)–C(50)	1.770(5)
Ag(4)–P(3)	2.4226(13)	C(9)–C(10)	1.350(7)
Ag(4)–S(2)	2.4822(13)	C(29)–C(30)	1.375(7)
Ag(4)–S(6)	2.5518(13)	C(49)–C(50)	1.367(7)
Ag(4)–Ag(5)	2.9803(5)		
S(3)–Ag(1)–S(5)	148.34(4)	P(4)–Ag(6)–S(1)	92.87(4)
S(3)–Ag(1)–S(2)	122.22(4)	S(3)–Ag(6)–S(1)	115.15(4)
S(5)–Ag(1)–S(2)	82.60(4)	C(10)–S(1)–Ag(5)	108.41(17)
S(3)–Ag(1)–Ag(2)	82.97(3)	C(10)–S(1)–Ag(6)	99.02(16)
S(5)–Ag(1)–Ag(2)	93.04(3)	Ag(5)–S(1)–Ag(6)	68.65(3)
S(2)–Ag(1)–Ag(2)	134.05(3)	C(10)–S(2)–Ag(4)	105.64(16)
S(3)–Ag(1)–Ag(5)	71.47(3)	C(10)–S(2)–Ag(1)	126.64(17)
S(5)–Ag(1)–Ag(5)	139.38(3)	Ag(4)–S(2)–Ag(1)	75.45(4)
S(2)–Ag(1)–Ag(5)	72.41(3)	C(10)–S(2)–Ag(3)	140.55(16)
P(1)–Ag(2)–S(6)	120.00(5)	Ag(4)–S(2)–Ag(3)	74.87(4)
P(1)–Ag(2)–S(4)	128.12(5)	Ag(1)–S(2)–Ag(3)	92.21(4)
S(6)–Ag(2)–S(4)	111.25(4)	C(30)–S(3)–Ag(1)	109.75(16)
P(2)–Ag(3)–S(5)	148.04(6)	C(30)–S(3)–Ag(6)	110.16(16)
P(2)–Ag(3)–S(2)	126.83(5)	Ag(1)–S(3)–Ag(6)	90.81(4)
S(5)–Ag(3)–S(2)	82.55(4)	C(30)–S(4)–Ag(5)	96.68(15)
P(3)–Ag(4)–S(2)	139.41(4)	C(30)–S(4)–Ag(2)	89.16(16)
P(3)–Ag(4)–S(6)	105.69(4)	Ag(5)–S(4)–Ag(1)	102.28(5)
S(2)–Ag(4)–S(6)	114.88(4)	C(50)–S(5)–Ag(3)	94.82(16)
S(1)–Ag(5)–S(4)	165.87(4)	C(50)–S(5)–Ag(1)	100.91(17)
P(5)–Ag(6)–P(4)	122.27(5)	Ag(3)–S(5)–Ag(1)	100.34(5)
P(5)–Ag(6)–S(3)	101.82(4)	C(50)–S(6)–Ag(2)	100.85(16)
P(4)–Ag(6)–S(3)	110.91(4)	C(50)–S(6)–Ag(4)	109.30(18)
P(5)–Ag(6)–S(1)	114.58(4)	Ag(2)–S(6)–Ag(4)	105.60(5)

233 K in CD_2Cl_2 , and we could not obtain well-resolved spectra (see the Supporting Information for details). A computer simulation of a $(\text{P}–\text{Ag})_4$ system in which the

phosphorus atoms exchange their positions through the migration around a square Ag_4 core (Figure 7) confirmed that the room-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **6** is the result of a dynamic process. The spacing between the peaks of the main quintuplet approximately corresponds to one-quarter of the mean of the coupling constants $^1J_{\text{P}–^{107}\text{Ag}}$ and $^1J_{\text{P}–^{109}\text{Ag}}$ and therefore can be interpreted as an average coupling of each of the P atoms with four Ag atoms. The further splitting into apparent quintuplets is attributable to the superposition of the spectra of the different isotomers. A related process has been reported for the hexanuclear derivatives $[\text{Ag}_6(\text{EAR})_4(\text{dppm})](\text{PF}_6)_2$ [EAR = SPh, S(*p*-To), SePh, or $\text{SeC}_6\text{H}_4\text{Me-}p$; dppm = bis(diphenylphosphino)methane], which led to the observation of a septuplet in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra at high temperatures, although in these cases, the splittings associated with the different isotomers did not resolve.³⁰ The present $^{31}\text{P}\{^1\text{H}\}$ NMR data prove that the dynamic process is intramolecular and are also an unequivocal demonstration that **6** is tetranuclear. In addition, since the Ag–P couplings are observed at room temperature, they reveal that the dppf ligands do not dissociate easily, which is consistent with the high stability observed for this complex in solution. We note that tetranuclear structures have been found for other silver(I) dithiolato complexes such as $[\text{Ag}_4(i\text{-mnt})_2(\text{dppm})_4]^{15}$ and $[\text{Ag}_4(\text{cpdt})_2(\text{dppm})_4]^{16}$ ($\text{cpdt} = \{(\text{EtO})_2\text{P}(\text{O})\}(\text{CN})\text{C}=\text{CS}_2^{2-}$), which have their metal atoms in a nearly planar arrangement and the dithiolato ligands acting as quadruply bridging ligands above and below the Ag_4 core. Complex **6** probably has an analogous structure, but with only two diphosphine ligands instead of four (Scheme 1).

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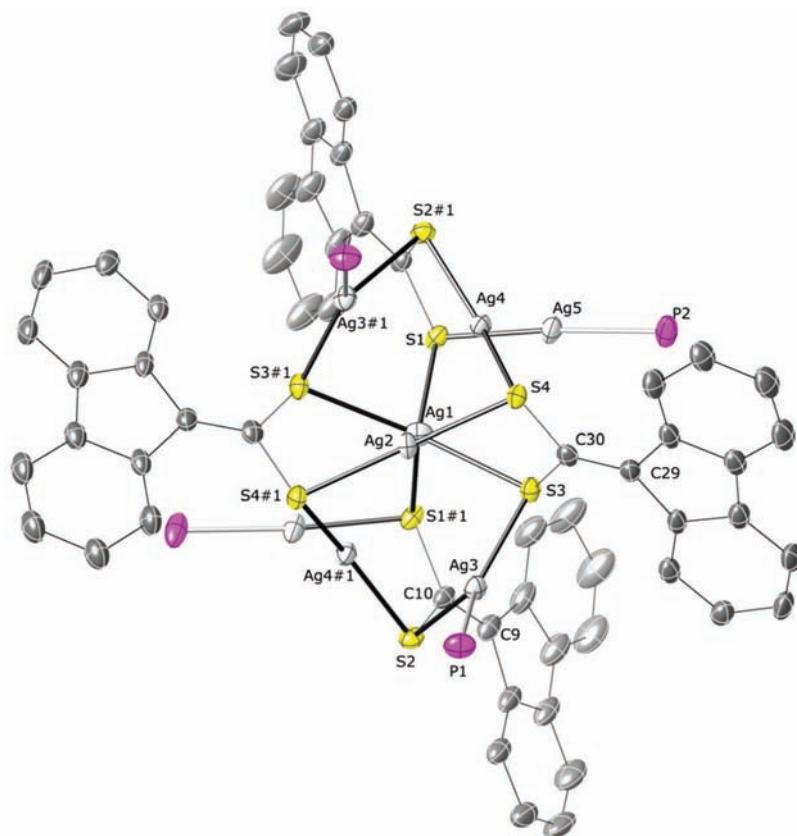


Figure 5. Thermal ellipsoid representation (50% probability) of complex **8**. H atoms and *t*-Bu and *i*-Pr groups have been omitted for clarity.

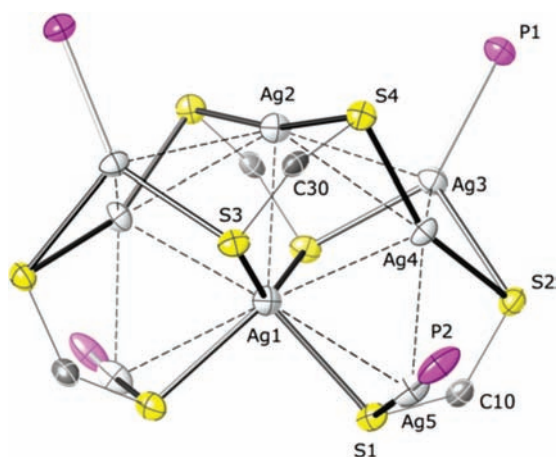
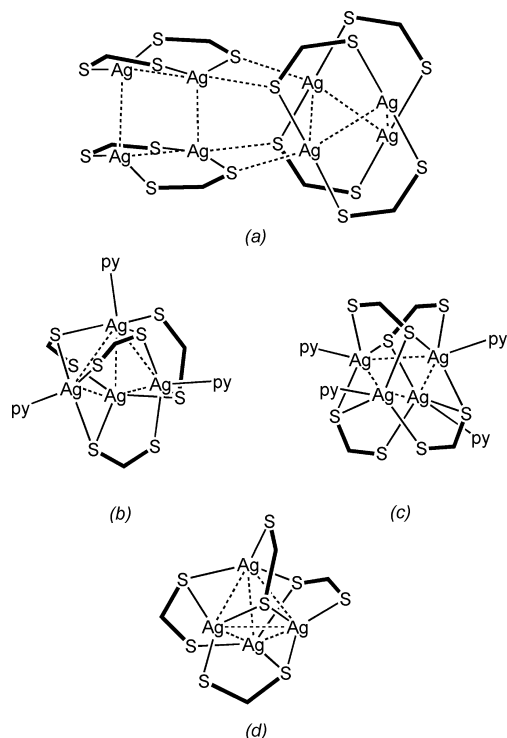


Figure 6. Perspective view of the $\text{Ag}_8\text{S}_8\text{P}_4$ core of complex **8**. Thermal ellipsoids at 50% probability.

Complex **7** gives rise to a very simple ^1H NMR spectrum at room temperature, which is indicative of symmetrical and equivalent dithiolato ligands, while the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a broad resonance at 41.7 ppm (CDCl_3). On cooling down to 213 K, the ^1H NMR spectrum showed no significant changes, while the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed two doublets arising from equivalent $[\text{Ag}\{\text{P}(i\text{-Pr})_3\}]^+$ units, thus revealing that this complex has a regular structure. A tetranuclear structure similar to that proposed for **6** would be consistent with the NMR data, but it could not be unequivocally established.

The room-temperature ^1H NMR spectrum of compound **8** shows broad signals for the protons of both the dithiolate

Chart 2



and the phosphine that are not consistent with the structure found in the solid state. The aromatic region of the ^1H NMR spectra in CD_2Cl_2 at temperatures between 203 and 296 K is shown in Figure 8. At 273 K, the resonances sharpen and reveal the presence of two different species, each one giving

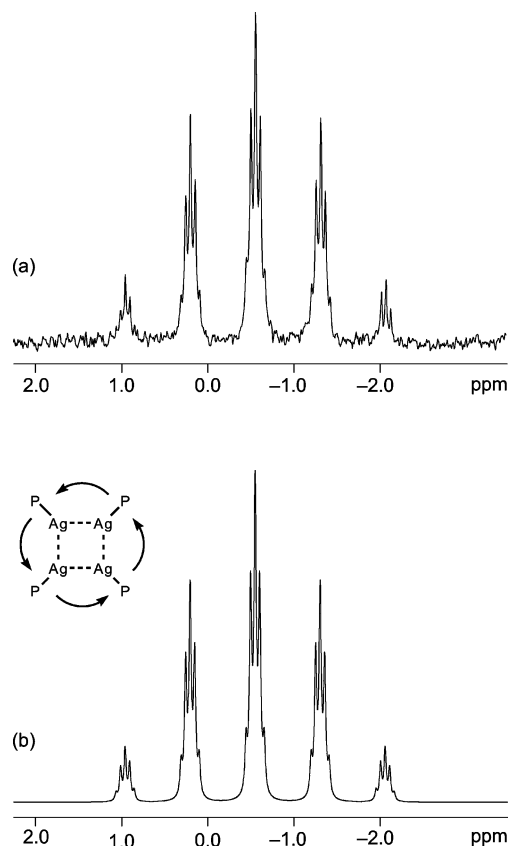


Figure 7. (a) Experimental $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **6** in CD_2Cl_2 at 298 K. (b) Simulated ^{31}P NMR spectrum for a $(\text{P}-\text{Ag})_4$ system in which the P atoms migrate around a square Ag_4 core ($^1J_{\text{P}-^{107}\text{Ag}} = 457 \text{ Hz}$, $k = 10^7 \text{ s}^{-1}$).

Table 4. Selected Bond Distances (Å) and Angles (deg) for **8**

Ag(1)–S(1)	2.5715(6)	Ag(3)–Ag(4)#1	2.8464(2)
Ag(1)–S(3)	2.6880(6)	Ag(4)–S(4)	2.3946(6)
Ag(1)–Ag(2)	2.8345(4)	Ag(4)–S(2)	2.4038(6)
Ag(1)–Ag(4)	2.9507(2)	Ag(5)–P(2)	2.3697(7)
Ag(2)–S(4)	2.4423(6)	Ag(5)–S(1)	2.3807(6)
Ag(2)–Ag(4)	3.0979(2)	S(1)–C(10)	1.774(2)
Ag(2)–Ag(3)	3.2584(2)	S(2)–C(10)	1.770(2)
Ag(4)–Ag(5)	2.9085(3)	S(3)–C(30)	1.773(2)
Ag(3)–P(1)	2.3946(7)	S(4)–C(30)	1.779(2)
Ag(3)–S(3)	2.4576(6)	C(9)–C(10)	1.364(3)
Ag(3)–S(2)#1	2.6564(6)	C(29)–C(30)	1.362(3)
S(1)#1–Ag(1)–S(1)	90.07(3)	C(10)–S(1)–Ag(1)	113.32(7)
S(1)–Ag(1)–S(3)#1	92.914(18)	Ag(5)–S(1)–Ag(1)	91.000(19)
S(1)–Ag(1)–S(3)	114.824(18)	C(10)–S(2)–Ag(4)	104.78(8)
S(3)#1–Ag(1)–S(3)	141.10(3)	C(10)–S(2)–Ag(3)#1	106.88(8)
S(1)–Ag(1)–Ag(2)	134.965(14)	Ag(4)–S(2)–Ag(3)#1	68.250(16)
S(3)–Ag(1)–Ag(2)	70.549(13)	C(30)–S(3)–Ag(3)	99.69(8)
S(4)#1–Ag(2)–S(4)	167.78(3)	C(30)–S(3)–Ag(1)	118.95(8)
P(1)–Ag(3)–S(3)	142.42(2)	Ag(3)–S(3)–Ag(1)	95.603(19)
P(1)–Ag(3)–S(2)#1	116.07(2)	C(30)–S(4)–Ag(4)	101.08(7)
S(3)–Ag(3)–S(2)#1	101.492(19)	C(30)–S(4)–Ag(2)	98.03(8)
S(4)–Ag(4)–S(2)	156.36(2)	Ag(4)–S(4)–Ag(2)	79.646(18)
P(2)–Ag(5)–S(1)	175.43(3)	S(2)–C(10)–S(1)	117.55(13)
C(10)–S(1)–Ag(5)	104.15(8)	S(3)–C(30)–S(4)	115.49(12)

rise to a single set of resonances for the pairs of equivalent aromatic protons, H1/H8, H3/H6, and H4/H5 (see Chart 1 for the atom numbering). As the temperature decreases, one of the sets broadens again and at 203 K resolves into four resonances for each of the pairs of protons,³¹ while the other

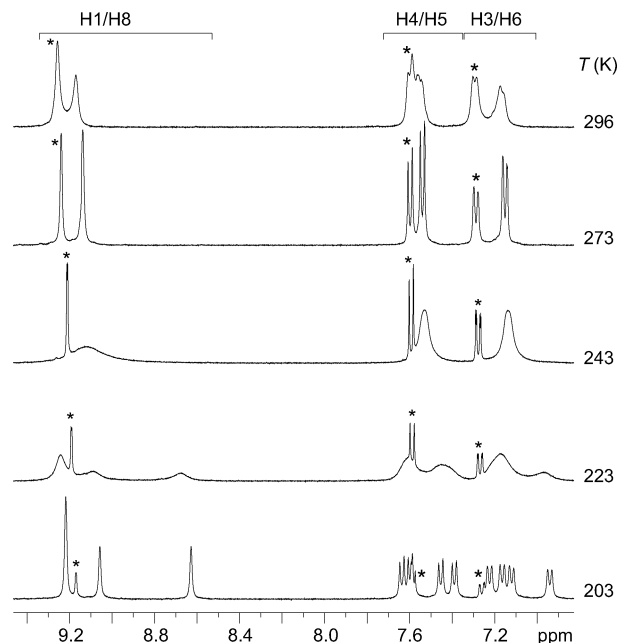


Figure 8. ^1H NMR spectra of complex **8** in CD_2Cl_2 at different temperatures (aromatic region). The resonances corresponding to the isomeric species **8*** have been labeled with an asterisk.

set undergoes a minor shift to lower frequencies and a drastic decrease in relative intensity. The resonances of the major species at 203 K are consistent with the structure found for **8** in the solid state, which contains two types of dithiolato ligands, neither of which have equivalent protons, thus giving rise to four signals for each of the H1/H8, H3/H6, and H4/H5 pairs. The other set of resonances must correspond to an isomeric species (**8***), which, as deduced from the integration of its signals, has the same Ag/dithiolate/phosphine ratio as **8**. We have labeled these signals with an asterisk in Figure 8. In the 0–2 ppm region, four resonances are observed for the *t*-Bu groups of **8**, while **8*** gives only one. The ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra also show the resonances of the two different $\text{P}(i\text{-Pr})_3$ ligands expected for **8**, while the isomer **8*** contains only one type of $\text{P}(i\text{-Pr})_3$ ligand (see the Supporting Information). In conclusion, the present NMR data show that (a) complex **8** is in equilibrium with an isomeric species (**8***) in solution, (b) the relative concentration of isomer **8*** decreases with the temperature, (c) complex **8** undergoes a dynamic process leading to equivalent and symmetrical dithiolates and equivalent phosphines above 273 K on the NMR time scale, and (d) isomer **8*** has a regular structure with equivalent dithiolates and phosphines. However, the nuclearity of **8*** cannot be inferred from its NMR data.

IR Spectra. The solid-state infrared spectrum of the dithiolato complex **2** shows a band at 1020 cm^{-1} assignable to one of the $\nu(\text{CS}_2)$ modes. For the phosphino complexes **3a–c**, this band is observed at around 1010 cm^{-1} . These values are slightly lower than those observed for other silver dithiolato complexes.³²

The dithiolato complexes **5a,b**, **6**, and **7** give rise to an intense band between 1485 and 1489 cm^{-1} , assignable to

(31) For the H1/H8 protons, three signals are observed, one of them of double intensity.

(32) Marsich, N.; Pellizer, G.; Camus, A.; Lanfredi, A. M. M.; Ugozzoli, F. *Inorg. Chim. Acta* **1990**, *169*, 171.

Table 5. Electronic Absorption Data for Compounds **2–8** in CH₂Cl₂ Solution (ca. 5 × 10⁻⁵ M) at 298 K (λ > 330 nm)

compd	λ _{max} /nm (ε/M ⁻¹ cm ⁻¹)
2	347 (6000)
3a	359 (6800)
3b	356 (6900)
3c	353 (4400)
4	363 (136600)
5a	375 (59000)
5b	395 (60500)
6	418 (34600)
7	386 (40900)
8	386 (100100)

the ν(C=CS₂) mode, while for **4** and **8**, two bands are observed at 1503 and 1473 cm⁻¹ and 1496 and 1464 cm⁻¹, respectively. These values are comparable to those found for neutral Au(I) complexes with the (*t*-Bu-fy)=CS₂²⁻ ligand.¹⁸

Electronic Absorption Spectra. The UV–visible absorption spectra of compounds **2–8** were measured in the range 200–700 nm in CH₂Cl₂ at 298 K. All of them show intense bands at around 230, 250–270, and 300 nm arising from the aromatic part of the dithioate or dithiolato ligands.^{18,19} The absorptions with λ > 330 nm are listed in Table 5. The dithioate complexes **2** and **3a–c** give rise to a relatively weak band in the range 347–359 nm. This absorption is only slightly modified with respect to that observed for the free dithioate **1** (346 nm), which can be ascribed to *n*–π* transitions within the CS₂ group.¹⁸ The spectra of the dithiolato complexes **4–8** show a broad and intense band in the range 363–418 nm. The energies and relatively large molar extinction coefficients observed for this band are typical of the π–π* transitions associated with the C=CS₂ moiety of the (2,7-di-*tert*-butylfluoren-9-ylidene)methanedithiolato ligand.¹¹ As expected, the molar extinction coefficients are larger for the clusters with a higher number of dithiolates per molecule (**4** and **8**). The molar extinction coefficient for complex **7** was calculated assuming a tetranuclear formulation and fits well within the observed values, although it cannot be considered as a confirmation of the proposed nuclearity.

Conclusions

A series of neutral silver complexes with 2,7-di-*tert*-butyl-9*H*-fluoren-9-carbodithioate and (2,7-di-*tert*-butylfluoren-9-ylidene)methanedithiolate have been prepared, including tetra-, hexa-, octa-, and dodecanuclear clusters. The compound [Ag₁₂{S₂C=(*t*-Bu-fy)}₆] (**4**) is the first neutral homoleptic 1,1-ethylenedithiolato silver complex, and its structure has no precedent in the chemistry of silver 1,1-dithiolates. Complex **4** is a useful starting material for the preparation of dithiolato complexes of silver with phosphine ligands. The compounds [Ag₆{S₂C=(*t*-Bu-fy)}₃L₅] [L = PPh₃ (**5a**), P(*p*-To)₃ (**5b**)], [Ag₄{S₂C=(*t*-Bu-fy)}₂(dppf)₂] (**6**), [Ag_{*n*}{S₂C=(*t*-Bu-fy)}_{*n/2*}{P(*i*-Pr)₃}_{*n*}] (**7**), and [Ag₈{S₂C=(*t*-Bu-fy)}₄{P(*i*-Pr)₃}₄] (**8**) also represent new types of silver clusters containing dithiolato and phosphine ligands. Compounds **5a,b** and **7** undergo phosphine dissociation and exchange processes in solution. Complex **6** undergoes a very fast dynamic process leading to an average coupling of each of the P atoms of the dppf ligands with four Ag atoms. The octanuclear derivative **8** is in equilibrium with a structural isomer in solution, but the nuclearity and structure of the latter could not be established. Complex **8** also undergoes a dynamic process leading to equivalent and symmetrical dithiolates and equivalent phosphines in solution. In contrast to the phosphine derivatives, the dodecanuclear cluster **4** does not exhibit fluxional behavior in solution.

Acknowledgment. We thank Ministerio de Educación y Ciencia (Spain), FEDER (CTQ2004-05396 and CTQ2007-60808/BQU), for financial support. Y.G.-S. thanks Ministerio de Educación y Ciencia (Spain) for a grant.

Supporting Information Available: Crystallographic data in CIF format for **4**, **5b**, and **8**; ¹H NMR spectrum of **4**; variable-temperature ³¹P{¹H} NMR spectra of **6**; simulations of the ³¹P NMR spectra of a (P–Ag)₄ system at different rate constants; variable-temperature ¹H and ³¹P{¹H} NMR spectra of **8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC802045J